



# University of Sheffield

PhD thesis

## Low temperature fabrication of lithium metatitanate and lithium orthosilicate combinatory ceramics for fusion breeding applications

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## Abstract

Nuclear fusion could one day satiate the world's thirst for energy. However, significant hurdles need to be surpassed to arrive at a functional fusion device. All components of a theoretical reactor must be designed with those hurdles in mind. One such component is the breeder blanket, functioning as both fuel — *via* the transmutation of lithium into tritium — and as a heat recovery system, transferring the kinetic energy of neutrons into usable heat. To this end, a variety of materials have been proposed to function as breeders, but currently ceramic breeders are leading the charge. Out of the many materials considered, two ceramics are generally understood to be the most suitable solutions:  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{SiO}_4$ .

Lithium containing materials suffer during fabrication as common methods require high temperatures, which results in lithium loss *via* vaporisation. This project aims to introduce novel, low-temperature fabrication methods to address this issue and expand the available pathways for ceramic breeder fabrication. In particular, the application of reactive cold sintering (RCS) allows for the facile introduction of different phases, which may enable the tailoring of ceramics composites.

In this project, single phase  $\text{Li}_2\text{TiO}_3$  has been synthesised using the DES method. Moreover, cohesive, single phase and multiphase pellets were generated applying the reactive cold sintering method. The capacity for this method to introduce different morphologies and phases through the use of the infill as an independent vector was demonstrated. Dense, single phase  $\text{Li}_2\text{TiO}_3$  pellets were produced with maximum temperatures 400 °C below those used in regular sintering. Biphasic,  $\text{Li}_4\text{SiO}_4$  –  $\text{Li}_2\text{TiO}_3$ , pellets were generated, resulting in exceptionally well-consolidated composites. Incompatibilities between the equipment and the materials used led to unpredictable shifts in stoichiometry, which ultimately led to sub-stoichiometric lithium content in the final pellets. This resulted in complex mechanisms leading to the sequestration and eventual retention of unreacted material.

**Keywords**— Lithium Metatitanate, Lithium Orthosilicate, Deep Eutectic Solvents, Cold Sintering Process, Biphasic, Bimodal, Ceramic Breeder, Composites, Reactive cold sintering, Method refinement.



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# 1 Introduction & Literature review

## 1.1 Fusion as an energy source

The demand for energy has become an ever expanding scientific and engineering problem. To keep up with population growth and energy demand, new and more efficient technologies must emerge as economically viable alternatives to the more conventional forms of energy generation. The added pressure of a dwindling supply of fossil fuels and increased likelihood of an environmental “collapse” [2] exacerbates the need for new reliable and environmentally benign power sources. Improvements in batteries and renewable energy sources may meet this demand eventually but are currently incapable of providing consistently the required power — without transcendental infrastructural changes this situation is likely unachievable.

Nuclear energy can provide a reliable, near constant supply of electrical energy which could easily be supplemented by renewables. This “baseline” provided by a potential nuclear power based infrastructure perfectly counteracts the main drawbacks of renewable energy; namely intermittency and reliability, and by developing functional fusion plants, the major negatives usually attributed to the technology may be completely erased.

Firstly, fusion power is intrinsically safe [3] — in stark contrast to fission — as the outrageously high temperatures within the reactor must be maintained to be operational, therefore any breach or damage to the containment vessel would simply result in quenching of the reaction. As well as this, the fuel, tritium, would be continuously generated *in-situ* therefore only the small amount currently within the vessel would leak in an emergency situation [3]. Plant design is also such that in a loss of coolant scenario the peak temperature reached should still be low enough as to prevent a runaway reaction from destroying the fusion device [3].

The word nuclear however has acquired a certain connotation in the current cultural zeitgeist — following the accidents at Chernobyl and Fukushima — poisoning most discussions related to nuclear power. This has led to an attempt by the fusion community to distance themselves from fission in order to highlight the fundamental difference in safety and environmental impact of a fusion device (the modern adoption of the term ‘device’ is a clear example of such an attempt).

Moreover, constant reviews are being undertaken to ensure the use of low activation materials in order to avoid the mistakes made with fission plant construction and operation [4,5]. Low activation materials are those which produce, as a result of their exposure to radiation, little to no amounts of long term radioactive waste [5]. This should result in close to no high-level nuclear waste generation, circumventing the need for a geological disposal facility and hence rendering moot one of fission’s biggest safety and political drawbacks.

Unlike fossil fuels and fission, the fuels required for fusion are not only readily available but some of the most abundant elements in the universe — hydrogen, or more specifically, two of its isotopes: deuterium and tritium. Deuterium (D) can be and has been extracted from sea water and is in plentiful supply and [3], although tritium (T) cannot be found in reasonable quantities (current civil stockpiles are almost exclusively generated in CANDU (CANada Deuterium Uranium) fission reactors and has been calculated at around £30,000

per gram) it can be ‘bred’ with the help of lithium; again a relatively abundant material which can be found plentifully in the oceans — although large scale oceanic extraction has not been demonstrated and may be one of the largest hurdles to jump before the widespread adoption of fusion energy [6]. The energy density of the fusion process is also remarkable, with 1 kg of lithium being roughly equivalent to 5700 barrels of oil [3].

Currently there are two main reactor designs: stellarators and tokamaks [7], although several private ventures into inertial confinement reactors (ICF), which have been commonly used in experimental facilities, are in testing. In essence, the first two groups aim to maintain a plasma localised in the centre of a containment vessel and continuously supply it with fuel to, in the future, generate energy, whilst the last group, confines the fuel to a highly compressed core, allowing the plasma’s inertia to maintain this highly pressurised environment for long enough for the thermonuclear burn to result in sufficient fusion reactions [8]. The goal is to reach “ignition” or a self-sustaining plasma; reaching this point with stability is the final step before proving the industrial viability of the reactor design [9]. Both stellarators and tokamaks are based on the same concepts and only differ in their practical approaches. Recently, the National Ignition Facility (NIF), an ICF experiment located in the US, were the first to achieve ignition, demonstrating the feasibility of this goal, even when using currently available technology.

In general, all magnetic confinement fusion reactor designs (*i.e.* stellarators and tokamaks) exploit the pinch effect — an application of the Lorentz forces a plasma can experience due to its charged nature — to immobilise the plasma and keep it from approaching the containment walls [10]. This is a requirement for two reasons: no material can resist the temperatures of upwards of  $1 \times 10^8$  K required for a D-T thermonuclear plasma and to avoid cooling of the plasma itself [11]. Cooling happens due to the temperature difference between the plasma and the walls of the vacuum tube, but, more importantly, due to heavier atoms ejected from the walls into the plasma which collide with the lighter atoms within it, decreasing their momentum and therefore decreasing temperature.

These outrageously high temperatures are required in order to satisfy the Lawson criterion, which describes the minimum possible temperature (more accurately plasma pressure) with which to achieve a self-sustaining nuclear fusion reaction [8, 12, 13]. This criterion has been further refined from the original research by Lawson *et al.* [12] and has differing key variables depending on the confinement method, as plasma pressure is achieved through different mechanisms in inertial *vs* magnetic confinement devices.

The toroidal design of most modern fusion concepts leads to a form of instability named the “kink”, where the plasma is pushed towards and collides with the walls of the container by the magnetic disparity created by the geometry itself. If magnets are added azimuthally, a disparity in the magnetic force experienced by the plasma arises as the inner radius of the torus has a greater magnetic field density [14]. To solve this issue, some rotation had to be introduced so that the kink instability would cancel out. Researchers in the USSR added another set of magnets in a poloidal position to generate a net helical magnetic field, causing the plasma to rotate and therefore stabilising it [15]. In contrast, USA researchers, and in particular Lyman Spitzer [16], decided to simply twist the torus, giving the plasma the rotation required. This is where the distinction between stellarators and tokamaks arose (shown in figure 1.1) [9].

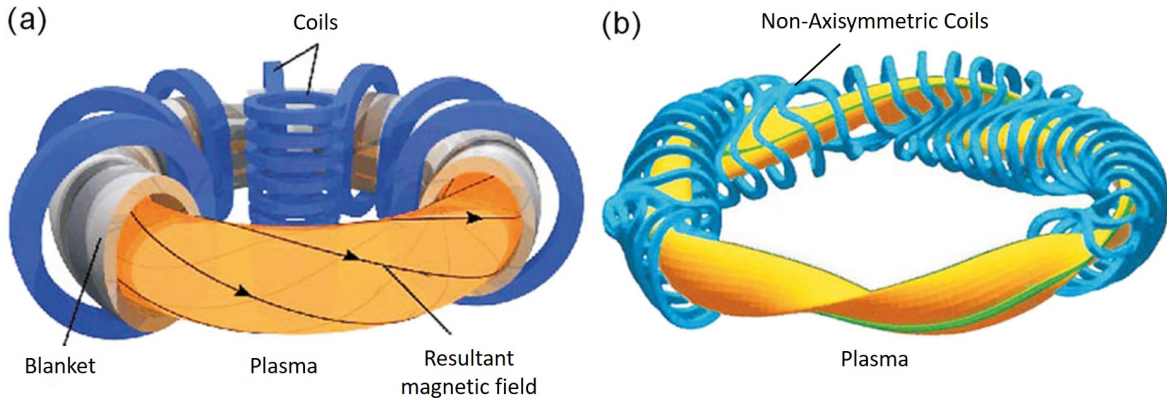


Figure 1.1: Schematic of confined plasma in both (a) tokamaks and (b) stellarators. Adapted from [7].

Nowadays, these designs are in constant iterative improvement with advancements like the tokamaks' D-shaped coils — which reduce both the tension forces in the inner radius and the magnetic field gradient — and the improved helically symmetric magnets of the more modern stellarators (shown in 1.1 b)). Tokamaks with their simpler designs and proven efficiency are usually the preferred solutions but plasma disruptions within them can cause catastrophic damage to the reactor. Stellarators have great potential however, as their possible configurations are greater than those of a tokamak and further optimization of stellarator design is possible [17].

In an attempt to simplify tokamak design and reduce the size and cost of the device, spherical tokamaks have come back into focus in recent years. These devices reduce the size of the torus' inner diameter leading to a plasma that almost takes on a spherical shape. This shift in aspect ratio results in an improvement in average magnetic field density within the plasma, theoretically leading to a reduction in required magnet size and therefore cost. The reduced size of the inner diameter however, results in a lack of space for proper shielding and cooling of the magnets used, casting doubt on their longevity, as the high fluxes of radiation coming from the plasma will result in rapid degradation without proper shielding [18].

## 1.2 Energy generation in fusion

The physical principle underlying all nuclear energy processes — and that which allows for energy generation — is the binding energy per nucleon (figure 1.2) [19]. The difference in this energy between parent and daughter products is what determines the energy of the reaction. Two different possible avenues to extract energy from such an event are evident from figure 1.2: a large atom could be split into smaller pieces *i.e.* fission (moving left towards Fe in figure 1.2) or very small atoms like hydrogen and helium could be joined together to form larger ones *i.e.* fusion (moving right towards Fe in figure 1.2).

Currently, out of the many exothermic fusion reactions, one has been singled out as the most promising to be successfully used in commercial energy generation. In this reaction an atom of deuterium and an atom of tritium would be fused together to form helium

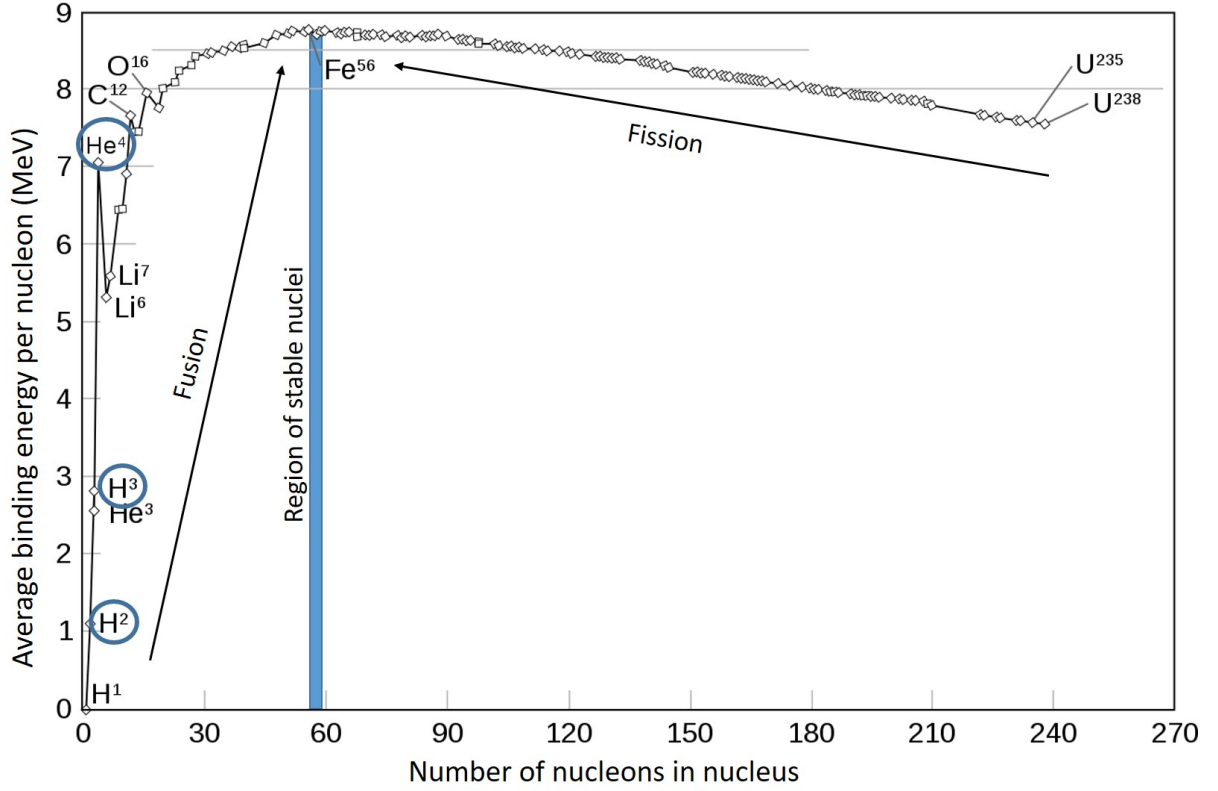
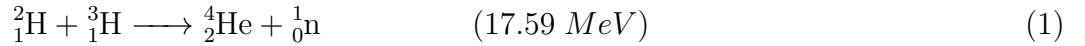


Figure 1.2: Average binding energy per nucleon vs. number of nucleons. Adapted from [20].

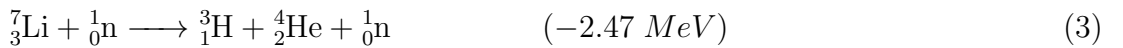
and a neutron as well as an enormous amount of energy [3].



Other fusion reactions have been considered and some have an even larger energy release but the atoms must, crucially, be close enough to react. Many of these other reactions, although more energetic, have a much smaller reaction cross-section (essentially how likely the reaction is to occur) than the proposed D-T reaction, which has by far the highest cross-section at the energies of interest [3].

A significant drawback when applying this reaction in a real system is the source of tritium. Not only would it be inadvisable to store significant amounts of it on site, but the 12-year half-life of tritium means that there are no naturally occurring stores that may be exploited and hence it must be generated in situ [21].

Luckily, a relatively simple solution is the utilisation of a lithium breeder to generate the required tritium in situ through a transmutation reaction with the help of neutrons, which would, conveniently, be generated by the D-T plasma itself [3, 22].



This requirement is what introduces the necessity for a breeder blanket. This element of the reactor is essentially a layer of lithium dense material adjacent to a neutron transparent first wall. The tritium and helium produced in this layer would then be separated, with the tritium being fed back into the reactor, maintaining the reaction. This layer is also the prime candidate to recover heat from [23] as the exuding neutrons dump their kinetic energy in the material. Hence, this breeder blanket must abide by two key design characteristics: efficient tritium generation and ease of energy extraction.

### 1.3 Breeder blanket design

Ever since the fusion community reached the general consensus of focusing on a DT plasma, the need for a breeder blanket was identified and researched [24]. This has resulted in a wide variety of design concepts that have shifted to match the constant influx of new research and design goals. In this review modern blanket systems will be described and studied to give a general overview of the current state of breeder blanket design.

Before considering specific breeder systems, it is important to understand the needs of a D-T fusion reactor. First, this blanket will both provide fuel to the plasma and allow for heat extraction and hence power generation. To fulfil these two functions, the blanket must occupy upwards of 85% of the in-vessel surface/volume around the plasma [23] — both to receive the necessary flux of neutrons and to extract a reasonable amount of energy. Materials around the blanket must also be carefully controlled, as those with high neutron cross-sections, such as steel, may reduce the number of neutrons reaching the breeder to unworkable levels [25].

As well as occupying a large volume of the vessel, the breeder blanket is in need of several large external auxiliary systems to maintain operation: a tritium extraction system, a heat transfer system and a power generation system [23]. All of these auxiliary systems are extremely dependent on the technology utilised in the blanket, hence the choice of technology will have a huge impact on the general safety and design concerns of the power plant as a whole.

Any material considered as a breeder must withstand the rigors of a fusion reactor, these being high magnetic fields, high temperatures (900 °C is accepted as the maximum allowable temperature within most breeder blanket designs) and high thermal and mechanical stresses [18]. All of this, of course, in addition to the damage incurred by transmutation of lithium to tritium as well as a dpa (displacements per atom — a dpa of 1 means that on average each atom in the material has been displaced from its original lattice site once) between 20 - 70, depending on the expected lifetime of breeder within the reactor [23]. Moreover, these dpa numbers are only relevant at the DEMO (DEMONstration power station) level, a commercial fusion power plant may require a breeder capable of resisting upwards of 150 dpa throughout the expected lifetime of the plant [26].

Four main technologies have survived the years of scrutiny and testing since the conception of the breeder blanket and are now being considered for use as the main tritium breeder in DEMO [23]. These are the Helium Cooled Pebble Bed (HCPB), the Helium

Cooled Lithium Lead (HCLL), the Water Cooled Lithium Lead (WCLL) and the Dual Coolant Lithium Lead (DCLL) [27].

Out of these four technologies, three are utilising what is termed “lithium lead”, this is a eutectic PbLi alloy enriched to 90%  $^6\text{Li}$  [23, 28]. The exact composition of this alloy fluctuates slightly around the eutectic point, with Pb-15.8Li being an average composition [23] and Pb-17Li being more commonly researched [28]. An offshoot of these technologies focuses on liquid salts, spearheaded by the Molten Salt Reactor Experiment (MSRE) in the US, and focuses mainly on lithium fluorides, chief among them FLiBe [27, 29]. These however have poor compatibility with the structural materials currently being considered, requiring a particularly tough combination of corrosion resistance and high temperature operation [30, 31] as well as forgoing some of the benefits introduced by the use of a liquid breeder. Manufacturing and safety concerns when manipulating salts containing elements with well-known high degrees of toxicity and reactivity should not be understated.

Originally, lithium-only liquid breeders were being considered but lithium metal reacts violently with water, and considering the large volumes required, would be too great a safety concern. This is why today; most researchers agree the PbLi is the more attractive avenue to pursue out of the two [18]. Liquid metal concepts have significant advantages over solid breeder concepts, providing a sufficient tritium breeding ratio and boasting a high thermal conductivity and low viscosity allowing for relatively easy heat recovery. Not only that but they are relatively immune to radiation damage as there is no lattice to preserve [18].

Being a more attractive technology does not, however, protect it from scrutiny and many issues have been raised when dealing with this eutectic alloy. Firstly, PbLi is corrosive and hence further limits the choices for structural materials, it is also very dense, which considering the high volumes required, would result in further structural considerations [18]. These are just simple drawbacks derived from the basic properties of the alloy; further issues arise from magnetic interactions between the magnetic fields and the high electrical conductivity of the material [18]. These interactions result in large pressure drops across the vessel due to strong flow-opposing forces induced within the liquid metal [18]. This drawback is the main reason as to why self-cooled breeder blankets are not being considered as an attractive technology — flowrates required when combined with the high pressure drops induced results in extremely high pressure stresses which could exceed material structural limits [18]. The DCLL concept design still uses some self-cooling to remove heat from the breeder material itself, but uses helium to supplement heat removal at the first wall interface [32].

Magnetohydrodynamic issues can be alleviated with more complex fluid channel designs, aligning the direction of flow with field lines for example. However, in the case of other conductive liquid lithium concepts, like molten salts, this issue is further compounded by the enhancement of corrosive REDOX interactions between the salt and the structural materials themselves [30].

The HCLL concept design is currently the European liquid metal reference design chosen for testing at ITER (International Thermonuclear Experimental Reactor) [33]. Here all the thermal energy is removed by a helium cooling system and the PbLi eutectic is used solely as a breeder [18]. This means that the whole system can operate at much

slower flowrates, decreasing the effect that magnetic interactions have on the system. One main issue of this design concept is the possible permeation of tritium into the He coolant stream. This could result in tritium loss as well as a tritium build-up in the coolant stream, which may have serious safety implications — due to the evident introduction of a potentially explosive stream [34].

The WCLL was one of the initial liquid metal conceptual designs [35] but was abandoned for the more promising HCLL concept. Recently, new WCLL designs have been proposed but further analysis is required to assess the cooling potential of the proposed arrangement [23]. An obvious issue however is the PWR-like (Pressurised Water Reactor) conditions the water stream would be in as well as the clear risk attached to having a potential leak which would allow the encounter between water and the PbLi eutectic — this reaction is highly exothermic and will generate hydrogen, another potentially explosive combination [36].

The last of the proposed liquid metal designs is the DCLL concept design, which combines the use of helium and of the breeder liquid itself as cooling [32]. In theory this design allows the PbLi eutectic to operate at much higher exit temperatures ( $\approx 700$  °C, comparable to temperatures required in molten salt concepts) than with other designs, providing a higher thermal efficiency [23]. It does this by utilising the helium to cool all materials around the liquid metal channels to under 550 °C (a requirement to maintain radiation damage to reasonable levels in ferritic steels) whilst only the flow of the eutectic will cool the alloy itself. This means that the material choice for the liquid metal channel is extremely important as it must resist neutron bombardment as well as provide enough thermal and electrical insulation to keep the rest of the components at the desired temperature and to help counteract the magnetically induced pressure drop [18]. Silicon carbide is proposed as a potentially viable material, but utilisation of SiC in practice needs significant further research in order to assess its response to neutron irradiation at the high temperatures required.

Finally, the HCPB concept is the only one utilising a solid breeder to generate the tritium required, and is arranged as shown in figure 1.3.

As it may be inferred from figure 1.3, the introduction of beryllium pellets aims to tackle a significant issue when dealing with ceramic breeder materials: lithium density [37]. In order to achieve stable fusion, the candidate breeder material must be capable of achieving a tritium breeding ratio (TBR)  $\geq 1.1$ , any lower and the reaction will not be self-sustaining [25,38]. The presence of beryllium aims to increase this ratio by acting as a neutron multiplier, enhancing the chances that a neutron will come in contact with a lithium atom and cause a transmutation event. In liquid metal breeders the lithium density is high enough due to a lack of voids, both within the pellets and between pellets (generally producing a TBR  $>1.1$ ), hence avoiding the need for neutron breeders

The multiplier is currently agreed upon to either be beryllium metal or  $\text{Be}_{12}\text{Ti}$  which has shown reduced swelling at pertinent conditions [18]. Lead has also been considered as a potential multiplier although its inferior performance and low melting point have precluded serious consideration of this technology as an independent supplement [39]. Some research has focused in the usage of lead-containing lithium ceramics,  $\text{Li}_8\text{PbO}_6$  as an example, these however will likely still require additional multiplier to arrive at the



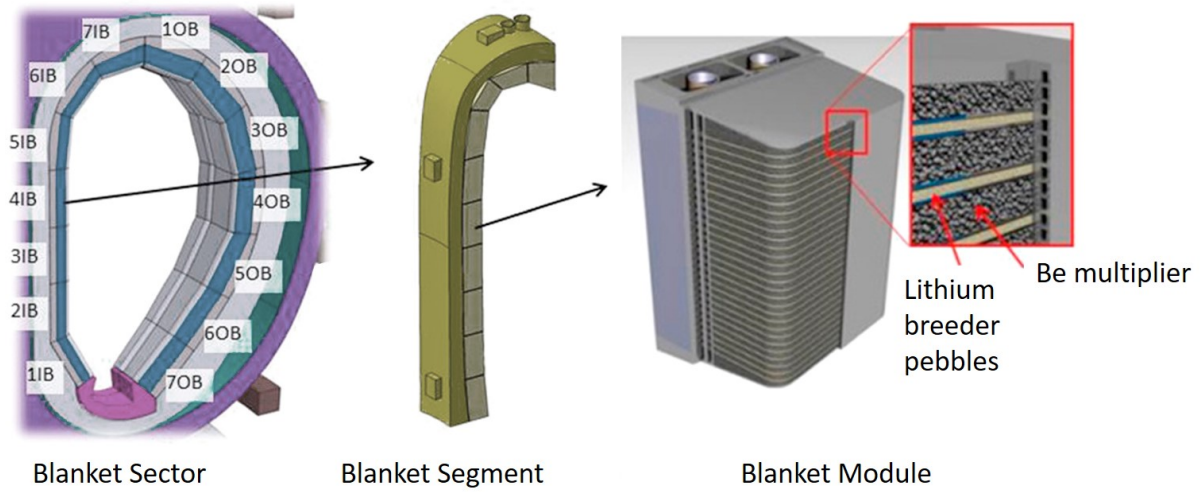


Figure 1.3: The HCPB concept design. Adapted from [23].

desired TBR [27].

Another approach which may be of interest is the addition of beryllia as a supplemental secondary phase into a candidate breeder material, generating a composite ceramic; but further research must be done to understand potential interactions when co-firing or the application of more flexible material synthesis methods [40].

However, a more interesting and nuanced academic debate is occurring with the breeder ceramic itself. Many different materials, synthesis and sintering methods are being researched in order to find a reliable and potentially upscalable method to produce the required material and microstructure. This project focuses on the application of alternative synthesis and sintering techniques to produce a variety of different breeder materials with variable composition and morphologies.

### 1.3.1 Ceramic breeder materials

A wide variety of lithium ceramics have been considered for use as the tritium source but there is yet to be international consensus on which results in the most practical solution [41]. Currently, ITER will act as the testing grounds for some of the more modern bed designs, with lithium metatitanate ( $\text{Li}_2\text{TiO}_3$ ) and lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ) as the principal candidate ceramics. The main reasons behind this lack of consensus are: the lack of relevant testing facilities — currently neutron bombardment experiments can't reach dpa levels that approximate the expected levels within DEMO let alone a full-fledged fusion reactor [25, 42] — and the lack of an ideal candidate material: all the ceramics that have been and are being considered have significant faults. What follows is a critical review of the different materials that have surfaced as plausible breeders, including their crystallographic characteristics and their place in current fusion breeder design. Table 1.1 summarises the crystallographic information as well as relevant properties of each of the ceramics discussed.

Table 1.1: Summary of relevant properties of the ceramic breeder candidates discussed.

| Material                                                                   | $\text{Li}_2\text{O}$<br>[37, 43, 44] | $\gamma\text{-LiAlO}_2$<br>[37, 43, 44] | $\text{m-Li}_2\text{ZrO}_3$<br>[37, 43–45] | $\text{Li}_4\text{SiO}_4$<br>[37, 43, 44] | $\beta\text{-Li}_2\text{TiO}_3$<br>[43–46] |
|----------------------------------------------------------------------------|---------------------------------------|-----------------------------------------|--------------------------------------------|-------------------------------------------|--------------------------------------------|
| Formula weight<br>(g mol <sup>-1</sup> )                                   | 29.9                                  | 65.92                                   | 153.2                                      | 119.85                                    | 109.75                                     |
| Theoretical<br>density (g cm <sup>-3</sup> )                               | 2.01                                  | 2.61                                    | 4.15                                       | 2.35                                      | 3.43                                       |
| Lithium atom<br>density (g cm <sup>-3</sup> )                              | 0.93                                  | 0.27                                    | 0.33                                       | 0.54                                      | 0.43                                       |
| Thermal conduc-<br>tivity at 400 °C<br>(Wm <sup>-1</sup> K <sup>-1</sup> ) | 6                                     | 2.6                                     | 1.4                                        | 2.5                                       | 1.7                                        |
| Melting<br>temperature (K)                                                 | 1706                                  | 1883                                    | 1888                                       | 1523                                      | 1535                                       |
| Crystal structure                                                          | Cubic<br>Antifluorite                 | Tetragonal                              | Monoclinic                                 | Monoclinic                                | Monoclinic                                 |
| Space group                                                                | $Fm\bar{3}m$                          | $P4_12_12$                              | $C2/c$                                     | $P2_1/m$                                  | $C2/c$                                     |

#### 1.3.1.1 Lithium oxide

Ceramic breeder candidate research started with the consideration of lithium oxide as a plausible solution [47, 48].

##### 1.3.1.1.1 Crystal structure

At ambient conditions lithium oxide adopts the antifluorite structure, with space group  $Fm\bar{3}m$ . The structure can be described as an array of ccp/fcc oxygen anions with lithium cations in fully occupied tetrahedral sites [49].

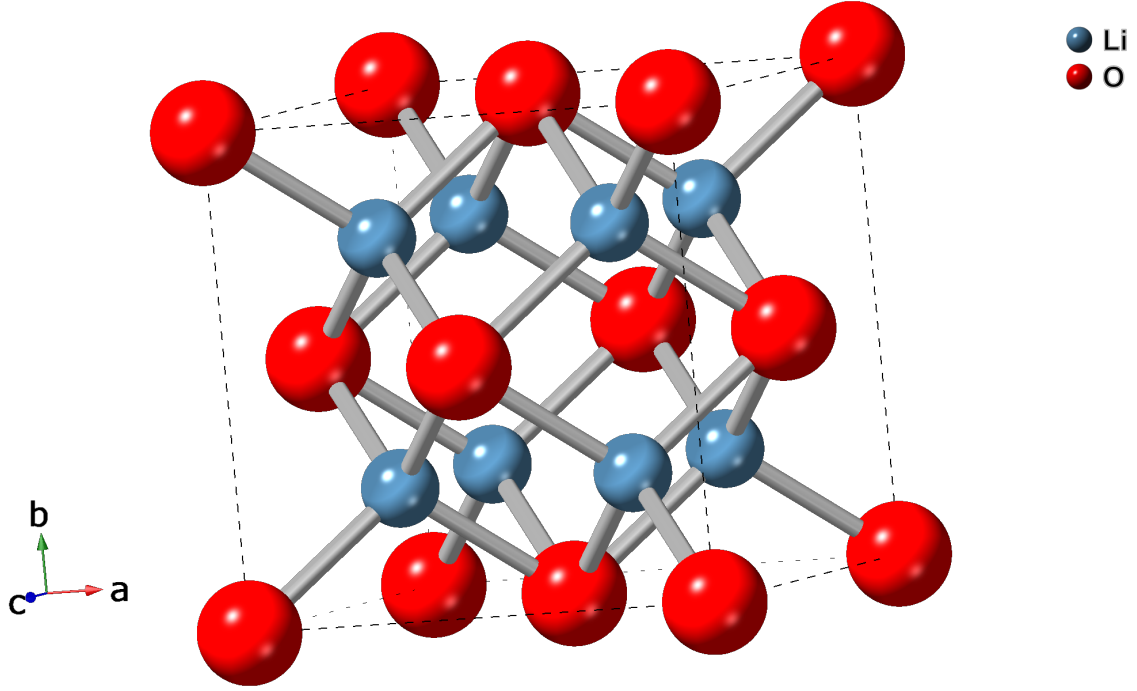


Figure 1.4: Structure of  $\text{Li}_2\text{O}$  according to ICSD card 54368 [49]. With lattice constant  $a = b = c = 4.61 \text{ \AA}$ . Generated using CrystalMaker<sup>®</sup>.

#### 1.3.1.1.2 Fusion properties

Having an extremely high lithium density, it was an obvious first step [50] in the search for a suitable tritium breeder. Regrettably however, just like lithium metal, lithium oxide reacts readily with water [48, 50] precluding its transport and storage and complicating its use within a reactor. This results in the necessity to fully water-seal any transport equipment and the breeder blanket itself, as well as disqualifying water as a possible cooling solution. Moreover, the reaction of  $\text{Li}_2\text{O}$  with water results in the formation of caustic  $\text{LiOH}$ , furthering the need for total humidity control as corrosion would now be a greater concern [48, 51]. The reaction is quite fundamental and is as follows:



Unfortunately, lithium oxide does boast the highest thermal conductivity among the ceramics considered (see table 1.1) making its poor chemical stability disappointing. Another issue affecting  $\text{Li}_2\text{O}$  is the measured lithium oxide vapour pressure, suggesting that lithium loss would be of great concern when utilising this material at the required temperatures [52]. It is worth noting that these measurements were not made under prototypical purge gas conditions [52] and hence may be an inaccurate representation of lithium oxide's behaviour. In Knudsen effusion method studies by Kimura *et al.* [53] and Kudo *et al.* [54], they found multiple lithium-containing ionic species in the gas phase at temperatures at and above  $900 \text{ }^\circ\text{C}$  ( $1225 - 1700 \text{ K}$ ). This implies that a breeder blanket fully composed of  $\text{Li}_2\text{O}$  pellets will need to address its lithium volatility in addition to all

other concerns, the rate of which may be high enough to render this ceramic unusable as an effective and efficient breeder solution.

### 1.3.1.2 Lithium aluminate

An alternative material adopted quite early on was lithium aluminate, one of many ternary oxides considered for this application.

#### 1.3.1.2.1 Crystal structure

$\gamma$ -LiAlO<sub>2</sub> has tetragonal crystals with space group  $P4_12_12$  and its enantiomer  $P4_32_12$  [55], shown in figure 1.5.

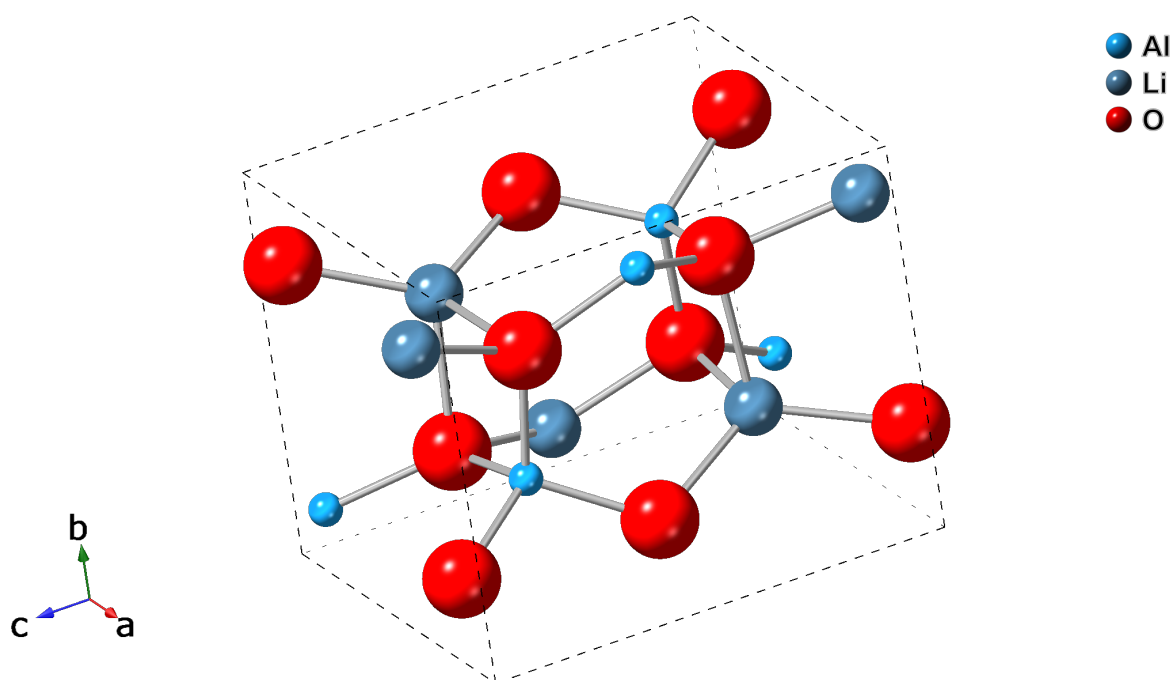


Figure 1.5: Structure of  $\gamma$ -LiAlO<sub>2</sub> according to ICSD card 23815 [55]. With lattice constants  $a = b = 5.17$  Å and  $c = 6.27$  Å. Generated using CrystalMaker<sup>®</sup>.

#### 1.3.1.2.2 Fusion properties

As seen in table 1.1,  $\gamma$ -LiAlO<sub>2</sub> has a series of very desirable properties: high thermal stability and conductivity as well as a relatively low lithium oxide vapour pressure, however, its activation characteristics are a cause for concern: the fusion community aims to utilise — wherever possible — low activation materials [51,56]. Not only this but throughout its time in the research limelight, as noted by Roux *et al.*, revealed a relatively poor tritium release performance [50].

These drawbacks have stopped this ceramic from being considered a viable candidate in a functional fusion device, however, due to their stability and resistance to temperature,

are still used to generate tritium for government stockpiles [57]. This has been done by replacing uranium in fuel rods with  $\gamma$ -LiAlO<sub>2</sub>, however, as noted by Kovari *et al.* in an IAEA report [57], these production methods are not economically or environmentally viable, and have been generally reserved for defence.

### 1.3.1.3 Lithium zirconate

Current international focus has shifted away from these ceramics and landed on three ternary oxides as materials of interest for functional breeder blankets: lithium zirconate, lithium metatitanate and lithium orthosilicate. All ceramic test breeder modules being prepared for ITER utilise these oxides, with shifts in preference occurring frequently [52]. Due to this international push, most current research focuses on these materials with a more recent bias towards lithium metatitanate and lithium orthosilicate [52].

#### 1.3.1.3.1 Crystal Structure

m-Li<sub>2</sub>ZrO<sub>3</sub> has a monoclinic unit cell and crystallises with symmetry  $C2/c$ . Similarly to both Li<sub>2</sub>SnO<sub>3</sub> and Li<sub>2</sub>TiO<sub>3</sub>, lithium zirconate has a rock salt structure in which the atoms form a distorted cubic close-packed network [58]. Layers of oxygen anions are interlaced with layers of mixed metal cations layers in a ratio of Li:Zr of 2:1 shown in figure 1.6.

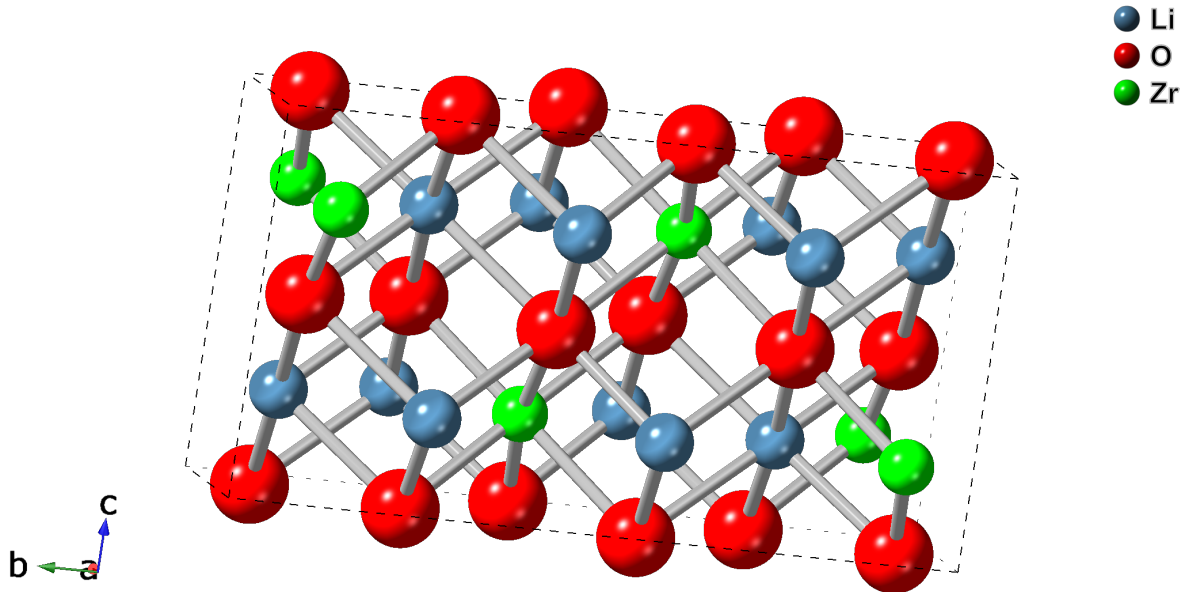


Figure 1.6: Structure of m-Li<sub>2</sub>ZrO<sub>3</sub> according to ICSD card 35236 [58]. With lattice constants  $a = 5.42 \text{ \AA}$ ,  $b = 9.02 \text{ \AA}$ ,  $c = 5.42 \text{ \AA}$  and  $\beta = 112.7^\circ$ . Generated using CrystalMaker<sup>®</sup>.

Figure 1.7 shows that single phase Li<sub>2</sub>ZrO<sub>3</sub> only forms at stoichiometric conditions, with no solid solutions forming around this point. This phase melts congruently at 1968

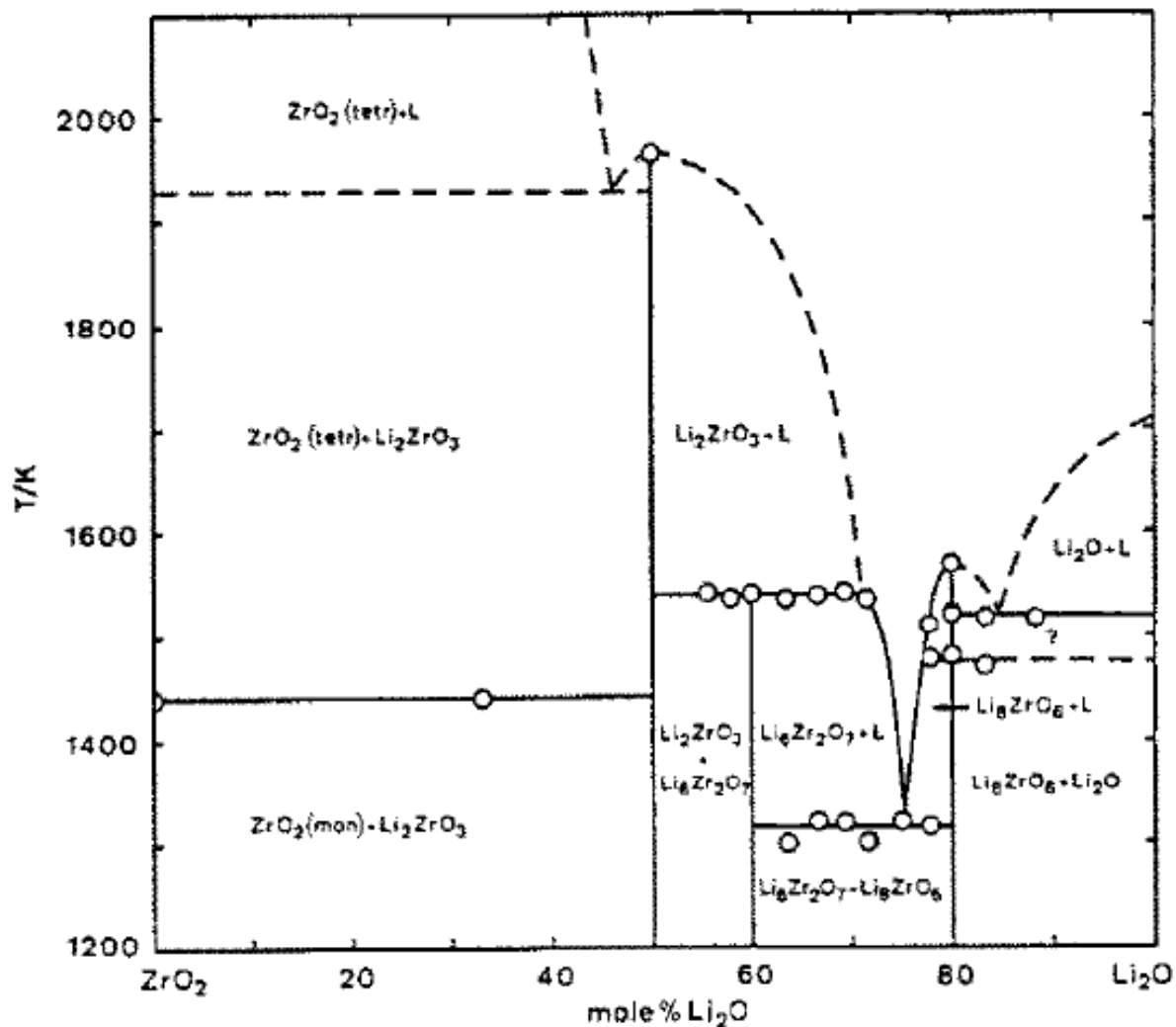


Figure 1.7: Phase diagram of the  $\text{Li}_2\text{O}$ - $\text{ZrO}_2$  system [59].

K [59], far higher than that required for use as a breeder within a fusion reactor and is stable at all the temperatures of interest [59]. A tetragonal phase of  $\text{Li}_2\text{ZrO}_3$  has been identified as forming at low temperatures but irreversibly transforms into the monoclinic phase of interest at around 900 K — lower than usual calcination temperatures [59].

#### 1.3.1.3.2 Fusion properties

Lithium zirconate appeared in literature as a more promising alternative to lithium aluminate, boasting improved tritium release characteristics. Similar concerns were raised by Roux *et al.* however, relating to possible activation issues [45].

Considering in-reactor use, lithium zirconate has no reported compatibility concerns with beryllium and has been shown to remain compatible with 316 L stainless steel in temperatures up to 800 °C [45]. It did, however, show significant solubility in water, with sintered samples being shown to completely dissolve within 1 month [45], limiting

its use within water-cooled breeder systems and raising concerns with regards to storage conditions. In a comparison of dissolution rates by Roux *et al.*, it was noted that, when compared against  $\text{Li}_2\text{TiO}_3$ , dissolution rates were significantly faster, with no dissolution occurring of the titanate detectable after a 40-day immersion.

#### 1.3.1.4 Lithium orthosilicate

Current breeder blanket concepts require a very large amount of beryllium to maintain a reasonable TBR (about 200  $\text{m}^3$  of bulk multiplier for the HCPB concept) [27], therefore ways of decreasing this have been considered. One of those would be the use of a fuel with a higher lithium density. Higher Li density would result in an increase in transmutation events and, therefore, a decrease in required multiplier. One such fuel in consideration is lithium orthosilicate. This ternary oxide is relatively well known as it has been used as an industrial  $\text{CO}_2$  absorber and its lithium density make it an enticing candidate for tritium breeding applications [27, 50, 60].

##### 1.3.1.4.1 Crystal structure

$\text{Li}_4\text{SiO}_4$  is monoclinic and of space group  $P2_1/m$  under ambient conditions [61, 62]. The structure contains 14 formula units and can be seen in figure 1.8.

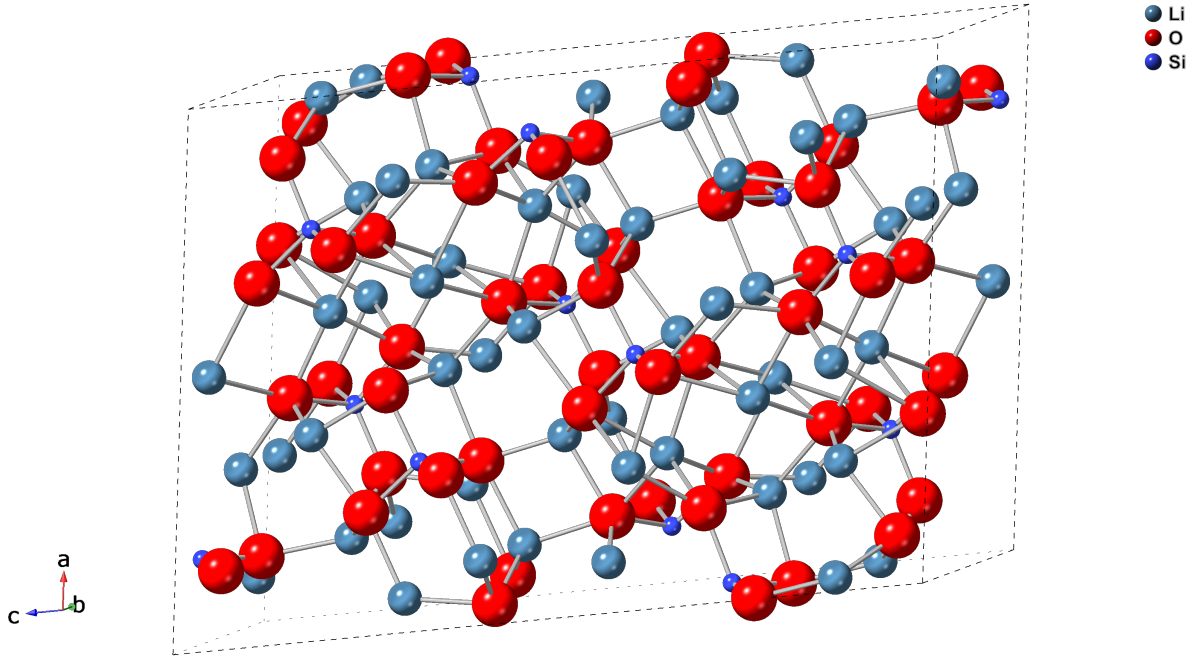


Figure 1.8: Structure of  $\text{Li}_4\text{SiO}_4$  according to ICSD card 21418 [63]. With lattice constants  $a = 11.55 \text{ \AA}$ ,  $b = 6.09 \text{ \AA}$ ,  $c = 16.72 \text{ \AA}$  and  $\beta = 99.1^\circ$ . Generated using CrystalMaker<sup>®</sup>.

According to the binary phase diagram (figure 1.9), single phase  $\text{Li}_4\text{SiO}_4$  forms at stoichiometric composition with a ratio of  $\text{Li}_2\text{O}:\text{SiO}_2$  of 2:1 (33.3%  $\text{SiO}_2$ ). No solid solutions

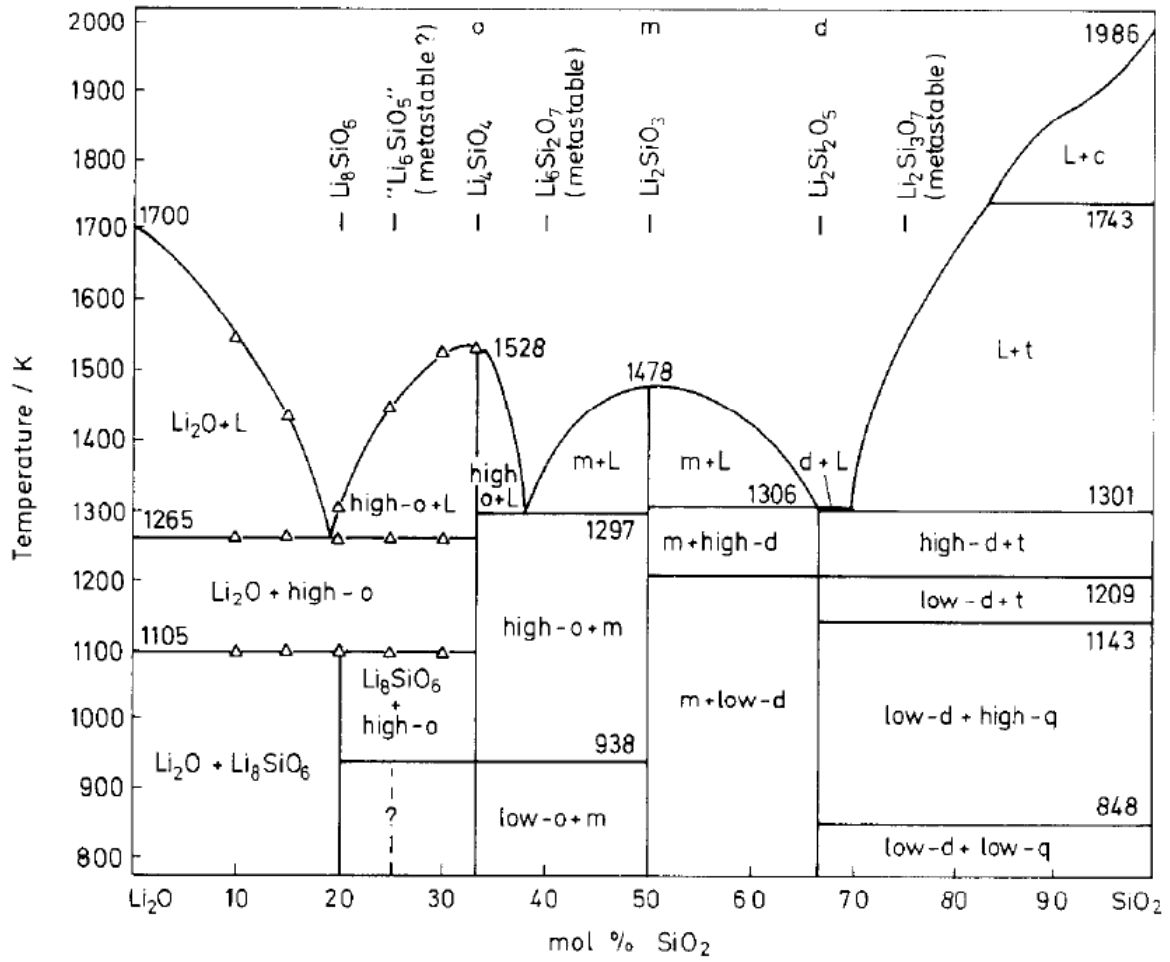


Figure 1.9: Phase diagram of the  $\text{Li}_2\text{O}$ - $\text{SiO}_2$  system [64].

form around this composition. This phase melts congruently at 1528 K and is stable at all the temperatures of interest [64].

Figure 1.10 shows the low symmetry of the crystal, with a large number of reflections with a high degree of overlap, making deconvolution from additional phases complex.



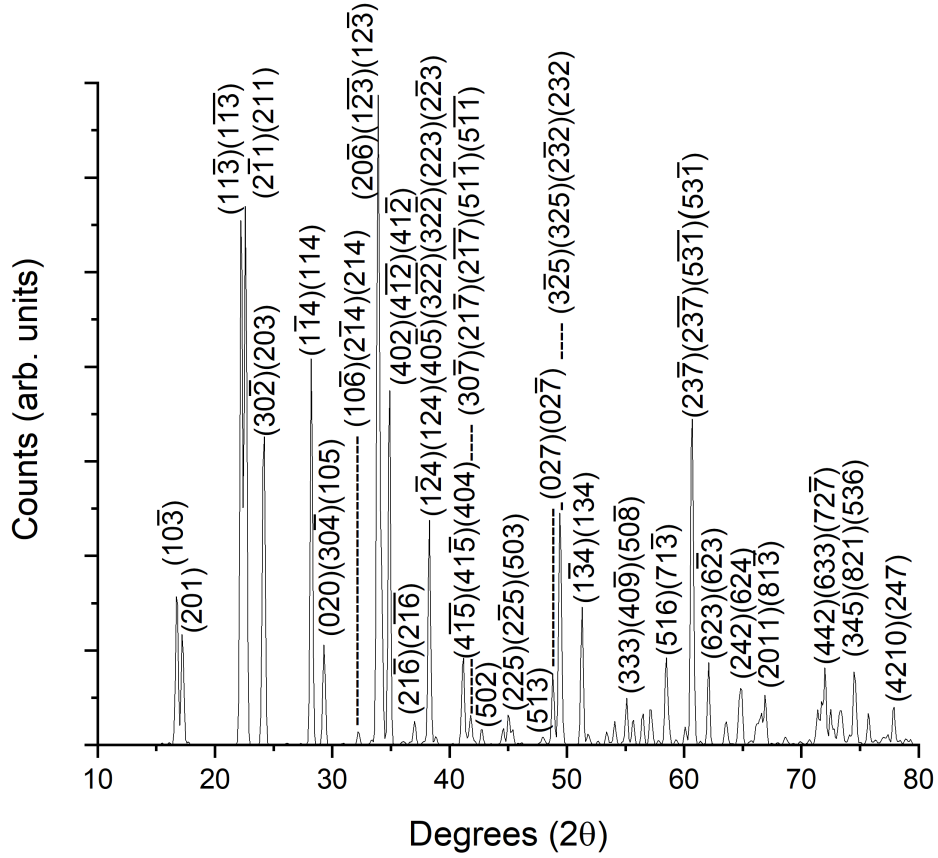


Figure 1.10: Simulated X-ray diffraction pattern of  $\text{Li}_4\text{SiO}_4$ , with fully indexed peaks, according to ICSD card 21418 [63]. Added for reference and comparison in future chapters.

#### 1.3.1.4.2 Fusion properties

Lithium orthosilicate is usually considered to be one of the most promising materials to be utilised as a breeder. However quite a few issues arise when considering its use. Firstly, as may be inferred from its use as a  $\text{CO}_2$  absorber, it quite readily uptakes the gas resulting in the formation of lithium carbonate and lithium metasilicate through the following reaction [65]:



This reaction is reversible [65] but would necessitate a further stage prior to utilisation within a fusion reactor to fully regenerate the material and ensure no metasilicate remains.

The formation of lithium metasilicate phases is undesirable as it has relatively unfavourable properties and a much lower lithium density [66]. These phases are quite common as quite a few mechanisms aid to stabilise them. One such mechanism is the

addition of a lithium metatitanate phase. This phase can form a solid solution with excess lithium therefore resulting in a lithium imbalance, impeding the crystallisation of the orthosilicate phase, as observed by Hanaor *et al.* [67]. Sub-stoichiometric lithium is one condition which leads to its formation and due to the high temperatures normally required to form this ceramic, lithium vaporisation aids to exacerbate the issue [66].

Not only is it susceptible to carbonation but, as with many of the ceramics considered, is hygroscopic [50, 52]. Water absorption is concerning with regards to storage and processing but this is only the case due to the effects of moisture within the reactor. Firstly, the material is intrinsically changed — lithium orthosilicate reacts with water by forming caustic lithium hydroxide and lithium metasilicate (equation 6) [68]. Secondly, the presence of water may have unwanted effects on the tritium release capability of the material. The adsorbed water may have damaged the structural properties [50] and, as noted by Hanada *et al.*, the now moistened surface will retain significant amounts of tritium, affecting release properties [69].



#### 1.3.1.5 Lithium metatitanate

Lithium metatitanate has long been considered a plausible breeder material, but has usually been overshadowed by the much more lithium dense lithium orthosilicate. Recently, as the drawbacks of lithium orthosilicate have become more apparent, lithium metatitanate has been promoted to the most likely candidate for the HCPB design [23].

##### 1.3.1.5.1 Crystal structure

Monoclinic  $\beta\text{-Li}_2\text{TiO}_3$  belongs to space group  $C2/c$  and forms in a distorted rock salt structure [46]. As mentioned previously, this structure is similar to both  $\text{Li}_2\text{SnO}_3$  and  $\text{Li}_2\text{ZrO}_3$ . However, in this case, oxygen anion layers are interlaced with alternate anion layers of exclusively lithium occupied planes and planes of titanium and lithium in a 2:1 ratio [46]. The structure is shown in figure 1.11, where this layered superstructure can be observed in the  $c$  direction.

As seen in figure 1.12 the polymorph of interest forms at stoichiometric conditions, forming solid solutions in a narrow range around this composition. This means that it can adapt in slightly lithium rich/deficient environments, explaining the mechanism noted by Hanaor *et al.* [67] and mentioned above. In lithium rich conditions  $\text{Li}_4\text{TiO}_4$  is formed in combination with  $\beta\text{-Li}_2\text{TiO}_3$  until a Li:Ti ratio of 4:1 is reached (around 33%  $\text{TiO}_2$ ), at which point single phase  $\text{Li}_4\text{TiO}_4$  is formed. This phase decomposes readily, forming  $\beta\text{-Li}_2\text{TiO}_3$  as lithium evaporates from the structure. It has a similar high reactivity to  $\text{Li}_4\text{SiO}_4$ . Conversely, in titanium rich scenarios  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is also formed until around 71%  $\text{TiO}_2$ , where it forms as single phase.

Above 1155 °C lithium metatitanate undergoes a reversible transition into a high temperature cubic phase, melting congruently at 1533 °C. The monoclinic phase is stable throughout the temperatures of interest [70].

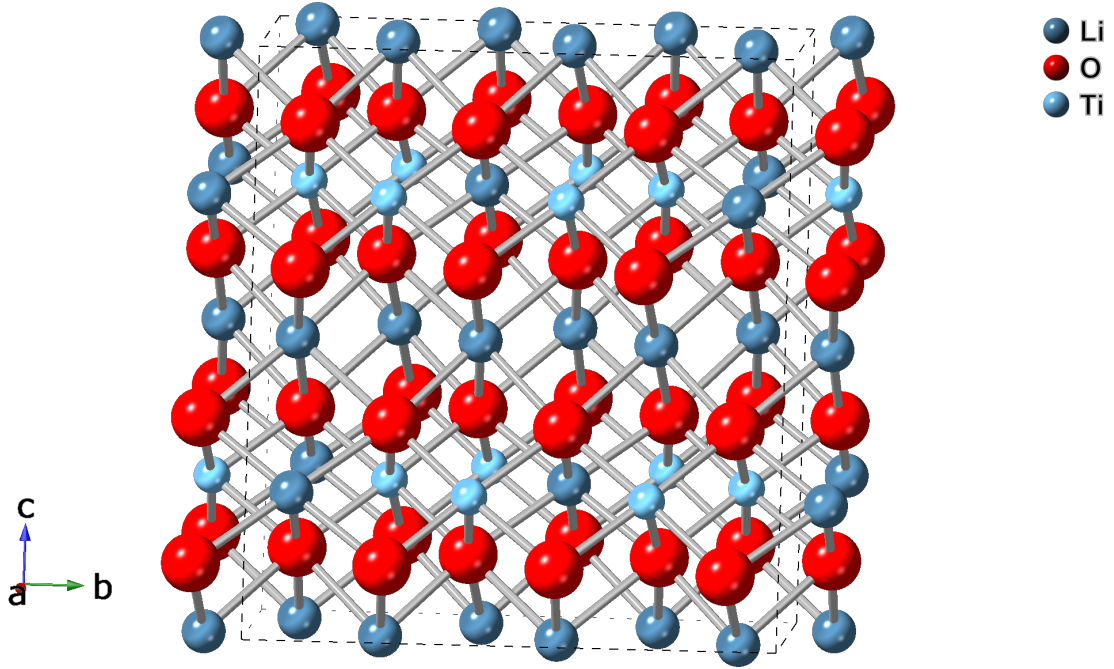


Figure 1.11: Structure of  $\text{Li}_2\text{TiO}_3$  according to ICSD card 162215 [46]. With lattice constants  $a = 5.06 \text{ \AA}$ ,  $b = 8.79 \text{ \AA}$ ,  $c = 9.75 \text{ \AA}$  and  $\beta = 100.2^\circ$ . Generated using CrystalMaker<sup>®</sup>.

As well as the high temperature polymorph a less common metastable cubic polymorph can form at low temperatures,  $\alpha\text{-Li}_2\text{TiO}_3$ . This thermodynamically metastable but kinetically stable phase has been formed at room temperature *via* mechanosynthesis by West *et al.* [71], however it reverts back to the stable polymorph on heating.

The layered structure of  $\beta\text{-Li}_2\text{TiO}_3$ , combined with this low temperature cubic–monoclinic transition leads to the presence of stacking faults, which, due to the slow kinetics of ordering along the  $c$  direction, results in a high annealing temperature for such defects and hence high variance in the X-ray reflections observed in samples processed at differing temperatures [72]. This makes comparing diffraction patterns taken using different temperatures and processing techniques complicated, with diffraction peaks changing intensity or being completely absent when compared to a simulated pattern (figure 1.13).

In part due to this and the different ways the mixed cation, titanium–lithium, layers can be arranged;  $\beta\text{-Li}_2\text{TiO}_3$  can be more accurately described by a probability of short-range ordering in the following three space groups:  $C2/c$ ,  $C2/m$  and  $P3_112$  [72, 73]. The ratio of these three space groups changes with temperature until  $C2/c$  becomes the primary space group when processed at high temperatures [73], hence why this is generally cited as the default  $\beta\text{-Li}_2\text{TiO}_3$  space group.

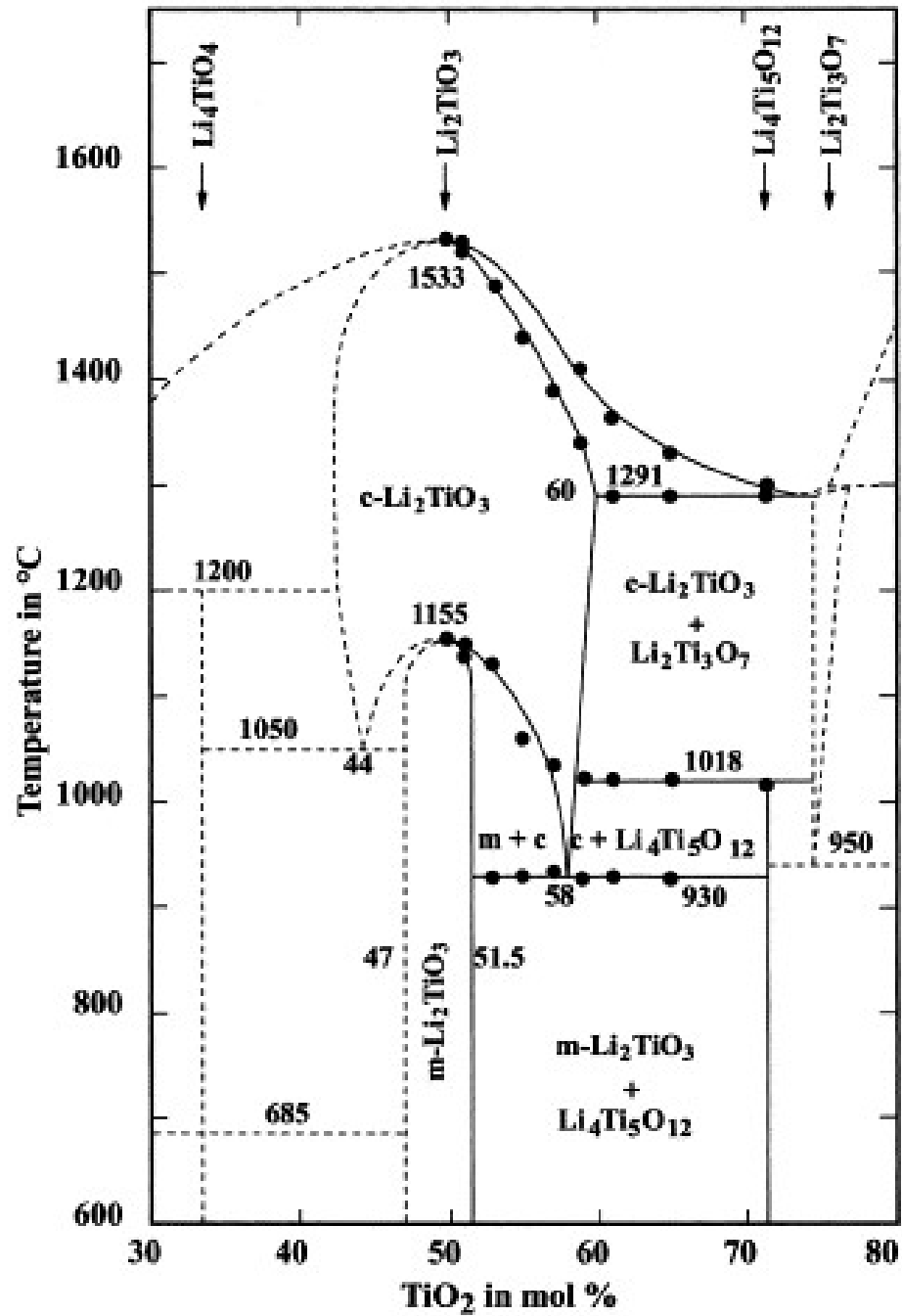


Figure 1.12: Phase diagram of the  $\text{Li}_2\text{O}-\text{TiO}_2$  system [70].

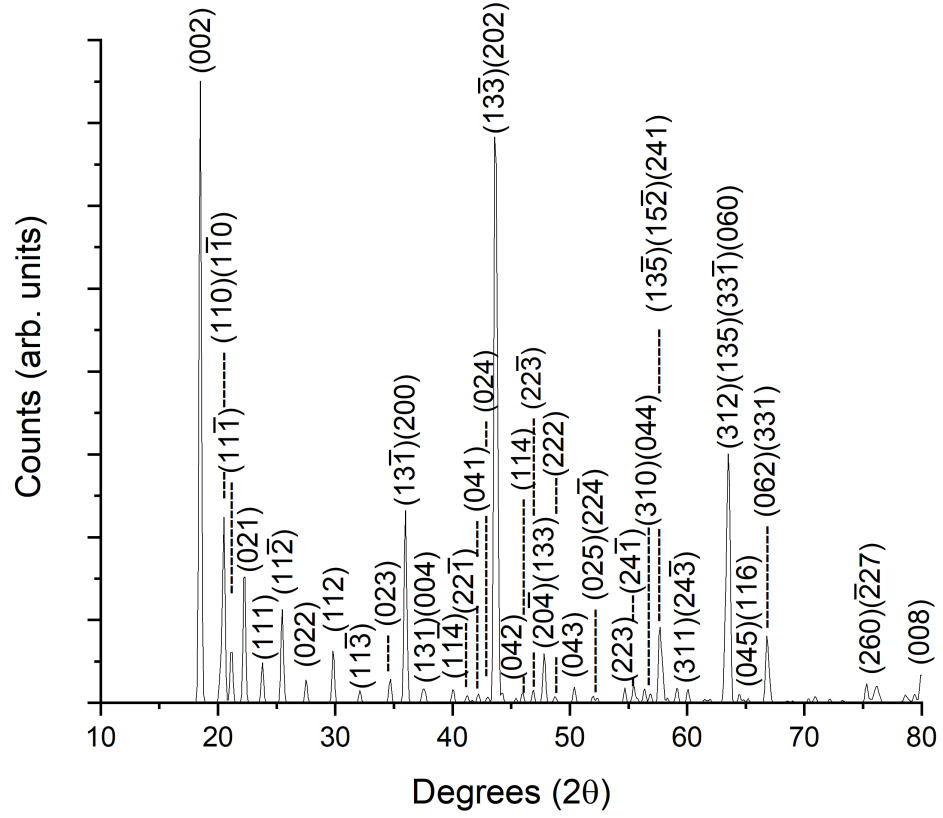


Figure 1.13: Simulated X-ray diffraction pattern of  $\text{Li}_2\text{TiO}_3$ , with fully indexed peaks, according to ICSD card 162215 [46]. Added for reference and comparison in future chapters.

### 1.3.1.5.2 Fusion properties

Lithium metatitanate manages to fulfil many of the desired criteria for a breeder material with few of the previously discussed drawbacks. Unlike lithium zirconate, it doesn't pose any activation concerns and unlike lithium oxide and lithium orthosilicate it has quite high chemical stability. Its mechanical strength is also of note, with the only real drawbacks being a relatively low lithium density and thermal conductivity [50, 74]. A value that exemplifies this is the lithium enrichment necessary for the viability of  $\text{Li}_4\text{SiO}_4$  vs  $\text{Li}_2\text{TiO}_3$ , with the former requiring around 30% enrichment and the latter double at 60% to arrive at a functional blanket (numbers based on the HCPB design to be tested in ITER) [75].

Chemical stability is commonly given as the main advantage of lithium metatitanate, as many other candidates are extremely susceptible to attack by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [50]. Roux carried out a comparative assessment of the dissolution of lithium zirconate and lithium metatitanate: no detectable amounts of dissolved metatitanate were found after 40 days [45]. This, however, fails to address any adsorbed/absorbed moisture which might have been introduced. This moisture has been shown to significantly affect the tritium release in the material [76]. Xiang *et al.* also discuss the apparent moisture insensitivity of lithium metatitanate [77, 78].

Research by Waters *et al.* [79] has demonstrated that even though lithium metatitanate may be more chemically resistant than other similar materials,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  desorption experiments have demonstrated both species are present. This effect is large enough to be of note and warrants consideration when addressing synthesis, storage and transportation of the ceramic. Low reactivity to these species is of close to no concern during operation however, as few current blanket designs are dealing with both solid breeders and a water cooling stream.

Solubility in water is a ubiquitous issue when dealing with these ceramics, for some more so than others. This, together with potential tritium absorption, are the main reasons behind the abundance of helium cooled beds and of principal concern when considering storage, transport and production methods.

In all of these cases a key design choice, when it comes to actual functional plant design, will be the amount of hydrogen utilised in the cooling/purge gas. The presence of hydrogen has been proven time and time again to aid the release of tritium [52] but this hydrogen addition will necessitate a larger tritium purification unit resulting in higher operational costs. As well as this, it has been noted by Hoshino *et al.* that this hydrogen rich atmosphere results in mass loss in at least lithium metatitanate, likely due to the reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  resulting in oxygen loss to maintain electroneutrality [80].

### 1.3.1.6 Other relevant ceramics

Increasing potential tritium breeding ratio whilst reducing the degree of lithium enrichment necessary is key to arrive at an economically sensible fusion device. Higher TBR results in smaller volumes of neutron multiplier required and less lithium enrichment leads to more economic material selection.

To this end, ceramics with higher lithium densities are desirable. Octalithium com-

pounds have been of interest recently due to precisely this [27]. They however are not well researched phases and many either melt/decompose at fusion relevant temperatures ( $\text{Li}_8\text{SiO}_6$  and most probably  $\text{Li}_8\text{PbO}_6$ ) [27] or are an activation concern (namely  $\text{Li}_8\text{ZrO}_6$ ) [44]. To reiterate, low radiation daughter products of applied materials is one of the key characteristics that attempts to minimise the waste management issues ubiquitous with other nuclear technologies; hence the need for low activation materials (*i.e.* materials which result in weakly radioactive waste). Of course as they are not as well researched as the other ceramics mentioned, their synthesis, melting points as well as their interactions with other phases are relative unknowns. However, these ceramics have been calculated by Hernandez *et al.* to result in a 5% increase in TBR, therefore, with further study, these phases may be found to be useable enough to be tested in a test reactor.

Aside from octalithium ceramics two other ceramics have been considered recently, although they run against similar problems to those discussed above. Firstly,  $\text{Li}_3\text{N}$  has likely the highest TBR of any (non  $\text{Li}_2\text{O}$ ) compound discussed [81], however its low melting point and the fact that it contains nitrogen (a problem material due to the formation of  $^{14}\text{C}$  through its activation) will likely preclude its utilisation in fusion applications. Secondly,  $\text{LiF}$ , boasting TBRs comparable to the octalithium compounds, however, it may dissociate at high temperatures leading to highly reactive fluorine gas reaching the separation unit [27].

An interesting research avenue pursued by an increasing number of researchers is the utilisation of a multiphase composite of a high lithium density ceramic such as lithium orthosilicate with lithium metatitanate as a strengthening phase [67, 82, 83].

### 1.3.1.7 Composite materials

Ceramic breeder material choice is an exercise in compromise. No ideal ceramic has been identified, be it for a lack of lithium density, poor stability or high activation. This lack of clear consensus over material selection has led to the consideration of ceramic-ceramic composites as a potential solution [41]. It must be noted that no publications attempt to describe the quasi binary systems relevant to the combinations of said ceramics. Miscibility, chemical interactions and solid solutions are unknown, all of which could potentially be relevant and will change on a per system basis. Higher order composites will compound this complexity and may require deeper study to fully understand and characterise [84].

#### 1.3.1.7.1 $\text{Li}_2\text{TiO}_3 - \text{Li}_4\text{SiO}_4$ system

Knitter *et al.* combines the melt spray method, used currently as a prospective reference material fabrication technique, with additions of titania, aiming to co-form  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{SiO}_4$  in the melt [85–87]. A combination of lithium hydroxide monohydrate, silicon dioxide and titania are mixed and the resultant powder is dehydrated at 150 °C. This dry powder is then slowly ramped to the melt temperature of between 1300 and 1400 °C (depending on lithium metatitanate content). This temperature as well as the fact that a melt is being generated, will increase the lithium vapour pressure, likely leading to lithium volatilisation. The molten material is homogenised for 30 min and dropped

into a liquid nitrogen bath, allowing the pellets to freeze into spheres. The size and shape of these spheres is determined by a multitude of factors (nozzle diameter, pressure of the delivery gas, falling distance), complicating pellet consistency. Additions to this technique are under way to improve process stability and yield [87].

An obvious result of this method is the dendritic microstructure of the resultant pellets, limiting control over said parameter using this method. Anneals at 900 °C in the order of days help transform these dendrites into more sintering-like grains, however, the lithium titanate phase remains dendritic even after a 3 week long anneal. Immediately after quenching the lithium titanate can be found in the metastable, disordered  $\alpha$  form, which Knitter *et al.* attribute to the rapid quenching of the droplets [85]. Other groups still find this phase forming at temperatures above its supposed stability window, however these do not perform quenching on their samples after sintering [88]. Just as with the dendrites, an anneal at 900 °C for a day transforms most of this into the  $\beta$  form.

This method is limited in potential compositions to those achievable with the available equipment, with compositions in excess of 40 mol% of  $\text{Li}_2\text{TiO}_3$  remaining inaccessible due to the increase in melting temperature [87]. Application of this technology to systems with melting temperatures higher than this (approx. 1500 °C) therefore is unachievable — not to mention the higher lithium vapour pressure as the temperature continues increasing. They observe a eutectic point at around 20 mol%  $\text{Li}_2\text{TiO}_3$ , after which, further increase in mol% results in significant increase to mechanical strength. They conclude that a pellet composed of 65 mol%  $\text{Li}_4\text{SiO}_4$  and 35 mol%  $\text{Li}_2\text{TiO}_3$  is the optimum composition for demonstration reactor purposes. This however doesn't include analysis of behaviour under neutron irradiation - including tritium release characteristics, which may be significantly impacted by the dendritic microstructure observed - and hence may be subject to change.

Other approaches aim to generate the desired  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{SiO}_4$  phases *via* hydrothermal method [83,88]. Both Dang *et al.* and Zeng *et al.* follow a similar hydrothermal process to co-synthesise both components together. Lithium hydroxide, fumed silica and titania are uniformly mixed in a solvent consisting of a 1:1 solution of deionised water and ethanol. This mixture was vigorously stirred and allowed to react in an autoclave vessel under autogenously produced pressure at 200 °C for 20 h. This powder was formed into green body pebbles *via* the wet method (freezing a slurry containing the powder using liquid nitrogen) and sintered. Interestingly, even when comparing X-ray diffraction (XRD) of two samples sintered at the same temperature from both groups,  $\text{Li}_2\text{TiO}_3$  seems to be a varying stages of the  $\alpha$ - $\beta$  transition, with no mention of the  $\alpha$  phase in Dang *et al.*'s work. Lithium carbonate was observed in both instances, likely due to the re-carbonation of lithium orthosilicate, with Zeng *et al.* observing complete dissociation in their precursor powders (no detectable  $\text{Li}_4\text{SiO}_4$ ). X-ray diffraction peaks for the resultant  $\text{Li}_2\text{SiO}_3$  were much more intense than those of the coeval  $\text{Li}_2\text{CO}_3$ . No discernible re-carbonation products were visible in XRD of samples post-sintering. This method generates pebbles of consistent nano-scale grains, however no further adjustment seems possible, aside from increasing sintering temperature or sintering time to allow for further coarsening.



### 1.3.1.7.2 Breeder—multiplier composites

Another potentially promising composite would be one combining the two necessary components of the blanket itself: the neutron multiplier and the breeder ceramic. The principal neutron multiplier candidate for such a combination would be beryllia has been attempted by Rath *et al.* [40]. Here  $\text{Li}_2\text{TiO}_3$  was synthesised *via* the sol-gel method as described by Vittal *et al.* [89], with the beryllia prepared separately *via* conventional solid state synthesis. Of note is the significant safety concern, with beryllium being highly toxic and its oxide powder potentially causing cancer and berylliosis [90] on inhalation. This danger is clear from the methodology used by Rath *et al.* to arrive at the precursors prior to synthesis; these were all done aqueously, reducing the potential for aerosolization of any powders produced. Preparation of the final composite was done *via* solid state sintering at a firing temperature of 1375 °C. Again, this temperature is high enough that lithium volatilisation is likely. They found no ternary phase formation as well as general improvements in strength and conductivity over  $\text{Li}_2\text{TiO}_3$  alone. This suggests that properties seem to combine well, although they did not run their own pure samples, relying on literature to assess these values in context. Crush load testing is very dependent on pellet geometry [91], and the validity of this comparison, therefore, must be questioned.

This combined breeder-multiplier simplifies breeder blanket design, as now all pebbles within the blanket would essentially be composed of the same composite material, however, a more pragmatic assessment would lead to questioning the practicality of using such a material. Respirators and other safety equipment were used by Rath *et al.* throughout their study and would now necessitate its use when dealing with the totality of the breeder material in a practical setting, as well as complicating its recycling.

### 1.3.1.7.3 Other composites

Variance in composition can be applied simultaneously with more advanced microstructures in order to further address the issues identified with each ceramic. Hong *et al.* improves lithium density *via* the addition of an  $\text{Li}_2\text{O}$  phase, proceeding to strengthen its stability by confining it to the core of a core-shell structure [92]. However, an immediate issue is identified:  $\text{Li}_2\text{O}$  will react with the  $\text{Li}_2\text{TiO}_3$  used as an initial base ceramic due to the final sintering temperature of 1200 °C, forming  $\text{Li}_4\text{TiO}_4$ , which has poor thermal and chemical stability (similarly to  $\text{Li}_4\text{SiO}_4$ ) [27]. The researchers then pivot to enclose the orthotitanate in a metatitanate shell. Gel casting method was used to “wash” layers of  $\text{Li}_2\text{CO}_3$  from a gel sphere containing  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{TiO}_3$ . The surface layers will therefore be mainly composed of  $\text{Li}_2\text{TiO}_3$  with the  $\text{Li}_4\text{TiO}_4$  confined to the core. The washing method uses the difference in solubility between the two components to preferentially remove one, however, poor control and loss of material in suspension will result in unintended variance in the results. Not only this, but this method will result in the formation of pores where the now dissolved lithium carbonate used to exist, leading to a porous “shell” which may expose the core to elements. Poor bonding between layers and lower Li/Ti ratios than expected were also reported, and may be related to the loss of the gel matrix as its burned during final sintering.

Other attempts at producing biphasic pellets with  $\text{Li}_2\text{O}$  as an enriching phase run into

similar issues due to the high sintering temperatures allowing for reactions between the phases to occur. Another such example is Xiang *et al.* where an attempt to generate  $\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{O}$  pellets resulted in the formation of  $\text{Li}_8\text{SiO}_6$  in combination with unreacted  $\text{Li}_2\text{O}$  [93].  $\text{Li}_8\text{SiO}_6$  is a poor tritium breeding candidate due to its low melting point and increased atmospheric and chemical instability [27].

Compositions with more phases add further complexity and little benefit, however, in the extreme end, “high entropy ceramics” may prove to be much more resistant to radiation damage and retain their mechanical properties throughout the life of the pebble bed [84]. However, these systems are complex and each composition must be tackled individually, with any benefit to the TBR being unclear.

### 1.3.2 Conclusions

Whilst no single ceramic satisfies all criteria required of a useable breeder, they all have their clear advantages over each other. Formation of composite materials is therefore of clear benefit to the pursuit of a viable tritium breeding ceramic, allowing for the generation of combinatory materials, combining the benefits of each of the individual components added.

Difficulties in formation of these composites however, has required the use of exotic synthesis and sintering methods to generate them. These result in limitations imposed by the methods themselves. High temperatures lead to issues such as incompatible sintering temperatures, reaction of phases of interest during heating, and uncontrolled grain growth. Co-synthesis complicates this further *via* the formation of complex chemistries during firing. Formation of advanced structures, such as core-shell, again require bespoke solutions with little capacity for scaling.

Therefore, flexible, low temperature and adaptable synthesis and sintering techniques are necessary in order to reduce the limitations imposed by other methods, and expand the potential compositions and microstructures accessible.

## 1.4 Synthesis methods

It is well-known that the synthesis method is an important consideration for both lab and industrial scale materials. Control over the composition and morphology of the resulting material is of the utmost importance, both for the scope of this project as well as for the application.

Fusion materials have certain requirements when it comes to microstructure and said microstructure is first defined during the synthesis process. A review carried out by Ying *et al.* [94] showed that in general, small grains ( $<5 \mu\text{m}$ ) were required in order to generate the required amount of tritium — tritium release is intrinsically related to the active surfaces available for tritium desorption and tritium propagation is more energetically favourable through intergranular spaces than within grains [95].

The following table (table 1.2) was generated by Knitter *et al.* to contextualise the current reference solid breeder candidates by country, with ITER in mind [1]. These focus on scalable capacity and hence smaller scale experiments are under-represented.

However, all experimental work should operate with these properties in mind and aim to improve upon them.

Table 1.2: Relevant properties, materials and fabrication processes of current reference solid breeder ceramics according to [1]. All methods aim for a pebble sizes of  $\approx 1$  mm.

| Country | Material | Fabrication process<br>(current capacity) | Pebble<br>density (%) | Open/closed<br>porosity (%) |
|---------|----------|-------------------------------------------|-----------------------|-----------------------------|
| CN      | LOS      | Melt-spraying (100 kg/year)               | 94                    | <4/<1.5                     |
|         | LMT      | Extrusion-spheronization<br>(50 kg/year)  | 85                    | <11/<3                      |
| EU      | LOS      | Melt-spraying (250 kg/year)               | 95                    | <1/<5                       |
|         | LMT      | Extrusion-spheronization<br>(150 kg/year) | 90                    | 5/5                         |
| IN      | LMT      | Solid state (200 kg/year)                 | 90                    | 6-9/2-5                     |
| JA      | LMT      | Sol-gel (100 kg/year)                     | 89                    | n.a.                        |
| KO      | LOS      | Slurry dropping (250 kg/year)             | 77                    | 11/12                       |
|         | LMT      | Sol-gel (200 kg/year)                     | 91                    | 5/4                         |

#### 1.4.1 Solid state synthesis

Solid state synthesis is perhaps the oldest form of ceramic chemistry as well as the simplest and most reliable. Even today, solid state synthesis is by far the most common synthesis route in academia. In general, a phase diagram (previously described by probing certain compositions and observing the resultant) is used to find desirable stoichiometries, then stoichiometric amounts of the required oxide precursors are milled and heated to form the desired product [96].

This simple process is driven by contact between reactant particles and subsequent diffusion of the reacting species through the reaction interface. Milling is needed to increase the surface area to accelerate this process and heat is needed to improve the kinetics of the reaction. Another required element is time. Even at temperatures close to the melting point, the reaction rate may be such that several days of firing are required to reach equilibrium. Also, due to the relative inhomogeneity of the system several milling/firing steps may be required in order to arrive at the desired product [96]. All the relevant materials to this project have been successfully produced following this method [66, 97–100].

Even though timescales are at times obstructive, the reliability of this process has resulted in its overreliance, especially for industrial processes [93, 101, 102], generating a high energy cost.

Two main drawbacks can be identified when utilising this method. The first is a lack of control of microstructure. Due to the high temperatures required being well above the recrystallization temperature, any microstructural properties that could have been

inherited from the reactants are lost, and significant grain growth occurs. This results in a large ( $> 1 \mu\text{m}$ ), consistent grain size after firing that offers little to no variation [96].

The second is material loss due to volatilisation. Elements such as sodium and lithium are highly volatile which often results in stoichiometric shifts during firing [103, 104]. A relevant and recurrent example identified in the literature is the formation of a lithium metasilicate phase when firing lithium orthosilicate due to the loss of lithium [66, 105]. This effect is exacerbated by the addition of phases capable of forming solid solutions with lithium, such as the previously mentioned lithium metatitanate example [67].

Measurements from Knudsen effusion mass spectrometry experiments have confirmed lithium volatilisation in all the breeder ceramics discussed [53, 106, 107]. And even though research such as that from West *et al.* [108] suggests that no significant volatilisation occurs in temperatures below  $1200^\circ\text{C}$  — well above the expected maximum operating temperature of  $900^\circ\text{C}$  — other research such as the work by Cruz *et al.* [66] shows that the effects of lithium sublimation can be observed at  $900^\circ\text{C}$  and suggests the onset could be at an even lower temperature. A 1998 review by Johnson *et al.* ranks these ceramics by their lithium oxide vapour pressure as follows:  $\text{LiAlO}_2 < \text{Li}_2\text{TiO}_3 < \text{Li}_2\text{ZrO}_3 < \text{Li}_4\text{SiO}_4 < \text{Li}_2\text{O}$  [52].

Finding an alternative synthesis route could not only aid in microstructural control but also reduce costs, improve lithium retention and possibly improve scalability.

### 1.4.2 Sol-gel

An alternative synthesis method employed quite commonly in the field of ceramic breeder materials is sol-gel synthesis [40, 109–112]. This procedure can be described as a wet chemical synthesis method, granting it a significant advantage over standard SS synthesis: homogeneous mixing.

In this process, a homogeneous, stoichiometric mixture of the desired precursors is prepared. When utilising metallic precursors, the most common form they take is metallic alkoxides [113]. This is mainly due to how readily these hydrolyse. Partial hydrolysis of the precursors is necessary in order to allow for condensation polymerisation between the precursors, resulting in the formation of colloidal particles, giving way to the gel [113]. This process leads to powders made up of branched polymers with complex 3D structures.

Since this process can occur at much lower temperatures, it also results in much smaller particle sizes, due in part to homogenous mixing at the start of the reaction. It also allows for some microstructural control through the use of acid or base catalysis which affects the final morphology [109, 113] (see figure 1.14).

Renoult *et al.* [115] used this method to synthesise all of the ceramics discussed in section 1.3.1, dissolving the alkoxide precursors (aluminium sec-butoxide, zirconium nbutoxide, titanium isopropoxide, tetraethoxysilane) in an organic co-solvent — ethanol in this case — prior to hydrolysis. This allowed them to produce ceramics at lower temperatures than solid state synthesis, with an associated reduction in average grain size. They note that  $\text{Li}_2\text{TiO}_3$  however showed increasing crystallinity until calcination at  $1000^\circ\text{C}$ , after which, sharp peaks in XRD patterns corresponding to monoclinic,  $C2/c$ ,  $\text{Li}_2\text{TiO}_3$  could be observed.

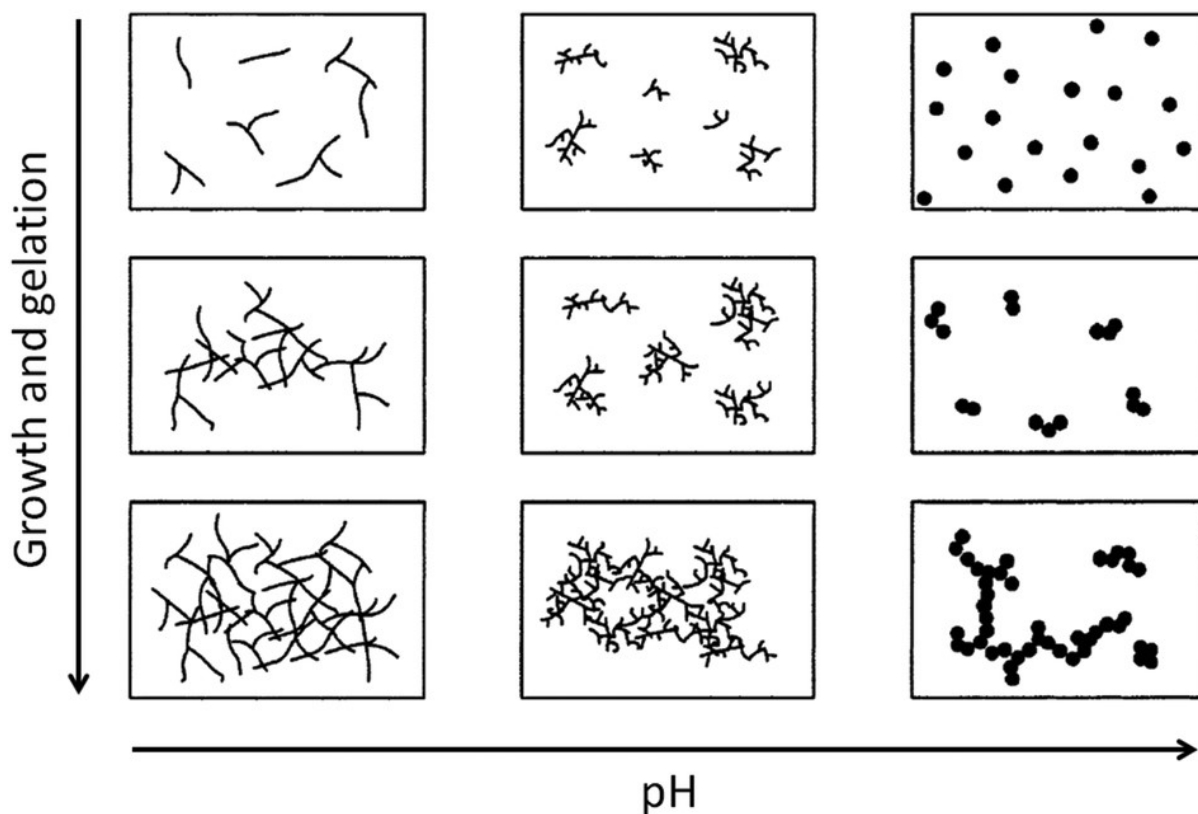


Figure 1.14: Figure showing how pH affects the structure of a gel. Adapted from [114].

The sol-gel technique however, is not limited to the use of alkoxides and organic solvents. Water-based systems are increasingly popular, where the sol may consist of fine colloidal particles or metal complexes with the common addition of chelating agents such as citric acid [114]. Most instances of water-based sol-gel use titanium tetrachloride as a titanium source [40, 116], a hazardous compound which may preclude its use in some labs. Another method was proposed by Wu *et al.* which has become the principal alternative [111]. Essentially they generate in situ tetrabutyl titanate through a series of reactions to then use as the precursor in water-based sol-gel with the aid of citric acid as a chelating agent [111]. Some researchers have noted however, that an alternative titanium source must be found as this method is quite expensive and moisture sensitive [116].

One main advantage of these water-based methods is their ability to produce sinterable beads directly from synthesis, removing the need for spherodization or melt dropping techniques following powder synthesis [111, 116].

### 1.4.3 Ionic liquids

Some alkoxide reagents are difficult to obtain, so synthesis methods which can use a combination of alkoxide and soluble reagents could be an advantage [117]. Non-aqueous solvents offer a solution, these including ionic liquids (ILs) (1-ethyl-3-methylimidazolium acetate most commonly). This approach has a number of advantages and may be used

in two modes which allow for further morphological control. First is their use as solvents for biotemplating. Biotemplating allows for the formation of complex and predictable microstructures through the introduction of biological agents with chelation sites which interact with the positive cations in the metallic precursors [118]. These biotemplates are effective at guaranteeing homogeneity and hence reducing reaction temperature, however the presence of the template itself could result in the formation of overly reduced species, requiring temperatures approaching those of solid state synthesis to ensure complete reaction of those reduced species. This is due to the reducing nature of the carbon-rich template [119].

The other mode of use is to utilise the IL as the chelating agent itself, hence avoiding the addition of any further carbon-rich elements. Many ILs have functional groups similar to those found in common biotemplates and therefore can themselves be used as chelation sites [118]. This reduces the microstructural control provided by the biotemplate but leads to the formation of nanoscale powders. Mottram *et al.* [120] found that following this method results in less formation of the highly-reduced  $\text{TiO}_2$  species and therefore the reaction occurs at a temperature of 600 °C rather than the >1000 °C usually required for solid state. This lower temperature also allows for protection of the nano-scale microstructure achieved through this method.

Green *et al.* identify a wide range of uses for ILs from energy generation and storage to actuators and magnetic field sensors, however there is no mention of its possible use in ceramic breeder materials [119]. No research so far has aimed to apply this synthesis method to create titanates for the ceramic breeder industry.

#### 1.4.4 Deep-eutectics

1-ethyl-3-methylimidazolium acetate, one of the most commonly-used ILs for synthesis has a significant drawback that affects its scalability and wider industrial use: cost. Even though it allows for great precursor flexibility, cost may limit its widespread use [121].

A similar alternative is deep eutectic solvents (DESs). These salt mixtures exploit eutectic points to produce a mixture with a melting point within the desired temperature range. A wide variety of such mixtures have been identified and categorised by Smith *et al.* [122]. The main advantage they have over ILs is their cost. As an example, one such salt mixture is choline chloride and malonic acid in a 1:1 ratio, with both components being of very common industrial use [121]. This wide range of possible compositions also allows for significant versatility whilst lowering costs [123].

DESs can be utilised as almost analogues of ILs as, even though their chemical properties differ, their physical properties and their chelating ability are similar enough that methods can be directly transferred [118].

Research by Boston *et al.* [124, 125] demonstrated its use with titanates by utilising the choline chloride/malonic acid DES to form barium titanate and strontium titanate. Using titanium isopropoxide and a barium acetate solution they managed to form single phase barium titanate at a temperature 400 °C lower than possible through conventional solid state [124].

A significant worry when dealing with some of the more common DES combinations

is chloride ion retention. In the previously mentioned work by Boston *et al.* they identify this as a possible issue but their data seems to suggest that, if it is indeed happening, it is happening at low enough concentrations that it is below the detection limit of the energy-dispersive X-ray analysis (EDXA) equipment used to characterise it [124].

As DESs have become more popular — seen as greener and cheaper alternatives to ILs — many reviews have been conducted looking at the potential applications of these solvents [121, 122, 126]. A wide variety of applications have been identified since the original work by Abbott *et al.* [123], however, this wet synthesis technique hasn't seen use in the production of lithium ceramics for breeder materials. Lower synthesis temperatures would be intrinsically beneficial, by reducing potential for lithium volatilisation, and would also allow for the formation of smaller grained precursor powders.

#### 1.4.5 Other methods

Other methods include hydrothermal [127] and melt spray [85, 128], as described in section 1.3.1. Researchers from the Kunming University of Science and Technology [128] and the Karlsruhe Institute of Technology (KIT) [85] have shown that melt spray technology can be utilised to produce high density lithium orthosilicate pellets by directly pouring the reacted melt into a cooling solution, therefore also simultaneously sintering it. This method however runs into several compositional issues due to lithium vaporisation and crucible contamination. Cracking is also an issue due to the extremely high cooling rates required to solidify the pellets from the melt, with long anneal times required to normalise the resulting dendritic microstructure.

#### 1.4.6 Conclusions

Lithium ceramics benefit from low temperature synthesis techniques as these avoid reaching the high temperatures related to lithium volatilisation. These low temperature synthesis techniques, by virtue of their lower operating temperatures, also allow for the formation of powders of smaller and more varied microstructures.

From the techniques addressed, DES synthesis seems to strike a balance between economically and environmentally sustainable while still showing promise in lowering synthesis temperature of ceramics, regardless of solubility of the relevant precursors. However, all of the work done to address temperature and microstructure at this stage can be undone when forming solid pellets from these starting powders. Hence sintering techniques must also adapt to retain microstructures generated during synthesis.

### 1.5 Densification methods

In very few applications the final form of the product is a powder and hence, ways of densifying this powder are necessary. Pellet densification aims to form a solid object from the powder and in many cases strives to reach a density as close as possible to the material's theoretical density. Depending on the densification technique, however, the work done during synthesis to guarantee a specific morphology could be completely undone as the temperature utilised may allow for significant grain growth.

With regards to the materials for breeder blankets, Knitter *et al.* suggested that improvements in densification techniques could result in higher densities but, subsequently, lower open porosity which has been linked to higher tritium release [129]. Ying *et al.* also note this balance between open porosity and density [94]. The fusion community however, now acknowledges that a higher density is more desirable in order to arrive at the desired tritium breeding ratio (TBR) [95]. The presence of pores (more specifically closed pores) also lends itself to possible tritium retention as well as swelling and cracking of the pellets. Improvements in densification techniques that still allow for microstructure control could be key in multiple applications, from batteries, to catalysts to, of course, fusion breeder materials.

### 1.5.1 High temperature sintering

No matter the synthesis route, the overwhelming majority of ceramics are densified through the same sintering process [124, 130–133]. High temperature sintering has been utilised since prehistoric times [134] and as such has demonstrated reliability and the capability to produce high density ceramics. Most modern methods introduce a pressing stage, forming a ‘green body’ which is then sintered in a high temperature furnace. Two fundamental phenomena occur during sintering: densification and grain growth [135]. The driving force behind this is the reduction in total surface energy of the system [135].

Generally, this reduction is primarily driven by surface curvature, although many other forces can be applied to allow for a reduction in free energy, such as application of external pressure and/or the use of a densifying chemical reaction [136]. The following equation shows how initial particle size relates to the decrease in free energy if a fully dense body were to be formed from a population of particles:

$$E_s = \frac{3\gamma_{sv}V_m}{a} \quad (7)$$

$E_s$  represents the decrease in surface free energy,  $\gamma_{sv}$  is the specific surface energy,  $V_m$  is the molar volume and  $a$  is the particle radius. It is clear that the decrease in surface energy is inversely proportional to the particle size. This is the reason behind the need for significant processing prior to sintering, with smaller particles (and therefore higher starting surface free energy) leading to faster and/or lower temperature sintering. Smaller particles also lead to an increase in fluidity which may aid in initial compaction of the green body and hence sintering times.



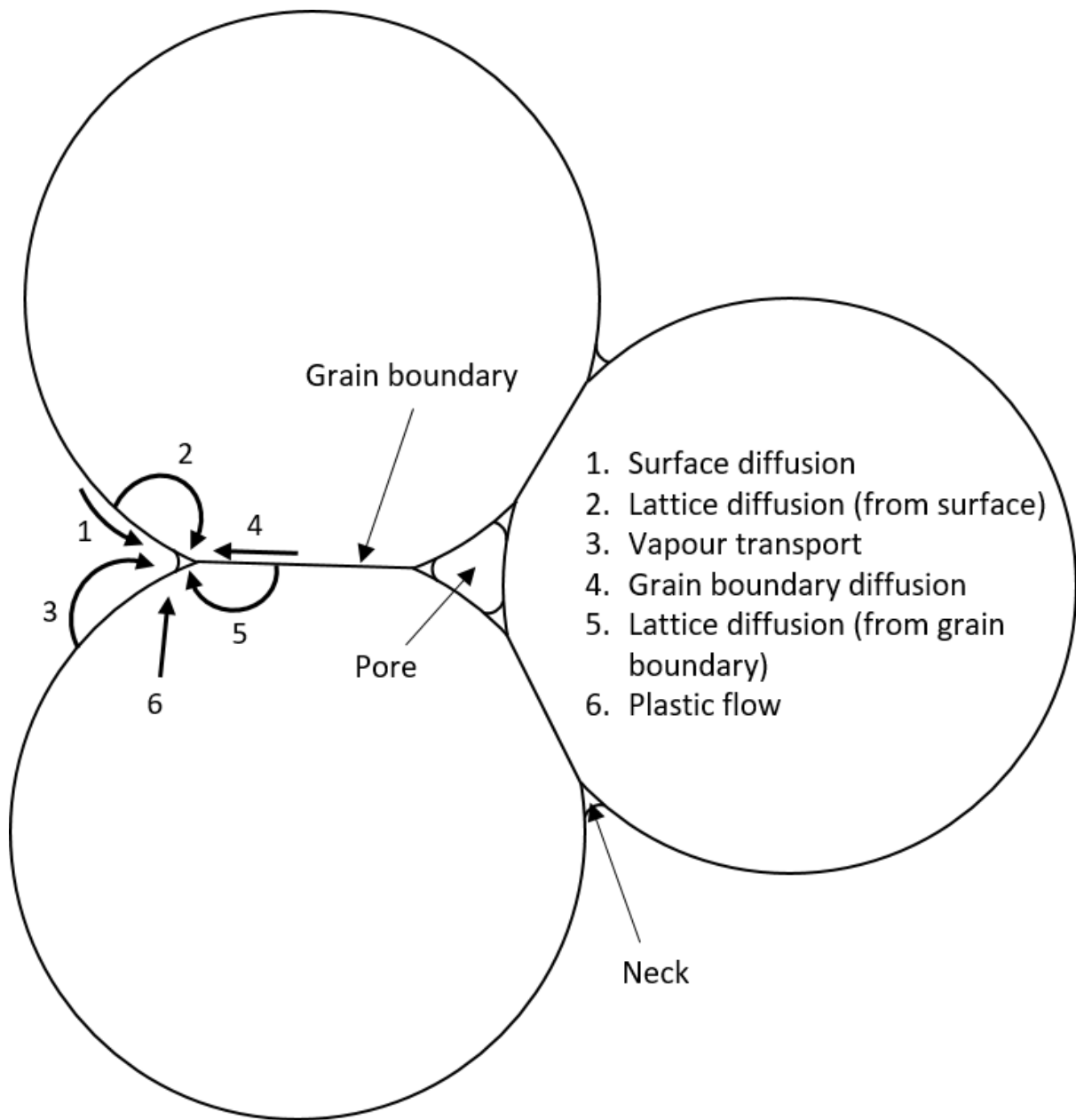


Figure 1.15: Diagram showing six mechanisms that contribute to the sintering of polycrystalline materials. Mechanisms 1 to 3 are non-densifying, 4 to 6 are densifying. Adapted from [136].

This is a greatly simplified relationship however, and in polycrystalline materials, a variety of mechanisms determine the progressive shape, size and porosity of the sintered ceramic (see figure 1.15). Firstly, there are the non-densifying, such as surface diffusion (1), lattice diffusion from particle surfaces to the neck (2), and vapour transport, (3) which is further limited by the material's vapour pressure as well as the contact area of the solid/vapour interface. Even though these mechanisms are non-densifying they still result in neck growth, reducing surface curvature and, as seen from equation 7, resulting in

a reduction in surface free energy and therefore slowing the rate of densification [136,137]. This provides a secondary way for the reduction of surface free energy: coarsening or grain growth.

Secondly, the principal densifying mechanisms, grain boundary diffusion (4) and lattice diffusion from the grain boundary to the pore (5), dictate the flux of matter from the boundaries to the pores. The relationship between this and grain size is shown in equation 8 as diffusion distance changes. Plastic flow by dislocation motion also leads to densification and neck growth, however it is much more common in the sintering of metal powders.

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{K}{G^m} \quad (8)$$

$K$  is a temperature-dependent constant and  $G$  is the grain size with the exponent  $m$  being larger for grain boundary diffusion (mechanisms 4 and 5) than lattice diffusion (mechanism 2). Essentially, rate of densification is inversely proportional to grain size, therefore, rapid coarsening causes a rapid reduction in densification rate, leading to the long sintering times required to achieve high densities [136]. The two fundamental phenomena that occur during high temperature sintering are at odds, and results in a high energy investment required to achieve the properties of interest, with grain coarsening being mostly unavoidable.

#### 1.5.1.1 Liquid phase sintering

Liquid phase sintering can improve densification rates. Many systems previously thought to simply involve solid state sintering involve a small amount of liquid during sintering. A disadvantage when utilising liquid phases is that they tend to remain as glassy intergranular phases that may affect the overall properties of the final sintered ceramic. In traditional, clay-based ceramics this intergranular phase is what leads to their glassy appearance after cooling [118]. The presence of a liquid phase allows for enhanced particle rearrangement of the solid grains as well as enhanced matter transport through the liquid.

The presence of the liquid also allows for the elimination of the solid/vapour interface, as now the pores will form in the liquid, with the reduction in the new liquid/vapour interfacial area being the driving force for densification.

$$\Delta p = -\frac{2\gamma_{lv}}{r} \quad (9)$$

Here,  $\gamma_{lv}$  is the specific surface energy of the liquid/vapour interface with  $r$  being the radius of a spherical pore and  $\Delta p$  being the compressive stress generated on the particles which is equivalent to placing the system under an external hydrostatic pressure of the same magnitude.

Generally, liquid phase sintering proceeds via first; the distribution of the liquid and rearrangement of the solid particles, then; densification via solution-precipitation, and finally; sintering driven by the mechanism described in equation 9 and dominated by Ostwald ripening. Coarsening together with grain shape accommodation, allows for more

efficient packing, which leads to the flow of liquid from these highly packed regions into pores, aiding further densification.

The solution-precipitation mechanism leads to the more rapid dissolution of smaller particles resulting in fast Ostwald ripening as diffusion through the medium is enhanced [136, 137]. This also means that as liquid volume is decreased, matter transport is accelerated, hence resulting in faster grain growth. This again introduces a balance between coarsening and densification, as a low liquid volume results in small amorphous intergranular material fractions with rapid coarsening, and high liquid volume results in higher densities with much higher amorphous intergranular material fractions, which may be deleterious to the device being fabricated.

It must be noted that in most liquid sintering systems the liquid phase is supposed to remain in the system post-sintering, *i.e.* the material should be persistent in order to see the benefits listed above. A transient liquid phase usually results in swelling of the compact as it either incorporates into the solid phase (increasing grain volume) or evaporates (increasing pore volume). This therefore limits the applicability and flexibility of the liquid sintering method to systems with eutectics or additives that don't significantly affect the properties of the final compact.

#### 1.5.1.2 In fusion

In applications where density is paramount this sintering method is usually applicable without any major drawbacks but, in situations where the microstructure produced through the synthesis route is of interest, this method will disrupt and permanently modify the microstructure. It is also commonly the case that the temperatures required to achieve high densities are high enough to induce severe volatilisation in systems with lithium or sodium content [130].

In the examples discussed in section 1.3.1 [40, 83, 85–87, 92, 93], they all use high temperature sintering to form final solid pellets — with the notable exception of Knitter *et al.* which use a melt spray method which combines synthesis and sintering into one step [87]. This high temperature, solid state sintering method is used in spite of it clashing against the aims of the research. Clear examples are Xiang *et al.* and Hong *et al.*, both of which are unable to form pellets with  $\text{Li}_2\text{O}$  as a component due to its reaction with other phases at sintering temperatures [92, 93].

Alternatives to high temperature sintering are sorely needed, from an environmental perspective, from an economic perspective, from a scientific perspective and may prove invaluable to refine and fine tune morphology and phase diversity in a multitude of industries desperately looking to do so (fusion breeder ceramics being a clear example).

#### 1.5.2 Cold Sintering

Diversifying densification mechanisms, especially at low temperatures, is singularly useful for dealing with particularly volatile species or particularly important microstructural characteristics. Many alternative sintering methods exist (field assisted sintering technology (FAST) [138], flash sintering [139], spark plasma sintering [138], microwave

sintering [88]) but most if not all still require the use of high temperatures (lowering conventional sintering temperatures by, at most 10 – 20%) [140] and introduce new issues: carbon contamination and reduction in the case of spark plasma sintering [138, 139].

A relatively new low temperature technique is the Cold Sintering Process (CSP) [141]. First identified by Jantunen *et al.* [141] and further developed by Randall *et al.* at The Pennsylvania State University [142], it shows promise for the fabrication of dense pellets at temperatures around 100 - 300 °C, with few of the drawbacks associated with regular sintering [142].

Similarly to liquid phase sintering, CSP works by introducing a transient solvent such as water to hydrate and dissolve the starting powder, as shown in figure 1.16. This dissolution produces a supersaturated solution around each particulate which will precipitate as the solvent is driven out *via* the application of heat (<300 °C) and pressure (100-800 MPa) filling in the intergranular voids [125]. This liquid phase also aids rearrangement of the particles enhancing densification [143]. Terrace ledge kink growth has been shown to be a major mechanism through which free surface energy is reduced [142, 144], although this mechanism is quite restrictive as it requires nanoscale powders with pristine crystalline surfaces, raising scalability concerns [125]. Most CSP work is carried out in a hot uniaxial press at ambient conditions — which have been shown to affect the resultant ceramic and hence, may be necessary to control in certain applications [145].

This process has been proven to produce pellets of density comparable to those formed through conventional sintering in materials such as  $\text{Li}_2\text{MoO}_4$  and  $\text{Na}_2\text{Mo}_2\text{O}_7$  [142, 146]. The development of this process is relatively material-dependent and parameters have to be optimised empirically [143]. For materials that readily dissolve in water this method works to reliably produce fully dense ceramics, but in cases where the material is more stable or insoluble, a more proactive approach is required [147].

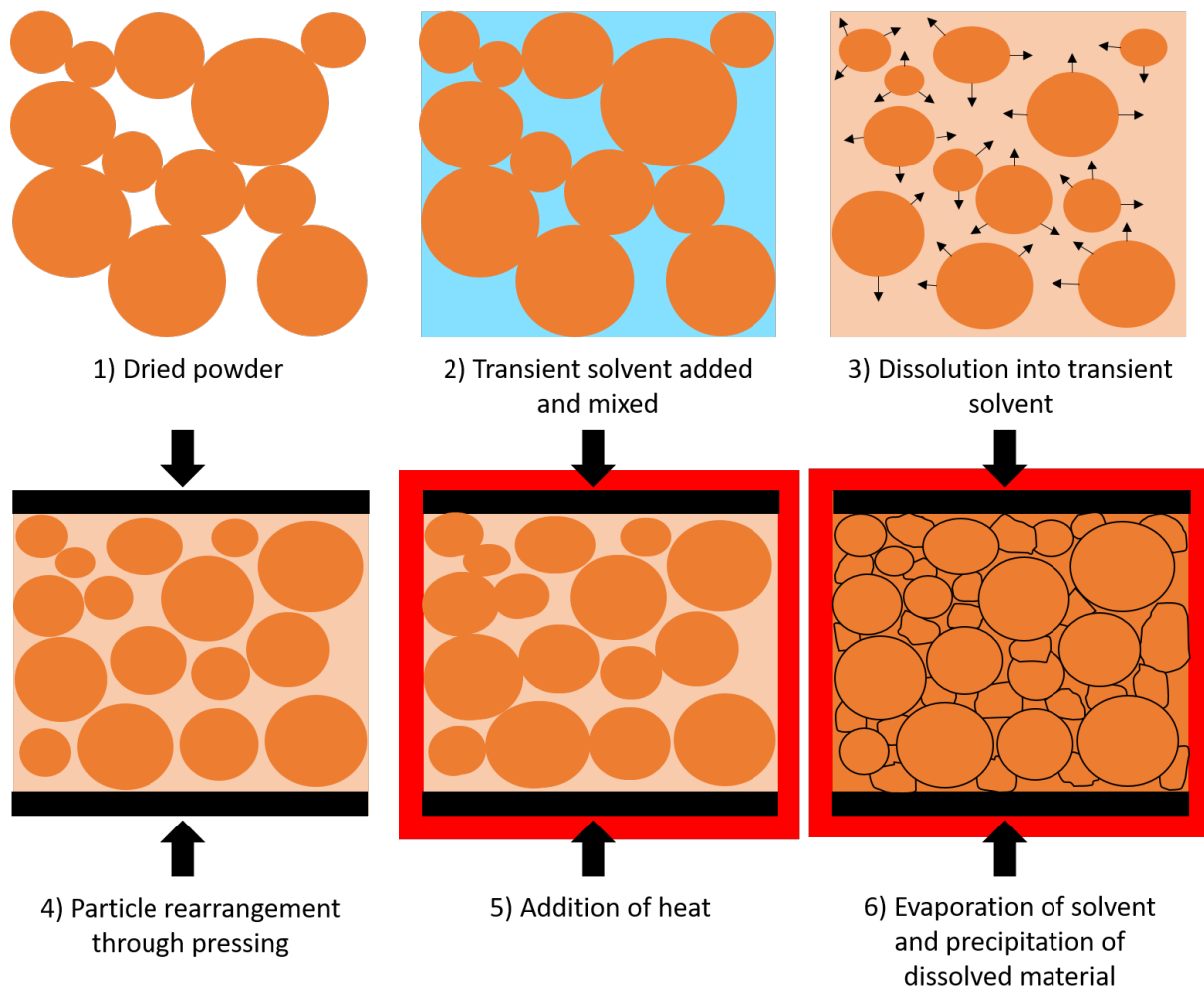


Figure 1.16: Diagram showing the steps in basic cold sintering operation. Adapted from [143].

In insoluble materials, an infill phase must be produced in order to imitate the intergranular redeposition mechanism without reliance on a dissolution-driven supersaturated solution. This mechanism was recently demonstrated by Boston *et al.* [125] through the utilisation of a  $\text{SrCl}_2$  and titanium dioxide nanopowder infill. On heating, this infill phase imitates the reaction found in the DES synthesis of  $\text{BaTiO}_3$  (see section 1.4.4) in order to produce micro-reactions around each particle, forming the desired product and allowing deposition around the grains, as shown in figure 1.17. This “reactive” CSP also changes the mechanism by which the infill phase is precipitated, removing the need for nano-scale powders and increasing the method’s flexibility, introducing the possibility of using starting powders of various sizes [125], since there is no direct interaction between the grains of bulk powder and crystallising infill.

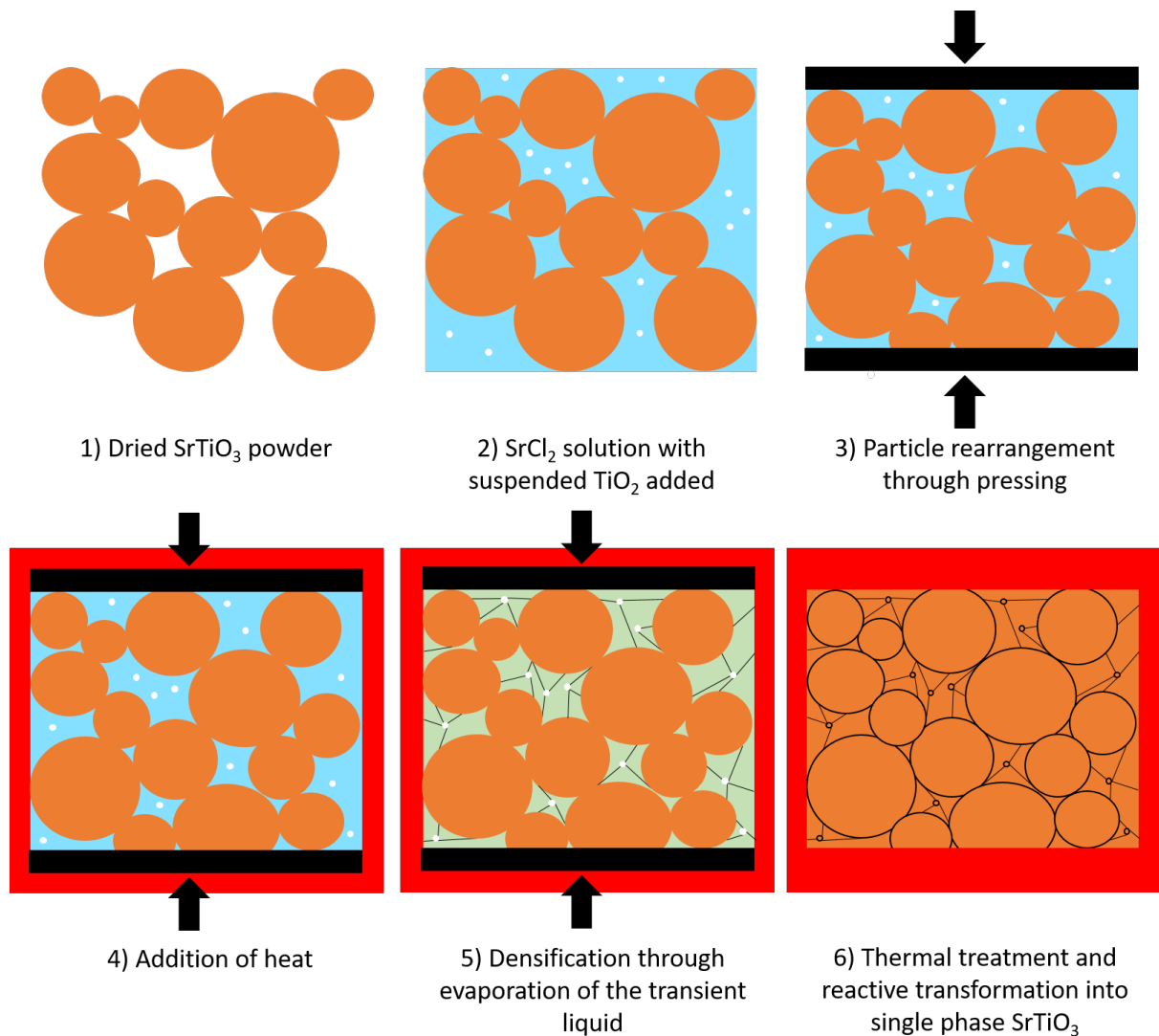


Figure 1.17: Diagram of the reactive cold sintering process in the  $\text{SrTiO}_3$  example. Adapted from [125].

The fact that the starting powder and the infill solution are independent of each other in reactive CSP allows for an intriguing possibility. Firstly, this could allow for the introduction of bimodality into fully dense ceramics; the infill will react to produce a nanoscale product and the starting powder could take any desired size (see figure 1.18) [125]. And secondly, this could allow for the formation of fully dense biphasic ceramics; the infill phase could be made up of a completely different material to the starting powder.

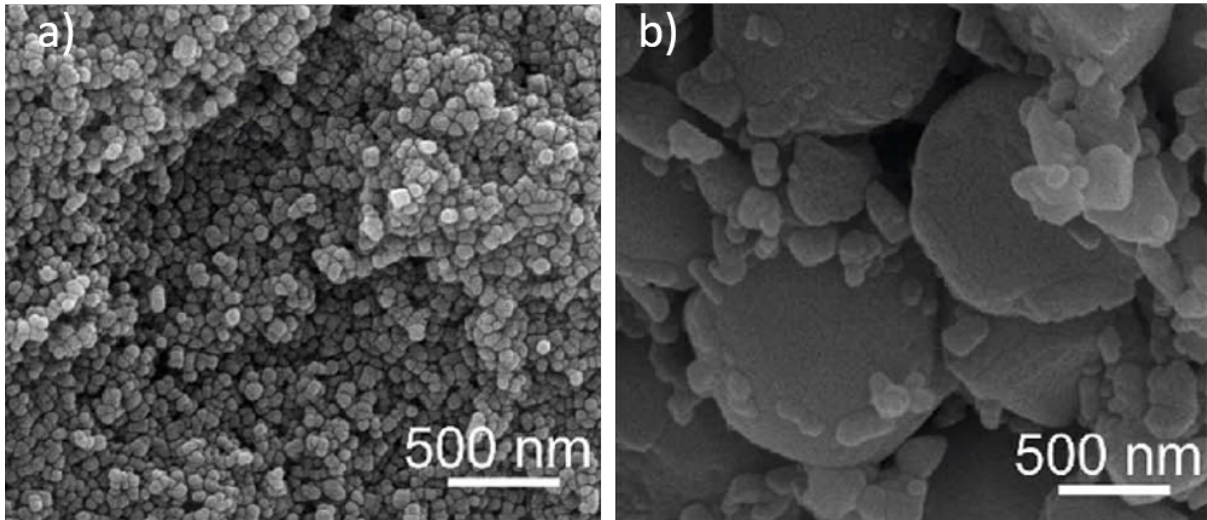


Figure 1.18: SEM micrographs of (a) fracture surface of cold sintered nano-scale and (b) fracture surface of cold sintered micron-scale  $\text{SrTiO}_3$  powder. (b) clearly shows the potential for bimodality with the technique [125].

As with liquid phase sintering, the use of a transient liquid phase may result in the trapping of the evaporated liquid in voids, as well as air trapped during the pressing stage. These flaws will result in poor wetting of the solid/liquid interface as well as the retention of significant pressing flaws. Flow rearrangement whilst under applied load should result in significant void reduction due to trapped air during pressing, which is expected as a drop in the applied load can be consistently observed [125]. As well as this, part of the reason behind the continuous application of pressure throughout the procedure is to drive the egress of the evaporated solvent, avoiding its concentration in any voids present, as the temperatures used aren't high enough for any conventional sintering or coarsening to occur. This pressure however, is limited by the equipment used and is normally in the order of 200 – 800 MPa [142,146] which is enough to drive pore reduction in liquid phase sintering (see equation 9), however the  $\Delta p$  required for pore reduction in this case will likely vary between systems (let alone between regular CSP and reactive CSP) and the time needed as well as the temperature required will also likely need refining in a per system basis.

Neither the CSP nor reactive CSP have been applied to ceramic breeder materials, and considering the low temperatures, high densities and microstructural control provided by the technique it could prove remarkably useful.

Furthermore, the prospect of finding a reliable method to produce biphasic and/or bimodal ceramics to a reasonably high density could be revolutionary in functional materials as well as advanced ceramic breeders. This could allow scientists to combine properties and give more control to tailor ceramics to their applications.

### 1.5.3 Conclusion

The high temperatures required to sinter dense ceramics is a clear limitation in the field. Many applications will benefit from the capacity to sinter at low temperatures yet few ways of achieving this exist. Even in the case of fusion breeding ceramics, where the lower rates of volatilisation and smaller microstructures achievable *via* lower temperature sintering methods are of clear benefit, high temperature sintering is still used in order to maximise density, even if it impedes the formation of compositions of interest. Retaining high densities whilst reducing processing temperatures significantly therefore opens up a wide variety of microstructures and compositions unachievable through higher temperature techniques.

Attempts to diversify densification techniques generally result in additional complexity without a significant reduction in processing temperatures. Cold sintering and reactive cold sintering may address both issues simultaneously; showing promise as a relatively simple, low temperature sintering technique without a significant impact on density or processing time.

## 1.6 General Aims

Based on the literature discussed, several unaddressed issues have been identified. Firstly, the lack of an ideal breeder candidate and the need to produce more advanced materials that tackle their issues. All ceramic solutions have their benefits, however their drawbacks result in significant impact to the efficiency, safety and economic viability of the fusion device as a whole. To address this, multi-phase ceramics aim to combine benefits and remove drawbacks, resulting in improvements to reactor design. New morphologies have not been studied in any detail with this application in mind and may also help in increasing tritium release characteristics.

Secondly, low temperature processing techniques, and especially sintering techniques, are complex, expensive and in many cases lack scalability or do not provide a large enough improvement to warrant their adoption. The benefits of accessing dense ceramic pellets at temperatures approaching room temperature are obvious: stabilising metastable phases, the mixing of previously incompatible phases, retaining bespoke microstructures introduced *via* synthesis and maintaining target stoichiometries susceptible to volatilisation. Considering the needs of the technology, ceramic breeder materials stand to benefit enormously from the development and application of low temperature processing techniques. Novel techniques, such as cold sintering therefore, may significantly improve the flexibility of composition and morphologies available to the industry as a whole; although their application in fusion breeder fabrication has remained untested.

This project aims to marry both, the push towards more advanced ceramic breeder material design and the potential application of novel, low temperature processing techniques.

Single phase  $\text{Li}_2\text{TiO}_3$  formed *via* both, solid state and DES methods, will aim to compare the difference in conditions required. Densification *via* reactive CSP will then be performed using both powder populations, aiming to observe retention of pre-sintering microstructure, therefore demonstrating the method's capability to retain any bespoke



microstructure introduced. Single phase  $\text{Li}_4\text{SiO}_4$  will then be generated and combined with the developed method aiming to introduce a distinct, independent phase, into a fully dense, cohesive, biphasic mass. This will further demonstrate the method's capacity to incorporate different phases at low temperatures.

RCS may allow for bimodality and multiple phases, introducing new fabrication pathways for a wide variety of composites.

## 2 Methodology

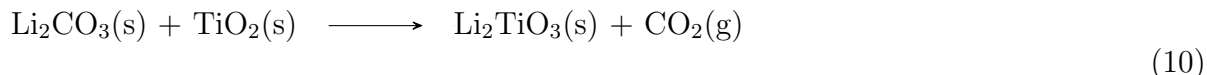
This chapter describes the methods utilised when synthesising, sintering and otherwise processing the materials generated throughout this study. All conditions used in the production of said materials are listed, including heating and drying protocols required, as well as any controls utilised. Characterisation methods and analysis techniques — including instruments used and relevant interpretation techniques — are also listed and thoroughly described. Any assumptions and/or limitations identified with the methods detailed will be listed where appropriate.

### 2.1 Synthesis methods

#### 2.1.1 *Solid state synthesis*

##### 2.1.1.1 Lithium metatitanate

Lithium metatitanate powders were produced *via* a solid state method following the reaction described:



Commercially available reagent powders were used in this synthesis;  $\text{Li}_2\text{CO}_3$  (Acros Organics  $\text{Li}_2\text{CO}_3$  99+% ACS Reagent) and  $\text{TiO}_2$  (Sigma Aldrich, anatase powder,  $\approx$  325 mesh,  $\geq$  99% trace metals basis).

$\text{Li}_2\text{CO}_3$  and  $\text{TiO}_2$  starting powders were fully dried for 12 h at 180 °C and 900 °C respectively. Following this drying step, the powders were batched ( $\text{Li}_2\text{CO}_3$ : $\text{TiO}_2$ ; 1:1 ratio) and ball milled under isopropanol with yttria-stabilised zirconia (YSZ) media for 24 h. The resultant slurry was dried at 80 °C overnight to remove the isopropanol. The dry powder was then sieved through a 250  $\mu\text{m}$  mesh sieve and calcined in an alumina crucible. Calcination was performed in air, in a box furnace. The program started with a 4 h dwell at 700 °C with a ramp of 5 °C/min, followed by a 4 h dwell at 730 °C with the same ramp rate. A first step at 700 °C is necessary to avoid a  $\text{Li}_2\text{CO}_3$  melt [79, 96]. The samples were then allowed to naturally cool down to room temperature. The reacted powder was again milled and dried as previously. The dry powder was then sieved using 150  $\mu\text{m}$  mesh and stored. Based on the propensity of this material to absorb  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (shown in work by Samuel Waters [79] and noted by Xiang *et al.* [77]) the powder was stored in an argon glove box.

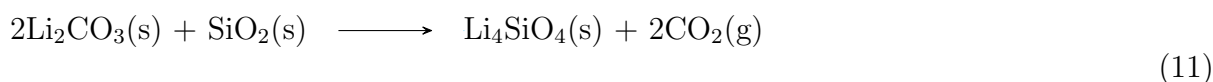
Additional powder was synthesised at an elevated temperature to produce a stock with larger grain size. This allowed for grain growth far above that produced by the method described above. The method was modified by changing the heating protocol: 4 h dwell at 700 °C with a ramp of 5 °C/min, followed by a 4 h dwell at 1100 °C with the same ramp rate.

Masses quoted to 4 decimal places were measured on standard laboratory balances, however the final decimal place was considered to have an accuracy of  $\pm 0.0005$  g to accommodate for fluctuations in the measurements due to changes in environmental conditions.

Changes to this degree were assumed to leave stoichiometry unaffected — transfer losses would far outweigh any potential fluctuation introduced *via* balances. As XRD was used as a first check in most cases, the effect of this mass fluctuation would be impossible to measure as the intrinsic limitations of bulk XRD would limit detection of any impurity or unreacted reagent to 5 wt% of total sample mass [148].

### 2.1.1.2 Lithium orthosilicate

Lithium orthosilicate powders were produced *via* a solid state method following the reaction described:



Commercially available reagent powders were used in this synthesis;  $\text{Li}_2\text{CO}_3$  (Acros Organics  $\text{Li}_2\text{CO}_3$  99+% ACS Reagent) and  $\text{SiO}_2$  (Sigma Aldrich,  $\approx 325$  mesh,  $\geq 99\%$  trace metals basis).

$\text{Li}_2\text{CO}_3$  and  $\text{SiO}_2$  powders were fully dried for 12 h at 180 °C and 900 °C respectively. Following this drying step, the powders were batched ( $\text{Li}_2\text{CO}_3\text{:SiO}_2$ ; 2:1 ratio) and ball milled under isopropanol with yttria-stabilised zirconia (YSZ) as media for 24 h. The resultant slurry was dried at 80 °C overnight to remove the isopropanol. The dry powder was then sieved through a 150  $\mu\text{m}$  mesh sieve and calcined in an alumina crucible. Calcination was performed in air, in a box furnace. The powder was pre calcined at 650 °C for 10 h with a 5 °C/min ramp, once again to avoid the formation of a melt during firing [79,96]. The resultant agglomerated powder was then ground using a pestle and mortar and re-calcined at 730 °C for 12 h with a 5 °C/min ramp in the same conditions. After re-calcination the powder agglomerated into a hard pellet (likely due to sintering aid properties of  $\text{SiO}_2$ ) which was then crushed with a percussion mortar and ball milled in the same conditions described above. The powder was then sieved through a 150  $\mu\text{m}$  mesh. Due to the air sensitivity of lithium orthosilicate, thoroughly understood [52,65,88], described in chapter 1.3.1 and explored in chapter 5, the resultant powder was quickly transferred to an argon glove box. Chapter 5 goes into more detail about the detectable effect and speed at which the reactions identified in chapter 4 affect the final product.

### 2.1.2 DES synthesis

A DES or deep eutectic solvent synthesis method was adapted from work by Boston *et al.* [124].

All chemicals were sourced from Sigma Aldrich. Starting reagents consisted of choline chloride ( $\geq 98\%$ ), malonic acid (99%), lithium acetate dihydrate and titanium isopropoxide (97%).

Choline chloride and malonic acid were mixed in a 1:1 molar ratio (6.8 g:5.15 g) and melted at 90 °C under gentle stirring. 1.0207 g (0.01 mol) of lithium acetate dihydrate was dissolved in the minimum amount of water. The resulting solution was added to the

now molten eutectic. This mixture was allowed to dehydrate completely under vigorous stirring ( $\approx 4$  h), forming a thick gel. A stoichiometric volume of titanium isopropoxide (1.4803 ml) was then slowly added to the dehydrated mixture under stirring. The pale yellow gel was then decanted into alumina evaporation trays and calcined at 650 °C for 4h with a 5 °C/min ramp. The use of evaporation tray-shaped crucibles is imperative to ensure even contact between the sample and air, particularly important for the removal of chlorine. Uneven contact may lead to partially unreacted samples as discussed in chapter 3. The reacted powder was then roughly ground using a pestle and mortar to break apart agglomerates and stored under argon.

## 2.2 Sintering methods

### 2.2.1 *Solid state synthesis*

#### 2.2.1.1 Lithium metatitanate

Lithium metatitanate powders ( $\approx 0.3$  g), synthesised following the methods described above, were uniaxially pressed into green bodies to sinter under atmospheric conditions in a box furnace. Generally, these pellets served as a standard to compare other samples generated throughout this project.

Pressing was done using 10 mm diameter dies. The powder was held at 0.8 T load (roughly equivalent to 100 MPa) for 2 minutes. The resultant green body was extracted and placed in an alumina boat and sintered in a box furnace in air at 1100 °C for 6 h with a 5 °C/min ramp. Sintering temperature was chosen following findings from Sam Water’s thesis [79], in order to give this pellet population the highest density possible whilst maintaining reasonable degrees of lithium volatilisation. Pellets removed from the furnace were immediately stored under an Ar atmosphere.

#### 2.2.1.2 Lithium orthosilicate

Portions of lithium orthosilicate powder ( $\approx 0.3$  g), synthesised following the methods described above, were uniaxially pressed into so called “green bodies” to sinter under atmospheric conditions in a box furnace. Generally, these pellets served as a standard to compare other samples generated throughout this project.

Pressing was done using 10 mm diameter dies. The powder was held at 0.8 T load (roughly equivalent to 100 MPa) for 2 minutes. The resultant “green body” was extracted and placed in an alumina boat and sintered in a box furnace at 1100 °C for 6 h with a 5 °C/min ramp. Sintering temperature was chosen following findings from Sam Water’s thesis [79]. Again, pellets removed from the furnace were immediately stored under an Ar atmosphere.

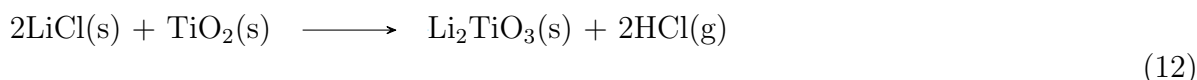
### 2.2.2 *Reactive cold sintering process*

Reactive cold sintering method was adapted from work by Boston *et al.* [125].

### 2.2.2.1 Infill stock production

Commercially available reagent powders were used in this stock material; LiCl (Sigma Aldrich,  $\geq 99\%$ ) and TiO<sub>2</sub> (Sigma Aldrich, anatase,  $< 25$  nm particle size, 99.7% trace metals basis).

This following describes the production of stock solutions — henceforth referred to as the RCS “infills” as their purpose is to fill in the space between particles of original powder material as described in chapter 1.5.2. All infills used in this work were stoichiometrically batched to produce Li<sub>2</sub>TiO<sub>3</sub> following the reaction described below in equation 12. Generally, 5 ml vials were produced containing a 6 M solution of LiCl and 3 M equivalent of a TiO<sub>2</sub> nano-powder ( $< 25$  nm) suspension. Under certain conditions other precursors were substituted for the LiCl to identify potentially unwanted reaction pathways.



Before usage of the stock infill, it was thoroughly shaken to allow the suspended TiO<sub>2</sub> nanoparticles to be mixed throughout and allow for the correct stoichiometry when calcined.

### 2.2.2.2 Introduction of Li<sub>2</sub>TiO<sub>3</sub> phase

Approximately 0.333 ml (equating  $\approx 27\%$  by mass of the final pellet) of the infill solution/suspension was added to 0.3 g of lithium metatitanate powder (produced following the methods outlined in section 2.1.1). The slurry was then ground by hand in a pestle and mortar until it formed a roughly homogeneous paste, at which point it was transferred to an evaporation tray and dried in a desiccator overnight. This step was required in order to address the deliquescent nature of LiCl and will be addressed throughout the thesis.

The now dried mass was briefly ground in a pestle and mortar to break up large powder agglomerates before being loaded in a uniaxial press die (10 mm diameter). The powder was pressed at room temperature with an initial pressure of 750 MPa for 15 minutes to allow for rearrangement and compaction of the particles [125]. The temperature was then raised to 180 °C whilst under load and held for 60 minutes. After this heating step, the system was allowed to cool down completely while under load, the load then released to extract the pellet.

The pellet was then post-annealed in air at 700 °C for 4 hours with a 5 °C/min ramp to allow the infill material to fully react (following reaction 12 and findings in chapter 3). This allowed for the introduction of a portion of material with a morphology unrelated to that of the original lithium metatitanate powder utilised.

Pellets were then transferred to a glove box to be stored under argon.

### 2.2.2.3 Introduction of $\text{Li}_4\text{SiO}_4$ phase

Approximately 0.333 ml (equating  $\approx 27\%$  by mass of the final pellet) of the infill produced was added to 0.3 g of lithium orthosilicate powder (produced following the methods outlined in chapter 2.1.1). The slurry was then ground by hand in a pestle and mortar until it formed a roughly homogeneous paste, at which point it was transferred to an evaporation tray and dried in a desiccator overnight.

The now dried mass was briefly ground in a pestle and mortar to break up large powder agglomerates before being loaded in a uniaxial press die (10 mm diameter). The powder was pressed at room temperature with an initial pressure of 750 MPa for 15 minutes to allow for rearrangement and compaction of the particles. The temperature was then raised to 180 °C whilst under load and held for 60 minutes. After this heating step, the system was allowed to cool down completely while under load and the resulting pellet was then removed from the die.

The pellet was then post-annealed in air at 900 °C for 4 hours with a 5 °C/min ramp to allow the infill material to react (following reaction 12). This allowed for the introduction of a portion of material chemically unrelated to that of the original lithium orthosilicate powder utilised, resulting in the formation of ceramic-ceramic composite pellets.

Pellets were then transferred to a glove box to be stored under argon.

## 2.3 Storage

Storage of all materials investigated required the utmost care and consistency. Both ceramics used have known interactions with components in air, specifically  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , hence storage under an inert atmosphere was deemed necessary in order to maintain the materials in question in pristine condition — reducing the effect of any transient change to the samples, ensuring consistency [45, 52, 65, 79, 88]. While lithium metatitanate is relatively stable in air for short periods of time [45], over long term storage significant adsorbance of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  can be observed; as identified by Sam Water’s [79].

In contrast lithium orthosilicate experiences rapid uptake of  $\text{CO}_2$  immediately upon contact with air. This reversible reaction (equation 5; explored in chapter 4 and 5) leads to the formation a crystallographically distinct phase which could lead to the erroneous conclusion that the experiment in question has resulted in an incomplete reaction or to the potential identification of an incorrect reaction pathway.

Therefore, again, in order to maintain consistency between samples and minimise the uptake of  $\text{CO}_2$ , samples and powders were all swiftly transferred into an inert atmosphere between experiments.

An mBraun glove box full of argon gas at an overpressure of 2 mbar was used to preserve the materials used in as close to their original state as possible.

## 2.4 Characterisation techniques

### 2.4.1 *X-ray diffraction*

X-ray diffraction is a key technique in the characterisation and identification of crystalline phases in both prepared powders and fully sintered ceramics. In this work this

technique is used extensively to identify present phases as well as to investigate and analyse the reaction pathways leading to the formation of the final pellets. The periodicity of crystalline structures allows for the diffraction of x-rays, leading to detectable peaks in intensity when certain conditions are satisfied that result in the constructive interference of the reflected X-rays. This condition is commonly called Bragg's law and shows that at angles of incidence other than the defined Bragg angle the reflected x-ray beams are out-of-phase and the destructively interfere, leading to no signal detection. When referring to x-ray "reflection" it is worth noting that in reality these x-rays are being diffracted, however only those diffracted at the Bragg angle result in the constructive interference which leads to a detection. Figure 2.1 shows a simplified scenario in which an incident x-ray beam is reflected off of two planes of atoms in an ideal crystal.

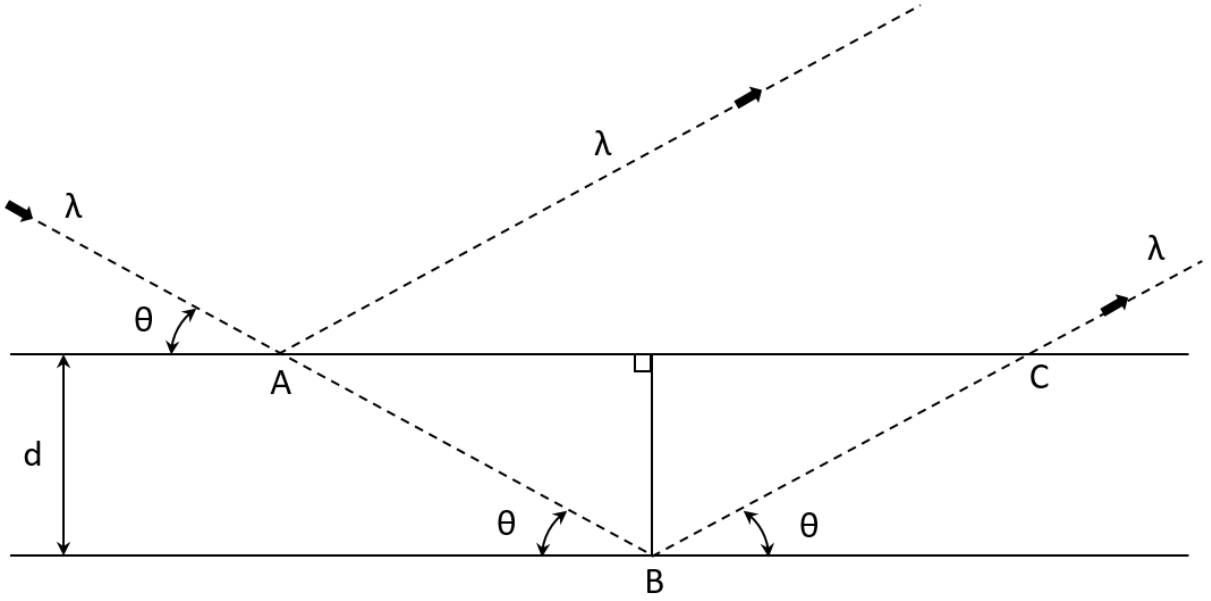


Figure 2.1: Schematic diagram of a simplified scenario portraying the diffraction of X-rays according to Bragg's law. Crystal planes are represented by solid horizontal lines, with waves shown as dashed lines. An arrow shows the direction of the wave.

From the diagram in figure 2.1 it is clear that the path length of the reflected beam is increased as we move deeper into the crystal.  $AB$  describes half of the extra distance travelled by the beam which can be derived trigonometrically from the angle of the incident beam  $\theta$  and the distance between the crystal planes  $d$ . The distance  $AB$  is the same as distance  $AC$  therefore the total additional distance travelled by the beam on this second plane,  $ABC$ , is twice this value, shown in equation 13.

$$AB = d\sin(\theta) \quad \text{and} \quad ABC = 2d\sin(\theta) \quad (13)$$

As constructive interference only occurs when the reflected beams are in phase, we can assume that the additional distance derived in equation 13 must be equal to an integer value,  $n$ , of the wavelength  $\lambda$ . This is shown in equation 14.

$$ABC = 2d\sin(\theta) = n\lambda \quad (14)$$

This equation is Bragg's law and describes the relationship between the incident angle and the distance between crystal planes or d-spacing. X-rays are used in these diffraction studies as the wavelength of X-ray radiation is commonly in the same order of magnitude as the interplanar spacing of crystals, essentially turning the planes in a crystalline material into a diffraction grating, and the diffraction peaks into a fingerprint for the crystal structure.

These diffracting or scattering atoms are directly related to the intensity of the detected signal. The intensity of the scattering produced by individual atoms is called the *scattering factor* [96], and its proportional to the number of electrons possessed by the atom and therefore directly related to its atomic number. This means that it is difficult to resolve the contribution of light atoms to measured diffraction patterns and therefore complicates structural analysis of crystals containing them.

Peak position can also give information on changes in lattice parameters, as changes in the size and shape of the lattice will result in changes to the angle at which the Bragg condition is satisfied. This may be due distortions induced by temperature, or by the addition of doping elements with different ionic radii. However, due to the geometry of the experimental set-up and variation in sample preparation — more commonly — shifts in peak position will be affected by sample displacement, *i.e.* slight differences in height from the expected analysis plane.

Relative intensities can give insight into a multitude other traits of the material being analysed. Assuming the sample to be fully crystalline, and if all the peaks present can be matched to specific materials, the relative intensities of the peaks corresponding to each material can be taken as very roughly proportional to the amounts of each present in the sample. Phase detection in real systems can be complicated as, small quantities of material will lead to small related signals, which may be impossible to deconvolute from background noise. This therefore results in a detection limit for trace materials which will vary between experimental set-ups, but is taken here to be  $\approx 5$  wt%.

Relative peak intensities can also vary for individual materials, perhaps most commonly due to preferred orientation of crystallites; distortion caused by preferred orientation is all but eliminated in powder samples as there are so many crystallites present it can be assumed to be a random system, as all possible orientations are equally likely to contribute to the signal. This issue however can be very visible when analysing solid surfaces as crystals will grow and re-arrange themselves to reduce the overall free energy in the system (which may lead to preferential growth in a certain direction).

Other peak characteristics can be related to certain physical or crystallographic attributes. Peak width observed in diffraction patterns can be related to lattice strain and crystallite size — significant increases in peak width can result in peak overlap which could lead to obfuscation of smaller peaks and increased peak distortion, which is of particular concern when analysing low symmetry crystals. In general, lower symmetry crystals result in more reflections as more features satisfy the Bragg condition.

A combination of three diffractometers were used in the work herein. A Bruker D2 phase, a Malvern Panalytical Aeries diffractometer and a Malvern Panalytical X'Pert<sup>3</sup>



all with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and arranged in Bragg Brentano geometry. Synthesised powders as well as a combination of as-fired and polished surfaces as well as re-ground powders were used to fully characterise the generated material. Re-ground powders were produced by crushing pellets using a percussion mortar and then ground to a fine powder using a pestle and mortar. Low volume material investigated (approx. 1 g) required the use of low-background silicon disk sample holders clipped onto metallic holders. Powder samples were deposited in the centre of the silicon disk, the surface flattened with the help of a glass slide to ensure consistency in sample height when taking measurements. Pellets were placed in a bulk sample holder and pressed down into a bed of putty to ensure measurements were taken with a consistent sample height. Irregular surfaces, particularly in bulk samples, may result in shift in peak positions and broadening which may be erroneously diagnosed as an inherent attribute during analysis.

Analysis and phase identification of XRD data was carried out utilising PDF4+ (ICDD) and EVA 3.1 (Bruker Diffrac Suite) using the database published by the Joint Committee on Powder Diffraction Standards (JCPDS) and the Inorganic Crystal Structure Database (ICSD).

#### 2.4.1.1 High temperature X-ray diffraction

High temperature XRD (HT-XRD) was employed using the Malvern Panalytical X'Pert<sup>3</sup>, fitted with an Anton Paar HTK12N furnace sample heating stage. This technique was used to elucidate potential reaction pathways and phase evolution during heating regimes relevant to synthesis and sintering methods use. Powder samples were loaded onto small alumina discs and once again flattened using a glass slide. Samples were then heated in air following programmed heating regime described in chapter 5.

#### 2.4.1.2 Sample preparation for cross-sectional study

Some of the generated ceramic pellets displayed differences in expected relative intensities consistent with preferred orientation effects (see chapter 3). These effects were thought to be surface-specific and hence a cross-sectional study was carried out to confirm this hypothesis and to quantify this effect.

Pellets were scanned as-fired and then layers of material were ground off, revealing a new, pristine surface to the X-rays. Material was ground off using an 800 grit SiC grinding paper and the new pellet thickness was recorded using a set of callipers. This process was repeated on both sides of the pellet. The ratio of the two largest peaks on the diffraction pattern was calculated. These values were used to calculate the Lotgering Factor of a certain family of peaks and plotted against the amount of material polished.

### 2.4.2 *Scanning electron microscopy*

#### 2.4.2.1 Imaging

Scanning Electron Microscopy was used to examine the morphology of the synthesised powder and as-sintered pellets. Micrographs were also used to estimate particle size and

to extract qualitative information about the ceramic: porosity, degree of grain growth, and general location of secondary and/or introduced phases.

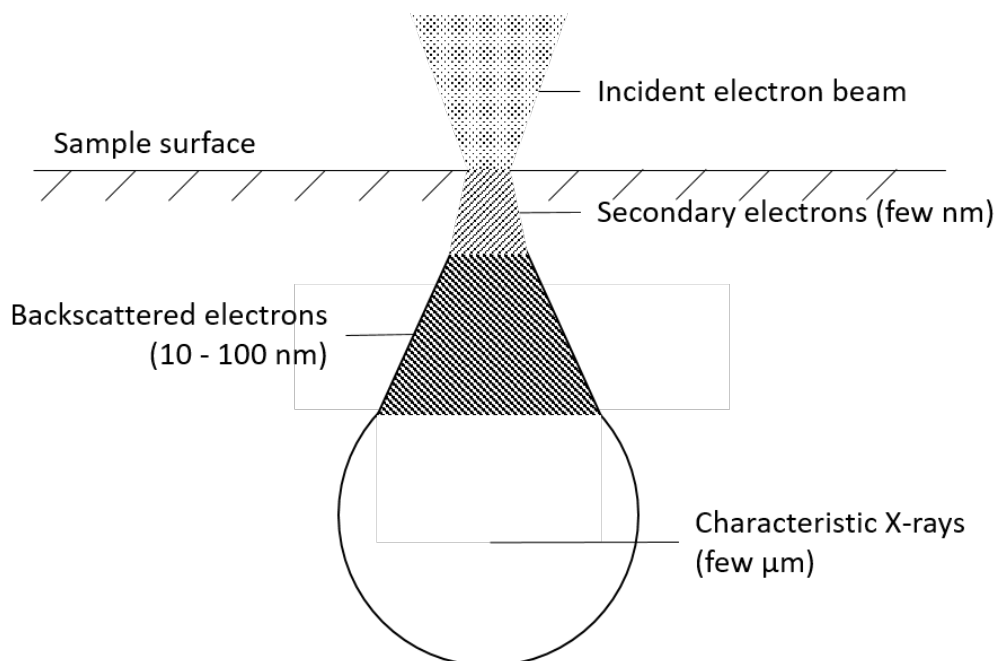


Figure 2.2: Basic diagram of interaction volume and escape depth of various quanta.

This technique utilises a beam of generated electrons, focused into a small probe with the aid of electromagnetic lenses, which is then rastered across the surface of the sample. These electrons interact with atoms in the sample, resulting in a range of energy release mechanisms (see figure 2.3). Secondary electrons are produced *via* inelastic scattering of the incident electron beam, resulting in the sufficient excitation of outer-shell electrons to overcome the coulombic forces confining them within the atom. Due to the energy lost during the scattering process, a majority of these secondary electrons come to rest within the interaction volume (see figure 2.2) and, therefore, only those close to the surface can escape and reach the detector. As only electrons generated at the sample surface can be detected, secondary electrons are used to capture topographical information.

Other beam interactions can also be used to further analyse the sample. Back-scattered electrons – those scattered through an angle greater than  $90^\circ$  *via* elastic collisions with atomic nuclei – have a kinetic energy comparable to that of the incident beam; this makes them significantly more energetic than the secondary electrons and hence, have a much greater escape depth. This results in detection of electrons from a much larger proportion of the interaction volume and, therefore, much of the topographical information is lost. However, since the cross-section for this type of scattering is proportional to atomic number, image contrast can provide information related to the elemental composition of the sample. It must be reiterated that detections are occurring from a much larger interaction volume and therefore, conclusions on elemental arrangement derived from BSE images should be addressed with due caution.

Powder and bulk samples were mounted onto aluminium stubs using a carbon adhesive

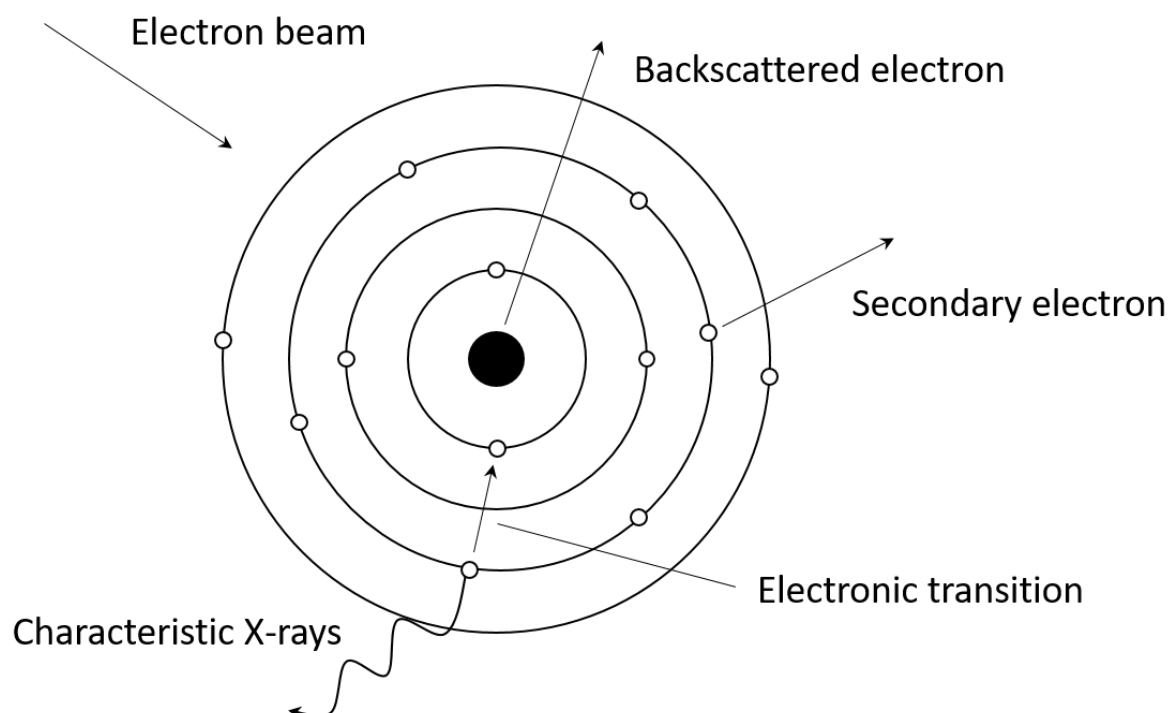


Figure 2.3: Simplified diagram of some of the processes occurring at the atomic level when exposed to the electron beam. Straight arrows signify movement of electrons. Adapted from [96].

pad. Samples were then sputter-coated with a conductive layer of either carbon or gold to reduce specimen “charging” when imaging. Charging occurs due to a build-up of electrons on the surface due to poor conduction and may result in a variety of artefacts which can affect the quality of the data obtained. This usually manifests on the obtained image as bright spots which increase in brightness through time as they are exposed to the beam. Charging can also result in “drifting” which can both be real – local differences in conduction resulting in small shifts in position (particularly common in powder samples) – and “apparent” – deflection of the electron probe due to changes in local charge, leading to the apparent displacement of the sample. As many of the samples investigated were bulk pellets of non-conductive ceramic material, silver dag was used to “bridge” the sample surface to the aluminium stub, giving a path to ground for the electrons building up on the surface; this generally lessens the charging effect.

SEM micrographs were obtained from a combination of three microscopes; an FEI Inspect F, an FEI Inspect F50 and a benchtop Hitachi TM3030 on BSE mode. Both FEI microscopes are equipped with field emission gun sources and the Hitachi with a thermionic emission source. These microscopes were operated with an accelerating voltage between 5 and 20 kV. Images were processed using ImageJ and Quantax 70 (Bruker).

### 2.4.2.2 Energy-dispersive X-ray analysis

The incidence of electrons on the sample also results in the emission of characteristic x-rays (see figure 2.3), the energy of which are quantised and determined by the elements present and can therefore be used to characterise the elemental composition of the sampled volume. This technique is generally referred to as energy-dispersive analysis of X-rays (the acronyms EDS, EDX, EDXA or EDAX are used interchangeably).

Small atoms, with fewer electron shells and therefore less available energetic transitions, are hard to identify using this technique as the peaks are obscured by background coming from stray radiation in the column and bremsstrahlung X-rays from secondary electrons. Any elements lighter than Be will be blocked by the window and will be undetectable anyway. Analysis of EDXA peaks can also be complicated due to its relatively poor energy resolution leading to the overlap of emission peaks of different elements – the technique is also limited by the accelerating voltage. The theoretical maximum transition energy would be equal to the accelerating voltage and, due to energy losses, it is generally advisable to operate at an accelerating voltage around twice as energetic as the theoretical critical excitation energy of the heaviest element of interest.

In this work EDXA was used to produce spectra and elemental maps of samples. These were taken at an accelerating voltage of 20 kV. EDX data was processed using Quantax 70 (Bruker) and AZtec (Oxford Instruments).

## 2.4.3 *Transmission electron microscopy*

### 2.4.3.1 Sample preparation

Samples were prepared by Dr Colm O'Reagan, using a FEI Helios Nano-Lab G3 UC, advanced FEG-SEM/Ga-FIB system. This equipment removes an electron transparent lamella of material from the surface of samples using a focused Ga ion beam. This lamella was then mounted on a copper grid.

### 2.4.3.2 Imaging

Transmission electron microscopy (TEM) operates similarly to SEM but with the observed electron beam having passed through the sample. This allows for the detection and analysis of a further series of interactions invisible in SEM (mostly limited to those alluded to in figures 2.2 and 2.3). Most importantly for the context of this research is the capacity of this technique to improve on SEM resolution and elucidate crystallographic information via electron diffraction (ED).

$$\lambda = \frac{1.22}{E^{\frac{1}{2}}} \quad (15)$$

Equation 15 shows the relationship between electron wavelength  $\lambda$ , and accelerating voltage in eV  $E$ . In a TEM a typical operating acceleration voltage is 200 keV, giving a  $\lambda$  of 0.027 Å, much smaller than the diameter of an atom, however, conventional electron lenses introduce aberrations which limit the resolution to around 1 Å [149].

This high resolution achievable can allow for the observation of bright and dark fringes, created by the convoluted reconstruction of the beam as it passes through the crystalline lattice. These are referred to as lattice fringes and gives information on the lattice spacing and orientation. Overlaps of these fringes and other distortions can result in moiré fringes, which can be extremely hard to deconvolute and may preclude the analysis of certain crystals with any certainty.

TEM was performed to elucidate information about the intergranular space of the cold sintered ceramics, in order to ascertain the potential mechanisms by which densification, recrystallization and lithium leaching was occurring.

TEM imaging was performed by Dr Colm O'Reagan, using a JEOL F200 80-200 kV, cold field emission gun high resolution analytical TEM/STEM, and a FEI Tecnai T20.

#### 2.4.3.3 Selected area electron diffraction

Selected area electron diffraction (SAED) is similar to XRD in that the wavelength of the incident beam (in this case an electron beam) satisfies the Bragg condition derived in equation 14. The pattern generated is a two dimensional projection of a reciprocal crystal lattice, hence the space visualised in SAED images is referred to as reciprocal space. Commonly, multiple crystallites contribute to the diffraction pattern observed and if enough crystallites are superimposed over each other a diffractogram composed of concentric rings can be observed as all possible orientations of crystallographic planes are interacting with the incident beam. In order to analyse the SAED pattern, the beam must be focused on individual crystallites as the relative distances between the spots is crucial in identifying the zone axis and, in turn, the crystal structure in question [149]. In highly polycrystalline samples, where no individual crystallite can be isolated with the beam, indexing may be impossible.

Incident beam angle is also crucial in the analysis of SAED patterns as if the beam is not perpendicular to the crystallite being investigated, then both the spacings and the angles used to analyse these patterns will be altered and likely impossible to index.

SAED was performed to further understand the formation mechanisms of the crystals observed and how the stacking faults generally expected from  $\text{Li}_2\text{TiO}_3$  were impacting the samples generated.

SAED patterns were taken by Dr Colm O'Reagan, using a JEOL F200 80-200 kV, cold field emission gun high resolution analytical TEM/STEM, and a FEI Tecnai T20.

#### 2.4.4 *Inductively coupled plasma – optical emission spectroscopy*

ICP-OES analysis was carried out by Shania E. Laming using a Spectrogreen ICP-OES with a 1150 W plasma, a 13 L/min coolant flowrate and a nebuliser flowrate of 0.8 L/min. Samples were run three times at 2 L/min. 5 mg of powder was dissolved in 5 ml concentrated HCl under sonication. Samples were then agitated in a mechanical shaker for 16 h being made up to a 50 ml solution with 1% nitric acid. The samples were then further diluted by a factor of 100 to reach the instrument's calibration range. The calibration range was 0-10 ppm for both Ti and Li, using calibration standards at 0, 5 and 10 ppm.

#### ***2.4.5 Differential scanning calorimetry/Thermogravimetric analysis***

Differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) are two techniques which, when performed simultaneously, complement each other and allow for the identification of events such as phase changes during calcination or anneal of a material, such as a decomposition or a melting event. TGA records the mass of material in the instrument continuously during the set thermal program. DSC can be very insightful when trying to categorise the mass loss/gain events identified in the TGA curve as, essentially, DSC measures the difference in the amount of heat needed to heat the sample vs a standard reference and may, therefore, be used to connect the change in mass to a change in enthalpy. The temperature at which the event took place, together with these two changes can therefore allow for the identification and description of the event in question.

DSC/TGA was carried out in a SDT 650 (TA Instruments) both under air and under nitrogen with varying heating regimes relevant to the calcination/anneal of the ceramics under investigation.

#### **2.5 Bulk density analysis**

Pellet density was measured using an Archimedes balance, adapting method from ASTM standard B962-17. The liquid used was isopropanol to reduce water adsorption into the materials. Three weights were taken to calculate the density of the pellets. Firstly, the pellets were weighed dry (1) then they were allowed to soak in the liquid for 5 minutes to allow the solvent to seep into pores and re-weighed after tapping the surface dry (2). Final weight was taken submerged in isopropanol (3). Measurement 1 represents the true mass of the pellet and measurement 3 is used to find the volume of the sample using isopropanol density at the temperature of interest. Measurement 2 allows for an estimation of the degree of open porosity of the sample and to identify the volume of solvent absorbed (as per ASTM standard B962-17).

### 3 Low-temperature synthesis and sintering of lithium titanate

#### 3.1 Introduction

Ceramic processing generally requires high temperatures to both synthesise and sinter – especially when high densities are prioritised. Ceramic breeder materials ubiquitously contain lithium in their structure – as is necessary to allow for tritium generation on transmutation – and lithium (as well as other species such as sodium) is particularly mobile and susceptible to volatilisation with high processing temperatures [103, 104]. Detectable amounts of lithium loss have been reported from temperatures as low as 800 °C [67] but generally starts to become an issue upwards of 1000 °C [108]. This issue results in loss of lithia, directly affecting stoichiometry and may result in structural and chemical shifts if severe enough. The main issue affecting ceramic breeder materials is the amount of lithium itself. The main drive in these ceramics is the push to ever-higher lithium densities, even to the detriment of all other properties, and hence processing conditions that may lead to lithium losses (even if limited to 1-2 wt%) are disadvantageous and will impact plant efficiency and design. Processing conditions, especially sintering conditions, have seen few advancements to address this; reading the literature feeling like there is a general acceptance that high temperature sintering is a necessary evil, that will lead to lithium volatilisation, but result in higher densities. High densities also increase overall lithium density and, in general, has a larger impact on this than any loss due to volatilisation. This creates even more dichotomical choices to be made with regards to fusion. Novel techniques may aid in falsifying this apparent dichotomy and allow the generation of pellets with high densities without compromising lithium content.

A side of material design that has seen no practical, fusion related, research is morphological control. A review carried out by Ying *et al.* [94] showed that in general, small grains (<5  $\mu\text{m}$ ) were beneficial for tritium release. Tritium release is intrinsically related to the active surfaces available for tritium desorption and tritium propagation is more energetically favourable through intergranular spaces than within grains [95]. Small grains are therefore understood to be likely a favourable trait in a ceramic breeder, however, even if available through synthesis (*via* hydrothermal synthesis for example), nano sized grains aren't retained after sintering, with coarsening occurring as a main drive for densification in high temperature sintering. Smaller size is known to be better, but other bespoke morphologies have not been tested with regards to tritium release. More complex structures may offer further benefits but a lack of straight forwards densification techniques capable of retaining these features have precluded their study.

Low temperature processing techniques may allow the study and assessment of compositions and morphologies previously inaccessible to the ceramic breeder community.

#### 3.2 Aims

The aims of this work were:

- Develop a method to produce nano-scale  $\text{Li}_2\text{TiO}_3$  using deep-eutectic solvent synthesis.

- Develop a method allowing for the sintering of dense pellets at lower temperatures than achievable with regular high temperature sintering.
- Introduce different microstructures into final pellets using the two vectors introduced with the RCS method.

### 3.3 Results and discussion

#### 3.3.1 Solid state synthesis

The RCS sintering process discussed in this section involves the combination of a pre-synthesised “main phase” powder, together with a mixture of precursors or infill. The resultant mixture is sintered (as described in section 2.2.2) with the aim of surrounding grains of the aforementioned pre-synthesised powder with a matrix of single phase material generated from the infill mixture added. This section discusses the production of  $\text{Li}_2\text{TiO}_3$  “main phase” powder to be used throughout the work.

Lithium metatitanate ( $\text{Li}_2\text{TiO}_3$ ) was successfully synthesised following the solid state synthesis method utilised by Sam Waters [79] and outlined in section 2.1.1. PXRD of the resultant powder was performed, with all peaks corresponding to  $\text{Li}_2\text{TiO}_3$  as identified by ICSD card 162215 [46] (figure 3.1).

This single phase material produced *via* solid state sintering will be used as the so-called “main phase” in the RCS process.

A feature of this material that can be observed from the X-ray diffraction pattern in figure 3.1 is inconsistencies in peak shape and intensity. The ICSD card followed when labelling this diffraction pattern contains several peaks not present in this figure. This is a well-known crystallographic characteristic of  $\text{Li}_2\text{TiO}_3$  (as it transitions from the cubic meta-stable form to the monoclinic  $\beta$  form) and noted by West *et al.* and Tarakina *et al.* [72, 108]. This feature is temperature dependent and generally disappears with increasing synthesis temperature, as the slow kinetics of ordering along the  $c$  direction lead to the slow annealing of stacking faults in the  $\text{LiTi}_2$  layer [72]. This effect has led some groups to separate  $\beta$ - $\text{Li}_2\text{TiO}_3$  into a high temperature and a low temperature form, due to undergoing a change in short range ordering probability with temperature between the space groups:  $C2/c$ ,  $C2/m$  and  $P3_112$ , finally arriving at a stable  $C2/c$  high temperature form [72, 73]. Even though no formal transition occurs, the increased disorder of the low temperature forms may lead to increased reactivity and Li ion mobility [72]. The impact this increase in mobility may have on the performance of the ceramic within a fusion device is unclear and outside the scope of the work shown here.

Morphological analysis of the resultant powder was undertaken *via* SEM imaging (figure 3.2) where a powder of particle size in the order of 150-300 nm was observed. This is consistent with sizes reported by Waters *et al.* [79] and as expected from the relatively low synthesis temperature. A Mastersizer particle analyser working in a water suspension under sonication, was used to confirm this observed scale. A  $D_{50}$  (median) value of  $1.32 \pm 0.02 \mu\text{m}$  was measured, showing perhaps a larger powder than identified through SEM. This discrepancy may be due to powder agglomeration however, as the  $D_{50}$  value reported slowly decreased in subsequent measurements and agglomeration was commonly



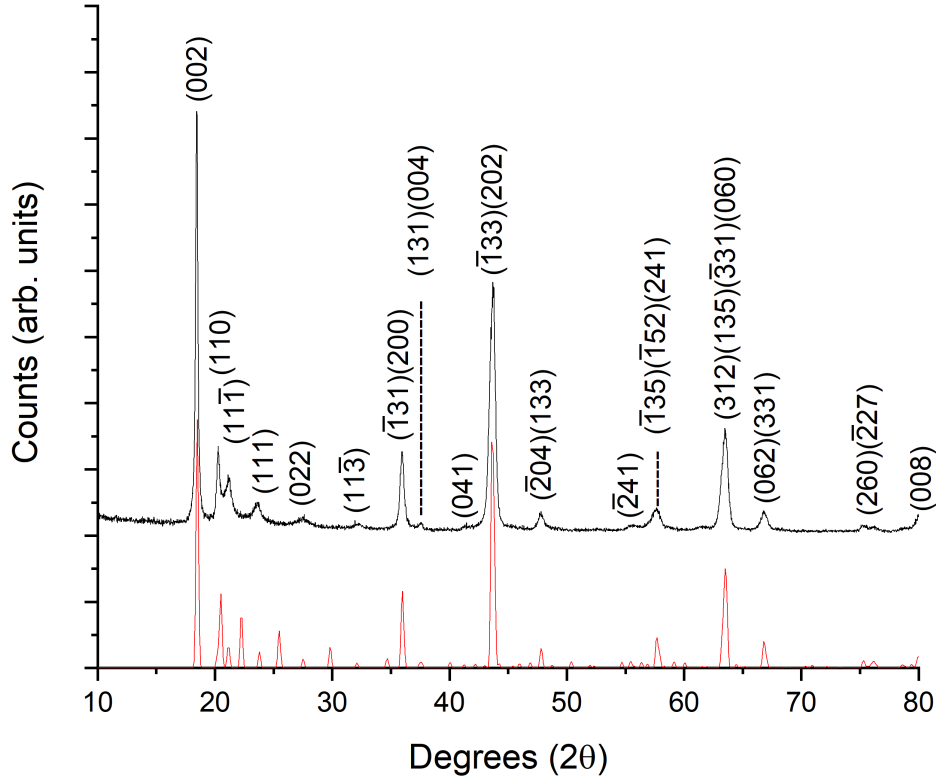


Figure 3.1: X-ray diffraction pattern of solid state synthesised lithium metatitanate. This was found to be phase pure lithium metatitanate after calcination at 730°C. Main peaks have been labelled with their relevant hkl's (some have been omitted for clarity). Simulated profile included in red according to ICSD card 162215 [46].

observed when manipulating these powders. Considering one of the main aims of this research is the introduction of a particle population of a different, independent morphology, these small particles might make identifying bimodality harder, as the difference in particle size between phases becomes less apparent.

This led to the synthesis of a second batch of  $\text{Li}_2\text{TiO}_3$  formed with a different set of thermal parameters, which would enable significant grain coarsening, increasing the difference in size between particle populations and, easing the identification of each post-sintering.

This larger-grained batch was produced following the same method (outlined in section 2.1.1) and precursors as previous, but calcined at a temperature of 1100 °C. This temperature was chosen due to its use as the default sintering temperature of pellets produced *via* solid state, hence allowing for a consistent grain size when comparing samples made using high temperature sintering and cold sintering. It also allowed for the production of a powder with a relatively predictable grain size, as the low temperatures used in the

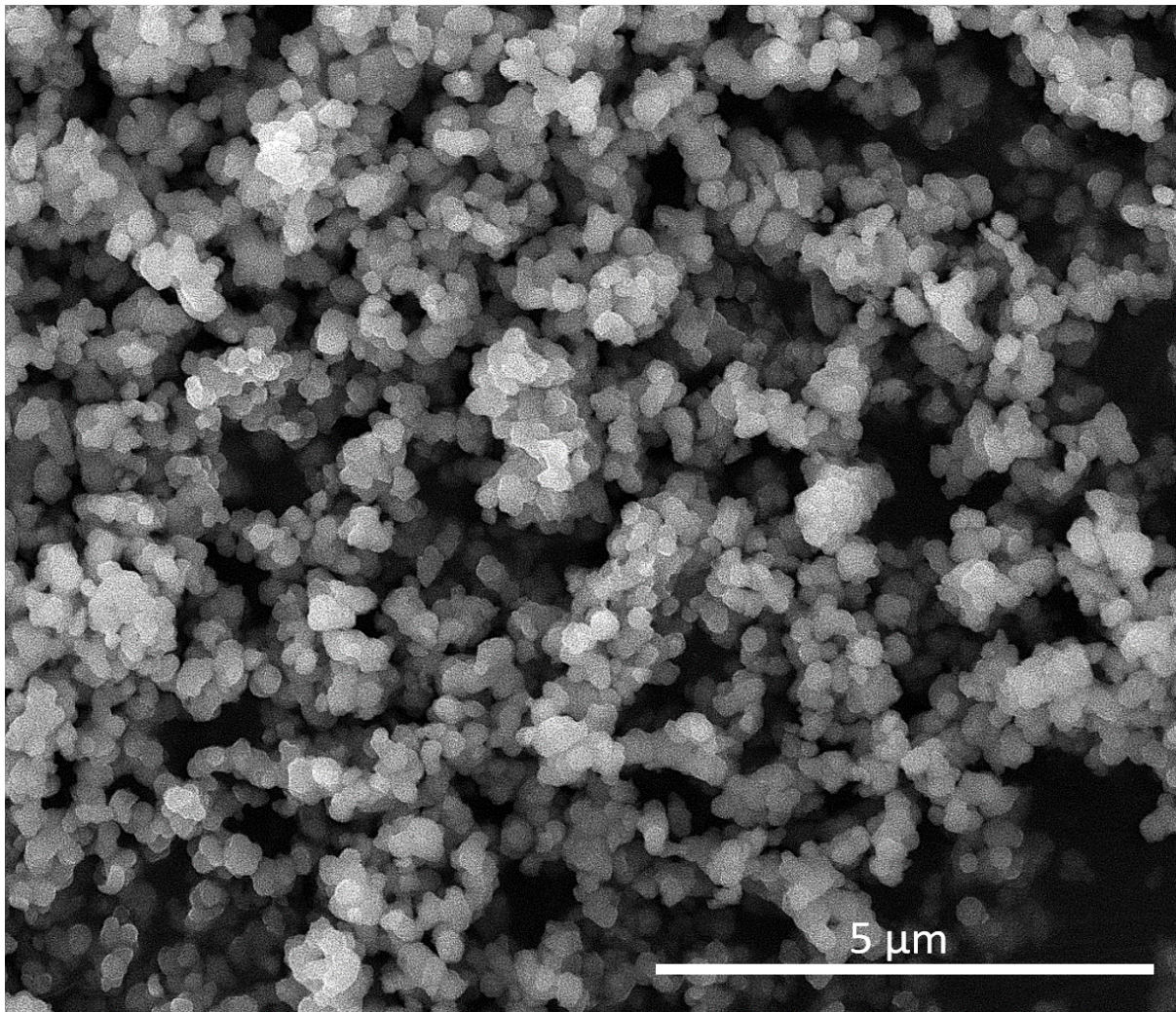


Figure 3.2: Secondary electron micrograph of the solid state  $\text{Li}_2\text{TiO}_3$  powder formed at  $730^\circ\text{C}$ .

reactive cold sintering method will result in negligible coarsening and hence retention of the grain size achieved in this step.

This higher synthesis temperature results in much sharper peaks than those shown in figure 3.1, clearly showing the effect that higher temperatures have on the structure of  $\beta\text{-Li}_2\text{TiO}_3$ . As referenced above, the stacking faults in the  $\text{LiTi}_2$  layer are annealed out of the structure leading to an XRD pattern which adheres more closely to the  $C2/c$  monoclinic space group.

SEM was used to ascertain the particle size in this new batch with increased grain size, as shown in figure 3.4. The  $\text{Li}_2\text{TiO}_3$  solid state powder can visually be taken to have a particle size in the range of  $1\text{-}10\ \mu\text{m}$ . This visual measurement for the  $\text{Li}_2\text{TiO}_3$  powder was confirmed using a Mastersizer particle analyser working in a water suspension, showing a  $D_{50}$  (median) value of  $3.86 \pm 0.035\ \mu\text{m}$ .

Here we have successfully produced two samples containing different powder popula-

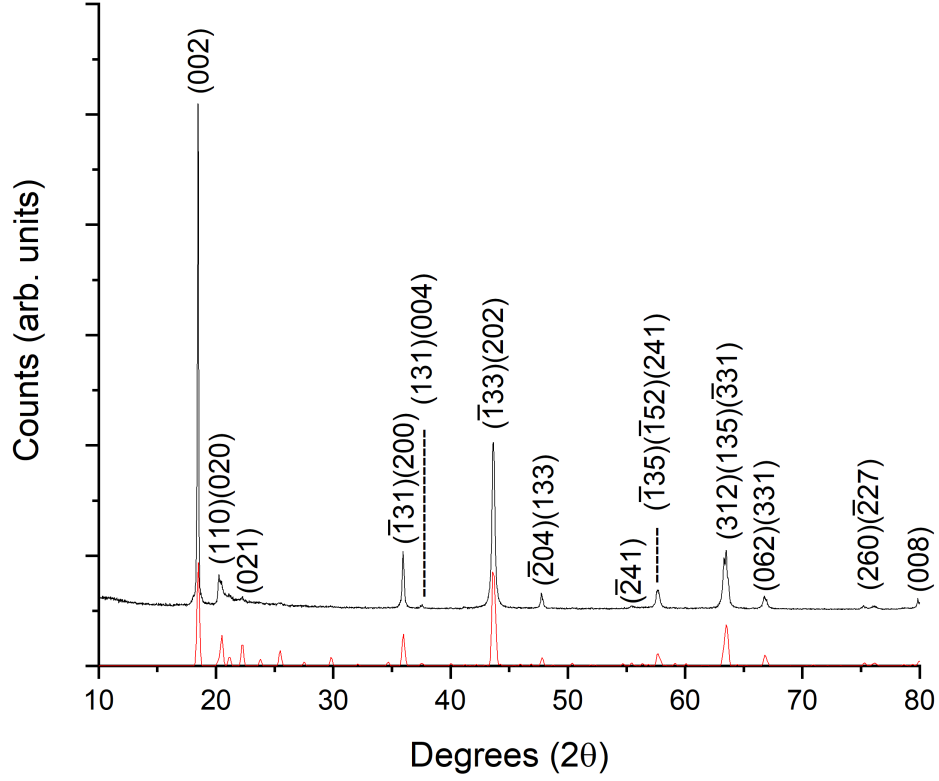


Figure 3.3: X-ray diffraction pattern of phase pure solid state lithium metatitanate after calcination at 1100°C. Main peaks have been labelled with the corresponding hkl's (some have been omitted for clarity). Simulated profile included in red according to ICSD card 162215 [46].

tions of single phase  $\text{Li}_2\text{TiO}_3$  *via* solid state synthesis: one at 730 °C with particle size measured at  $D_{50}$  (median) value of  $1.32 \pm 0.02$ , and another at 1100 °C with particle size measured at  $D_{50}$  (median) value of  $3.86 \pm 0.035$   $\mu\text{m}$ ; at minimum a factor of three increase in grain size, however in the smaller scale powder significant agglomeration was observed and therefore the size difference under SEM is expected to be larger.

These will be used as the stock powders in the sections to follow, generally referred to as the “main phase” powder and differentiated by their synthesis temperatures.



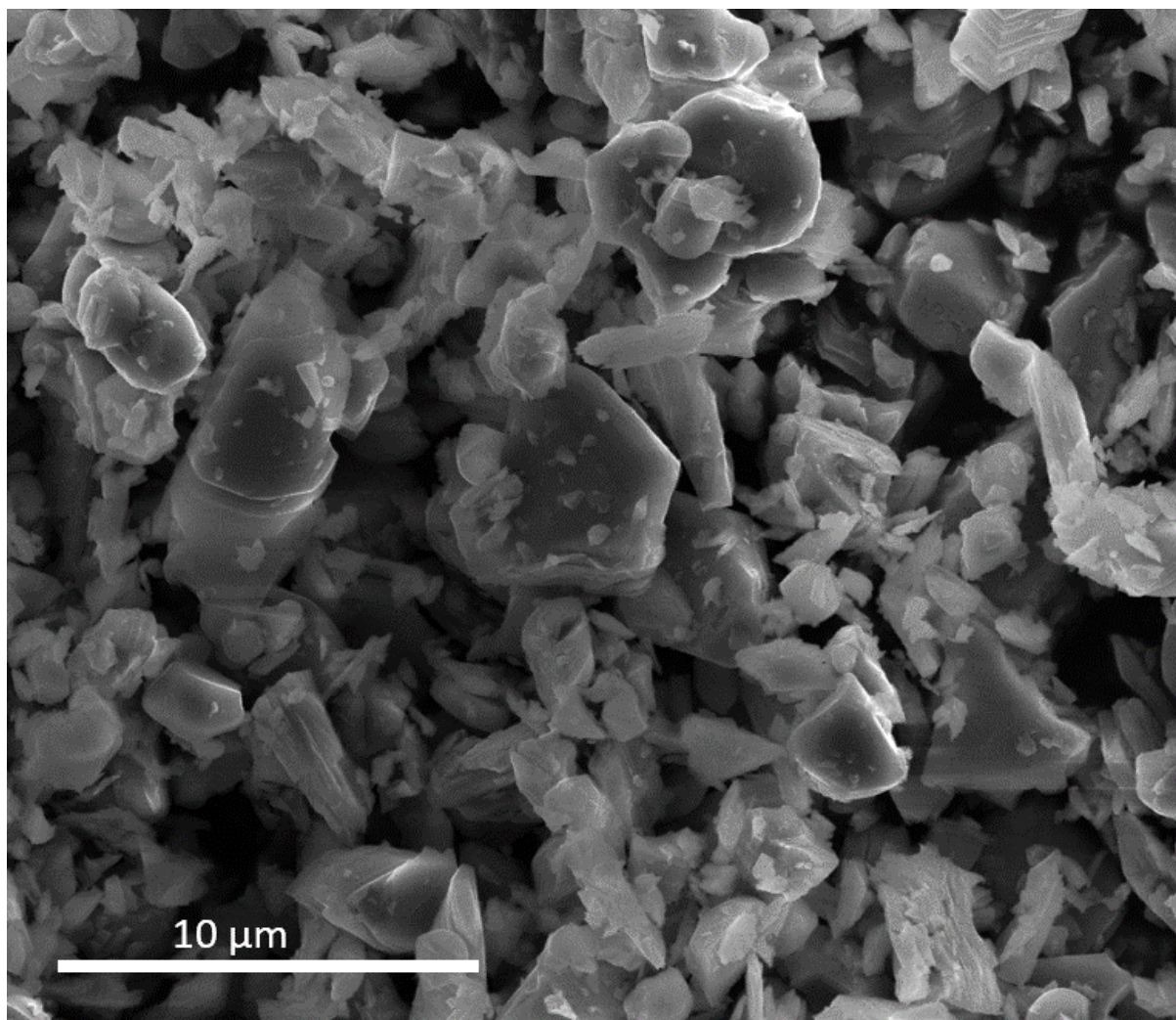


Figure 3.4: Secondary electron micrograph of the solid state  $\text{Li}_2\text{TiO}_3$  powder formed at  $1100\text{ }^\circ\text{C}$ .

### 3.3.2 Deep-eutectic solvent synthesis

Synthesis of  $\text{Li}_2\text{TiO}_3$  using a malonic acid/choline chloride deep-eutectic solvent (DES) synthesis method was performed. This was done for two reasons: the *ex-situ* generation of a powder representative of the material expected to be produced by the precursor mixture added during the RCS process, as well as the reduction of processing temperature when synthesising the ceramic.

We postulate that - based on previous work on strontium titanate showing DES synthesis of titanates is proceeding *via* the formation of a chloride salt and  $\text{TiO}_2$  [124] - lithium titanate prepared using the DES synthesis method will mirror the reaction expected from the  $\text{LiCl-TiO}_2$  mixture used during the RCS process as described. If indeed this is the case, this will allow an estimation of the expected particle size as well as elucidate information about the reaction occurring within the RCS pellets.

A series of 10 distinct DES powders were synthesised during method refinement.

Table 3.1: Summary of key variables tied to each sample batch. Notes added for clarity and context.

| Material | Malonic acid (g) | Choline chloride (g) | Drying regime (h) | Vessel           | Calcination temperature (°C) | Notes                                                      |
|----------|------------------|----------------------|-------------------|------------------|------------------------------|------------------------------------------------------------|
| DES 1    | 5.15             | 6.8                  | 4                 | alumina crucible | 650                          | -                                                          |
| DES 2    | 5.15             | 6.8                  | 5                 | alumina crucible | 650                          | wash volume was reduced to keep water content minimal      |
| DES 3    | 5.15             | 6.8                  | 12                | alumina crucible | 650                          | drying regime increased                                    |
| DES 4    | 5.15             | 6.8                  | 4                 | alumina tray     | 650                          | switch to trays during calcination                         |
| DES 5    | 5.15             | 6.8                  | 4                 | alumina tray     | 650                          | -                                                          |
| DES 6    | 5.15             | 6.8                  | 4                 | alumina tray     | 650                          | -                                                          |
| DES 7    | 5.15             | 6.8                  | 4                 | alumina tray     | 650                          | crystals spotted in Ti isopropoxide stock                  |
| DES 8    | 5.15             | 6.8                  | 4                 | alumina tray     | 650                          | switch to fresh Ti isopropoxide, aluminium contaminant     |
| DES 9    | 5.15             | 6.8                  | 4                 | alumina tray     | 700                          | calcination temp. increased                                |
| DES C    | 25.9             | 34.7                 | 4                 | alumina tray     | 650                          | 5x increase in eutectic solvent based on previous research |

Initially, DES powder synthesis of lithium metatitanate yielded both the desired phase and both of the known precursors which are produced during the DES reaction pathway ( $\text{TiO}_2$  and hydrated forms of  $\text{LiCl}$ ) [124] as can be seen from all samples in figure 3.5. The powder was visibly oily, confirming the presence of lithium chloride, as this is deliquescent and draws moisture out of the air.

This was, at first, attributed to a poor drying procedure of the eutectic, leading to moisture retention in the gel and therefore titania precipitation upon the addition of titanium isopropoxide;  $\text{TiO}_2$  is highly stable and would be unlikely to react at the relatively low temperatures in use if not in solution. However, during the synthesis of batch DES 2, extra care was taken to ensure full water evaporation prior to the addition of the alkoxide. Figure 3.5 shows this still yielded a partially unreacted powder. DES 3 was dried for 12 h and still resulted in unreacted material.

In agreement with previous work, [124] and as outlined in section 2.1.2, consistent contact with air seemed to be key when approaching the DES reaction pathway. DES 1-3 were synthesised in large alumina crucibles with a relatively low surface to volume ratio. It was postulated that an atmosphere which was retaining large quantities of outgassed material could be produced within the crucibles, leading to poor air flow, and so a different crucible shape was utilised to avoid this potential issue.

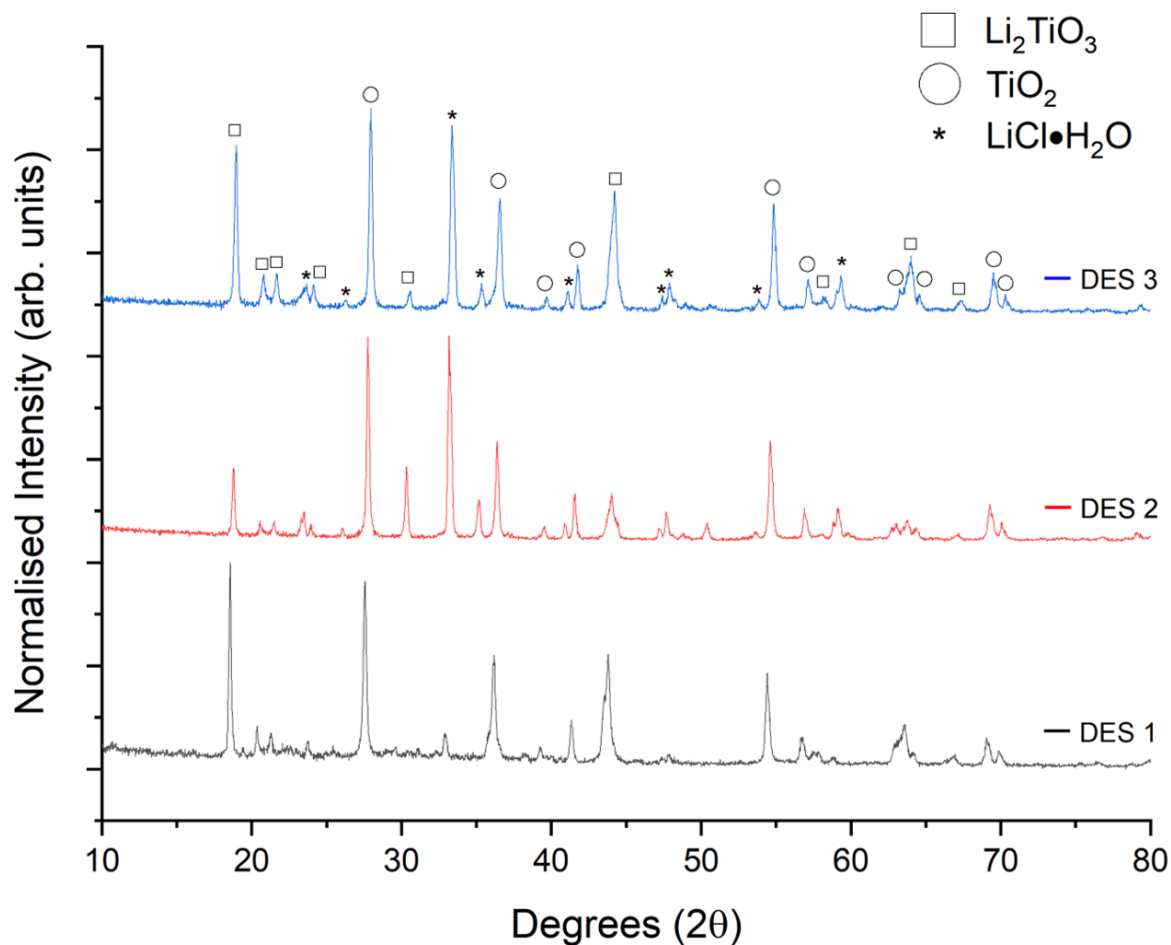


Figure 3.5: X-ray diffraction pattern of powders DES 1-3 sintered at 650 °C for 4 h. Both precursors were found in all iterations, with DES 2 not even having  $\text{Li}_2\text{TiO}_3$  as the dominant species.

DES 4 was poured as a gel onto flat crucibles to increase the sample's contact with air. Figure 3.6 shows the improvement realised by this subtle change in procedure with the X-ray diffraction pattern showing a much cleaner material with slight  $\text{TiO}_2$  peaks still remaining. Some peaks where  $\text{Li}_2\text{TiO}_3$  and  $\text{TiO}_2$  overlap appear larger than might be expected for  $\text{Li}_2\text{TiO}_3$  alone (at 27° and 36° for example), suggesting the presence of some unreacted titania remaining in the powder. Minor peaks at 40° and 54° also suggested the presence of titania (rutile). DES 5-7 were produced using the same method and yielded similar diffraction patterns as seen in figure 3.6. Care was taken to fully dehydrate the DES during synthesis to ensure no titania precipitated into the gel and yet it proved persistent. Mottram *et al.* show evidence this titania may still precipitate at low temperatures even without any water present in the gel [120]. During the synthesis of DES 7 the presence of crystallised titania was noted in the titanium isopropoxide stock; this could also be a source of  $\text{TiO}_2$  contamination.

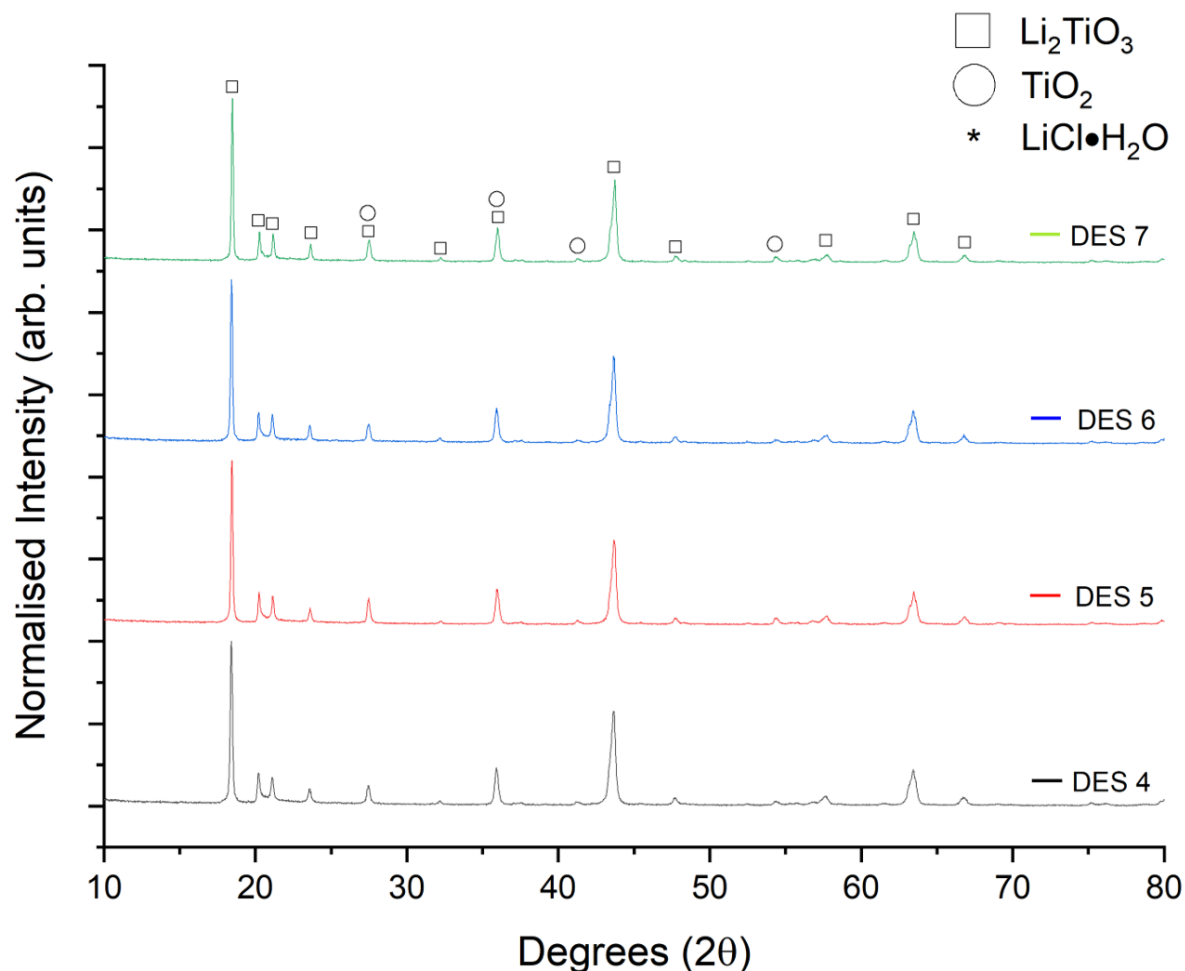


Figure 3.6: X-ray diffraction pattern of powders DES 4-7. All iterations were apparently lithium chloride-free but with subtle titania (rutile) peaks.

SEM in combination with EDX was used to further analyse the resultant powders to further elucidate the reason behind the retained presence of titania in the diffraction pattern.

Figure 3.7 shows the presence of a particle population with large grains, the presence of which, considering the highly homogenised environment as well as the low synthesis temperature (650 °C in this case) used, was unexpected. EDXA of each morphologically distinct species shows a clear difference: the larger crystal population contains no chlorine. Based on previous XRD results and research into the mechanisms involved in DES synthesis [124] it is predicted that lithium chloride is formed as a precursor during the reaction. It stands to reason, then, that if the reaction did not reach completion, the reacted powder would exhibit an EDXA peak related to chlorine. The absence of such, together with the expected size of the resultant powder being well under one micron (calcination temperature and residence time used should not result in this degree of coarsening), and the previously mentioned titania crystals observed in the isopropoxide,



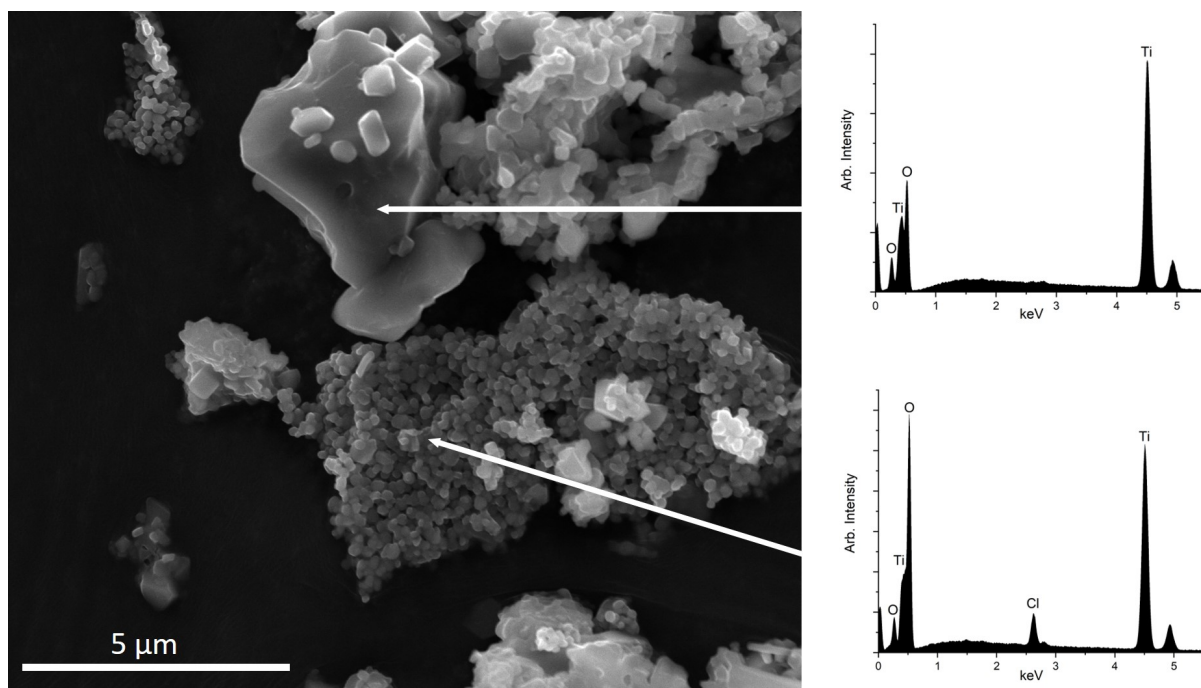


Figure 3.7: Secondary electron micrograph of powder DES 7 with EDXA spectra of two points with different morphology. Sample was carbon coated.

suggested that the large particles seen under SEM could have been introduced from the isopropoxide stock and may have resulted in the segregation of reactants, leading to the partially unreacted powder produced, as well as explaining the presence of the large, titanium-rich, grains.

DES 8 was synthesised using a fresh isopropoxide stock. Figure 3.8 shows the X-ray diffraction pattern of this new batch, with significantly improved purity. Now, the titania peaks identified in previous iterations are not present, however a new unidentified peak has appeared (at  $33^\circ$ ). SEM and EDXA analysis were carried out to identify both the morphology and phase of the powder.

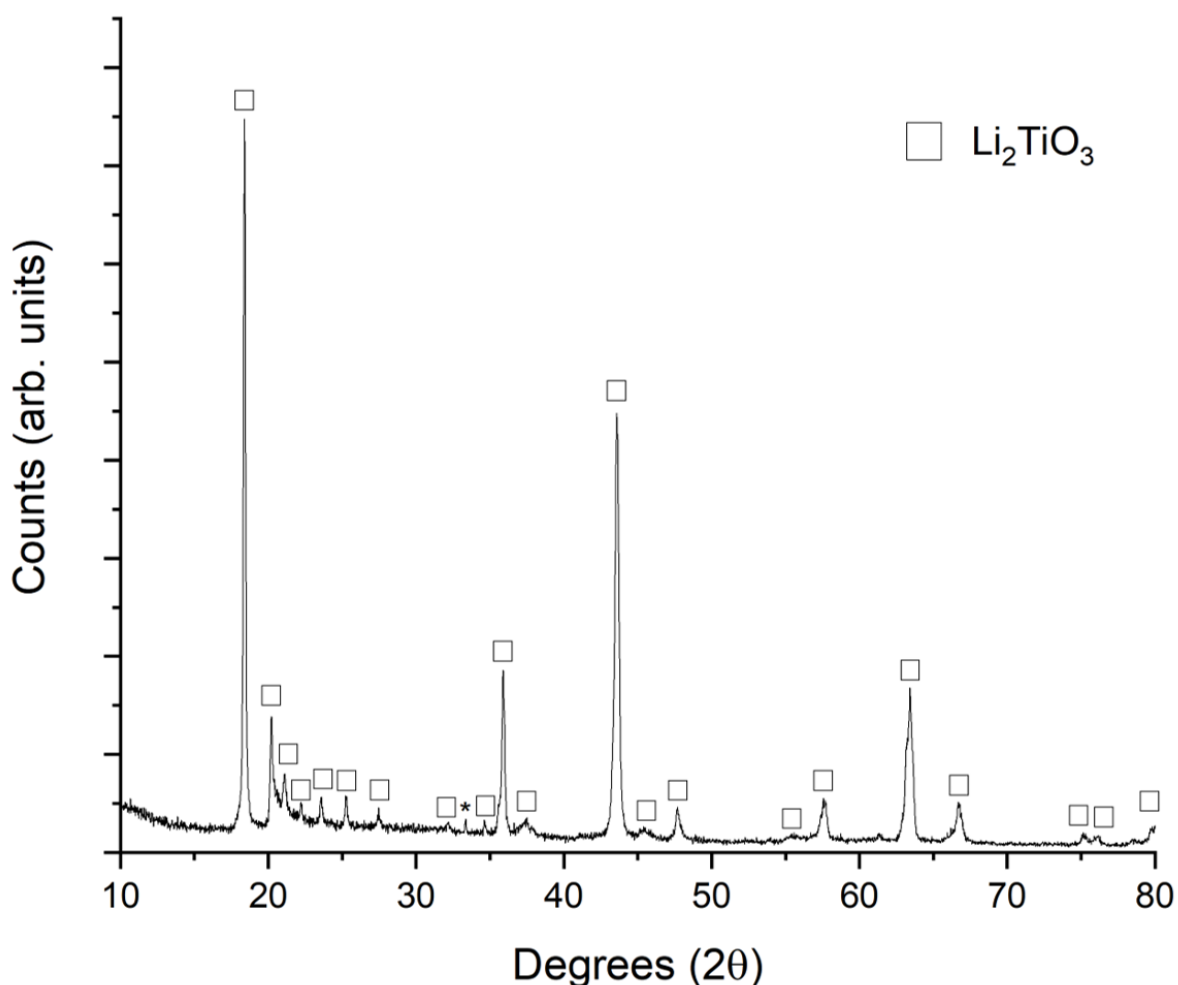


Figure 3.8: X-ray diffraction pattern of powder DES 8. \* signifies the unidentified phase.

Figure 3.9 shows the overwhelming presence of chlorine. No large titania particles were found however, signifying that multiple factors may be resulting in the partially reacted powder observed in figure 3.7. The unidentified phase contained aluminium, according to the EDXA and elemental maps. Overlap with characteristic energies of other elements was checked but only aluminium could have produced the peak observed. This aluminium species could have either been introduced through the new isopropoxide stock or possibly from the alumina refractory bricks lining the furnace, which were seen producing unusual amounts of dust prior to calcination. The aluminium phase seems to be spread quite evenly across the surface however, which suggests that this phase was introduced during the mixing stage of the DES process. Titania produced by the hydration of the titanium isopropoxide stock was checked using SEM and EDXA for aluminium (figure 3.10) and none could be found so it was assumed that the aluminium presence in DES 8 had been randomly introduced and remaking it should solve the problem. Particle size also seemed to vary widely, with large agglomerates being clearly visible. Looking at figure 1.18 (in the introduction section 1.5.2) the nano-powder produced utilising this method is in the

order of tens to a few hundred nm, clearly smaller than those observed in figure 3.9. Agglomeration may be obscuring the true particle size of the powder produced.

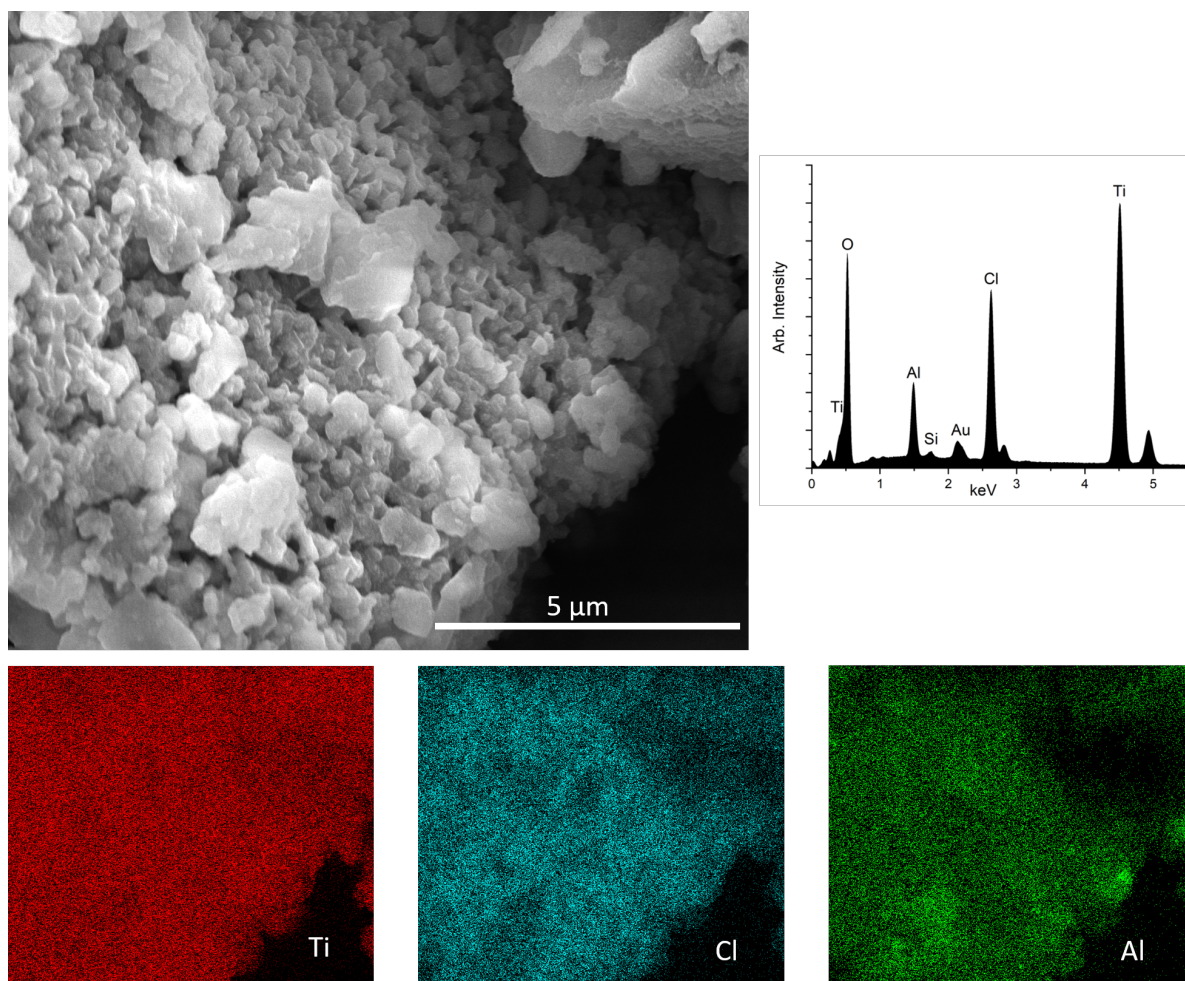


Figure 3.9: Secondary electron micrograph of powder DES 8 with EDXA spectrum and elemental maps. Sample was gold coated.

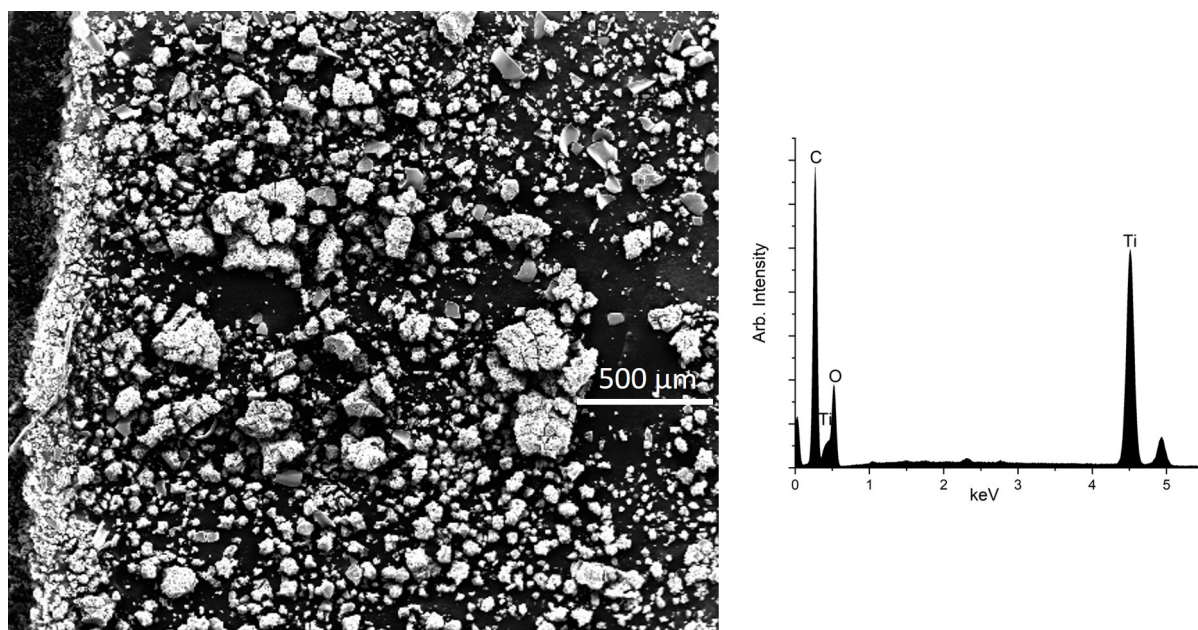


Figure 3.10: Secondary electron micrograph of titania derived from the titanium isopropoxide stock with EDXA spectra. Sample was carbon coated.

The overwhelming presence of chlorine in the EDXA clearly suggested a partially reacted powder and hence, there must be some limiting factor preventing the reaction from going to completion.

Two potential factors were identified as the most likely to be impacting the reaction: firstly, considering the mechanism by which DES creates a homogeneous mixture (refer to section 1.4.4), the number of chelation sites may be insufficient to fully process the amount of material being reacted and, secondly and perhaps much simpler, the reaction temperature used so far may be insufficient to fully react the powder.

In summary, the increased kinetics related to the improved system homogeneity may be limited by the chelation sites present, or, the rate of reaction may be limited by the reaction conditions, and an increase in reaction temperature or dwell may allow the reaction to reach completion.

To this end DES C was produced with a fivefold increase in deep eutectic solvent used (34.7 g of choline chloride to 25.9 g of malonic acid) in order to increase the number of chelation sites available, previous work in the group suggested that working with such an excess resulted in single phase material. DES 9 was produced with a synthesis temperature of 700 °C as a first approach in finding the reaction temperature required. In both cases the rest of the method was kept identical to that described in section 2.1.2.

As with DES 8 (figure 3.8), all peaks observable are related to lithium metatitanate (figure 3.11). The unidentified peak at 33° is not present, confirming the hypothesis that it may have been a random contaminant affecting that batch alone. Peak shape and peak expression are almost identical, with no significant differences to report. SEM and EDXA must be therefore performed to address the Cl content identified as an issue in samples previous.

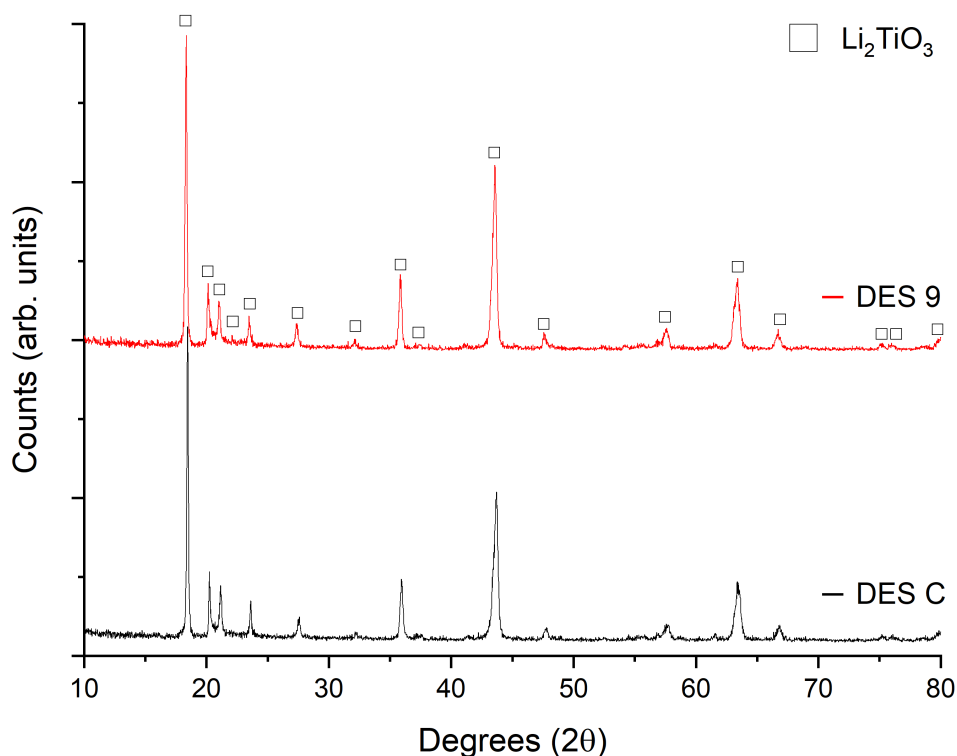


Figure 3.11: X-ray diffraction pattern of powders DES 9 and DES C.

Small grains surrounding larger ones can still be observed, although significantly smaller than the suspected titania grains. Here however, no clear difference between the two particle populations was observed in the EDXA. Particles are generally globular and collect in tight agglomerates that, under low magnification, often appear to be large individual particles. It must be noted that larger particles were observed in DES 9, calcined at a higher temperature, although not enough were captured to state a difference in particle size with any certainty.

More clear however is the EDXA of both of these powders, evidently showing the higher calcination temperature as the limiting factor in the system. Considering the lack of chloride in DES 9 all DES powders produced hereon were generated at this temperature.



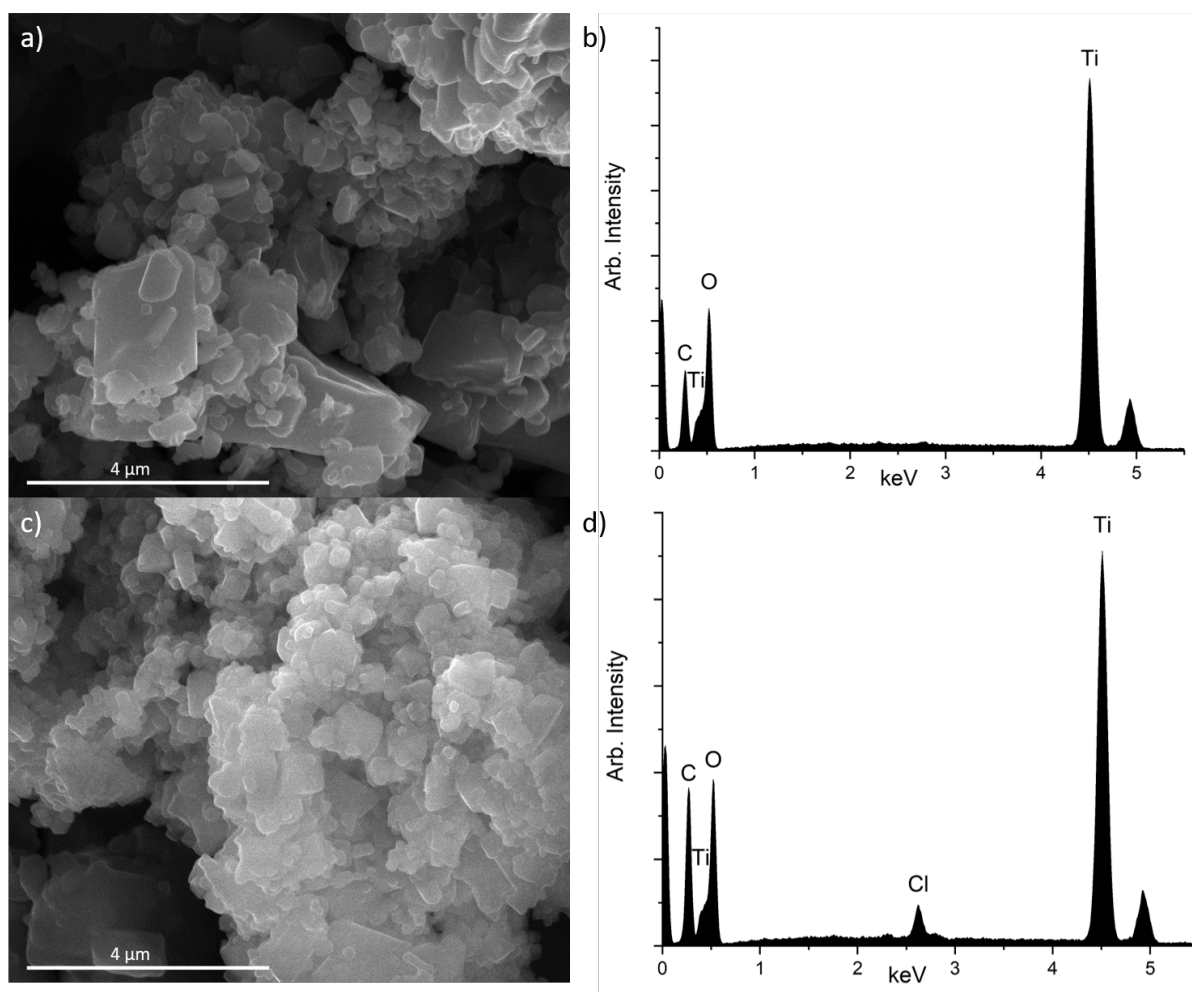


Figure 3.12: Secondary electron micrograph of DES 9 (a and b) and DES C (c and d) with respective EDXA spectra. Samples were carbon coated.

### 3.3.2.1 Conclusions and key conditions for synthesis

Lithium titanate synthesis has been demonstrated using the DES method. Synthesis temperature has been decreased from the 730 °C used during solid state synthesis; this could potentially be decreased further as the minimum synthesis temperature in this system can be concluded to be somewhere between 650 and 700 °C. Further research is needed to precisely determine the minimum synthesis temperature.

Following the findings outlined in this research, a successful  $\text{Li}_2\text{TiO}_3$  batch using the DES synthesis method requires the following:

- Fully dehydrated eutectic mixture prior to addition of the alkoxide.
- Use of a dry *i.e.* clean (no obvious suspended solids) alkoxide stock.
- Good air contact during calcination *i.e.* a high surface area crucible should be used to ensure high surface area to volume ratio of the pre-reacted gel when it is loaded

into the furnace.

- A calcination higher than 650 °C (700 °C was shown to be sufficiently high in this work, but the minimum temperature could be potentially lower than this)

### 3.3.3 Cold sintering method – bimodal

An issue with tritium breeder ceramics lie in their expected tritium-generating capacity. Each transmutation event will lead to the generation of a tritium atom but the extraction of these atoms from the bulk represents a further challenge. Tritium permeation is a key factor in the breeder equation and closely linked to pellet microstructure.

This issue establishes a key dichotomy in the design of a functional breeder ceramic: high densities are desirable to maximise lithium content, however, high densities generally lead to a decrease in tritium diffusion rates [94, 95]. This last point is mainly caused by generally larger grains due to coarsening during densification, the loss of intergranular space directly related to this and, also relevant, the loss of open porosity [75]. In essence, the loss of low free energy diffusion pathways.

Even with these well-understood microstructural issues, very few groups have focused on the impact of pellet microstructure on tritium release characteristics – a big reason behind this gap in the research is the lack of applicable densification techniques which allow for any kind of control over the resultant microstructure. Choosing to alter the microstructure would necessitate the application of a different densification technique entirely; one that would allow for the retention of the desired morphology.

Flexible, low temperature techniques which allows for control over final pellet microstructure would be key to streamline this kind of research and aid the development of consistent, highly tailored microstructures, maximising potential for tritium release. Benefits of such a technique would not be limited to ceramic breeders of course.

One technique with the potential to achieve this is cold sintering [141] or, more specifically, reactive cold sintering [125]. Independence between the primary powder introduced and the particles formed *via* the added infill mixture, allows for two opportunities for independent particle design and, the ratio between these two components allows for further tailoring. This plus the low temperatures required for highly dense bodies may lead to a maximisation of density whilst allowing for the retention of low free energy tritium diffusion pathways.

$\text{Li}_2\text{TiO}_3$  was selected as an infill material as the formation mechanisms could be simulated using the DES method outlined above and due to the conventional disregard for titanates in cold sintering, primarily due to their poor solubility. Hence, the successful use of this mix phase infill will demonstrate the capacity for the RCS method to operate with insoluble, previously inaccessible, systems.

#### 3.3.3.1 Preliminary experiments – method refinement

Initially, a 3 M solution of LiCl and equivalent  $\text{TiO}_2$  nano-powder was used as the infill with both the DES and the SS (solid state lithium metatitanate sintered at 730 °C) powders. As the powders were left to dry it became increasingly obvious that they would

Table 3.2: Summary of the initial powders, infill concentrations, relative mass of infill, drying regimes applied and maximum pellet density of the different CSP experiments.

|       | Initial Powder (0.3g) | Infill concentration              | Relative mass of infill | Drying Regime                            | Max Density |
|-------|-----------------------|-----------------------------------|-------------------------|------------------------------------------|-------------|
| CSP 1 | SS & DES 5            | 3 M LiCl (1.5M TiO <sub>2</sub> ) | 15.45%                  | -                                        | -           |
| CSP 2 | DES 6                 | 1.5 M LiCl                        | 8.37%                   | -                                        | -           |
| CSP 3 | DES 6                 | 0.75 M LiCl                       | 4.37%                   | -                                        | -           |
| CSP 4 | SS & DES 7            | 0.75 M LiCl                       | 4.37%                   | -                                        | 79%         |
| CSP 5 | SS                    | 6 M LiCl                          | 26.76%                  | 180 °C overnight                         | 71%         |
| CSP 6 | SS                    | 6 M LiCl                          | 26.76%                  | RT desiccator overnight                  | 78%         |
| CSP 7 | SS                    | 6 M LiCl                          | 26.76%                  | RT desiccator overnight (ground pre-CSP) | 78%         |

not dry completely; prior to pressing the material is expected to produce a loose powder, however, in this instance the powder never dried past a thick slurry consistency. Even though the use of LiCl and TiO<sub>2</sub> was informed by the reaction pathway of the DES powder [124], using LiCl directly as a reactant rather than as an intermediate produced during the reaction resulted in the introduction of clear methodological issues [67].

The issues related to the use of LiCl arise from its extremely hygroscopic nature [67], readily pulling water from the air under ambient conditions. This was first observed in the oily texture of the partially reacted DES powders (DES 1-3 in section 3.3.2) and the difficulties of working with LiCl have been noted by other researchers, for example by Hanaor *et al.* [67]. The mixture to be cold sintered would not dry fully just with grinding and air contact and was added to the die with a paste-like consistency.

The RCS method as described uses a pressure of 750 MPa. This was enough to extrude out almost all of the paste initially introduced, yielding very small pellets (resulting in mass losses of up to 80% of the 0.3 g of initial powder used) which shattered during the post-anneal step (initially 650 °C as described in section 2.2.2). The solid state powder showed extrusion to a lesser degree but the difference was relatively minor and was attributed to differences in fluidity due to their differing particle sizes.

CSP 1 (name given to this initial experiment) outlined a very clear issue that needed addressing before this method could be used to produce pellets reliably: moisture control and adequate drying of the powder pre-sintering. Poor tolerances in the equipment and high variance between die diameters only helped compounding this issue.

Initially, mass loss issue was tackled by reducing the amount of LiCl present. Table 3.2 shows the infill concentration used in the subsequent experiments. CSP 2 halved the amount of LiCl present using the DES powder (as it had shown to be the most sensitive to extrusion). This still resulted in significant extrusion and with the production of a



pellet of uneven shape with an 80% mass loss, which again shattered during post-anneal. CSP 3 again halved the previous amount of LiCl, now using a 0.75 M infill solution with the DES powder. This time a very thick paste formed which experienced significantly reduced extrusion during pressing. The 0.144 g pellet cracked during post-anneal and was visibly powdery.

This method of moisture control was repeated with CSP 4 where a 0.75 M infill was used to sinter both the SS (730 °C) and DES 7 powders. Extrusion was significantly reduced with pellets weighing in at 65.2% and 83.8% of the original mass respectively after post-anneal. Using an Archimedes density balance, their density was calculated as 79% vs theoretical density (TD) and 75% TD respectively (using  $3.43 \text{ gcm}^{-3}$  as TD from literature shown on table 1.1). The pellets were pre-soaked in isopropanol to increase the accuracy of the result but closed porosity may still be inflating the values stated as these values were taken before a precise density measurement method was developed for this ceramic. Even so, these densities were deemed too low, smaller than the >90% TD achieved using a similar method by Boston *et al.* [125] and far from the as-high-as-possible target set as an aim by the fusion community for ceramics of this kind. This lack of density was attributed to the reduction in infill mass brought about by this approach to reduce the deliquescence of the to be sintered mixture. This approach was inherently flawed as: in an attempt to address the moisture retention and therefore to reduce mass loss during processing, the environment that allows for densification in the RCS process has been compromised. The infill itself is key to densification as, without significant coarsening mechanisms, its deposition around grains and subsequent reaction is the main mechanism behind it. Decreasing the overall amount of this infill will therefore affect the degree of densification achievable by the system. Considering the aims of this project involve the production of composites using this infill as a point of ingress for one of the relevant phases, this approach to reduce extrusion was deemed at odds with the project and a different avenue was pursued to address the concerns raised above.

Further instances of RCS would now be carried out using a 6 M LiCl infill solution (with 3 M  $\text{TiO}_2$ ), yielding a relative infill mass of  $\approx 27\%$ . Lower than this and the eutectic found by Knitter *et al.* [87] may start to become an issue, and high enough to clearly show under analysis. The DES powders produced (section 3.3.2) failed to generate single phase  $\text{Li}_2\text{TiO}_3$  when used in the RCS method and so, the next set of pellets were all produced utilising the solid state synthesised  $\text{Li}_2\text{TiO}_3$  (synthesised at 730 °C) whilst that issue was resolved. This however still has not solved the moisture issue, hence differing drying regimes were tested in an attempt to control the moisture of the to-be-sintered mixture.

The CSP 5 mixture was dried overnight at 180 °C prior to pressing. This resulted in no extrusion during the pressing step, however, the density of the pellet produced after post-anneal was 71% TD, lower than in the previous attempts and this value is likely inflated above the actual value, as the pellet was visibly powdery and did not feel fully cohesive. Considering that the mechanisms involved in the CSP process (see figure 1.17) are intrinsically related to the wetting of the powder used, the cause for this decrease in density was obvious: there was no moisture left to aid in particle rearrangement during the pressing stage. Evidently, a fully dry powder would not result in the production of

a dense pellet and hence this drying method on its own was deemed unsuccessful, the heating being too intense, fully desiccating the mixture.

A less intense drying regime was trialled with CSP 6 and CSP 7 with the to be sintered powder left overnight in a silica gel desiccator. Control of moisture is of utmost importance in CSP, with ambient conditions having significant effects in the resultant pellet [145], therefore, a method which enables the precise control and measurement of moisture would be preferred. In the future this could be achieved using saturated salt solutions [105]. After the desiccating step, CSP 6 was cold sintered directly around a minute after removal from the desiccator. This resulted in a pellet with 78% of theoretical density. During post-anneal, the pellet cracked with enough force to be ejected out of the crucible. This was assumed to be due to a combination of the expansion of the remaining moisture, together with stresses introduced due to the pressing of “scales” of powder (powder as removed from the desiccator had agglomerated into layered structures resembling scales). End-capping of compacts is understood to be exacerbated by the presence of agglomerates and further magnified with the presence of high compaction pressures [150]. This capping, and subsequent ejection of the resultant pellet was presumed to have been induced by pressing those powder agglomerates directly, and hence, CSP 7 was ground prior to pressing to avoid the impact of these layered agglomerates on the final sample. The brief time spent under pestle and mortar was enough to re-absorb enough moisture to, once again, allow some material to be extruded out of the die. CSP 7 resulted in a pellet of 78% TD, matching the previous iteration.

In order to confirm this measurement (as the accuracy of the Archimedes density balance was in question ) and assess the theoretically introduced bimodality, SEM micrographs of the CSP 7 pellet surface and fracture were taken together with EDX to check that the infill had fully reacted during the post-anneal step.

Figure 3.13 (a) indicates that the pellet is relatively dense, with no significant porosity, suggesting that the Archimedes density balance may not be overestimating the density after all. The fracture surface shows the presence of needle-like crystals which, based on the elemental maps, contain sulphur. The EDXA agrees with this, showing the presence of sulphur  $K\alpha$  peak at 2.3 keV. The source of the sulphate presence throughout the pellet could not be identified, as none of the chemicals utilised have resulted in introducing such a contaminant previously. One possible source of contamination could have been the ethanol used during measurements taken in the Archimedes density balance. Subsequent pellets were carefully analysed with this contaminant in mind as, if recalcitrant, its introduction vector must be properly identified.

Chlorine is present homogeneously throughout the pellet, indicating the infill material hadn't fully reacted.

Initially, this system was postulated to generate pellets with a bimodal distribution of particles: due to the formation of two distinct populations, coming from the infill and the pre-synthesised powder independently from each other. However, the difference between these populations was not large enough to clearly identify them in figure 3.13. The use of an  $\text{Li}_2\text{TiO}_3$  powder synthesised at a low (730 °C) temperature, in combination with an infill generated at a post-anneal temperature of 650 °C likely leads to the formation of particles of very similar sizes due to the limited coarsening achievable through the

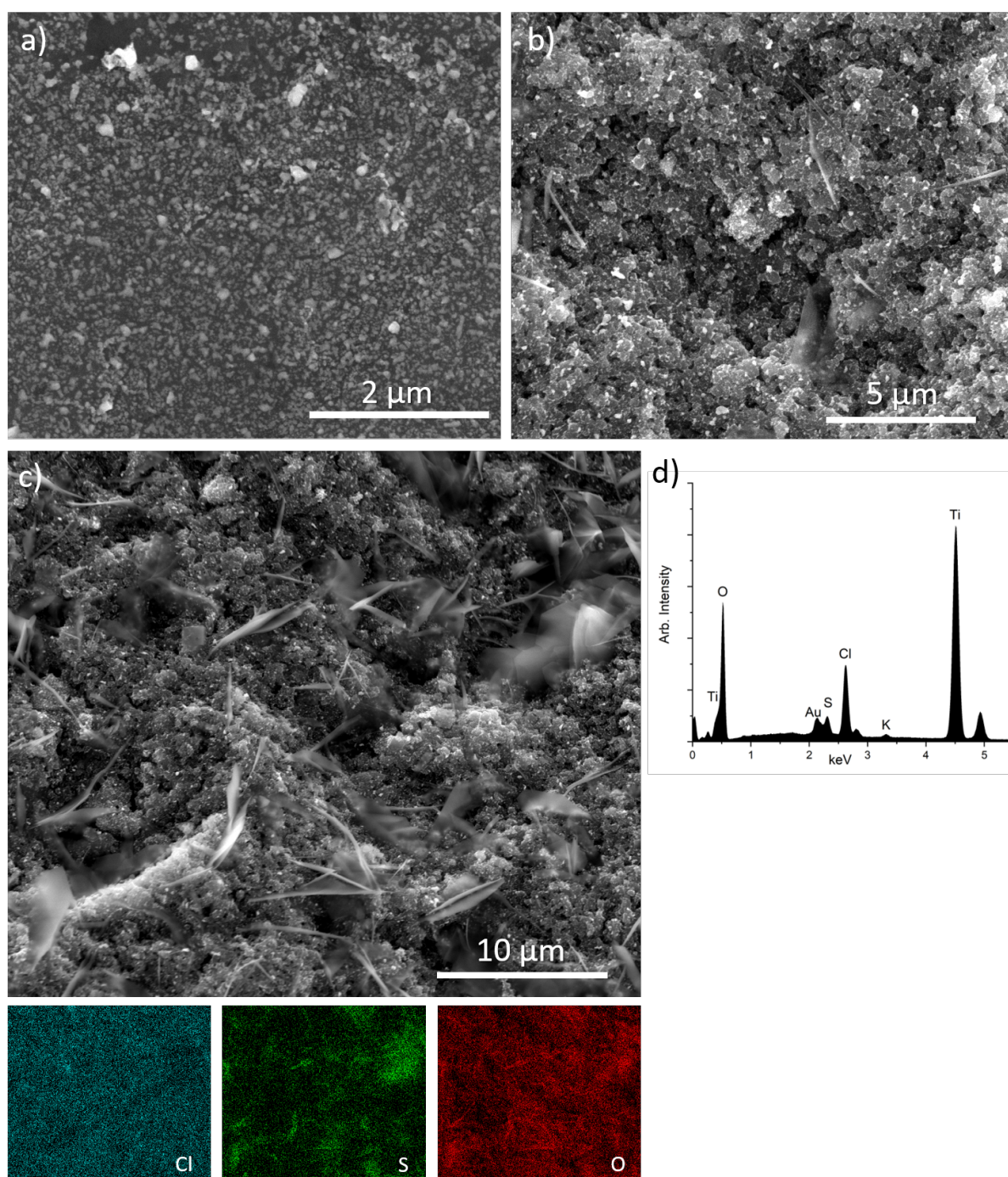


Figure 3.13: Secondary electron micrographs and corresponding EDXA spectra of the CSP 7 pellet. (a) pellet surface; (b) fracture surface; (c) fracture surface with elemental maps; (d) EDXA spectra. Sample was gold coated.

heating regimes applied.

Moisture control is of importance to aid replicability and consistency at the front end of the method applied, however the chlorine presence noted implies issues with the

proceeding steps and hence may be addressed and approached simultaneously.

Presence of chlorine in the EDXA was taken as an indication of unreacted material, just as when refining the DES synthesis method (section 3.3.2). Using the lessons learnt during the development of said method, it was concluded that a calcination temperature of 700 °C may be required in order to produce a fully reacted product. Considering the expected use of the DES powder as an analogue of the infill within the CSP pellets, it was decided that such a limitation was also likely of relevance here. Therefore, the post-anneal temperature was increased to match the DES powder synthesis method.

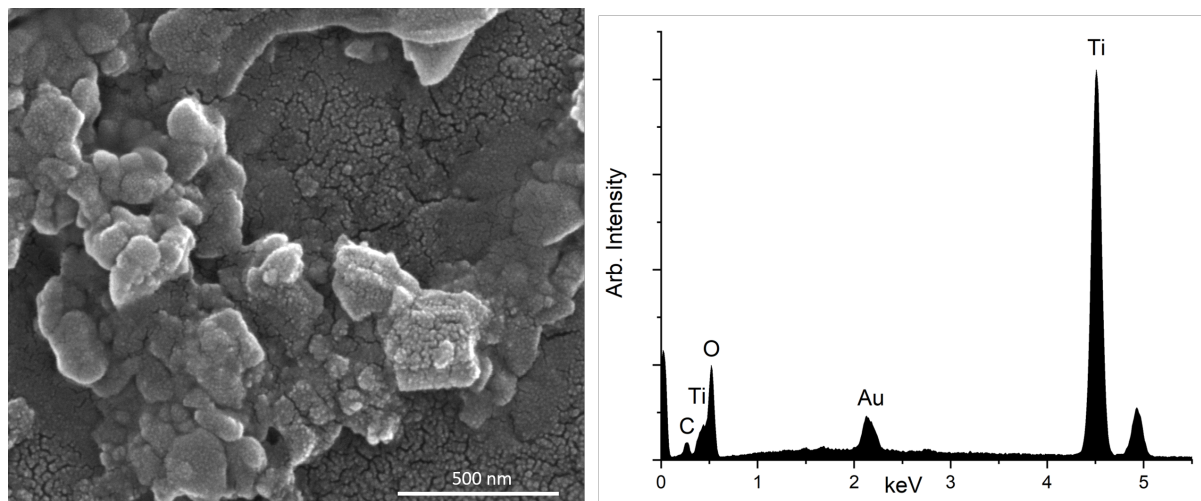


Figure 3.14: Secondary electron micrographs (left) and corresponding EDXA spectra (right) of an RCS sample, post-annealed at 700 °C.

As expected, no detectable chlorine was found on the EDXA of the RCS sample produced at this increased post-anneal temperature (700 °C). This further confirmed the applicability of the DES powder as an *ex-situ* analogue to that generated through the infill in RCS.

Small particulates can be observed. This was due to this sample being gold coated (as is also apparent from the EDXA). Gold particles are significantly larger than those deposited when carbon coating; considering the expected nm scale of the particles formed *via* the processes analysed, carbon coating was always used when available. As an aside, the sulphur containing phase present in CSP 7 could not be identified in figure 3.14 and therefore was taken as arising from random contamination during handling.

Hereon, all RCS pellets produced with the  $\text{TiO}_2$  –  $\text{LiCl}$  infill were post-annealed at a minimum temperature of 700 °C, as this was deemed sufficient to arrive at a fully reacted product. Density of these pellets still remained at 78%, as measured in previous samples.

Again, and as was expected from the micrographs generated during the DES experiments, no clear bimodality could be observed. The grain size of both populations of  $\text{Li}_2\text{TiO}_3$  are of comparable size and therefore are unidentifiable from each other in the bulk.

During polishing of these latter pellets (CSP 7 onwards) in preparation for SEM (using method outlined in section 2.4.2), an intriguing feature was found in all the surface XRD

done thereafter: certain peaks appear to double when compared to XRD of the as-sintered pellet surface.

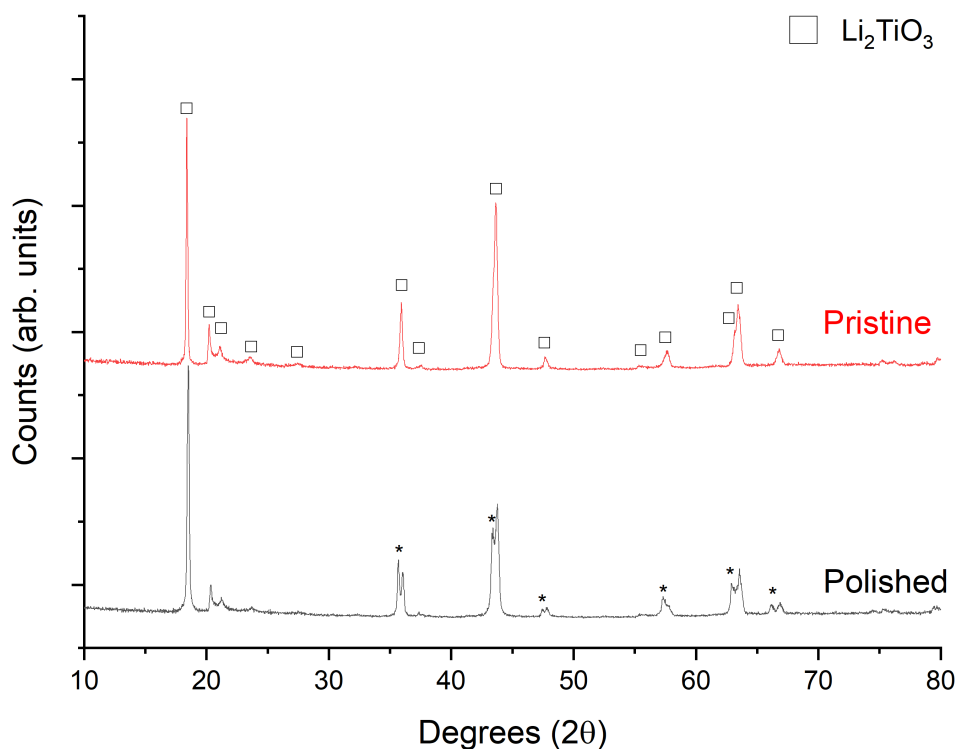


Figure 3.15: X-ray diffraction pattern of a pristine and a polished pellet surface. Unknown phase marked \*.

Initially, these pellets were identified as single phase, showing XRD patterns (figure 3.15) indicative of single phase  $\text{Li}_2\text{TiO}_3$ , however upon removal of the top surface, doubling of certain peaks was observed. As the diffractometers in use were not fitted with monochromators, this effect could potentially be representative of  $K\alpha_1$  and  $K\alpha_2$  peak detection, except, following this logic, the  $K\alpha_2$  peak should be found at higher angles than the  $K\alpha_1$  peak and should be of lower intensity than the  $K\alpha_1$  peak. Neither of these apply to the peaks in the observed diffraction pattern.

This indicates the presence of a structurally distinct phase within the bulk of the pellets produced. Bearing in mind the EDXA results (figure 3.14), showing a fracture surface containing exclusively Ti and O related peaks, as well as the similarity between the newly identified phase and the  $\text{Li}_2\text{TiO}_3$  phase already characterised, this could potentially be described by the presence of a second, structurally distinct, lithium titanate.

The addition of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (figure 3.16) led to a fully indexed diffraction pattern. This is a lithium-deficient spinel phase, the presence of which suggests a stoichiometry veering from that initially intended — the source of this imbalance, and mechanisms resulting in the appearance of this phase will be further analysed in section 3.3.3.4.



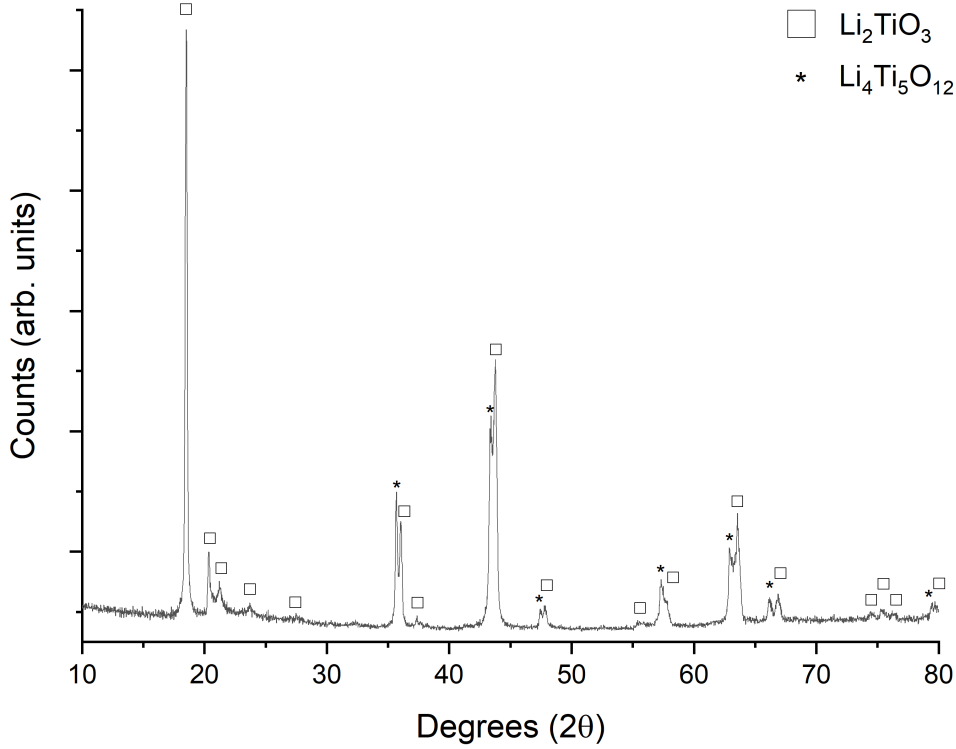


Figure 3.16: X-ray diffraction pattern of a characterised polished surface.

#### 3.3.3.1.1 Conclusions

Densification of  $\text{Li}_2\text{TiO}_3$  into useable pellets was demonstrated using the RCS method. This was achieved using temperatures 400 °C lower (700 °C) than those required during solid state sintering of similar powders (1100 °C) [40, 79, 83, 85–87, 92, 93]. The grain size of the phase introduced was not conducive to the formation of a bimodal material but this will be addressed in section 3.3.3.2.

The presence of a lithium deficient species ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) suggests further methodological concerns as, even if the material has fully reacted, a stoichiometric imbalance is likely introduced during the procedure. Further analysis is required in order to understand where this occurs and how to address it.

Two key factors were identified during method refinement as barriers to the replicability of the RCS method:

- **Moisture control.** Wetting of the grains of introduced powder is key in order to allow for particle rearrangement in the system [143]. However, excessive wetting will result in enhanced powder mobility which may lead to phase segregation as well as uncontrolled extrusion. The limits of this will likely vary in a per system basis, depending on initial particle size and powder chemistry. Identification of these limits may aid repeatability, however, full control of this necessitates the use

of some form of complete atmospheric control. Ambient temperature, atmospheric pressure and ambient humidity all will affect the rate of evaporation as well as the moisture content of the powder mixture pre-RCS. The design of such a piece of equipment is outside the scope of this project.

- Equipment condition. Non-parallel plungers and poor tolerances between said plungers and the dies themselves will lead to uneven pressure distribution as well as allow for excessive extrusion respectively. Both of these effects compound each other and lead to the generation of unique, non-repeatable samples. Good care and control of the equipment is required in order to allow for consistency.

### 3.3.3.2 Morphological control

The method developed in section 3.3.3.1 allows for the generation of fully reacted pellets containing both, a pre-synthesised material and an independent infill phase. One of the key benefits identified previously of such a procedure lies with this independence between the two components at play in the RCS method, allowing for the combination of two particle populations with different thermal histories, and therefore, morphologies.

Using the method as described however, leads to a generally homogeneous morphology, as is visible under SEM. This was attributed to the relatively consistent particle size between the powder synthesised using the solid state technique at 730 °C and the DES analogue produced in section 3.3.2.

In order to demonstrate the capacity of the RCS method to generate pellets using two independent components, the particle size difference between these two components needed to be increased. This would allow the two different populations to be clearly identifiable when analysed under SEM.

To this end, a batch of lithium titanate was synthesised following the method described in section 2.1.1, with a final dwell at 1100 °C for 4 hours.

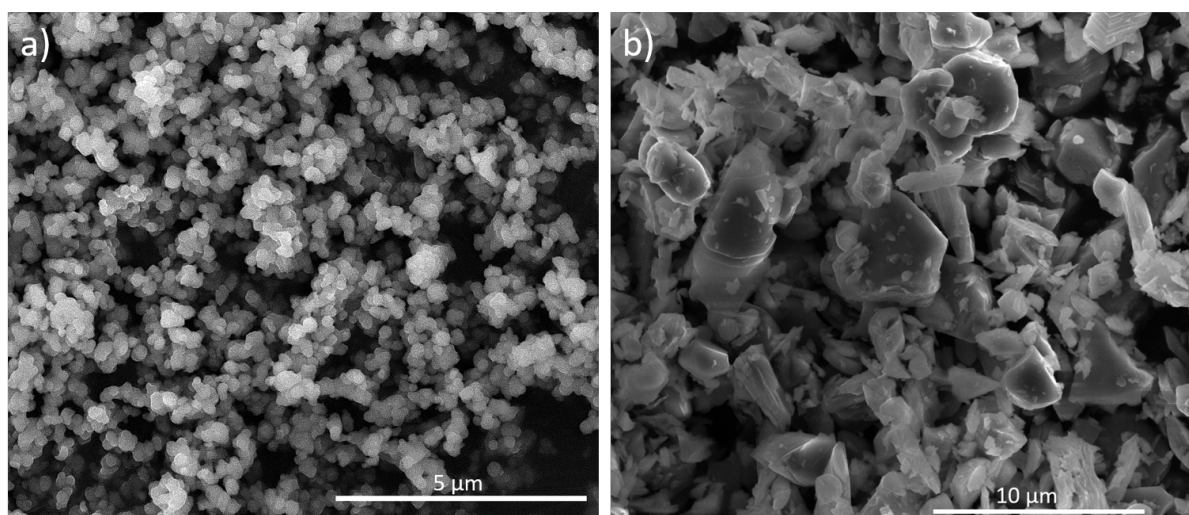


Figure 3.17: Li<sub>2</sub>TiO<sub>3</sub> powders synthesised at (a) 730 °C and (b) 1100 °C.

As can be observed from figure 3.17 the difference is stark between the two particle populations; as can be assumed from the 370 °C firing difference between them. Considering the expected size of the particles coming from the infill after post-anneal (refer to DES analogue in figure 3.7), this size increase in the main phase powder should be sufficient to identify both particle populations when observing the final pellets under SEM.

Following the method used for pellet CSP 7 (outlined in section 3.3.3.1), 0.3 g of the powder synthesised at 1100 °C was combined with 0.333 ml of the 6 M LiCl – 3 M TiO<sub>2</sub> infill (27% of infill by mass) and left to dry in a desiccator (humidity sensor reading < 5%). The resultant powder was briefly ground to loosen any agglomerates and loaded into a press. The pressure was allowed to equilibrate at 750 MPa for 15 minutes, followed by an hour hold at 180 °C under load. The pellets were then extracted and loaded into a furnace where they were post-annealed at 700 °C for 4 hours (temperature increased following findings in section 3.3.3.1).

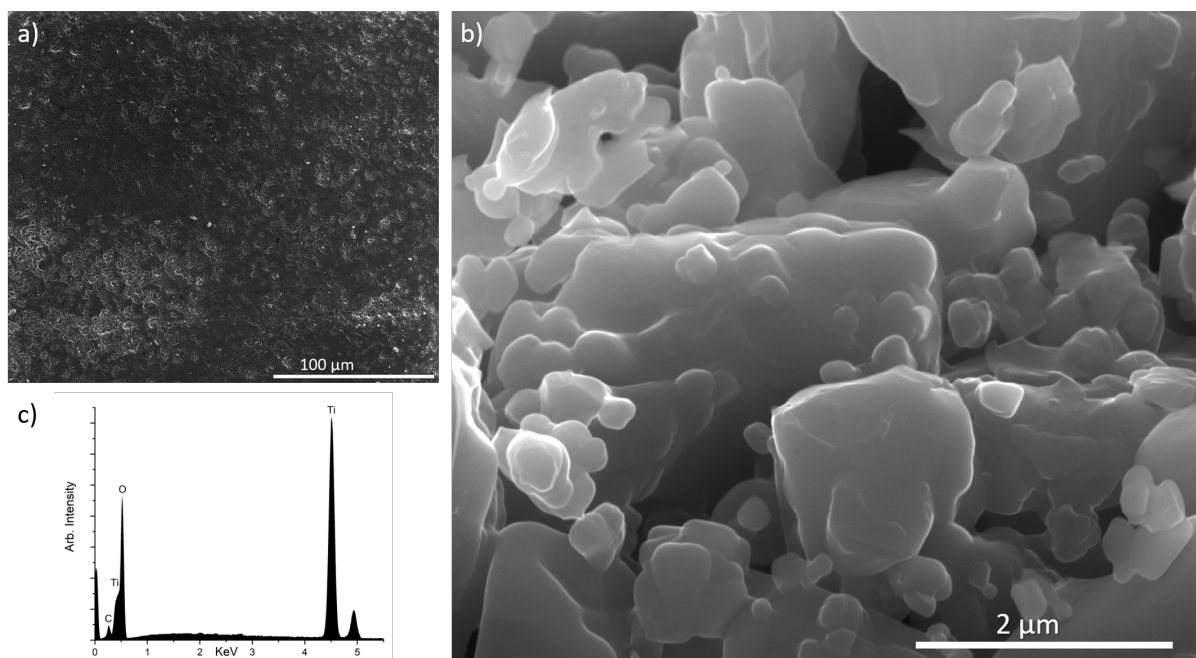


Figure 3.18: Secondary electron micrograph of (a) the pellet surfaced after polish and (b) a high magnification micrograph of a pellet fracture. EDXA of material in the fracture shown in (c). Sample was carbon coated.

The difference between the micrographs shown in figure 3.18(b) and those produced in section 3.3.3.1 is clear. Bimodality is clearly present, with a population of particles in the order of 100 - 400 nm surrounding micron-sized grains from the newly generated 1100 °C main phase powder. Crucially, comparing these to the starting powders utilised shows retention of the original particle size (fig 3.17), demonstrating the ability of this method to produce pellets from a powder of a predetermined size.

Surface SEM suggests relatively dense ceramics, however, in order to maintain the thermal history of the pellets no thermal etch was carried out prior to SEM. This reduces



the clarity and reliability of the resultant micrographs, so no conclusions could be derived from this measurement alone. In addition to this, previous work has suggested that cold sintering in general tends to preferentially densify pellets at the surfaces perpendicular to the pressing axis [151], and hence, density cannot be informed solely from surface SEM of any kind.

Both bulk and surface XRD analysis of these pellets was performed in order to confirm the added infill had fully reacted, as well as address the potential presence of the lithium deficient titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) identified in section 3.3.3.1.

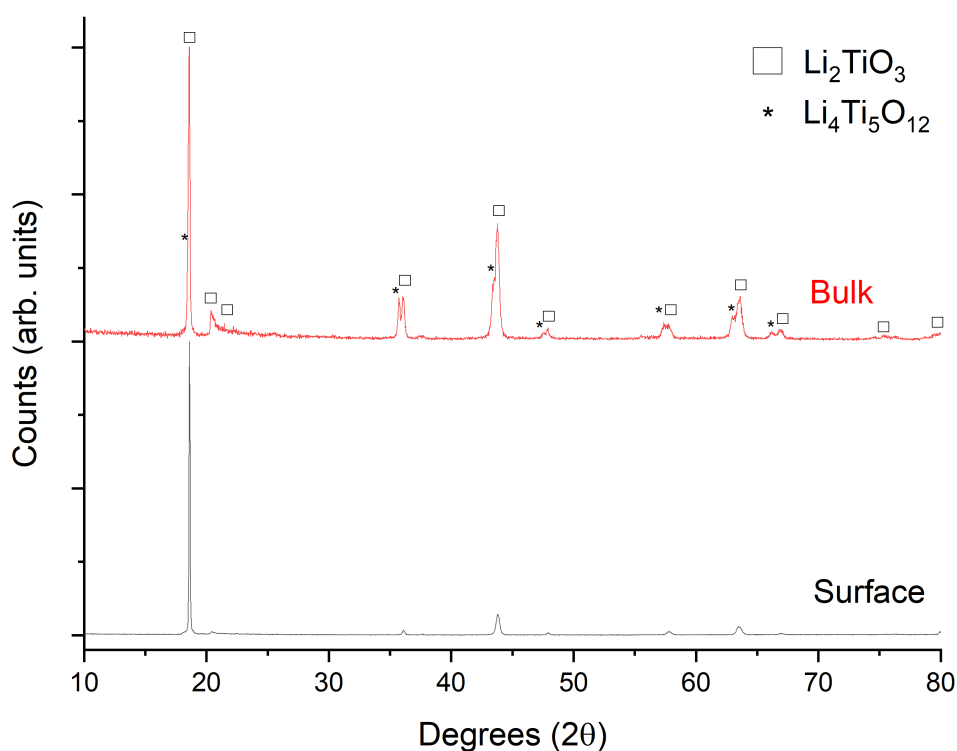


Figure 3.19: X-ray diffraction pattern of a pellet sintered using the RCS method (700 °C post-anneal) and a main phase powder fired at 1100 °C. Pristine surface in black, reground in red.

As expected, the bulk XRD (reground pellet post-sintering refer to 2.4.1) reveals no further phases aside from  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ; the presence of which leads to the conclusion that its appearance is entirely dependent on the conditions experienced by the infill component of the pellet.

Comparing both the XRD pattern of the as-sintered surface to that of the bulk shows an intriguing difference in relative peak intensities. The 002 peak exhibits a dramatic increase in relative intensity when compared to the rest of the peaks, suggesting an induced surface effect during processing. This will be further analysed in section 3.3.3.3.

With the introduction of the  $\text{Li}_2\text{TiO}_3$  powder synthesised at 1100 °C the capacity of

the RCS method to produce pellets with two different, independent particle populations has been demonstrated. Particle size is retained from pre-sintered powders, allowing for predetermination of the final size of either population.

Two characteristics of the pellets generated still remain to be addressed: further analysis and characterisation of the preferential orientation effect of the peak related to 002 observed, as well as, identification of the mechanism behind the formation of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase identified and an attempt to correct it.

### 3.3.3.3 Preferential orientation

Orientational effects in pressed ceramics are well known [152], although not usually addressed as through solid state sintering these effects are generally annealed out and hence can't be observed in final pellets. Certain applications, such as batteries and functional materials, benefit from this induced texture, as specific crystallographic orientations tend to be better at certain forms of conduction than others. The benefit of this effect in a fusion context, if any, has not yet been investigated.

With uniaxially pressed pellets this orientation effect is generally understood to be pressure induced, however the exact mechanism is less clear. On one hand pressure induced mechanical deformation of the powder particles themselves, and therefore leading to crystallographic distortion, could result in the overexpression of certain orientations [153], on the other, and especially when considering relatively anisotropic crystals, grain alignment may lead to a reorientation of particles in specific directions due to vertical deviatoric stresses on the crystallites from the compression load [154]. The latter is also aided by the presence of an interspersed fluid which facilitates inter-grain motion. It follows then that the presence of a powder with an anisotropic crystal structure, in combination with the particle rearrangement already allowed by the conditions introduced during the RCS method, may lead to increased texturing through the latter mechanism than in green bodies produced before conventional solid state sintering.

Preferred orientation could be observed in the pellets generated in this project and what follows is an analysis of the degree of texture as well as the conditions leading to this observed effect.

#### 3.3.3.3.1 Surface vs Bulk

This preferential orientation effect was initially observed on pellet surfaces when using the RCS method and the 1100 °C synthesised main phase powder.

In order to quantify and compare the degree of texture observed in these samples the Lotgering factor (LF) will be used [155]. This is defined as follows:

$$LF = \frac{p - p_0}{1 - p_0} \quad (16)$$

where  $p$  is the fraction of the sum of all peak intensities related to a specific family of peaks to that of the sum of all peak intensities, and  $p_0$  is the same for a randomly oriented sample (or a specific reference sample as is the case here). An LF of 0 refers to a perfectly random sample (or containing the same proportional intensities as the reference

sample) and an LF of 1 refers to a perfectly oriented sample (or one which only contains peaks of the peak family in question, 002 in this case)

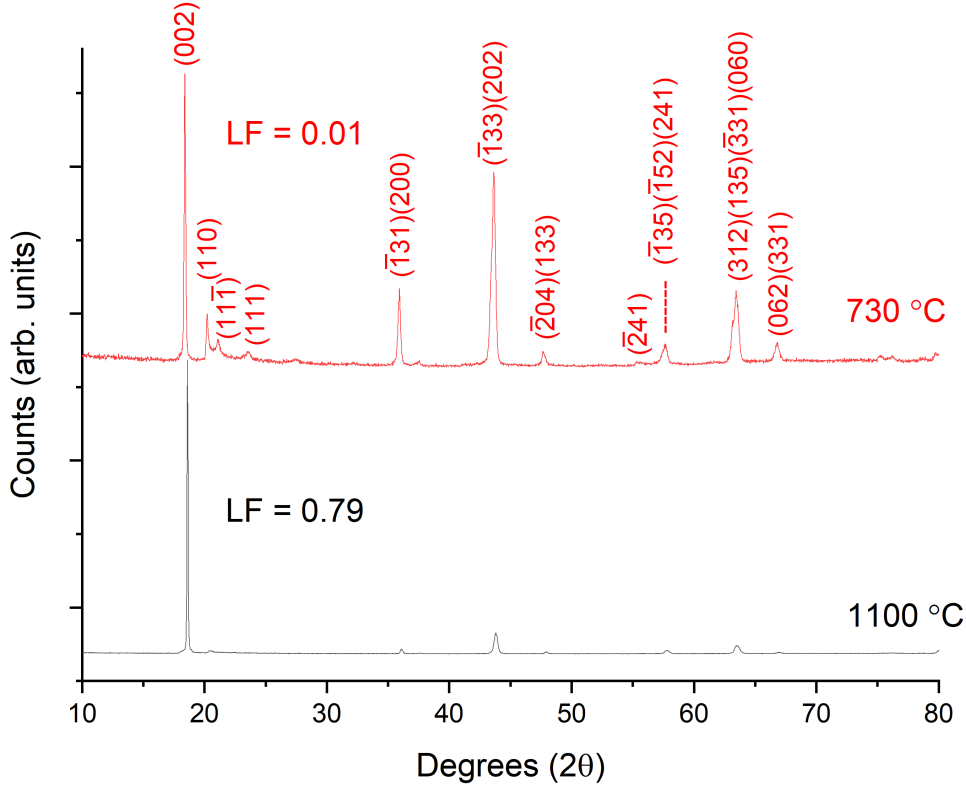


Figure 3.20: X-ray diffraction pattern of two pellet surfaces, using a main phase powder synthesised at 730 °C (in red) and at 1100 °C (in black). Relevant HKLs have been added for clarity. Calculated Lotgering factor shown.

Interestingly pellets generated using the lower temperature (730 °C) powder don't exhibit the same degree of preferred orientation as their high temperature counterpart (fig 3.20). An LF of 0.01 suggests that these pellets have essentially no texture when compared to a random sample of lithium metatitanate powder. The main difference between these two pellet groups is the average crystallite size of the main phase powder. Considering the mechanisms likely at play here, perhaps this increased number of crystallites allows for enough additional randomness to lead to this reduction in texture.

Lithium titanate, especially compared with *e.g.* YBCO (yttrium barium copper oxide), is a much less anisotropic crystal ( $a = 5.05 \text{ \AA}$ ,  $b = 8.76 \text{ \AA}$ ,  $c = 9.68 \text{ \AA}$ ), hence particle rearrangement – although one of the key mechanisms leading to densification in the RCS method as applied in this study – is unlikely to have resulted in the high degree of texture observed. An LF of 0.79 shows that indeed, surface orientation is preferably aligned in the 002 direction in samples made using this main phase powder with a larger crystallite size.

Crystallite size may explain why preferred orientation only occurs in samples made

with the larger powder, however, the reason behind the effect observed is still unanswered. Following the sample through the method may elucidate which step is inducing it and hence may clarify what mechanism may be resulting in this effect.

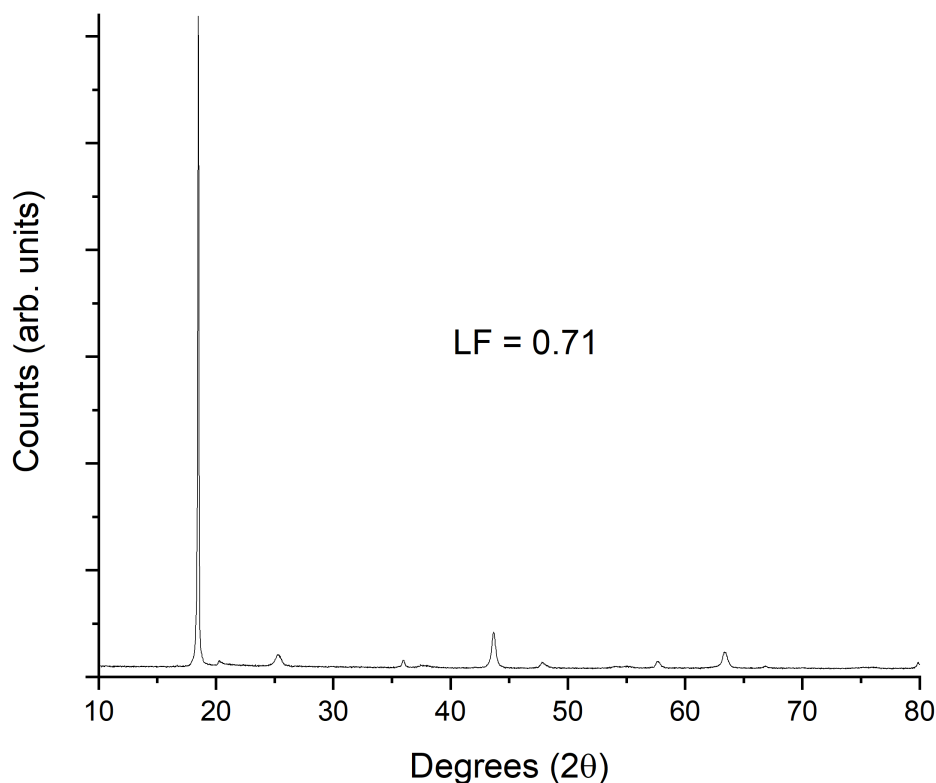


Figure 3.21: X-ray diffraction pattern of a green body pressed at 100 MPa. Lotgering factor shown.

Further, to remove any variables introduced through the RCS method, a sample of 1100 °C powder was pressed into a green body at 100 MPa. This green body material was then analysed by XRD and the preferred orientation effects were once again apparent. An LF of 0.71 was calculated, not as stark as the sample XRD after post-anneal but extremely significant nonetheless. This implies that the increased pressure, added heat, added moisture, secondary phase and pressing time have little effect on the introduction of texture and, just by virtue of pressing the powder, preferred orientation of the 002 peak is induced. The higher LF on a pellet that has been cold sintered may simply be due to the higher pressure (750 MPa) and longer pressing times (one-hour vs a few minutes) involved compared to the formation of a simple green body.

Of course, this effect is only able to be retained in final pellets due to the reduction in sintering temperature (400 °C lower than conventional solid state sintering) brought about by the RCS method used and if these pellets were to be sintered using conventional steady

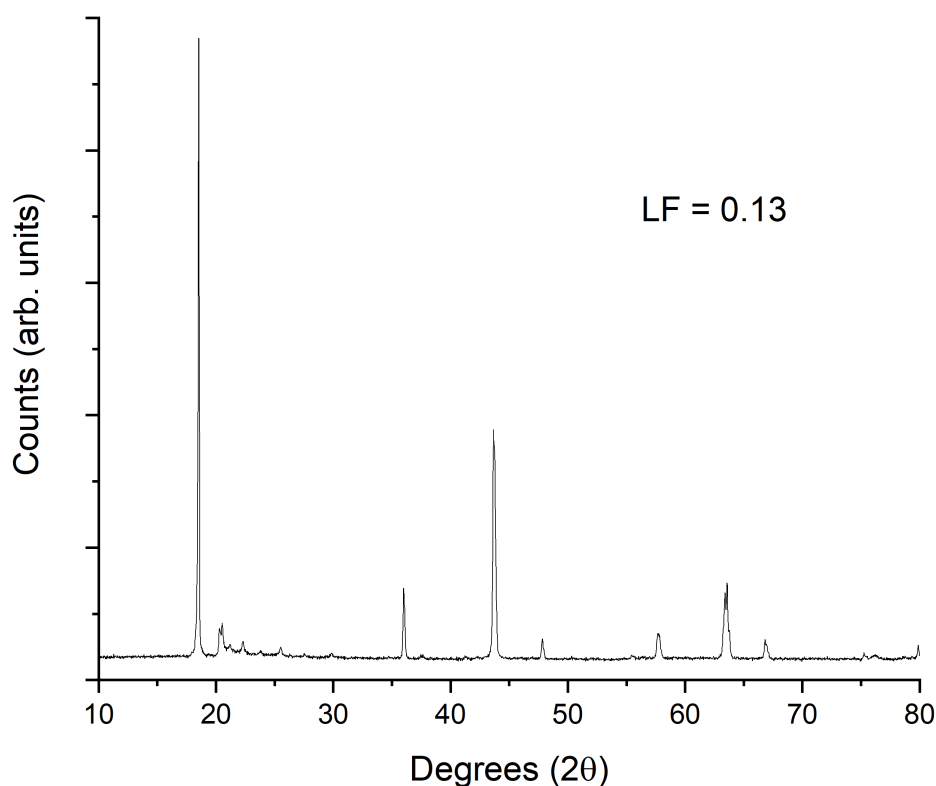


Figure 3.22: X-ray diffraction pattern of a pellet sintered at 1100 °C for 4 h. Lotgering factor shown.

state the texture induced will be all but completely annealed out. Figure 3.22 clearly shows this, with a reduction in LF from 0.71 as a green body, down to 0.13 as a fully sintered pellet.

As expected, grinding up an RCS pellet results in a loss of most of the induced texture as, through processing, crystallites become randomly oriented. This results in a drop from 0.79 after post-anneal to 0.22 after grinding it down. Some texture remains but is likely due to the hardness of the final pellet preventing the powder from being reduced to a small enough size using a percussion mortar. Of note is the sudden expression of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase after powdering the pellet, revealing the bulk characteristics identified in section 3.3.3.1.

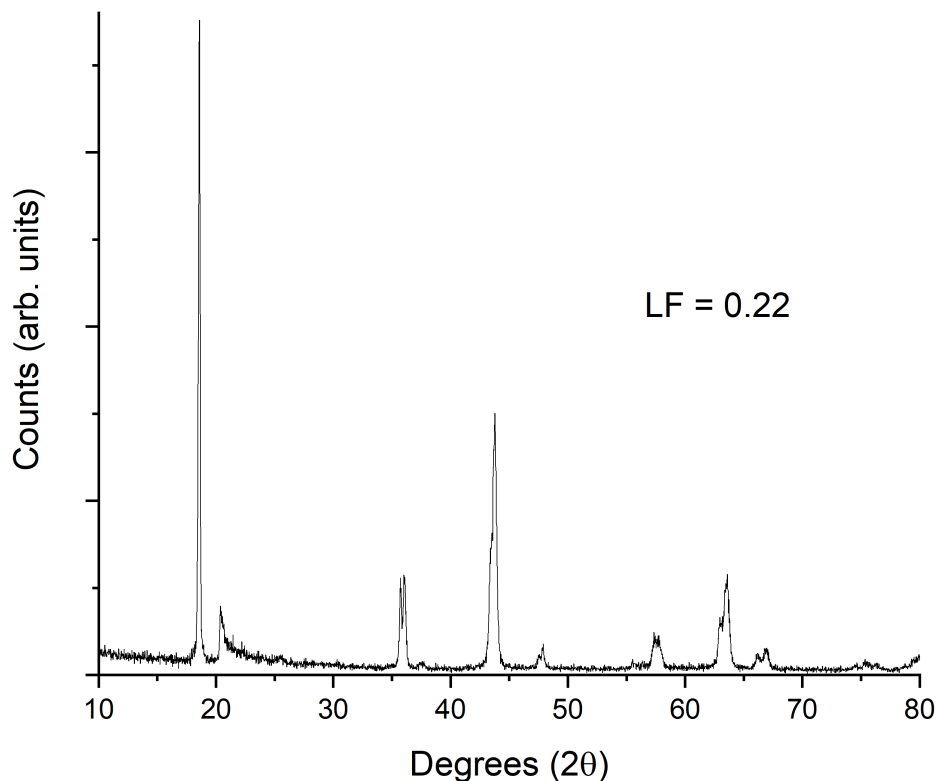


Figure 3.23: X-ray diffraction pattern of a crushed RCS pellet with the main phase powder synthesised at 1100 °C. Lotgering factor shown.

In summary, XRD reveals a pressure induced preferential orientation effect, leading to the over-expression of the 002 peak in all pellets generated using a starting powder synthesised at 1100 °C, regardless of pressure applied. Using a powder with smaller crystallites led to little to no texture, with a calculated LF of 0.01, meaning it was essentially exactly as random as the un-sintered powder. However, a sample made *via* RCS using a starting powder synthesised at 1100 °C led to an LF of 0.79. Clearly the larger crystallites in the second powder have some effect on the preferred orientation effect observed.

Even though the crystal itself is relatively anisotropic, especially when compared to the likes of YBCO, it does show anisotropy in other ways. The layered nature of the  $\text{Li}_2\text{TiO}_3$  crystal leads to the presence of cation channels running through the *ab* plane. This results in improved tritium diffusion and thermal conductivity down this plane [73, 156, 157] compared to other directions — the benefits of these two properties on fusion applications would be enormous as part of the issue with ceramic breeder materials is potential tritium retention issues as well as slow heat dissipation. The overexpression of the 002 plane implies the alignment of surface grains with this *ab* plane, meaning the pressing direction

is parallel to the  $c$  direction. This should result in surface grains with cation channels running parallel to the surface and not perpendicular, as would be necessary to benefit from the anisotropic thermal conductivity and tritium diffusion. However, the capacity of this method to retain this texturing means that if a method that allows for the alignment of the  $ab$  plane perpendicular to the surface could be found, RCS could then be used to sinter the resultant ceramic and retain said induced texture.

Separating the powder from the RCS method still showed preferred orientation, with a sample which was simply pressed into a green body still showing an LF of 0.71. This is slightly smaller than found when processed with RCS but still large enough to conclude this is likely a pressure induced effect, the difference then, likely due to the increased pressures in the RCS method. A pellet sintered at regular sintering temperatures (1100 °C) showed an LF markedly reduced (0.13), implying that this effect can be annealed out with increased temperature. After crushing, the pellets made *via* RCS show a previously invisible phase ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) and a reduction in LF down to 0.22, the slight texture present likely due to poor sample grinding.

An additional question to further describe this effect is: is this effect seen throughout the pellet or could it be limited to the surfaces perpendicular to the applied force?

### 3.3.3.3.2 Cross-sectional Analysis

Considering the likely introduction of this preferred orientation effect through the pressing process, it was postulated to be a pressure induced surface effect. Initially, to confirm this assertion and to observe the likely change in relative peak intensities across the sample an experiment was devised in order to take sequential XRD measurements through the samples' cross-section.

This was done by taking XRD patterns of the pellets' surface and subsequently grinding off part of said surface – at least three times over the 31  $\mu\text{m}$  attenuation length (distance where beam intensity has dropped to  $1/e$  [158]) of  $\text{Li}_2\text{TiO}_3$  at the surface normal – revealing a pristine surface, after which the new pellet thickness would be noted using a set of Vernier callipers and the surface re-examined using XRD. This would be repeated from both surfaces perpendicular to the pressing axis until no more material could be removed or the pellet crumbled. Due to the amount of material necessitating removal, a set of 4 mm thick pellets was produced for this analysis.

The Lotgering factor of the 002 family of peaks on the resultant scans was plotted vs pellet depth generating a pellet profile with degree of preferred orientation throughout.

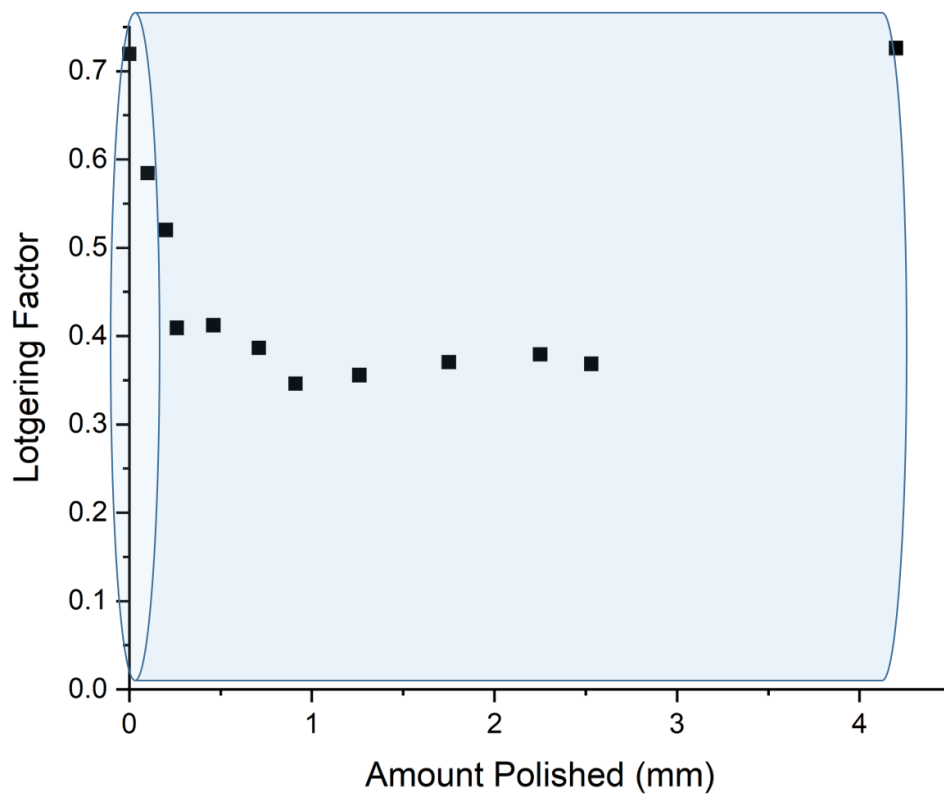


Figure 3.24: Lotgering factor plotted against amount polished off of an RCS pellet. Visual representation of said pellet added for clarity. Last point at 4.2 mm is the other pristine surface, scanned at the start. Pellet started breaking apart after 2.5 mm of material was removed.

Clearly, the degree of preferred orientation very strongly correlates with distance from the surface perpendicular to the pressing axis. Both surfaces show high degrees of preferred orientation, slowly approaching an LF of 0 although stabilising around the middle of the pellet at an LF of around 0.35. Lotgering factor sharply drops as material is removed, with a drop from 0.72 to 0.4 in the first 260  $\mu\text{m}$ . This clearly indicates a heavily surface dependent effect. Texture is likely still induced throughout the pellet simply due to being exposed to the pressures needed to cold sinter it, although the effect is much more subdued.

Previously, two potential pathways to this preferred orientation effect were identified (section 3.3.3.2), one of which was grain alignment. Considering the relative isotropy of the crystal structure in question ( $a = 5.05 \text{ \AA}$ ,  $b = 8.76 \text{ \AA}$ ,  $c = 9.68 \text{ \AA}$ ) grain alignment was considered to be unlikely, however, now knowing the effect was surface dependent, cross-sectional SEM could be used to attempt to observe a difference between crystallites at the sample surface vs bulk.



In order to confirm the arrangement of crystallites in the samples, a cross-section of a pellet generated through RCS was produced and analysed with SEM imaging.

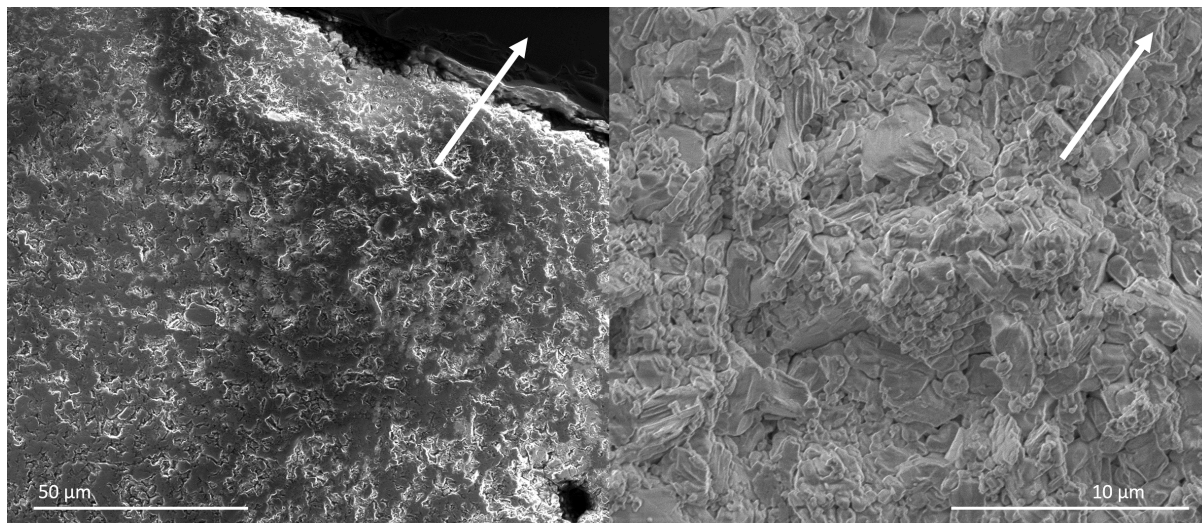


Figure 3.25: Secondary electron micrograph of a cross-section of an RCS pellet using the  $\text{Li}_2\text{TiO}_3$  powder synthesised at 1100 °C. Low magnification (left), high magnification (right) of areas immediately beneath the surface. Arrow pointing in the direction of the pellet surface.

No clear particle alignment could be identified, as expected due to the relative isotropy of the crystal. However, the larger grains did seem to be somewhat columnar, although no clear alignment could be spotted with these columns pointing in random directions. If there is any texture due to the alignment of these elongated particles it isn't immediately apparent from the SEM.

In conclusion, this preferred orientation effect is pressure induced and surface dependent. The effect is retained due to the low temperatures used during the RCS method, as has been seen elsewhere [159]. Even though RCS presents the perfect conditions for particle rearrangement (high deviatoric stress and presence of an interspersed fluid), the relative isotropy of the crystal makes this unlikely to lead to the high degree of texture observed, further confirmed by the lack of particle alignment observed in the cross-sectional SEM. Pressure induced crystallographic distortion is therefore the more likely mechanism at play here.

#### 3.3.3.4 Infill composition and air mix

With the first unusual characteristic of the Bimodal pellets addressed, now the presence of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase must be analysed.

Initially, a variety of potential factors resulting in the introduction of this secondary lithium titanate were identified. Firstly, lithium content during the post-anneal step may be lower than anticipated, either due to losses prior to heating or due to lithium volatility during the ramp to and hold at 700 °C. Volatility concerns were partially the reason behind the use of the RCS method and literature suggests that no significant

volatilisation occurs before 800 °C [53,106–108], however, the presence of the pre-reacted LiCl may alter the lithium partial pressure at low temperatures and could, perhaps lead to an increase in lithium loss *via* volatilisation, although this was seen as very unlikely at the temperatures in question.

Secondly,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is not only lithium deficient, but oxygen deficient as well when compared to the target  $\text{Li}_2\text{TiO}_3$  structure.

Thirdly, lithium content may be as calculated through the post-anneal, however,  $\text{Li}_2\text{TiO}_3$  can form a lithium rich solid solution [70] and has been shown to leech lithium from multi-phase systems due to this [67]. This effect could be further exacerbated if the initial  $\text{Li}_2\text{TiO}_3$  powder sintered at 1100 °C is already somewhat lithium deficient, as the material’s capacity to accept lithium would be enhanced. Fourth, the deliquescence of the LiCl itself may be leading to excess hydration of the pre-RCS mass and therefore resulting in excessive die extrusion and material loss, ultimately leading to the introduction of a stoichiometric imbalance in the system.

Finally,  $\text{Li}^+/\text{H}^+$  ionic exchange in the  $\text{Li}_2\text{TiO}_3$  structure may lead to leaching of lithium, perhaps to a large enough degree that the lithium deficient species begins to form. Large degrees of protonation have been noted on lithium conductors such as LLZO [160]; lithium’s highly mobile nature may exacerbate any potential protonation in the hydrated RCS system. In order to expose and observe the lithium deficient phase using XRD, the generated pellets were ground using a percussion mortar to produce a sample representing the bulk material.

A potential source of stoichiometric imbalance has been identified above and is the potential lack of oxygen leading to the formation of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as an oxygen deficient lithium titanate. This was addressed by firing a pellet using the LiCl-TiO<sub>2</sub> infill under oxygen.

As is clear from the resultant XRD (figure 3.26), the addition of pure oxygen during post-anneal has not changed the proportion of the phases to any significant degree so it can be concluded that the presence of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is likely dependent on a lithium deficiency rather than oxygen.

Different infill compositions were trialled in an attempt to address the final three factors identified above.

At first the solid solution hypothesis was considered the most approachable, both due to its appearance in similar systems in the literature [70] and the apparent simplicity of the explanation: saturate the solid solution. To this end a LiCl infill was produced with  $\approx 35\%$  Li excess to both saturate the hypothetical solid solution and form the  $\text{Li}_2\text{TiO}_3$ .

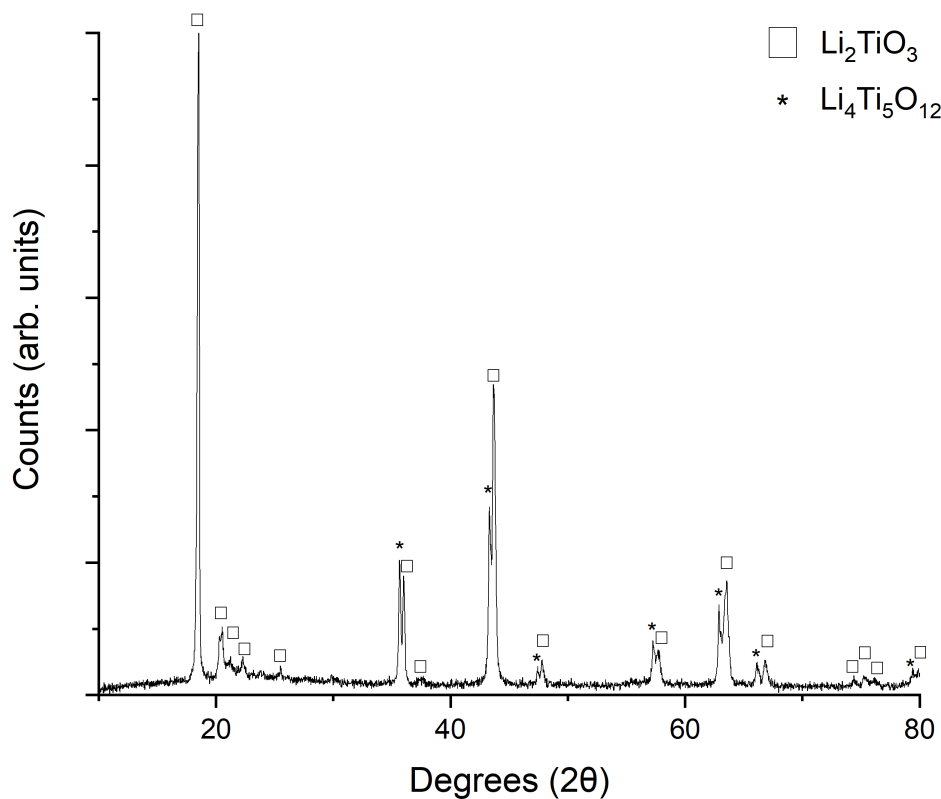


Figure 3.26: X-ray diffraction pattern of an RCS pellet post-annealed under an  $O_2$  atmosphere.

Clearly, this additional lithium has not resulted in the formation of single phase  $Li_2TiO_3$  and it has not even reduced the proportion of  $Li_4Ti_5O_{12}$  by any discernible amount, see fig 3.27. From an abundance of caution and to fully address the possibility of adding a lithium excess through the infill, a second test was done using an infill with  $LiCl$  at 100% lithium excess; the thought process being that if the problem could be solved through this vector, doubling the amount of available lithium should lead to single phase  $Li_2TiO_3$ , even if some unreacted  $LiCl$  remained.

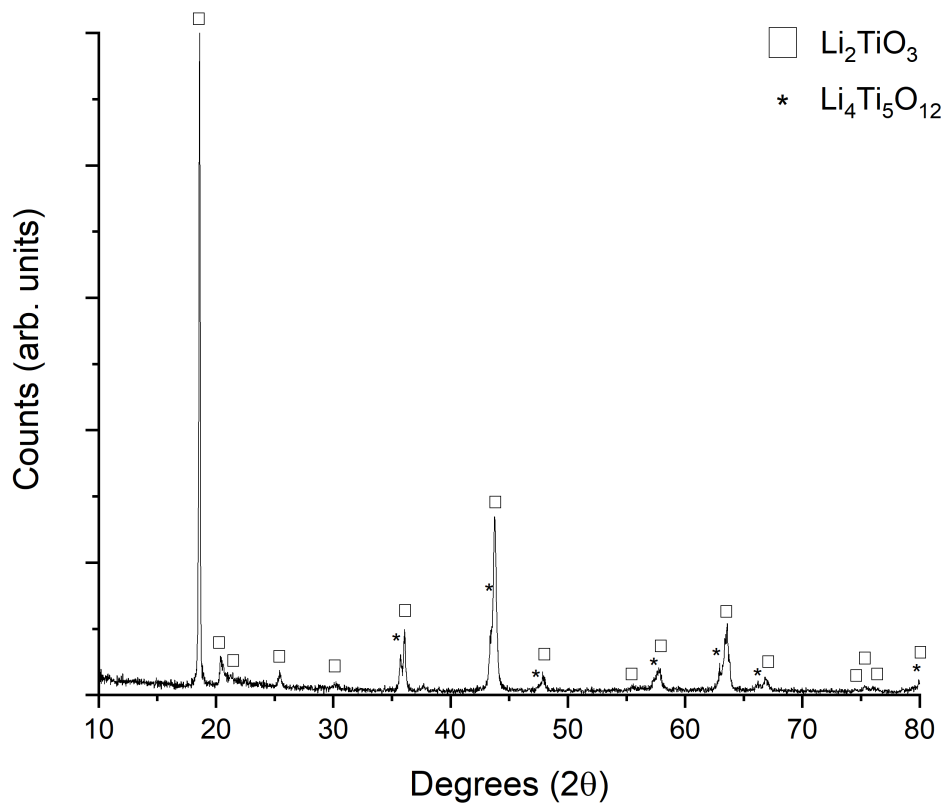


Figure 3.27: X-ray diffraction pattern of an RCS pellet using a starting infill with a 35% Li excess.

Working with such a lithium excess meant use of higher LiCl concentrations. This led to RCS batches with high failure rates as extrusion some days was enough to remove most of the material from the die. Even though the initially available lithium was doubled, no significant decrease in the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase could be identified. This result logically led to the following three potential situations: a) the added lithium may be somehow being lost preferentially prior to post-anneal, b) a pathway exists that enables the rapid volatilisation of lithium at post-anneal temperatures or c) the lithium remains within the pellets unreacted. The final point can be called into question as no other phase aside from the two titanates mentioned can be observed from the XRD.

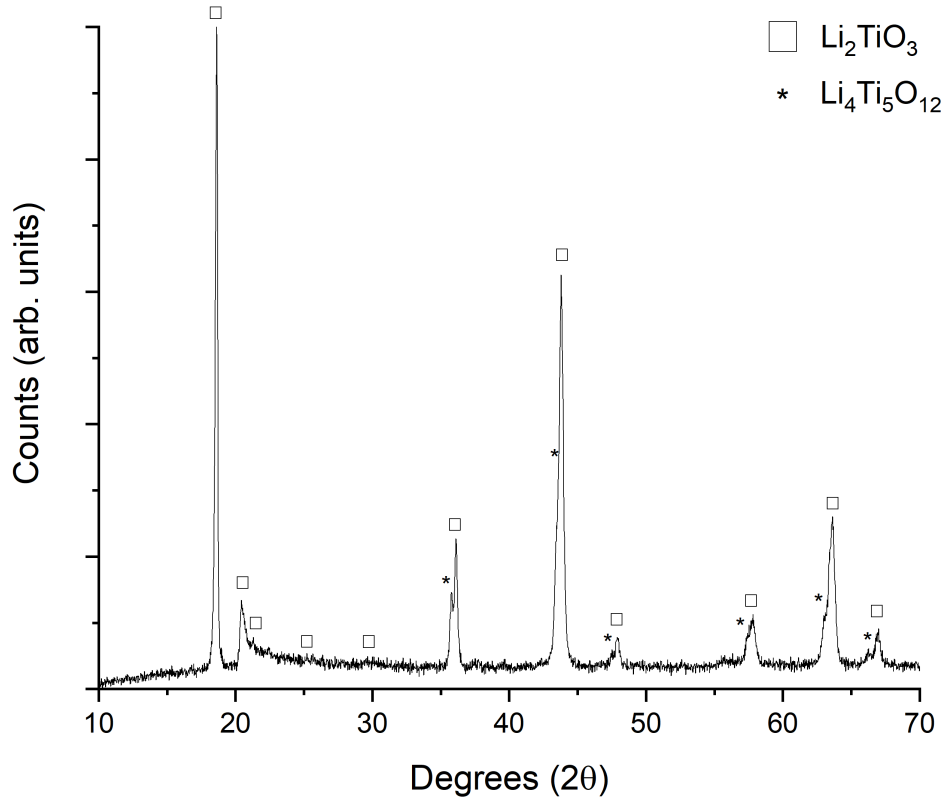


Figure 3.28: X-ray diffraction pattern of an RCS pellet using a starting infill with a 100% Li excess.

To address the deliquescence of the LiCl and therefore to attempt to approach the loss of material prior to post-anneal an infill was produced using lithium acetate as the lithium source (figure 3.29). After grinding the main phase powder together with this newly generated infill, the resultant powder was seemingly dry. However, during pressing significant extrusion could still be observed, even with a powder without the previously persistent paste-like consistency induced by the LiCl in the infill.

As expected from the similar degree of extrusion observed, the switch to lithium acetate did nothing to correct the proportion of phases in the final pellet. Further repeats of this experiment led to the same or similar degrees of extrusion. Potentially this may be due to water of crystallisation being released from the acetate as the temperature increases during pressing or, perhaps, the tolerances of the equipment in use have deteriorated to the point where the enough space exists to allow for extrusion of even dry material.

Considering the need for a transient solvent for the RCS to allow for low temperature densification, the potential issue of protonation poses a challenge. In most cold sintering systems this transient solvent is either water or some aqueous solvent [142] and if protonation is indeed causing the formation of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , addressing this by changing to a

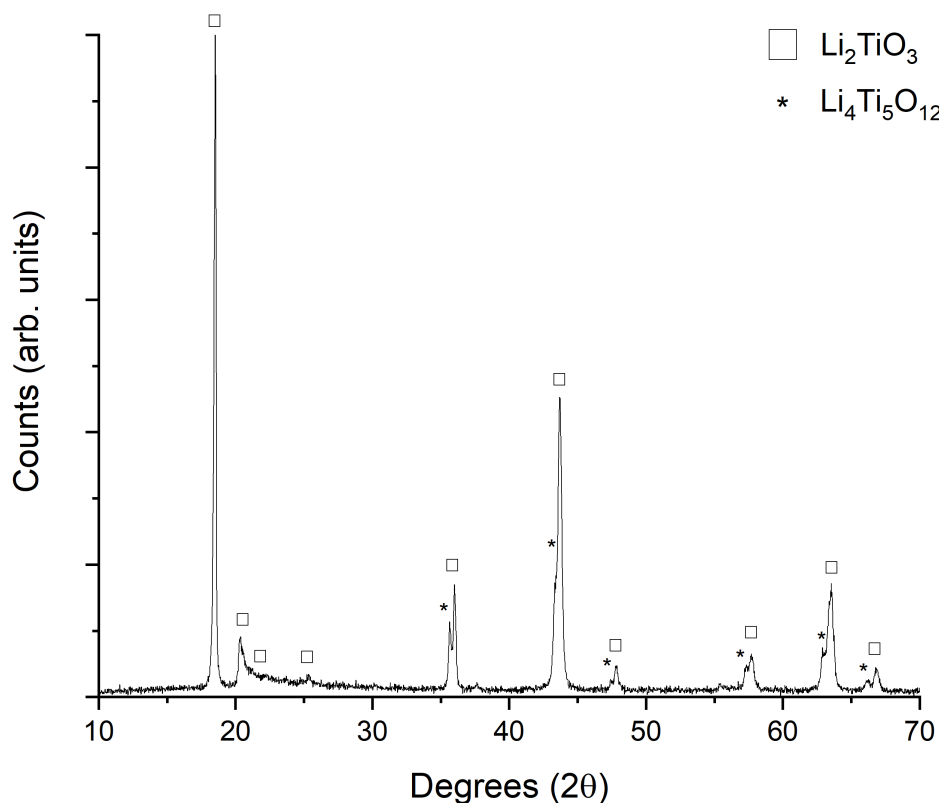


Figure 3.29: X-ray diffraction pattern of an RCS pellet using a starting infill using lithium acetate as a lithium source.

different solvent may impact the densification pathways involved with RCS by changing the intrinsic characteristics of the solvent, such as the surface tension and boiling point. Nonetheless, to assess the potential protonation issue (ignoring the likely impact on final pellet density for now), an infill was produced using ethanol as a solvent and LiCl as the lithium source. Ethanol was chosen as it has a higher  $pK_a$  than water, therefore resulting in a lower concentration of  $H^+$  in solution ( $pK_a$  of water = 14,  $pK_a$  of ethanol = 16) [161]. Solubility limits and solvent availability also limited the potential solvent-solute combinations usable as an infill in the RCS system.

The higher vapour pressure of ethanol over water led to faster evaporation of the solvent during sample preparation. This resulted in the grinding of a dry powder during homogenisation prior to pressing. In less than 2 minutes of grinding the now dry LiCl re-hydrated rapidly, leading to the re-introduction of water into the system and, once again, the production of a paste-like pre-RCS mass.

The rapid evaporation of the solvent due to the mechanical work, combined with the rapid re-hydration of the now dry LiCl resulted in a sudden change in texture that was hard to load into dies. This overly-hydrated mass extruded completely during the pressing

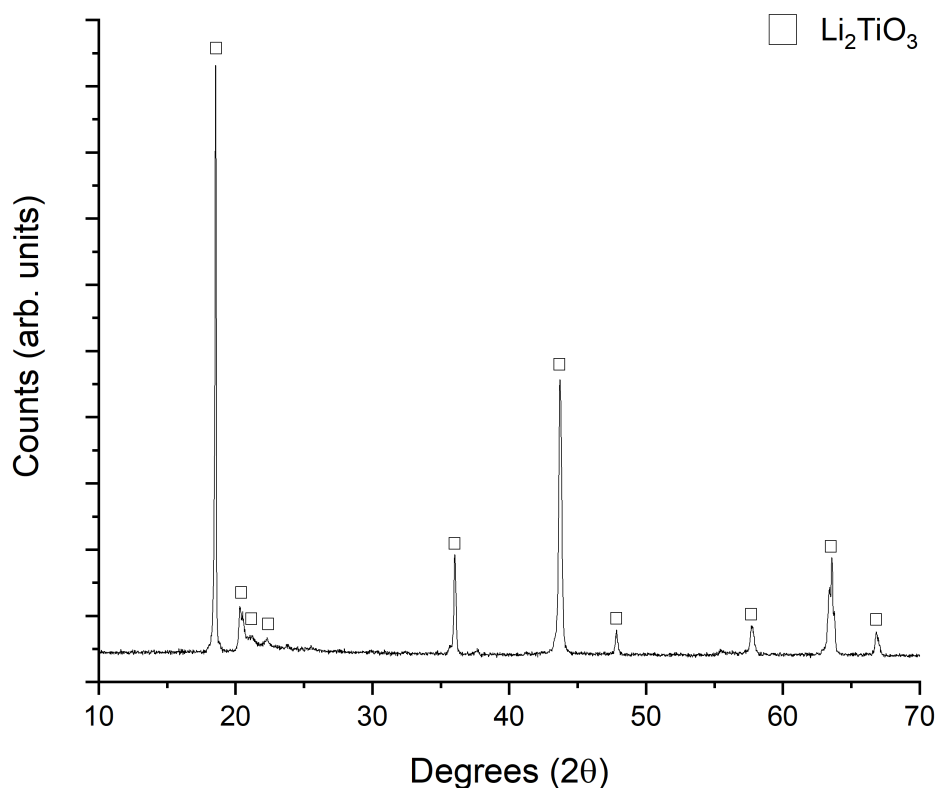


Figure 3.30: X-ray diffraction pattern of extruded material post-annealed. Ethanol was used as a solvent.

step of the RCS method.

The extruded material was re-homogenised and post-annealed nonetheless resulting in the XRD seen in figure 3.30. A lack of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is immediately apparent. This suggests that if all of the previous samples had been fired in their totality (*i.e.* no loss of material to extrusion), this would have been the result: a pellet composed of single phase material.

The re-hydration of the sample resulted in a failure to test for deprotonation, however the post-anneal of the extruded material shows that this isn't a stoichiometric or chemical issue; it's likely a methodological one.

From the results shown in this section, it is clear that there is indeed a stoichiometric imbalance in the system, most likely due to lithium leaching during pressing. The question now becomes; how can this be addressed?

### 3.3.3.5 Lithium loss - extrusion

The largest loss of material throughout the process occurs during pressing. The pressures used (750 MPa) are large enough and the material mobile enough that the forces applied

lead to extrusion through the gaps between the die and the plungers. The three components of the RCS mixture are the main phase powder, a LiCl solution and a titania nanopowder suspended therein. Clearly the most mobile component in the system is the dissolved LiCl and, considering this, a preferential loss of lithium through the extruded material seems like the logical conclusion.

The solution therefore seems obvious, tighter tolerances reducing the gap between the die and the plungers. However, in order for RCS to work the transient fluid needs to exercise its transiency: if the tolerances get too tight there won't be enough time for the fluid to fully evaporate through the smaller gaps and hence won't allow for the RCS method to work as intended. A balance must be struck to arrive at tolerances which stop extrusion and still allow water vapour to escape.

As obvious a solution as this is, refining the equipment to this degree was unachievable given the tools and expertise available, therefore, other methods were employed in an attempt to minimise material lost *via* this route.

A logical first step would be reducing pressure and therefore lowering the driving force leading to material extrusion. A pellet was generated following the exact same method as described in section 2.2.2, with the compressive force reduced by half, resulting in a final pressure of 325 MPa. This was considered a large enough reduction to see a decrease in extrusion whilst still providing enough pressure to allow for enough densification to produce a cohesive pellet.



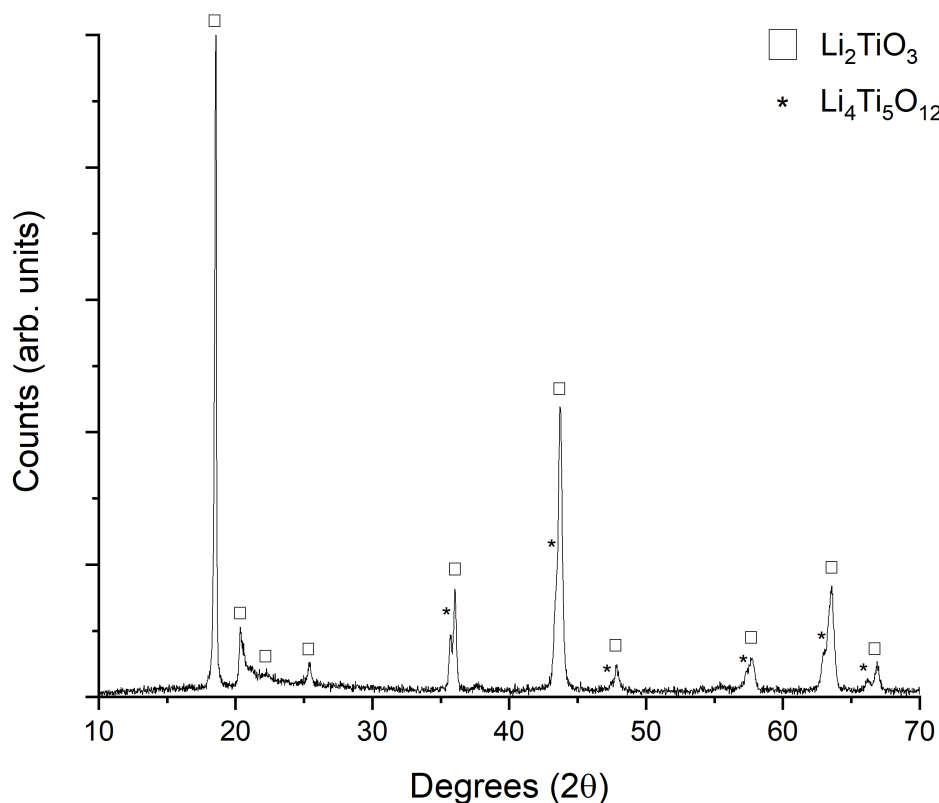


Figure 3.31: X-ray diffraction pattern of an RCS pellet pressed at 325 MPa.

A slight reduction in extruded material was noted but not to any meaningful degree. As can be seen from figure 3.31, the amount of material lost was still enough to lead to the formation of the lithium deficient titanate identified throughout this chapter.

As RCS requires these high pressures to allow for particle rearrangement and densification, even if this method had significantly reduced material extrusion, further analysis would be required in order to strike a balance between material extrusion and densification. Any material extrusion leads to the introduction of an uncontrollable source of off-stoichiometry, therefore even if there was a pressure which achieved this balance, replicability would be close to impossible.

To reiterate, even if it had not impacted the sample's chemistry, extrusion must be minimised if not eliminated. The stoichiometric imbalance introduced by the uncontrolled loss of material significantly reduces the replicability and therefore applicability of the related methodology.

Other methods of reducing space available for material extrusion were attempted. This included the addition of PTFE (polytetrafluoroethylene) plungers on top of the stainless steel ones used under normal operation. The RCS method as used requires temperatures of 180 °C and therefore other available materials to fill gaps, such as Parafilm<sup>®</sup> would be

unsuitable (melting point around 60 °C).

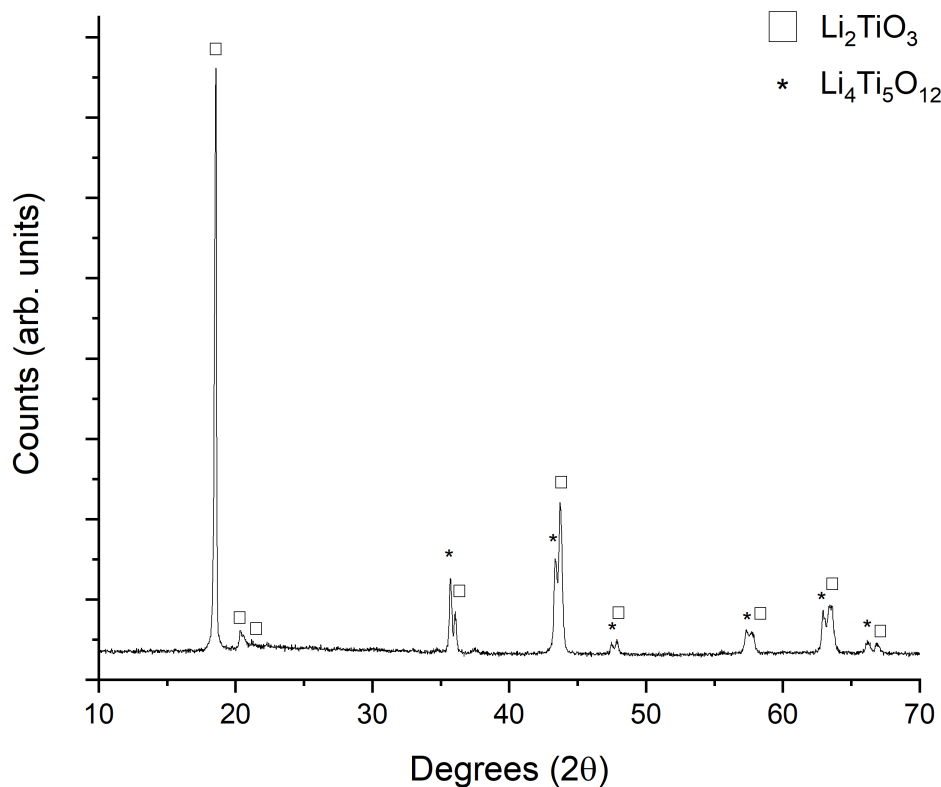


Figure 3.32: X-ray diffraction pattern of an RCS pellet pressed using PTFE pucks between the sample and plungers.

The addition of PTFE plungers resulted in added complexity as the highly mobile RCS material worked its way in between these plungers and the steel ones normally used with the method. This meant that although visibly less material escaped the die, a significant amount extruded into the gaps surrounding the PTFE plungers; drying and resulting in difficulty extracting the pellets.

Cracks usually formed due to the stresses applied during pellet extraction. Not only did this introduce complexity when extracting the pellets but the presence of the lithium deficient species – the entire reason for the use of these additional plungers – did not seem to be affected as can be seen in figure 3.32.

### 3.4 Conclusion

One of the principal functions of a useable breeder ceramic is as a fuel to the fusion device, generating tritium *via* lithium transmutation reactions. Therefore, the lithium content of the ceramic is key in maximising tritium generation. Hence, analysing the

avenues resulting in the lithium loss observed is crucial to understand how to potentially address it in the future. However, tritium permeability of the ceramics is also important as no matter how much tritium is generated if it cannot be released and used as fuel, increasing density and/or chemical improvements would be futile.

Pellets containing  $\text{Li}_2\text{TiO}_3$  were generated using the reactive cold sintering method at temperatures 400 °C below regular sintering temperatures. This method demonstrated the capacity to generate seemingly dense pellets whilst retaining the morphology of the added components. Microstructural design and tailoring is therefore possible and may allow for the study of the effect specific morphologies have on tritium release characteristics.

The unexpected characteristics of the pellets produced in this section of the work, namely the overly exaggerated preferred orientation and the presence of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , can all be concluded to arise from intrinsically methodological issues. The pressures necessary for densification under RCS lead to the induction of texture and the subsequent retention of said texture due to the low processing temperatures involved. Similarly, the pressures used combined with the poor tolerances of the equipment, lead to material extrusion which, in turn, lead to a loss of stoichiometric control over the RCS mass. Due to the differences in mobility of the components of the RCS mixture, lithium happens to be lost preferentially.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$  is a good lithium ion conductor and sees regular use as an electrode [162], its individual performance in a fusion device hasn't been assessed however, let alone its performance when combined with  $\text{Li}_2\text{TiO}_3$  as produced in this work. This lack of research into the materials that have been made in this section of the work make their suitability in a fusion context hard to qualify, even if their apparent sub-stoichiometric lithium content makes them inherently undesirable.

Chapter 5 attempts to quantify the degree of lithium loss and analyses the potential mechanisms by which the remaining lithium is being segregated.

### 3.5 A note on contextualisation and further work

As described throughout the work, development of advanced synthesis and sintering techniques of these ternary lithium ceramics has all been done with nuclear fusion as a target application. To this end some way of comparing the generated ceramics to others produced utilising more conventional methods (i.e solid state processing) would be ideal.

Several key characteristics have been identified as important when considering their successful deployment in a functional fusion device, chief of which is overall lithium density [27, 67, 82, 83]. This covers both the lithium capacity of the crystal itself and the density of the final pellet. As previously discussed in chapter 1.3.1, a balance must be struck between the final density and the ceramic's ability to release tritium as it is generated. High densities result in a reduction in low energy tritium escape vectors and low densities result in an increased need for neutron multipliers and worsening economic prospects.

An adequate thermal conductivity and crush load strength are also important when considering the pebble bed designs generally viewed as the most likely method for ac-

tual implementation [41]. Thermal conductivity needs to be high enough to ensure the kinetic energy deposited by the neutrons generated in the core is dissipated fast enough to maintain a stable operating temperature below the 900 °C maximum operating temperature [18]. And, similarly, the crush load strength needs to be high enough to stop the pellets from failing under their own weight.

The impact of irradiation on these characteristics has yet to be fully studied and is a clear limitation of these measurements, likely rendering them somewhat irrelevant as loss of strength is inevitable as structural lithium is lost as part of the process itself.

As well as lacking irradiation performance assessment of these ceramics, other important characteristics have been generally ignored, namely pellet microstructure. No in depth analysis of tritium release characteristics of different microstructures exist in the literature, likely due to a limit on the available sintering and synthesis techniques and expertise on said techniques in the community.

Density, thermal conductivity and crush load strength were important to contextualise the samples generated to those in literature. However, methodological issues resulting in differences from the desired stoichiometry, as well as a lack of consistency made these measurements irrelevant; densities seemed promising but if the chemistry is uncontrolled, maximum theoretical density will fluctuate uncontrollably.

## 4 Lithium orthosilicate synthesis and composite fabrication

### 4.1 Introduction

As a logical next step in demonstrating the flexibility and adaptability of the RCS method a ceramic-ceramic composite was produced utilising a solid state  $\text{Li}_4\text{SiO}_4$  main phase powder, and the  $\text{LiCl} - \text{TiO}_2$  infill discussed previously.

Ceramic breeder approaches struggle against other technologies as they have a low potentially achievable TBR (tritium breeding ratio). This is simply limited by the overall lithium concentration of each of the materials considered, with technologies generally following: liquid metal > liquid salt > solid ceramic.

Liquid breeder solutions introduce a myriad other issues such as increased toxicity, increased handling concerns and increased system complexity, however, they usually result in better TBRs. The relatively weak achievable TBRs of ceramic solutions requires the presence of supplemental neutrons. This therefore leads to an increased need for neutron multipliers which, as discussed in section 1.3.1, leads to faster burnup (more frequent re-fuelling) and increased complexity (use of Be pellets and necessary fuel compartment design to contain it).

Maximising TBR results in a decrease in the necessary amount of neutron multiplier required to arrive at a ratio greater than one. Less multiplier also results in higher overall lithium density and therefore longer burnups. To this end, as well as to remain competitive with other technologies, ceramic breeders with high TBRs are desirable.

As mentioned in section 1.3.1 no single ceramic meets all the qualifications required to be a serviceable solution without significant drops to TBR. All compositions excel in different parameters – that being crush load, lithium density or chemical stability – but no singular criteria can be prioritised without significantly compromising the others; that is if only single phase materials are considered. Ceramic-ceramic composites can address this “no singular solution” issue, however their physical properties make some of them incompatible when co-sintering.

The reactive cold sintering process, key to this project, presents a unique way of combining ceramics at low temperatures, avoiding the usual sources of co-sintering incompatibilities. To this end, RCS was applied to the lithium orthosilicate – lithium metatitanate system.

### 4.2 Aims

The aims of this work were:

- Continue developing the reactive cold sintering method, now adding a chemically distinct phase into the system.
- Develop said method to allow for the sintering of dense biphasic pellets at low temperatures, *via* the two vectors introduced with the RCS method.
- Analyse and investigate the stability and chemistry of said pellets.

### 4.3 Results and discussion

#### 4.3.1 *Solid state synthesis*

As with lithium titanate, the way the RCS process is being applied in this work necessitates the presence of a pre-synthesised “main phase” powder, together with a mixture of precursors; the aim being the production of a final pellet composed of said pre-synthesised powder surrounded by a matrix of single phase material generated from the added precursor mixture or “infill”. This section discusses the production of single phase  $\text{Li}_4\text{SiO}_4$  as a “main phase” powder to be used throughout this work.

The two step solid state calcination method described in methods section 2.1.1 was used to synthesise lithium orthosilicate.

Significant agglomeration occurred during  $\text{Li}_4\text{SiO}_4$  synthesis — likely due to a combination of two factors: the second calcination step occurring at the melting temperature of  $\text{Li}_2\text{CO}_3$  [96] and the well-known sintering aid properties of  $\text{SiO}_2$  [163]. This agglomeration was so recalcitrant that several milling iterations still resulted in particles retaining diameters of  $> 4$  mm. The hardness and resistance to crushing of these agglomerates — even though their occurrence was ubiquitous through different batches — seemed to change significantly between batches. As no other difference could be identified this variance was attributed to some environmental factor or due to initial heterogeneity, which may have led to  $\text{SiO}_2$  rich pockets sintering together preferentially.

All material was eventually homogenised to ensure formation of single phase  $\text{Li}_4\text{SiO}_4$ , although potential presence of YSZ (yttria stabilised zirconia) in the final powder was likely, due to the number of steps needed and, as previously noted in research by Sam Waters [79]. All material was passed through a  $100\text{ }\mu\text{m}$  sieve.

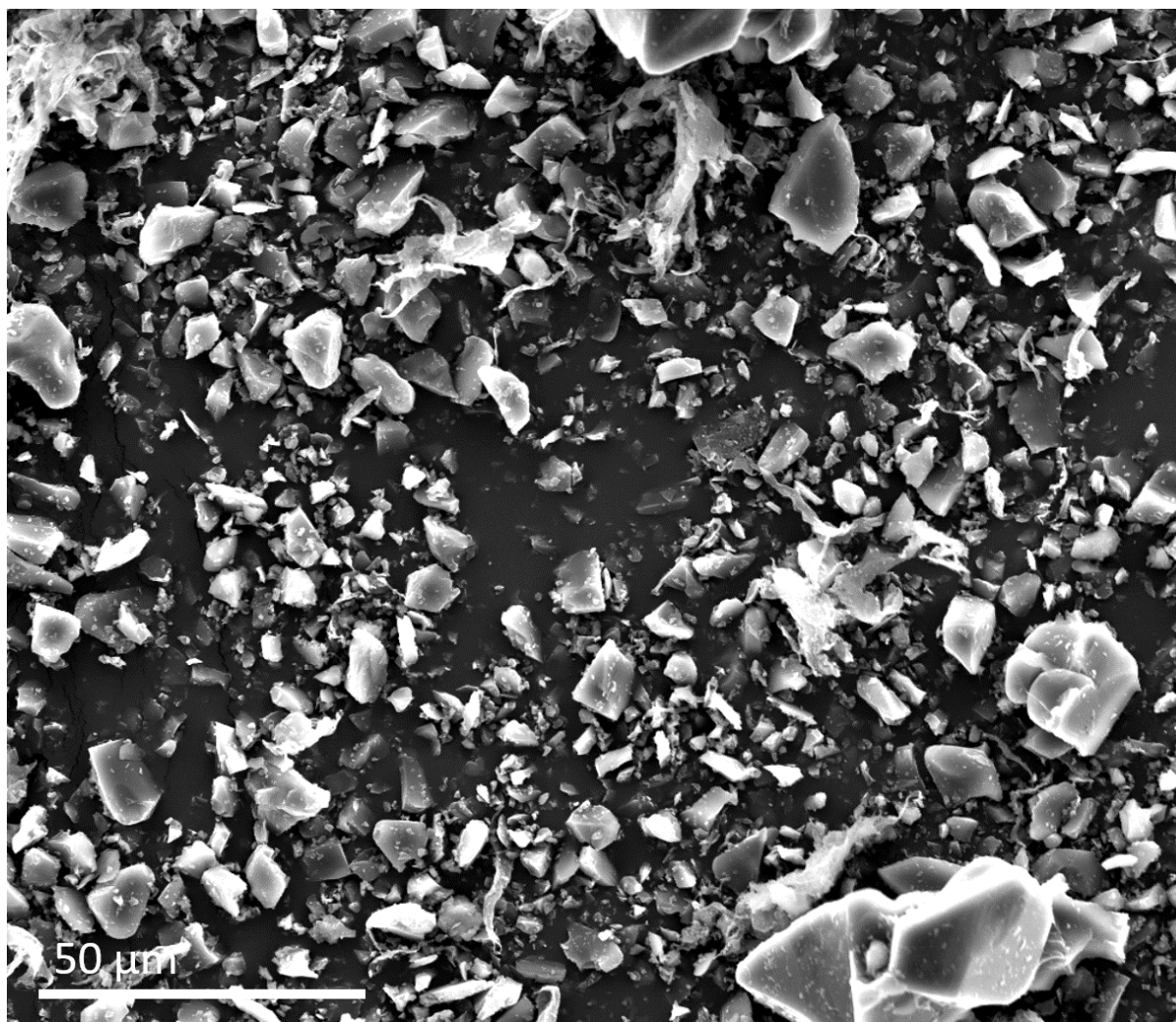


Figure 4.1: Secondary electron micrograph of loose  $\text{Li}_4\text{SiO}_4$  powder.

Figure 4.1 shows the loose  $\text{Li}_4\text{SiO}_4$  powder produced following the method described in section 2.1.1. Immediately apparent is the broad range of particle sizes present, with some reaching upwards of  $50\text{ }\mu\text{m}$  in diameter. Another characteristic of the powder produced is the highly angular, shard-like shape of the particles, which may be explained by the hardness of the monolith removed after calcination, leading to larger particles shattering into smaller pieces rather than ground into globular particles. It was postulated this morphology would aid in phase identification in the final pellets produced using this powder. Particle size analysis using the Mastersizer was deemed too unreliable to attempt as the relatively high solubility of lithium orthosilicate would rapidly impact the particles in suspension. This of course compounded by the issues with agglomerates identified in chapter 3.

As is clear from figure 4.2,  $\text{Li}_2\text{CO}_3$  was present in the powder sample. This initially was attributed to a potentially incomplete reaction, perhaps introduced due to a poorly homogenised powder, however being aware of the low ambient stability of  $\text{Li}_4\text{SiO}_4$  [18] as

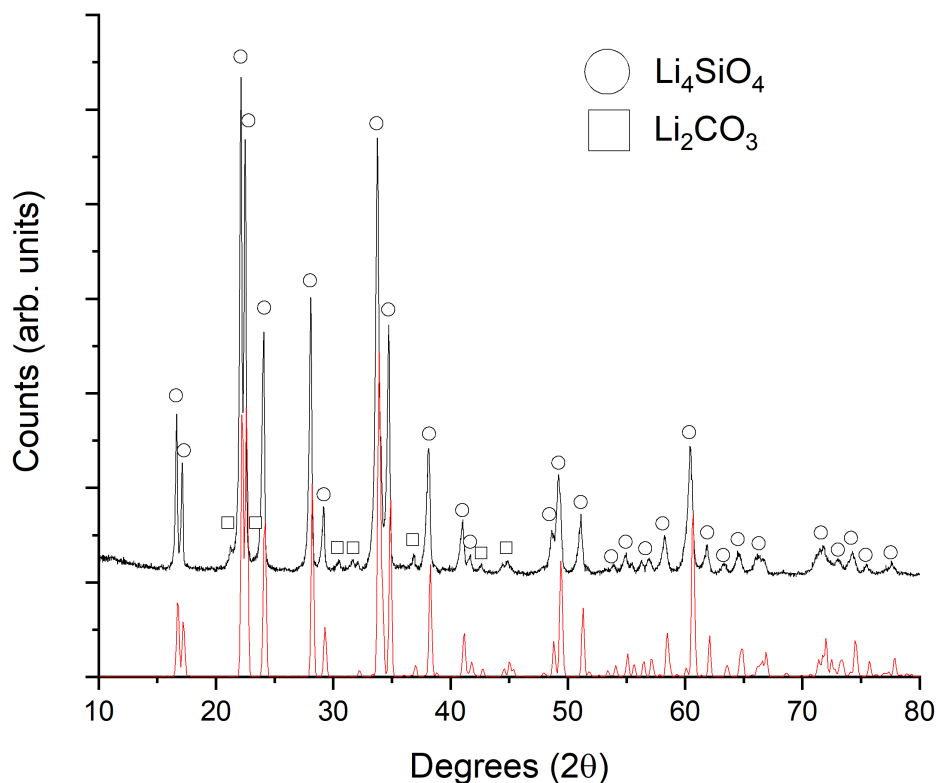


Figure 4.2: X-ray diffraction pattern of a solid state sintered lithium orthosilicate. Lithium orthosilicate was produced as the dominant phase, with detectable lithium carbonate. Simulated profile included in red according to ICSD card 21418 [63].

well as its industrial use as a  $\text{CO}_2$  scrubber [65], re-carbonation of the orthosilicate into a metasilicate and  $\text{Li}_2\text{CO}_3$  was also considered, following reaction 5.

A portion of the calcined powder was added into a furnace at  $650^\circ\text{C}$  for 10 hours, replicating the first calcination step during synthesis. This was done to see if a temperature low enough to avoid the main  $\text{Li}_4\text{SiO}_4$  forming reaction, but high enough to allow for regeneration, would result in single phase material. After firing the powder was subjected to XRD within 5 minutes to keep potential ambient contamination to a minimum, with the XRD pattern of the powder produced by this second reaction shown in figure 4.3.



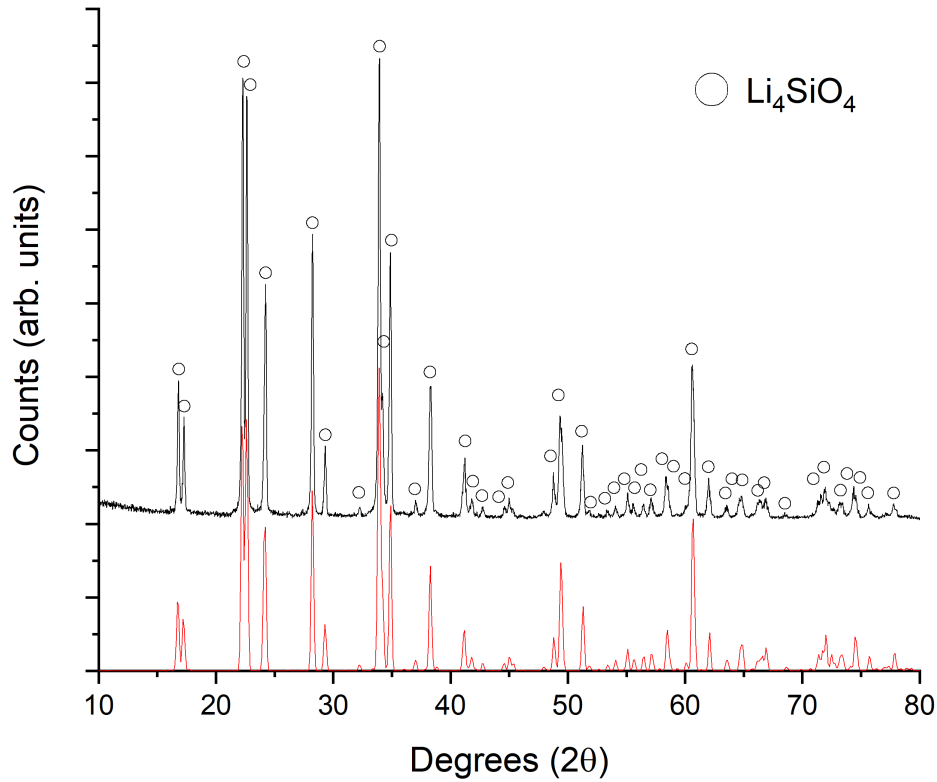


Figure 4.3: X-ray diffraction pattern of a solid state sintered lithium orthosilicate after further firing at 650 °C for 10 h. Simulated profile included in red according to ICSD card 21418 [63].

No detectable lithium carbonate was left on the XRD pattern after re-firing, indicating that, indeed, the carbonate presence was likely due to post-synthesis re-carbonation under atmospheric conditions. Bulk powder material was therefore stored under argon to minimise contact with air as much as possible, however through transfer and processing it was thought impossible with the current experimental setup to fully curtail the re-carbonation of the lithium orthosilicate. This led to most powder samples containing a small amount of  $\text{Li}_2\text{CO}_3$  by the time they reached the diffractometer.

Formation of single phase  $\text{Li}_4\text{SiO}_4$  has been performed, with any secondary phases being eventually introduced *via* the material's reaction with ambient  $\text{CO}_2$ . Any post-anneal or post-synthesis firing should allow for this to react back to form the orthosilicate and, considering the RCS method involves a firing step, maintaining the lithium orthosilicate pristine was not initially a priority.  $\text{Li}_4\text{SiO}_4$  is cited in previous studies [79] to be commonly accompanied by the products formed *via* this re-carbonation. The work presented here suggests that these lower purities may simply be the result of the re-carbonation reaction rather than any intrinsic off-stoichiometry.

### 4.3.2 Cold sintering method - biphasic

Next, lithium orthosilicate - lithium metatitanate ceramic-ceramic composites were fabricated using the LiCl – TiO<sub>2</sub> infill previously discussed.

Theoretically, the RCS method should allow for a flexibility not achievable by other cited methods such as co-firing and melt spray techniques, which are limited by cross-reactions and disparate melting points [85–87]. Generating pellets of different proportions of Li<sub>4</sub>SiO<sub>4</sub> to Li<sub>2</sub>TiO<sub>3</sub> should be as simple as altering the ratio of main phase powder to infill, although there will be a lower limit to the mass of main phase powder before structural stability is lost.

#### 4.3.2.1 Preliminary experiments - method refinement

Mirroring the work done in chapter 3, a 3 M solution of LiCl and equivalent TiO<sub>2</sub> nanopowder was used as the infill, using the previously synthesised Li<sub>4</sub>SiO<sub>4</sub> as the main phase powder. This infill has been shown to form the expected Li<sub>2</sub>TiO<sub>3</sub> phase through the work presented in the previously referenced chapter.

The same issue, as previously reported, presents itself with the use of LiCl as a lithium source. The highly hygroscopic nature of LiCl results in a pre-sintered mass with a paste-like consistency rather than the preferred free-flowing powder. Although the presence of water in this pre-sintered mass is necessary to allow for particle rearrangement in the RCS (Reactive Cold Sintering) process, this uncontrolled excess leads to a particularly mobile mixture, leading to significant and irreproducible mass losses during the pressing stage of the RCS process. This occurs through extrusion of material around the edges of the die during pressing. The water content of the mass is directly related to ambient conditions during its preparation which may change unpredictably throughout the day let alone throughout a year. Other research groups have also noted the difficulty of working with LiCl under ambient conditions due to this [67].

Using findings from chapter 3 the pre-sintered mass was kept overnight in a desiccator to limit the amount of water absorbed into the mixture without completely avoiding it altogether; the presence of water within the mass is necessary to allow for particle rearrangement, therefore fully drying the sample, although much more consistent, is undesirable and will result in densities close to those of a green body. The degree to which this step aids in avoiding large mass losses during pressing is difficult to estimate. Ambient conditions are ultimately what determine the amount of water absorbed (*i.e.* humidity) and are essentially uncontrollable without a much more advanced experimental setup. The addition of this step onto the process, however, led to an increase in mass retained in the final pellets. It was hence seen as beneficial to the experiment, even if the control necessary to predictably regulate the water content within the mass wasn't achieved.

The pre-sintered mass (a combination of the main phase powder together with the infill mixture, allowed to equilibrate in a desiccator for a day) was homogenised (roughly ground together with haste to avoid the excessive re-hydration of the mass) and added to a press to be cold sintered using the same regime as that used in chapter 3 and described in the methodology (section 2.2.2).

As the infill used in this system is identical in composition and proportion to that used in the bimodal system (chapter 3) it follows that, to allow the infill to fully react, the densified pellet should be fired at 700 °C for 4 h after the pressing stage to allow for the complete removal of Cl from the sample.

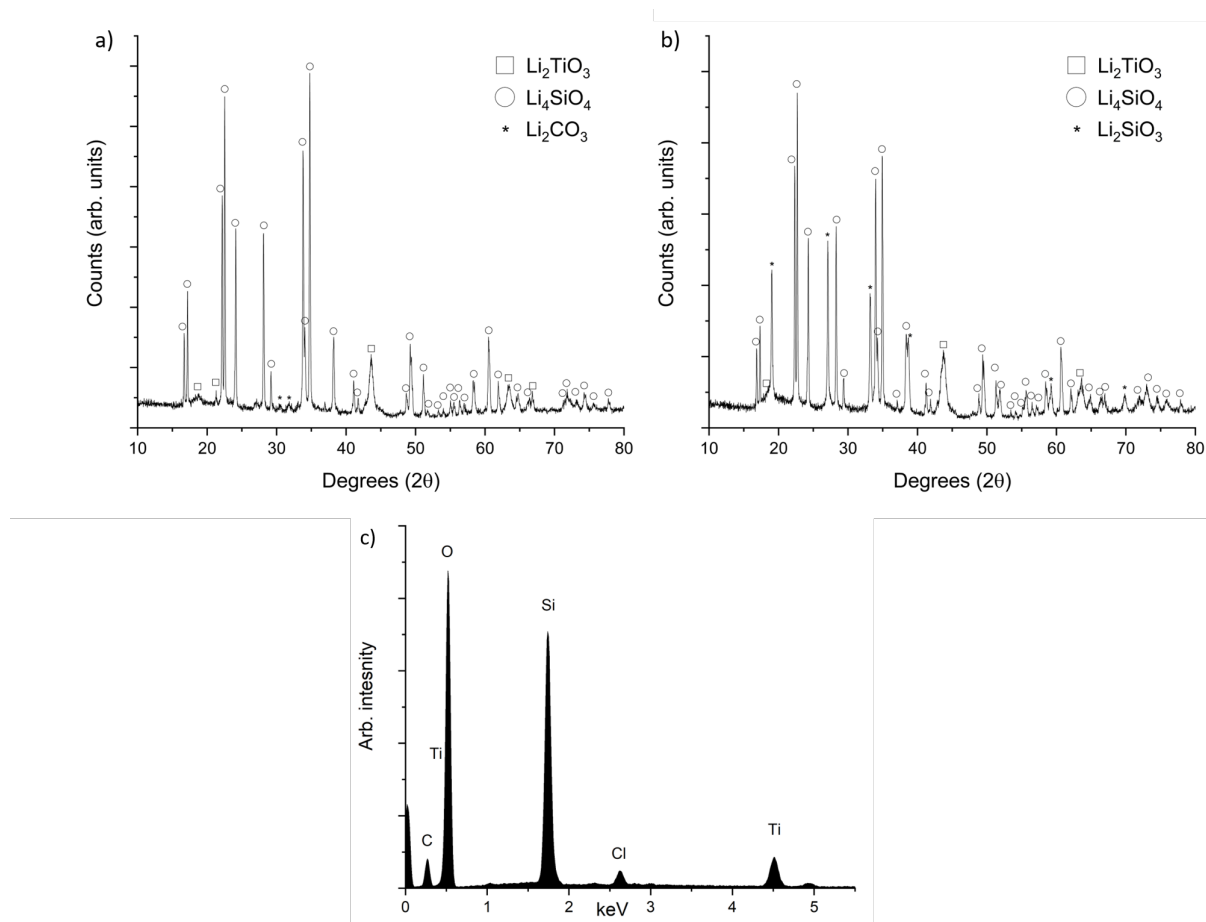


Figure 4.4: X-ray diffraction pattern of (a) a pristine surface of the biphasic sample and (b) a crushed biphasic sample, post-annealed at 700 °C. (c) shows an EDXA scan of a fracture surface, clearly showing the remaining Cl.

Pellets looked well-sintered with no clear cracks or porosity. When crushing, the resultant powder started agglomerating as if it had been moistened, perhaps  $\text{LiCl}$  re-hydration. Figure 4.4 presents the XRD and EDXA of a pellet produced using this method, with a post-anneal of 700 °C. In figure 4.4(a), both the lithium titanate and the lithium orthosilicate are present, however there are a few peaks related to  $\text{Li}_2\text{CO}_3$  visible as well as there being an alarming lack of a peak at 18.6°, the 002 peak discussed in chapter 3.3.3.3. Figure 4.4(b) shows the two expected phases, now with a lack of those  $\text{Li}_2\text{CO}_3$  peaks and the sudden appearance of  $\text{Li}_2\text{SiO}_3$ , undetectable on the pristine surface. The EDXA shows that the moistening of the material through crushing was indeed, likely to be  $\text{LiCl}$  presence.

There are then three unexpected features which show significant deviation from the

results presented in chapter 3. Firstly, there is the clear presence of Cl in the EDXA of final pellets, suggesting a potentially incomplete reaction; secondly, there is the unexpected presence of  $\text{Li}_2\text{SiO}_3$ ; and thirdly, an absence of the  $\text{Li}_2\text{TiO}_3$  (002) peak, present in every other previous XRD pattern in this work.

A presence of Cl in the EDXA suggests that the same issues identified in the bimodal system described in chapter 3.3.3.1 may be repeating themselves, namely incomplete reaction of the added infill. This is the case, despite keeping the post-anneal temperature which was shown to rectify this issue. It has been shown through the bimodal system as well as through the powders generated using the DES method that the heating regime used (700 °C for 4 h) should be enough to fully react the infill to produce lithium metatitanate leaving no detectable Cl behind. The only difference here is the presence of the lithium orthosilicate phase, and as such, its presence might be causing the reaction pathway to change, allowing for the retention of chlorine in some form.

Following from this, the appearance of large amounts of  $\text{Li}_2\text{SiO}_3$  in the ground up sample without any significant  $\text{Li}_2\text{CO}_3$  — the presence of which should be expected following equation 5 — suggests that this is unlikely due to re-carbonation happening through the process of breaking the pellet apart and loading into the XRD apparatus, but rather, always present, and generated during the post-anneal process. Considering the  $\text{CO}_2$  absorbing capacity of lithium orthosilicate at high temperatures [65], its re-carbonation during post-anneal is not wholly unexpected, however, if this is indeed the case, this leads to question where the lithium carbonate related to the now orphaned lithium metasilicate went.

The lack of the characteristic (002) lithium metatitanate peak remains intriguing however as the remaining peaks previously ascribed to lithium metatitanate not only don't fully agree with the characteristic pattern (PDF 01-080-7163) but neither do they agree with the lithium-deficient titanate  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  identified in chapter 3.3.3.4. Another feature visible when comparing between figure 4.4(a) and figure 4.4(b) specifically, and consistent with the bimodal system of chapter 3.3.3.3, is the presence of some degree of texturing. Just as with the previously mentioned bimodal system, this is likely a pressure-induced effect, retained due to the relatively low temperatures involved in the production of the final pellets. Observing this effect in a completely different system gives further credibility to the theory that this is simply pressure induced texturing and occurs independently from the crystal structure of the ceramic involved. The same effect has been observed in cold sintered YBCO by Boston *et. al* [152].

Further study of the XRD patterns suggest the titanate phase clearly present was most likely the metastable cubic form of lithium metatitanate,  $\alpha\text{-Li}_2\text{TiO}_3$  (PDF 01-080-7159). Both  $\beta$  (the monoclinic, stable form of  $\text{Li}_2\text{TiO}_3$  considered as a breeder material) and  $\alpha$  forms, share most peaks, but the latter phase lacks the characteristic (002) peak at  $18^\circ 2\theta$ . This suggests that rather than just the (002) peak being missing from the pattern, these peaks actually represent the  $\alpha$  phase. Considering that the metastable  $\alpha$  form transforms irreversibly to the  $\beta$  form at 300 °C [164] its presence after a 4-hour dwell at 700 °C was unexpected and not present in any other systems previously analysed. Zeng *et al.* [88] found a similar effect when dealing with the same system, with the  $\alpha$  form persisting until calcination at 900 °C (600 °C above the expected transition temperature),

suggesting that some characteristic introduced by  $\text{Li}_4\text{SiO}_4$  may be somehow stabilising this meta-stable phase, shifting its transition to much higher temperatures. Research by Knitter *et al.* also identifies this disordered phase [85], however attributes it to the rapid quenching involved in their method, a characteristic the method described herein doesn't share. The only similarity between these methods is the combined use both  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{TiO}_3$ .

In order to confirm this, a pellet formed using the same heating regime as previous (4-hour dwell at 700 °C) was XRD to confirm the absence of the (002) lithium metatitanate peak and then fired for 4 additional hours at 900 °C.

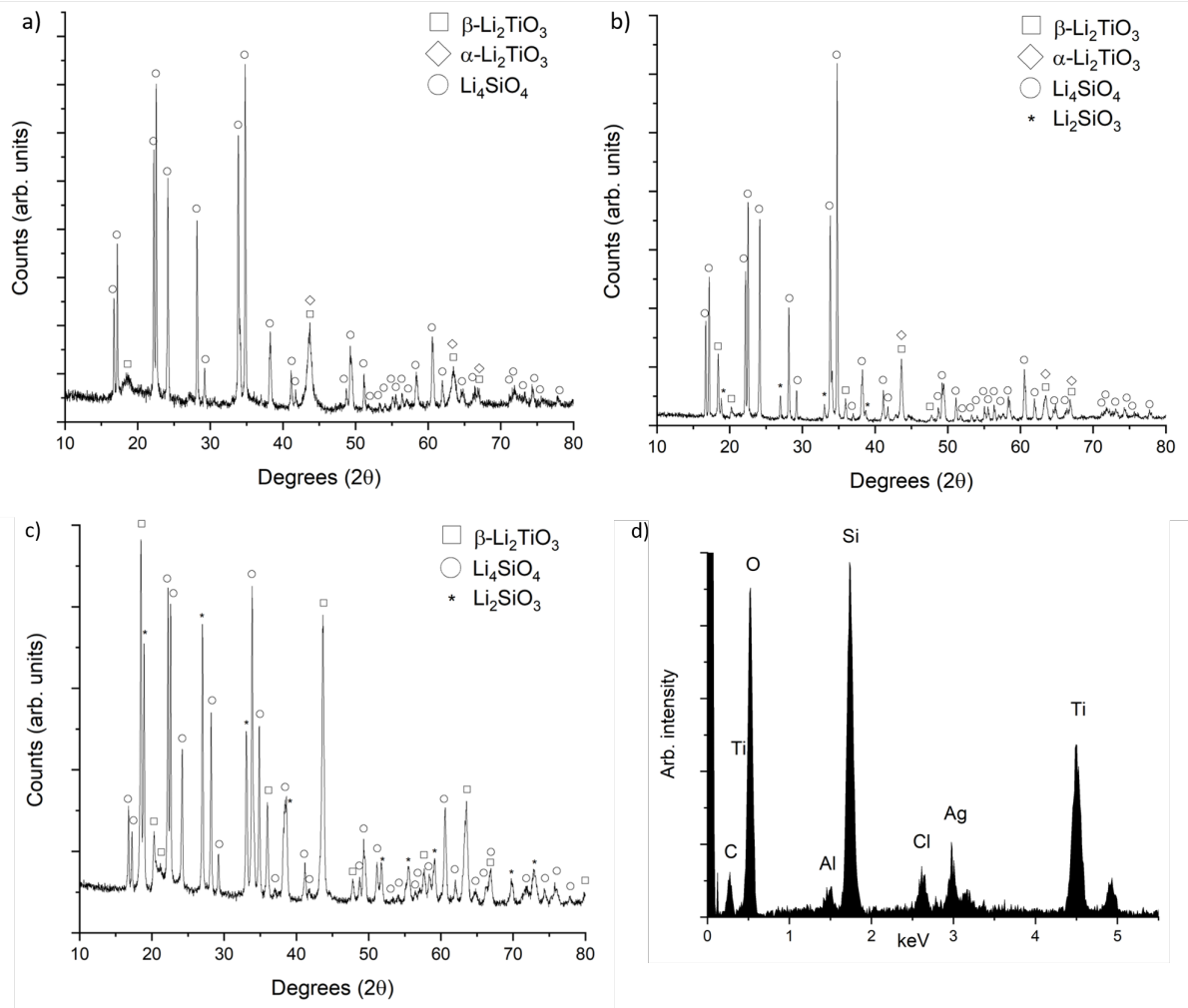


Figure 4.5: X-ray diffraction pattern of (a) a pristine surface of a biphasic sample as removed from post-anneal at 700 °C, (b) pristine surface of a biphasic sample as removed from post-anneal at 900 °C and (c) crushed biphasic sample as-removed from post-anneal at 900 °C. (d) shows an EDX scan of the fracture surface after final heating step, clearly showing the remaining Cl. Aluminium and silver content due to surface contamination during handling.

Again, pellets looked well-sintered with no clear cracks or porosity when removed at

either temperature. Figure 4.5 presents the XRD and EDXA of a pellet produced using the RCS, removed with a post-anneal of 700 °C and subsequent post-anneal of 900 °C. In figure 4.5(a), both the lithium titanate and the lithium orthosilicate are present, however, just as before close to no signal related to the 002 titanate peak can be observed. This is likely due to an incomplete transition between the  $\alpha$  and  $\beta$  phases. Figure 4.5(b) now shows the two expected phases, with the clear presence of  $\beta$ -Li<sub>2</sub>TiO<sub>3</sub>. Full transformation of the  $\alpha$  phase is hard to judge as all peaks are shared between those two forms. Li<sub>2</sub>SiO<sub>3</sub> now can be observed even at the surfaces of the pellet, although this may have been exacerbated by the re-carbonation reaction of Li<sub>4</sub>SiO<sub>4</sub>. Figure 4.5(c) shows  $\beta$ -Li<sub>2</sub>TiO<sub>3</sub> has clearly been formed with peak ratios commensurate with this form, it however also shows the same effect as seen previously, Li<sub>2</sub>SiO<sub>3</sub> at the surfaces being subdued significantly when compared to the bulk of the sample; now showing large amounts, with peak heights comparable to the introduced lithium titanate phase. The EDXA shows remaining Cl, implying an incomplete reaction, although, unlike with the bimodal scenario in chapter 3.3.3.1, no lithium deficient titanate can be detected.

As postulated, raising the post-anneal temperature to 900 °C resulted in the complete transformation of the  $\alpha$ -Li<sub>2</sub>TiO<sub>3</sub> to the monoclinic  $\beta$  phase just as seen by Zeng *et al.* [88]. Grinding the pellet reveals the large proportion of both Li<sub>2</sub>TiO<sub>3</sub> and Li<sub>2</sub>SiO<sub>3</sub> in the resultant material, again with a lack of peaks related to Li<sub>2</sub>CO<sub>3</sub>. This, combined with the persistent detection of Cl in the EDXA and the lack of a lithium deficient titanate phase in the ground XRD shows that this is unlikely an incomplete reaction issue. In fact, this implies the TiO<sub>2</sub> in the infill has fully reacted to form lithium metatitanate, which, considering the loss of material due to extrusion in the pressing process, should not occur as has been shown in chapter 3.3.3.4. The next section addresses this detail and characterises the introduced phase versus the Li<sub>4</sub>SiO<sub>4</sub> main phase powder.

Subsequent pellets made were post-annealed at 900C for 4 h following the findings of Zheng *et al.* and the replicated results presented here [88].

#### 4.3.2.2 Introduced phase characterisation

As previously mentioned, a new heating regime was chosen for consequent pellets, in order to ensure formation of the target phase,  $\beta$ -Li<sub>2</sub>TiO<sub>3</sub>. Now that the formation of lithium metatitanate has been confirmed – even though Cl retention still needs to be addressed – SEM in combination with EDXA was used to identify areas of phase segregation between the two ceramic components, and further confirm the presence of both the Li<sub>2</sub>TiO<sub>3</sub> and Li<sub>4</sub>SiO<sub>4</sub> existing simultaneously and independently of each other.

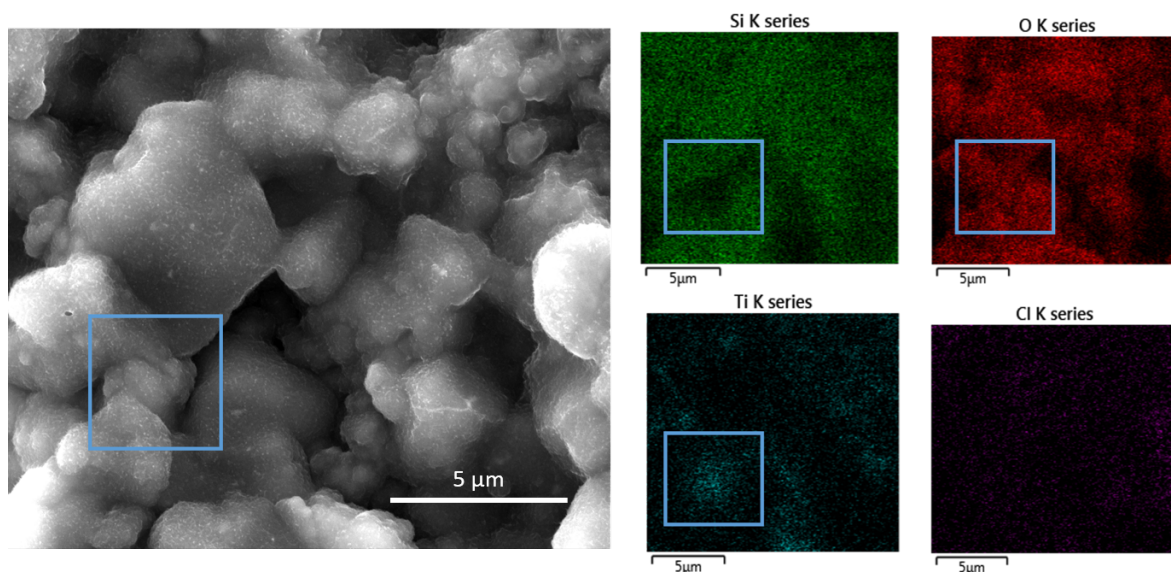


Figure 4.6: Secondary electron micrograph of a biphasic fracture surface. Ti, Si, O and Cl EDXA maps shown. Blue box highlights one area of Ti/Si segregation, however it can be seen that high Ti areas correspond to low Si areas in the maps.

Visual identification of the infill phase is much harder than in the bimodal system described in chapter 3.3.3.2. The wide particle size distribution of the lithium orthosilicate powder may be obscuring the previously clear areas of small particles, normally ascribed to the introduced infill phase. It may well also be the case that the increase in post-anneal temperature has resulted in the coarsening of the lithium metatitanate grains vs the bimodal samples, leading to a more homogeneous distribution. Not only this but all the grains in the fracture surface seem to be covered by some sort of “patina” that obscures any grains smaller than a micron.

The EDXA maps in figure 4.6 reveal clear areas of phase segregation. Several Ti rich/Si deficient areas can be seen, showing the introduction of an independent ceramic phase therefore confirming the capacity of the reactive cold sintering (RCS) method to produce ceramic-ceramic composites.

A Cl signal can still be detected throughout the surface of the sample however, again raising the question of how can Cl remain at these temperatures considering the presence of fully reacted  $\text{Li}_2\text{TiO}_3$ , which theoretically should only form *via* the added  $\text{LiCl/TiO}_2$  infill.

Even though the introduction of  $\text{Li}_2\text{TiO}_3$  to a  $\text{Li}_4\text{SiO}_4$  matrix was successfully achieved, the persistent presence of  $\text{Li}_2\text{SiO}_3$  and detection of Cl in the EDXA suggests that the system and reaction pathway is not fully understood. This will be further analysed in chapter 5.

As mentioned in chapter 1.3.1 lithium orthosilicate reversibly reacts with carbon dioxide to produce both  $\text{Li}_2\text{SiO}_3$  and lithium carbonate. Considering the need for  $\text{CO}_2$  to form the carbonate, as well as the wide  $\text{CO}_2$  absorption range of lithium orthosilicate [65], a logical first step in addressing its presence is firing the pellet in a controlled ( $\text{CO}_2$ -free)

atmosphere.

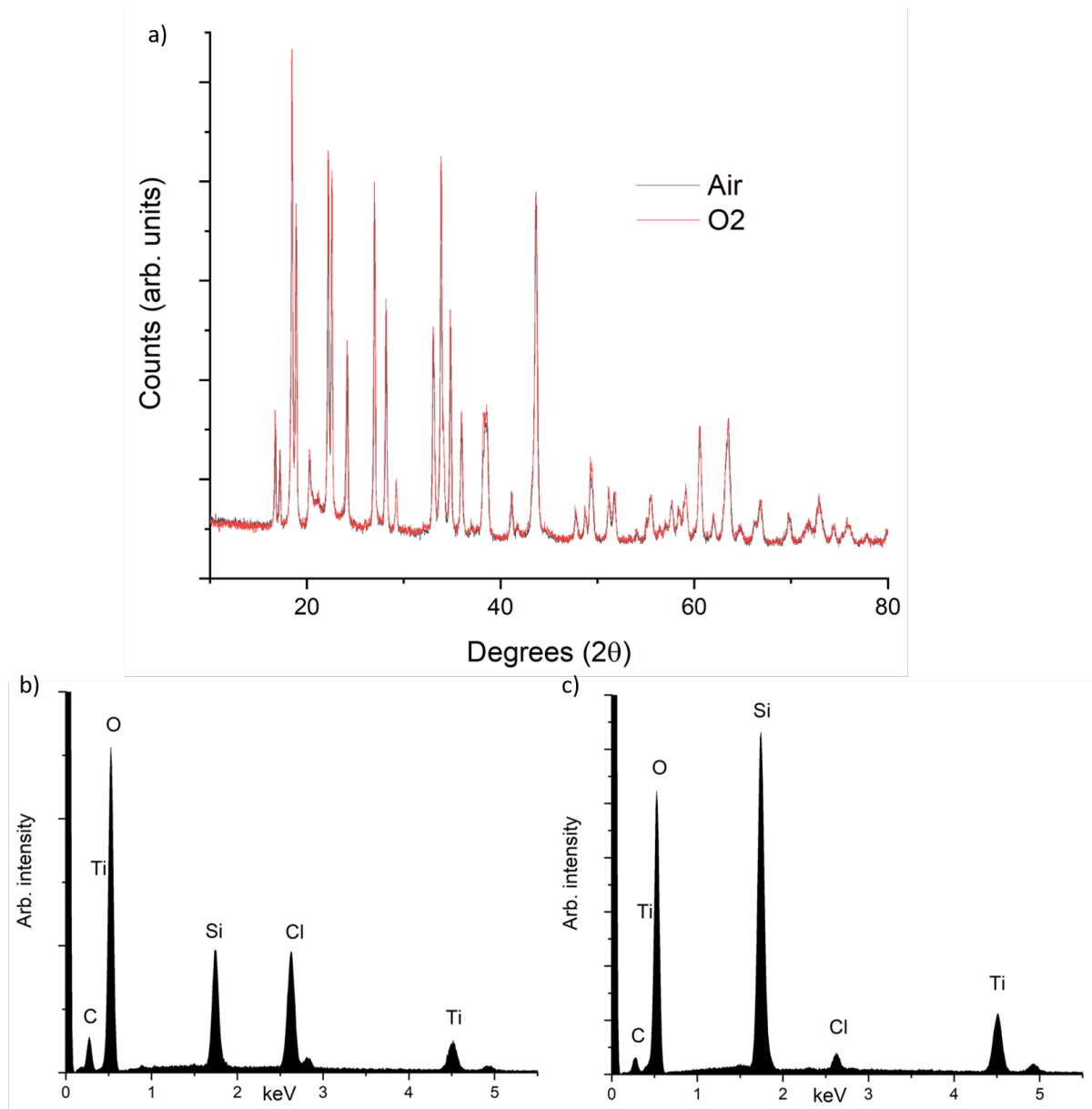


Figure 4.7: Superimposed X-ray diffraction pattern, (a), of a crushed pellet post-annealed under air and under O<sub>2</sub> to highlight the similarities between them. Identical composition to figure 4.5(c). EDXA of (b) fracture surface of sample fired in air and (c) fracture surface of sample fired in O<sub>2</sub>.

The XRD patterns taken from a pellet fired in air and one fired under O<sub>2</sub> have been plotted together in figure 4.7 to highlight the similarity between patterns, where no discernible difference could be identified. The EDXA however suggests a significant decrease in the Cl signal from air to O<sub>2</sub>. It must be noted that the strength of the chlorine signal varied significantly between samples and sometimes between sections of the same sample



(see figure 4.5(d)), although no pattern could be identified at this time. The silver and aluminium presence in figure 4.5(d) were likely, as postulated, introduced through handling; likely through the silver dag used to bridge the sample and the powdery alumina bricks used to line the furnaces.

This difference in the Cl signal suggests that, even though the system arrives at similar phase fractions after post-anneal (clear from the identical patterns in figure 4.7(a)), the pathway to get there is different. Considering the postulate that significant re-carbonation is occurring during the post-anneal, significant amounts of lithium carbonate will be generated which may be utilised as an alternate lithium source by the  $\text{TiO}_2$  and may be doing so preferentially. In the  $\text{CO}_2$ -free scenario this lithium source ( $\text{Li}_2\text{CO}_3$ ) will be significantly reduced (essentially only the  $\text{Li}_2\text{CO}_3$  generated during the pressing stage will be available), resulting in more of the LiCl reacting with the  $\text{TiO}_2$  left after the reaction with the available carbonate.

The fact that the reduction in the Cl signal is not matched by a reduction in the apparent proportion of  $\text{Li}_2\text{SiO}_3$  seems to disagree with this postulate. This however may be explained by the resolution of the techniques used. It may be that a slight change in available  $\text{Li}_2\text{CO}_3$  results in a large proportional impact on the amount of available LiCl. Hence a change that may be imperceptible in XRD (a slight reduction in the  $\text{Li}_2\text{SiO}_3$  present) may be very noticeable in EDXA (a significant reduction in the already small LiCl population).

All the pellets generated using the methods and materials described in this section have the following similarities:

- Clear presence of the expected phases, namely  $\text{Li}_4\text{SiO}_4$  and  $\beta\text{-Li}_2\text{TiO}_3$  in XRD.
- Large presence of  $\text{Li}_2\text{SiO}_3$  with a distinct lack of detectable  $\text{Li}_2\text{CO}_3$  in XRD.
- Constant presence of Cl peaks in the EDXA.

#### 4.3.2.3 Proposed schematic

The similarities between the mechanisms shown in this chapter and those shown in chapter 3 led to the following. It was postulated that, the presence of lithium metasilicate as well as the Cl signal in the EDXA were related and therefore the issues are likely associated with the source of lithium used in the formation of the  $\beta\text{-Li}_2\text{TiO}_3$ .

The lack of lithium carbonate in the final pellet implies the uptake or loss of it resulting in the orphaning of the lithium metasilicate in the final pellet. HT-XRD in combination with TG/DSC was performed in order to elucidate this further and is described in chapter 5.

If the lost lithium carbonate is assumed to be preferentially reacting with the titania (introduced by the infill) to produce the final lithium metatitanate (following reaction 10), this would both explain the lack of  $\text{Li}_2\text{CO}_3$  in the final pellet as well as the presence of unreacted LiCl. The carbonate is reacting, leaving  $\text{Li}_2\text{SiO}_3$  remaining in the final pellet and, as a significant amount of said carbonate is reacting with the titania, the remaining LiCl has been similarly left behind. Essentially the preferential uptake of one lithium

source over another is stopping the reverse, de-carbonation reaction, leaving the  $\text{Li}_2\text{SiO}_3$  unable to react back to form  $\text{Li}_4\text{SiO}_4$ . This is visualised in figure 4.8.

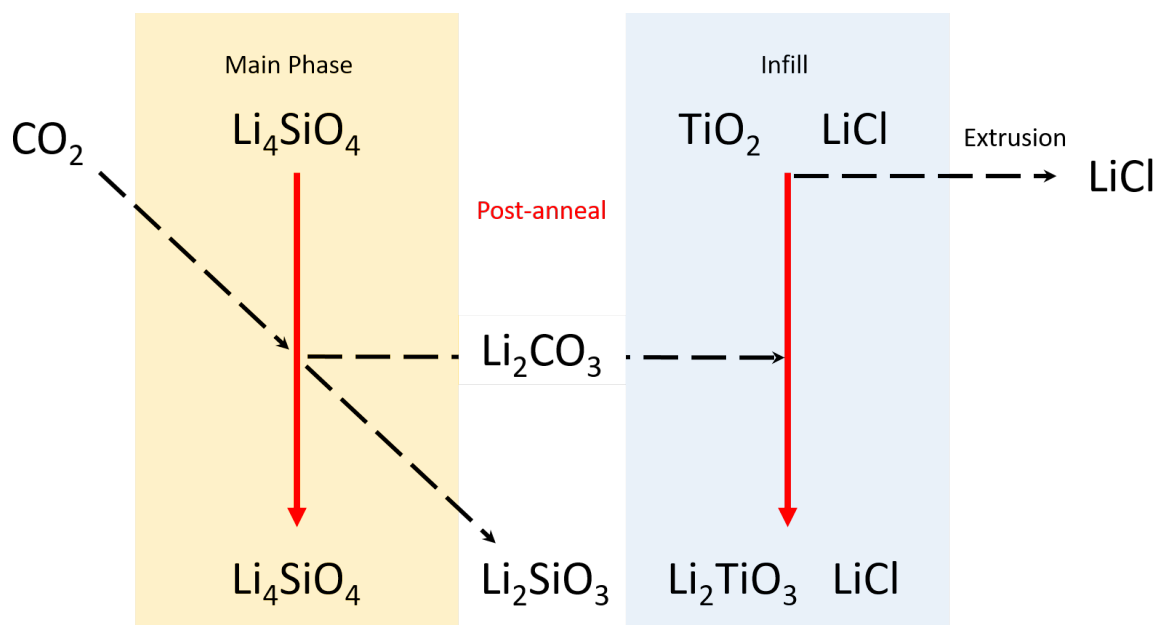


Figure 4.8: Schematic showing the postulated mechanism behind the formation of  $\text{Li}_2\text{SiO}_3$  together with the Cl retention and the absence of  $\text{Li}_2\text{CO}_3$ . Movement of species depicted by dashed arrow, red arrow depicts the calcination step of the post-anneal. Reactions related to the main phase powder on the left, those related to the infill to the right. Bottom of the figure shows the species conforming the final pellets.

Considering this together with the known, large degree of material loss (extrusion from the die) during the pressing stage — and how that material loss results in the formation of a lithium deficient titanate in the bimodal system described in chapter 3.3.3.4 — it can be postulated that, aided by the inherent off-stoichiometry induced *via* extrusion, lithium carbonate generated *via* the re-carbonation of the main phase powder ( $\text{Li}_4\text{SiO}_4$ ) is being preferentially utilised by the titania present in the infill to form  $\text{Li}_2\text{TiO}_3$ , obscuring the fact that the system is still operating with a lithium deficiency.

Enhancing this mechanism is the potential formation of a salt eutectic between  $\text{LiCl}$  and  $\text{Li}_2\text{CO}_3$  which may be coalescing the two potential lithium sources into one, allowing for easier access to the previously dispersed carbonate. This specific theory will also be investigated through the analysis of the system using differential scanning calorimetry (DSC), applied and characterised in chapter 5.

#### 4.3.2.4 Lithium loss

Considering the results from chapter 3.3.3.4 indicated the lithium loss in the pellets was likely due to methodological issues (die extrusion during pressing), this was taken as the most likely case in this system as well. Based on previous research on the  $\text{Li}_2\text{TiO}_3$  -  $\text{Li}_4\text{SiO}_4$  system, however, it is also possible for the lithium metatitanate itself to start

leaching lithium out of the lithium orthosilicate structure, forming a lithium rich solid solution and transforming the orthosilicate into the less lithium dense metasilicate [67].

To investigate whether this proposed leaching effect was occurring, the two fully reacted ceramic powders were co-fired following the same heating regime as used during post-anneal of the samples herein.

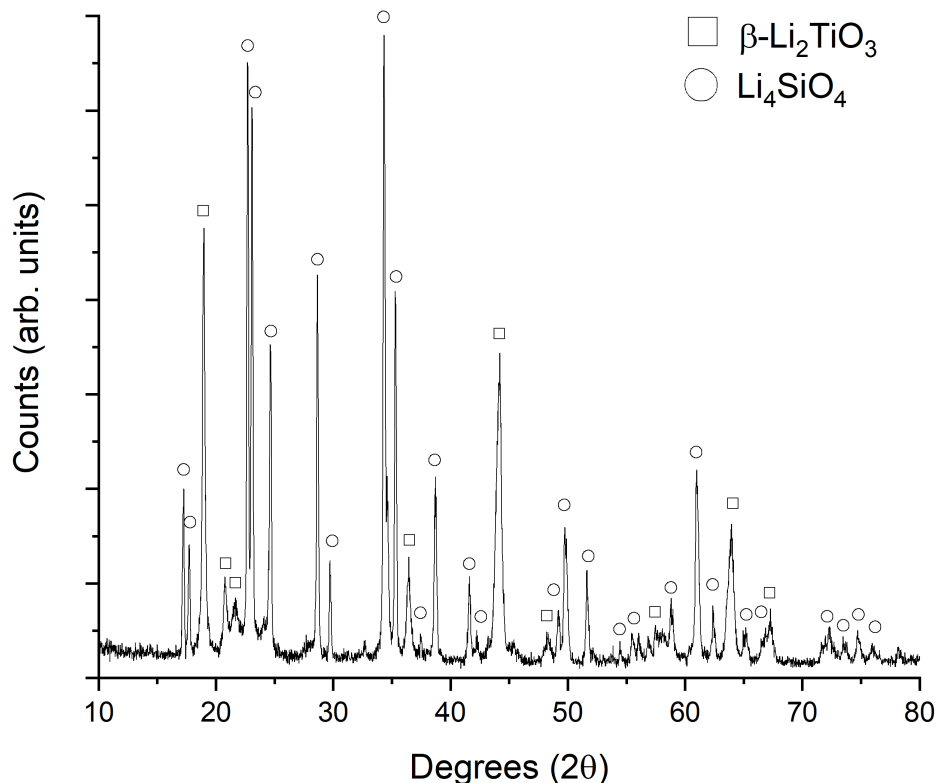


Figure 4.9: X-ray diffraction pattern of a crushed pellet made by co-firing an equivalent mix of  $\text{Li}_4\text{SiO}_4$  and stock  $\text{Li}_2\text{TiO}_3$  powder to an RCS pellet. Both phases can be seen after calcination, without the large  $\text{Li}_2\text{SiO}_3$  presence visible in previous figures.

Co-firing of the two, fully reacted ceramics shows little to no deviation from the expected XRD pattern of  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{SiO}_4$  individually, suggesting that, even if lithium metatitanate is indeed leaching some lithium from the orthosilicate, this effect is not large enough to cause the appearance of  $\text{Li}_2\text{SiO}_3$ , especially to the degree observed in the previous ground up samples (figure 4.5). Humps around  $27^\circ$  and  $33^\circ$  may be suggesting a minor presence of the metasilicate however, this is so minimal in comparison to the RCS samples that it likely is solely due to re-carbonation of the orthosilicate.

This again points towards an interaction during post-anneal, between the re-carbonation of  $\text{Li}_4\text{SiO}_4$  and the synthesis of the infill-derived,  $\text{Li}_2\text{TiO}_3$ . The mechanism by which this occurs (postulated in section 4.3.2.3) will be further addressed in chapter 5, however, the

fact that this interaction is likely to blame introduces a high degree of uncertainty when quantifying the effect.

Essentially, the observed effect leading to the retention of  $\text{Li}_2\text{SiO}_3$ , is clearly determined by the two reactions identified, these reactions however are governed by uncontrollable, extrinsic atmospheric conditions - namely humidity and  $\text{CO}_2$  exposure. Processing time, time of day, time of the year, even specific room conditions all can affect these two factors. All of these elements compound complexity leading to two uncontrollable systems and hence, leading to unquantifiable degrees of material loss (and hence loss of stoichiometric control *i.e.*  $\text{LiCl}/\text{TiO}_2$  ratio) and re-carbonation respectively.

Even though this effect is consistent, due to the randomness inherent in performing the experiments in an uncontrolled environment, accurate quantification may be impossible and therefore measurements will fluctuate depending on the atmospheric conditions. In short, only qualitative information may be extracted from the observed measurements; essentially, whether or not this has occurred and to what comparative extent.

#### 4.3.2.5 Surface reactions

Another detail of the pellets generated in this chapter that was of interest was the “patina” identified on the SEM taken in section 4.3.2.1. This layer was too thick and consistent to be due to over-coating of any of the surface sputter coatings used in the lab (C and Au). The layer was ubiquitous and obscured any grains smaller than a micron, suggesting that it was relatively thick and had been introduced or produced by a substance that entirely permeated the sample surface.

It follows that this is then either an introduced contaminant, likely from the infill material as it permeates the sample, or a result of reactions within the sample, leading to the formation of this material coating all the surfaces viewed. This latter theory may be correct as another group working on lithium garnets has identified the rapid formation of  $\text{Li}_2\text{CO}_3$  at the sample surface as it is exposed to air, resulting in a very similar layer identifiable in their micrographs [165].

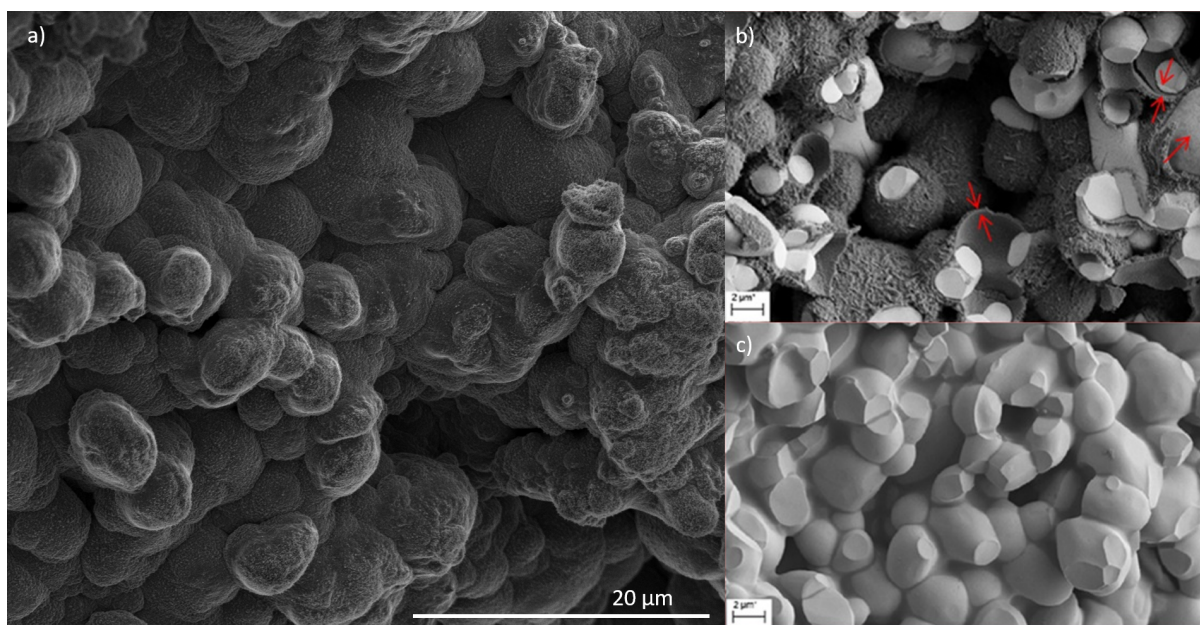


Figure 4.10: Secondary electron micrograph of (a) a fracture surface of a biphasic sample after exposure to air, (b) morphology of the garnet studied by Abdel-Basset *et al.* after 2 days of air exposure, (c) sample after an acid etch of the same material [165].

The “patina” looks in both cases like a cluster of cubes surrounding all the grains visible from the micrograph. In figure 4.10(b) you can see areas where grains have fragmented or detached from other grains revealing a pristine surface; this surface containing no “patina”. If this is indeed a reactivity issue, it appears between transfer and processing of the samples, enough time has passed to allow for the entire surface to be covered by this layer. In the case of the  $\text{Li}_4\text{SiO}_4$  -  $\text{Li}_2\text{TiO}_3$  composite produced in this work and as seen from the SEM shown in figure 4.10, this layer expands to fully obscure even the lithium titanate grains, hindering this phase’s identification from SEM micrographs alone.

Abdel-Basset *et al.* [165] acid etched the surface of their samples revealing the actual surface beneath the layer of re-carbonated material (figure 4.10(c)). Considering the similar atmospheric instability of the materials involved, as well as the visual similarities between the surfaces of both, this is likely due to the same or a very similar process.

In their case this “patina” was identified as a metastable, low-temperature form of  $\text{Li}_2\text{CO}_3$  (ICSD 259172). In the samples studied this phase could not be identified *via* XRD so, to confirm this, a more surface specific technique was used to attempt to detect it and perhaps to see how it forms.

#### 4.3.2.5.1 Raman spectroscopy

Lithium metasilicate is being generated in the biphasic pellets in noticeable amounts, a second, unexplained phenomena can be seen at the surface of grains in SEM. This may be the low-temperature form of  $\text{Li}_2\text{CO}_3$  identified by Abdel-Basset *et al.* [165], formed by re-carbonation of the garnet. The re-carbonation reaction likely to blame is usually ascribed

to a core-shell phenomenon described in figure 4.11. This forms a layered structure with lithium carbonate at the grain surfaces, preceded by a layer of  $\text{Li}_2\text{SiO}_3$  with a lithium rich core of  $\text{Li}_4\text{SiO}_4$ .

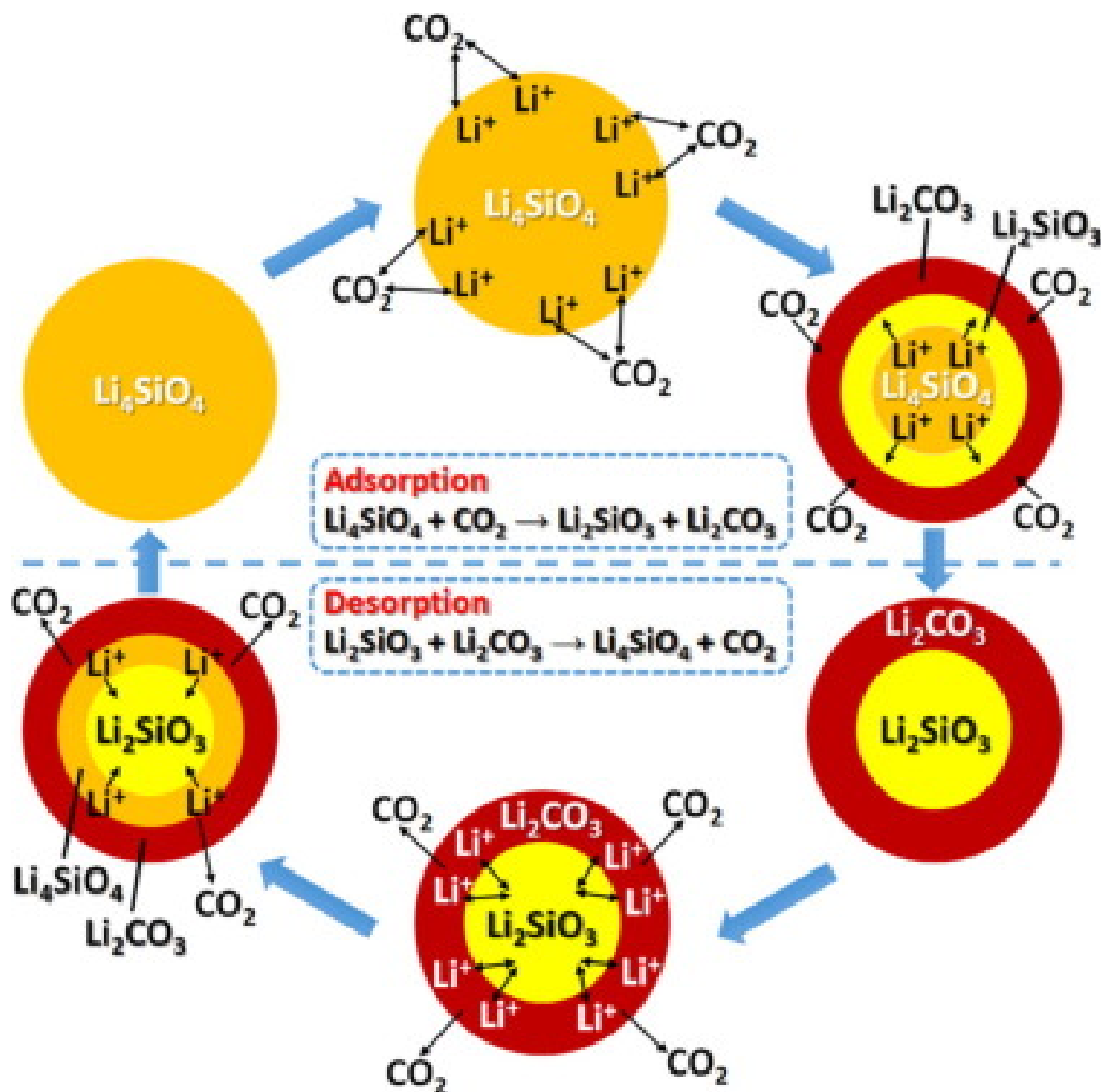


Figure 4.11: Schematic showing a simplified reaction scheme for the  $\text{CO}_2$  absorption and desorption on  $\text{Li}_4\text{SiO}_4$ . From [166].

Understanding the limitations of this reaction is important and hence the depth to which this occurs needs to be characterised. As a surface specific technique, capable of detecting Li bonds, Raman spectroscopy lends itself perfectly to this purpose.

The aim is to identify the extent of the carbonation, *i.e.* if it is isolated on the surface of the pellet or if it penetrates into the bulk at all. To this end, a fresh pellet surface of a sample stored in air will be polished and scanned using a 532 nm laser, which will then

be aged for 5 hours in air and subsequently re-scanned in order to observe any products of the reactions naturally occurring in air and the difference between bulk and surface compositions.

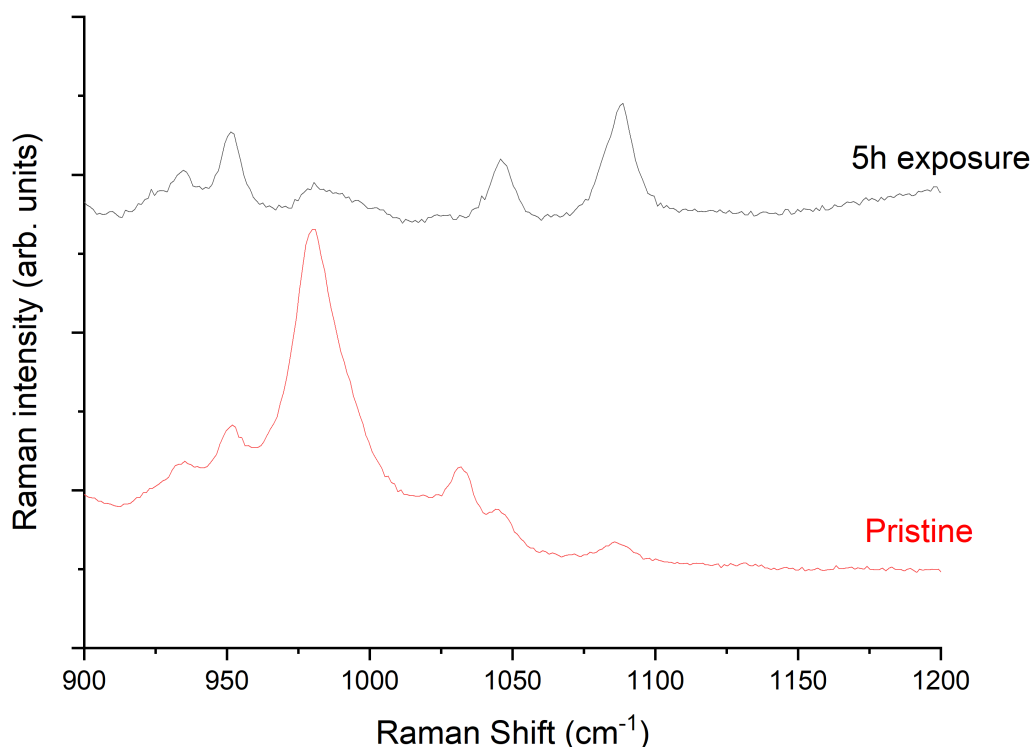


Figure 4.12: Raman spectra between 900 and 1200  $\text{cm}^{-1}$  of a pristine surface (bottom) and a surface (top) exposed to air for 5 hours.

There is a clear difference between the revealed and the aged pellet surface. A peak at 1082  $\text{cm}^{-1}$  has appeared after aging at the same time as the peak at 980  $\text{cm}^{-1}$  has been heavily subdued. Using the reaction mechanism suggested in figure 4.8 it may be surmised that an aged surface will be rich in  $\text{Li}_2\text{CO}_3$  and a revealed, polished surface may have abraded the carbonate layer revealing the lithium silicates in the core.

This measurement confirms the suggested mechanism, as the 1082  $\text{cm}^{-1}$  peak corresponds to the symmetrical stretching vibrational modes of the C–O bonds of isolated  $[\text{CO}_3]^{2-}$  triangles in the  $\text{Li}_2\text{CO}_3$  and the 980  $\text{cm}^{-1}$  corresponds to the symmetrical stretching vibrational modes of the Si–O bonds of isolated  $[\text{SiO}_4]^{4-}$  tetrahedra in the now revealed  $\text{Li}_2\text{SiO}_3$  [167].

For there to be a lithium carbonate signal the newly revealed surface must be composed of, at least partially, unreacted  $\text{Li}_4\text{SiO}_4$  and therefore it can be assumed that the re-carbonation under ambient conditions occurs exclusively at the surface of the pellet and is likely incomplete, *i.e.* only material exposed to air can re-carbonate, and the carbonate layer itself acts as a barrier preventing further re-carbonation of the lithium orthosilicate

beneath. The speed of re-carbonation was also notable. This test was carried out within 5 hours, however many SEM images were taken minutes after the pellets' removal from storage under argon.

#### 4.4 Conclusion

No single lithium ceramic manages to combine all of the properties beneficial to a tritium generating material. To this end, multi-phase ceramics can help marry the properties of multiple different materials to form ceramic-ceramic composites, improving flexibility and efficiency. Formation of ceramic-ceramic composites, especially at low temperatures, heavily depends on the properties of each component and may require highly specialised techniques [85–87].

Single phase  $\text{Li}_4\text{SiO}_4$  was produced using conventional solid state synthesis. Other groups report incomplete reactions, with  $\text{Li}_2\text{SiO}_3$  and  $\text{Li}_2\text{CO}_3$  as main by-products. This was found to be potentially due to either, re-carbonation of the powder or an incomplete reaction. A re-fire at 650 °C led to single phase material and was deemed too low to allow for a continuation of the reaction but high enough to allow for regeneration of the  $\text{Li}_4\text{SiO}_4$ . Rapid re-carbonation of the lithium orthosilicate powder under atmospheric conditions was clear.

To demonstrate the capacity for the reactive cold sintering method to form cohesive ceramic-ceramic composite pellets, pellets were generated replacing the lithium metatitanate main phase powder with the aforementioned lithium orthosilicate. These biphasic samples had clear phase segregation, with areas of either containing titanium or silicon, as expected if the infill had successfully been introduced into the pellet.

However, previous temperatures used to post-anneal the cold sintered  $\text{Li}_2\text{TiO}_3$  pellets (700 °C) resulted in the persistence of metastable  $\alpha\text{-Li}_2\text{TiO}_3$  in the final samples. This phase was likely stabilised by some unknown interaction between lithium metatitanate and lithium orthosilicate. The  $\alpha - \beta$  transition temperature occurs at 300 °C under normal conditions, however, the transition now has shifted up in temperature, reaching complete transition when the post-anneal temperature is raised to 900 °C. Not only this but, similarly to the  $\text{Li}_2\text{TiO}_3$  pellets, hints of lithium deficiency were observed, namely a large proportion of both  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_2\text{SiO}_3$ , with a distinct lack of  $\text{Li}_2\text{CO}_3$  related peaks. This lack of carbonate implying the lithium metasilicate present was not generated *via* re-carbonation post-sintering.

A proposed mechanism to explain this system was shown in figure 4.8. It was postulated that, aided by the inherent off-stoichiometry induced *via* extrusion, lithium carbonate generated *via* the re-carbonation of the main phase powder ( $\text{Li}_4\text{SiO}_4$ ) is being preferentially utilised by the titania present in the infill to form  $\text{Li}_2\text{TiO}_3$ , obscuring the fact that the system is still operating with a lithium deficiency.

A layer of material was seen to commonly obscure any SEM generated with any  $\text{Li}_4\text{SiO}_4$  content. This had been seen in work by Abdel-Basset *et al.* [165] and was found to be a low temperature, meta-stable  $\text{Li}_2\text{CO}_3$  phase. Their garnet material produced this “patina” due to re-carbonation; the similarities leading to the consideration that this may also be the mechanism at play here. Raman was performed to identify the appearance of this



“patina” and characterise it as  $\text{Li}_2\text{CO}_3$ . Within 5 hours of exposure to air  $\text{Li}_2\text{CO}_3$  could be identified in the Raman spectra, confirming the obscuring material to be  $\text{Li}_2\text{CO}_3$ , produced *via* re-carbonation of the  $\text{Li}_4\text{SiO}_4$  at speed.

#### 4.5 A note on contextualisation and further work

As discussed in chapter 1, these advanced sintering techniques and generation of composite ceramics has all been performed with nuclear fusion as a target application, and some way of contextualising the material produced with the wider community would be of interest.

This chapter interests itself in the formation of a ceramic-ceramic composite using a relatively low temperature sintering method to achieve this. Therefore, the key difference between the material produced herein and that seen in literature is the combinatory effect of microstructure and composition to the sample as a whole. As such, to fully contextualise the samples produced, a wide range of tests should be performed to fully understand the benefits and limitations of generating samples the way they have been described in this work.

To reiterate, the combination of the two phases chosen ( $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{TiO}_3$ ) was selected to attempt to strike a balance between beneficial properties of each of these ceramics. Lithium orthosilicate has a larger lithium density than many of the other lithium ceramics considered viable by the fusion community [41], a property required to reduce the amount of material needed to populate a reactor. And lithium metatitanate is generally agreed upon to have the best atmospheric stability and crush strength among the viable ternary lithium ceramics [75].

It is therefore of importance to quantify these in an attempt to contextualise them and see where the generated material fits within the rubric of potential breeder material solutions. The issues encountered during fabrication however, call into question the usefulness and relative value of any number derived as methodological concerns limit the repeatability and expected compositions of the pellets generated.

Density of course is of interest, especially when considering the target application. However, the high sensitivity of lithium orthosilicate to ambient conditions will lead to the continuous re-carbonation and hydration of the pellet surfaces. This may introduce variance to the results that will be hard to deconvolute from the actual density.

Another key factor when measuring density is the context. Density may be measured but without a complete understanding of the material in question contextualising this number, *i.e.* understanding the value as a percent of the potential maximum density, the values extracted may be all but meaningless. The inherent variability of the materials being generated in this chapter - having varying proportions of  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_2\text{SiO}_3$  depending on uncontrollable atmospheric conditions - make this attempt at contextualisation close to impossible, and would require detailed analysis in a per-sample basis to arrive at an accurate value.

Due to this and similar issues encounter in the other sample population, measurement of these was forgone in order to address the methodological and chemical concerns addressed. Any future work must identify avenues to aid contextualisation, although this

may need a stable and consistent procedure to work.

## 5 Factors leading to lithium loss and high temperature analysis

### 5.1 Introduction

Throughout this work the final generated material has stayed persistently inconsistent. From  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  forming consistently in the bulk in single phase and chlorine retention combined with the formation of  $\text{Li}_2\text{SiO}_3$  in the biphasic population. Both in a single phase as well as in a biphasic scenario, the end product has never been as expected. Not only that but these issues are seemingly unrelated and result in very different final compositions. Lithium loss is likely partially to blame but this has just been a working hypotheses and has yet to be confirmed experimentally. However, even if this were the case, the way this loss has affected each system is still unknown.

Understanding the factors and mechanisms behind these inconsistencies is key in both, developing the method further and addressing the issues themselves.

Fusion hinges on material scientists to provide the necessary materials to arrive at a functional reactor. Rarely do industries require so much out of each of the decisions made over material choice and component morphology, with every part of the final device operating at, or close to, its absolute physical limits just to function. As such, the materials analysed herein, namely lithium metatitanate and lithium orthosilicate, were chosen deliberately and purposefully.

Predictable tritium release behaviour and lithium density are key to accurately design and simulate a functional breeder blanket; as the potential volume of generated tritium is key to estimate the final capacity of the device. This need for predictable performance is further complicated by the highly specific conditions the material experiences during operation: high neutron fluxes at high energies and high temperatures. Currently, no experimental setup in the world can simulate all of these conditions simultaneously and hence the predictability required is hard to come by. Certain breeder ceramic candidates have been studied to a large enough extent that through combining a large series of experiments, it is possible to estimate their performance inside a reactor in the described conditions [168–170]. This has led to the limited spread of potential ceramics in consideration today, from which lithium metatitanate and lithium orthosilicate stand out as the most likely candidates.

This fact leads to materials considered to require a high degree of consistency and adherence to the phases recognised, this all in an effort to improve confidence in the application of the pellets produced into a fusion device. Variance from these phases therefore, even if potentially beneficial, must be approached with a certain degree of scepticism as performance in fusion conditions cannot be assessed without thorough analysis.

All this to say, the variance observed in the compositions produced in this work is pernicious and affects its relative practicality as a fusion breeder ceramic and, as such, the source of this variance must be understood in order to address and explain the issues present in the experimental setup as well as how to potentially remediate them.

## 5.2 Aims

The aims of this work were:

- Identify the mechanisms behind and the factors leading to the formation of lithium-poor phases in both single phase (bimodal) and the biphasic systems described in chapter 3 and 4, respectively.
- Once understood, identify how these mechanisms relate to the method and hence, if possible, how to approach and address them.

## 5.3 Results and Discussion

### 5.3.1 *Characterisation*

#### 5.3.1.1 Preliminary transmission electron microscopy of RCS ceramic bodies

TEM was used over further SEM in order to further elucidate the formation mechanisms of the samples in question. Grain boundaries, and the transition between starting powder grains and those formed during post-anneal were of particular interest. This technique would also allow the use of SAED to analyse individual crystallites and, perhaps, allow for the inference of the presence of transitional intergranular phases, which may leach lithium out of the structures of interest and result in the lack of lithium observed throughout the work.

This technique shares several shortcomings with SEM however, chief among them being incapable of detecting lithium specifically. Not only this, but SAED analysis becomes increasingly complex with decreasing crystal symmetry which, considering all the expected structures are monoclinic and formed at relatively low temperatures, may result in patterns that are impossible to index. Crystallite size may exacerbate this issue as isolating individual crystallites may be unachievable.

An important note on this technique is the focus on extremely small features within samples. Consider that an SAED pattern may be taken of a section of  $\approx 1 \mu\text{m}$  crystallite, coming from an extremely specific location on the surface of the 10 mm diameter pellet. Making conclusions about bulk characteristics based on analysis of such a specific area, in such a small scale must be approached with caution.

##### 5.3.1.1.1 Bimodal $\text{Li}_2\text{TiO}_3 - \text{Li}_2\text{TiO}_3$

Figure 5.1 shows the area the lamella was extracted from. The morphology looks as expected, with large micron sized grains surrounded by much smaller debris. The porosity perhaps looks worse than as seen previously, however this surface was not polished or etched, so comparison between this and other, previous, micrographs taken on polished surfaces aren't directly comparable.

The TEM micrographs in figure 5.2 show some expected features and others which bring up further questions. Figure 5.2(a) shows the expected morphology previously observed under SEM, with micron sized grains surrounded by smaller material. Starting with (b) however, odd features start to be observed. Most of the grains observed here

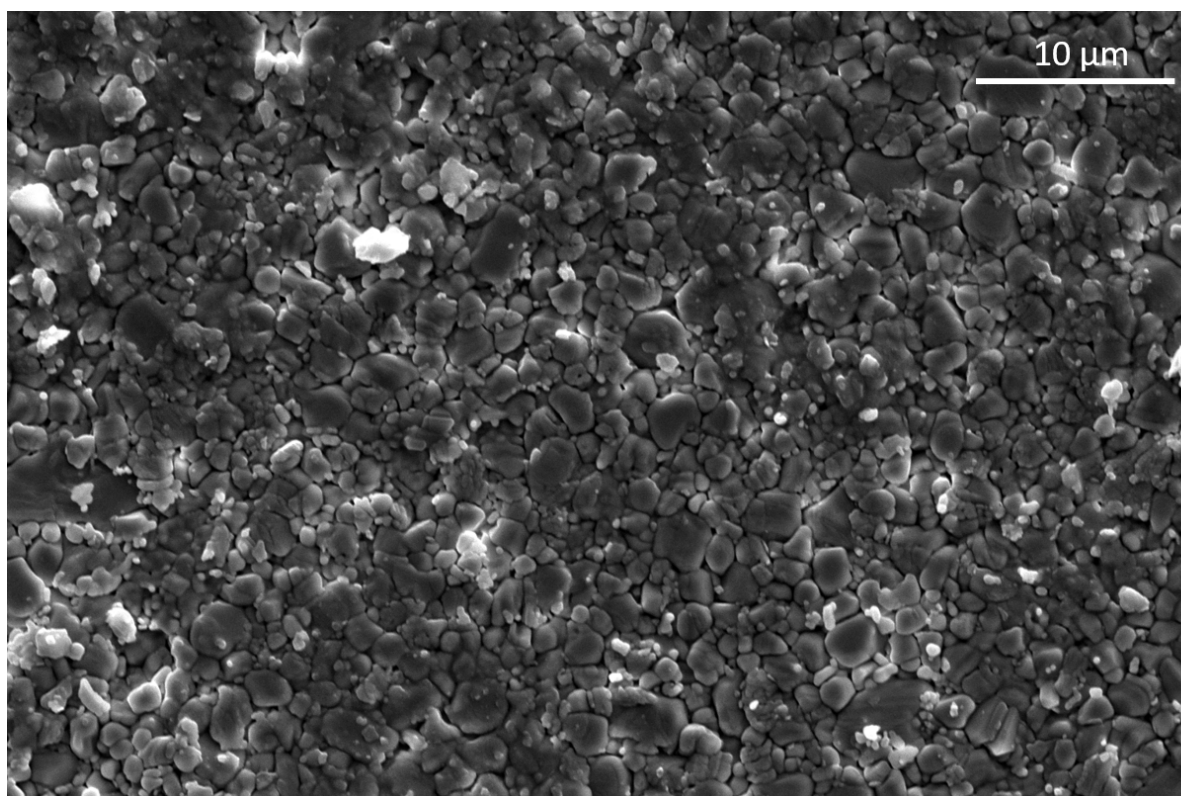


Figure 5.1: Secondary electron micrograph of a bimodal pellet surface prior to FIB lamella extraction.

appear to have intragranular bubbles. Whether this is due to beam damage or an inherent feature of some of the grains in the pellets is difficult to ascertain. These bubbles were not ubiquitous but their presence was concerning.

Figure 5.2(c) shows a crystalline grains with what seems like lattice fringes as well as moiré fringes, surrounded by a glassy, likely amorphous, material. Other grains in the micrograph exhibit much less conventional patterns and spotty contrast which may suggest the presence of nanodomains.

Finally, figure 5.2(d) once again shows this glassy layer surrounding the more crystalline grains, with some grains visible with the spotty contrast previously mentioned. EDXA was used in STEM mode to confirm the chemistry of the material visible and all of the grains probed contained comparable elemental composition.

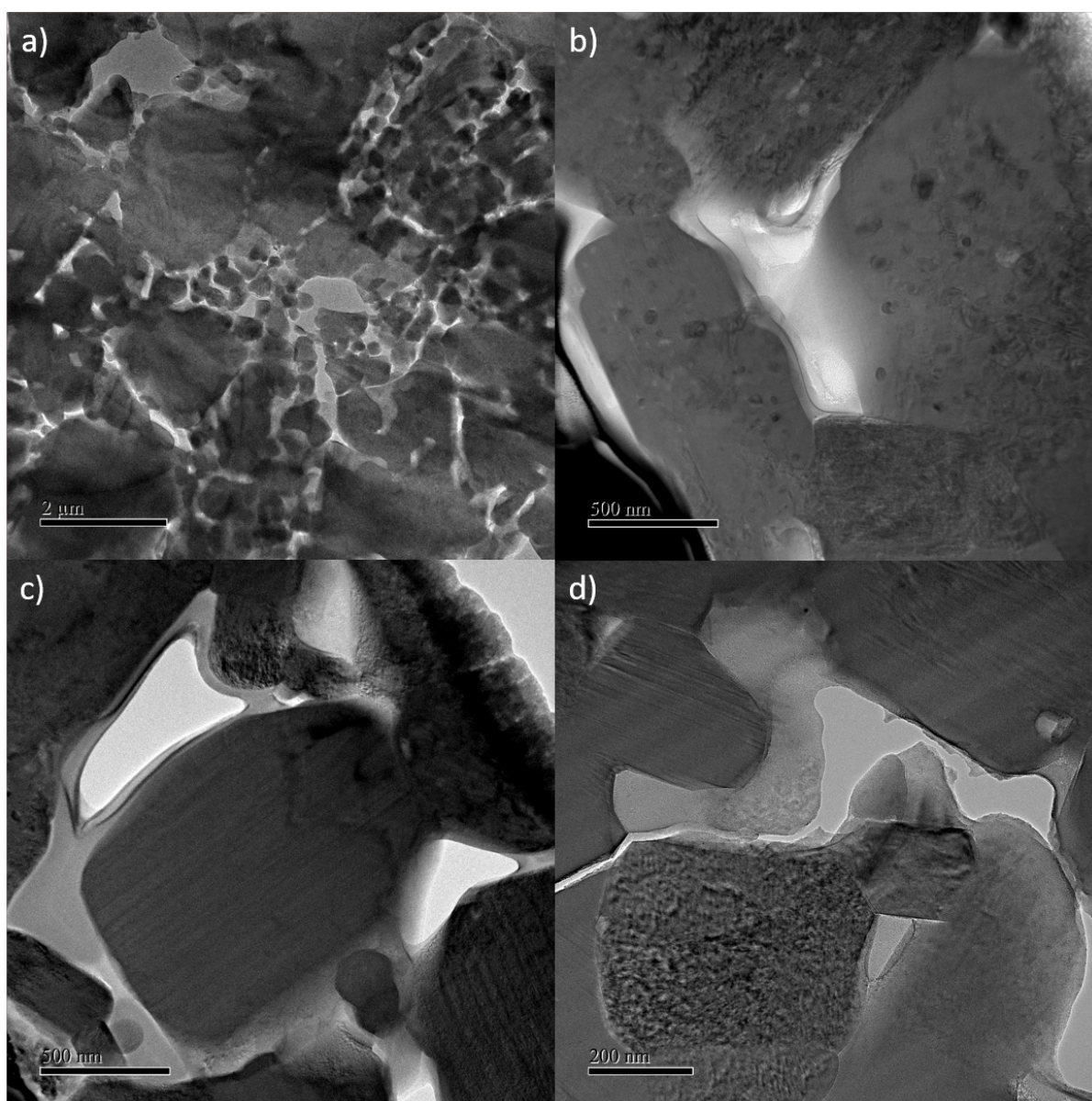


Figure 5.2: TEM micrographs of a bimodal pellet surface lamella. Magnification increases with subsequent letters. Bimodality is clearly apparent from low magnification imaging (a), with areas of seemingly amorphous material surrounding larger grains when observed under higher magnification (c and d).

Observing the SAED patterns taken from figure 5.2(d) (figure 5.3) shows a variety of artefacts. Figure 5.3(a) shows a diffuse pattern with some poorly defined spots. This diffuse appearance may be due to the targeting of the boundary between grain and the amorphous material. Figure 5.3(b) has an oval shape, implying some amount of distortion, which could be due to the crystallite surface not being perpendicular to the incident electron beam. The spot pattern however seems to suggest the presence of nanodomains within the crystallite in question. Figure 5.3(c) is the closest to an indexable





Figure 5.3: TEM micrograph of a bimodal pellet surface lamella (figure 5.2 d) with SEAD of three different areas.

pattern, however, diffraction spots show some rotational symmetry. All of these patterns were deemed above the skillset of this group to index, however, considering the likelihood of stacking faults, this effect may be due to their presence. This could not be concluded with any certainty however, and further analysis of these materials as well as further study of the TEM data would be required to fully characterise and understand the effects at play.

#### 5.3.1.1.2 Biphasic $\text{Li}_2\text{TiO}_3 - \text{Li}_4\text{SiO}_4$

Figure 5.4 shows the surface from which the FIB lamella was extracted. The ‘patina’ described in chapter 4 is clearly visible and completely engulfing the visible surface. The size of this shell of re-carbonated material is still in question and may preclude the extraction of a lamella consistent with the bulk material.

Initially, observing figure 5.5(a), no crystallites could be identified, which was concerning until magnification was reduced and figure 5.5(b) was observed. The shape and size of these circles clearly showed severe beam damage, ablating the material completely in some areas.

The material could be seen, seemingly boiling off. Figure 5.6(a) attempts to show this with a one minute timelapse of the degradation of one area of the sample. Figure 5.6(b) shows the aftermath of this timelapse. The damage is overwhelming the image, leaving little material to analyse. Some grains seem to be revealed by the evaporated material and, considering their size, may be the added  $\text{Li}_2\text{TiO}_3$  phase. The re-carbonated material at the surface of the ceramic is clearly too beam sensitive to be analysed and may be forming a layer thick enough for FIBing of the direct surface to form an unusable lamella. Future analysis should be conducted on lamella generated after removing material from the surface using the Ga ion beam, until pristine grains can be observed. This may introduce other issues, as the impact of beam damage on the pristine material is unknown.

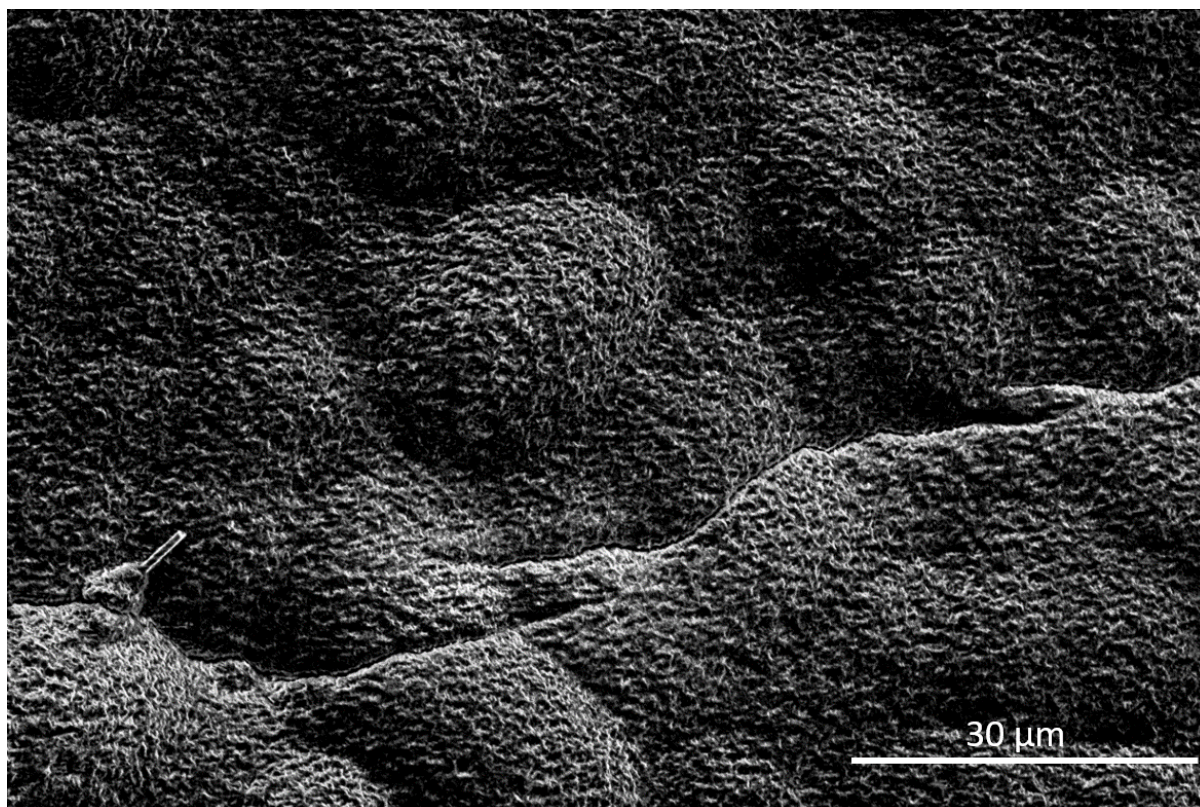


Figure 5.4: Secondary electron micrograph of a biphasic pellet surface prior to FIB lamella extraction. Surface reaction identified in chapter 4 can be clearly visible.

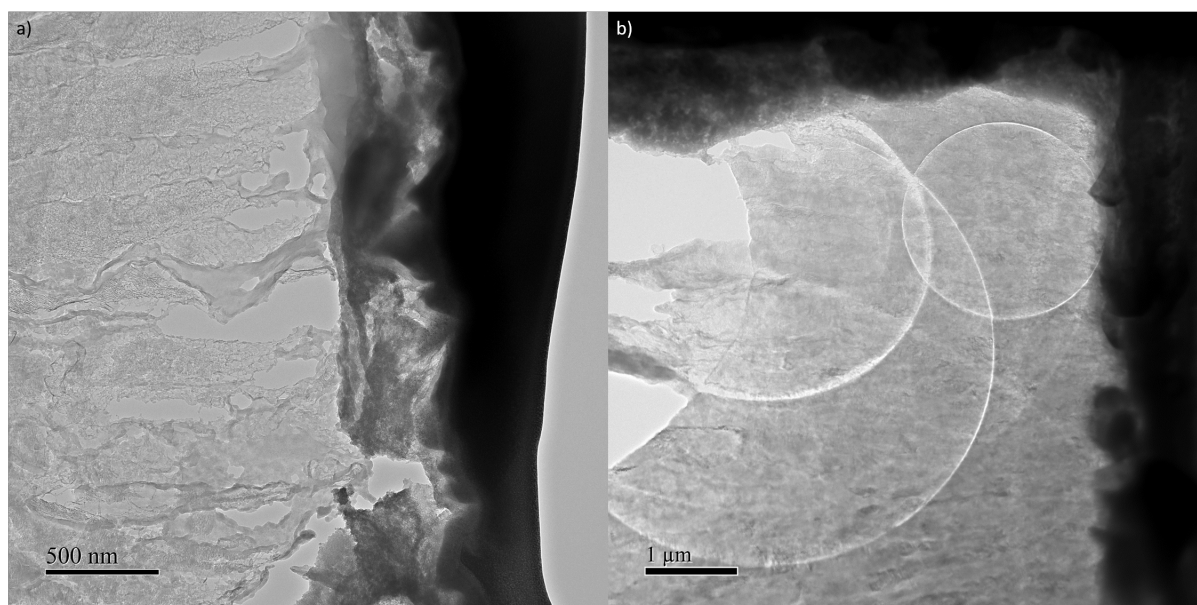


Figure 5.5: TEM micrographs of a biphasic pellet surface lamella. Microstructure seemed unusual when observed (a), and after reduction in magnification it was apparent that significant beam damage had occurred (b).



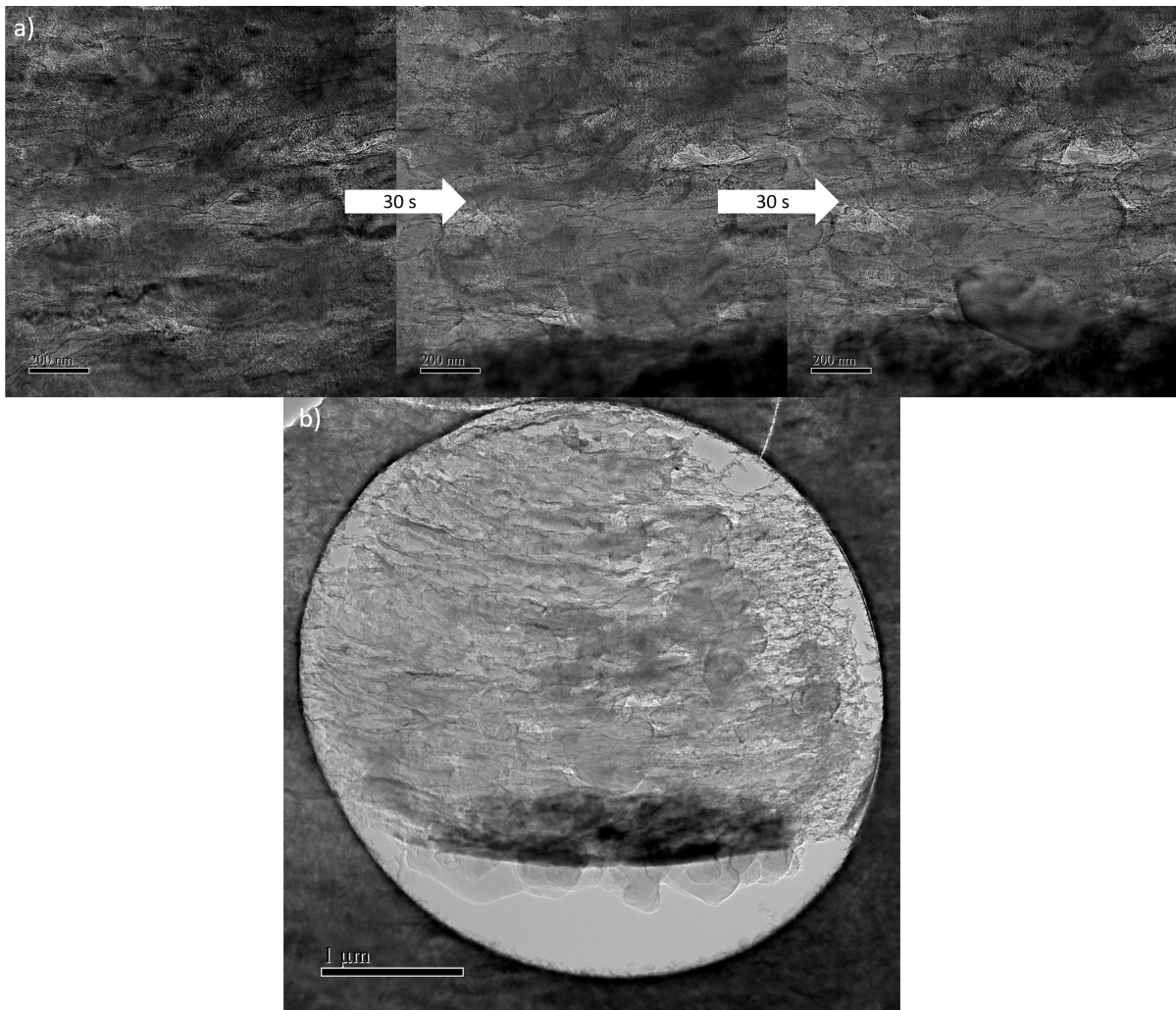


Figure 5.6: Timelapse of TEM micrographs of a biphasic pellet surface lamella. Images were taken every 30 seconds showing the rapid deterioration of the surface due to exposure to the beam. b) shows the final state of the lamella after  $\approx 1$  minute of exposure.

### 5.3.1.1.3 Summary

TEM of the RCS ceramics was ultimately inconclusive, yet intriguing. The main conclusions that may be extracted from these micrographs have already been observed using other techniques or inferred from other similar systems. Two different grain populations can be observed, as previously noted in chapter 3. An amorphous material could be observed surrounding the larger  $\text{Li}_2\text{TiO}_3$  grains, as was assumed to be likely, based on research by Boston *et al.* and similar systems using liquid sintering techniques [125,136]. Re-carbonation of  $\text{Li}_4\text{SiO}_4$  is indeed occurring and results in a layer of  $\text{Li}_2\text{CO}_3$  which permeates the entire surface. This layer is thick enough to preclude the extraction of a lamella with enough  $\text{Li}_4\text{SiO}_4$  to be representative of the pellet as a whole.

More samples are required and more time is needed to conclude anything else with any degree of certainty. SAED in the bimodal system seems to suggest the presence of nanodomains as well as perhaps the retention of stacking faults, this however needs further analysis of the patterns to fully evaluate.

### 5.3.1.2 Inductively Coupled Plasma - Optical Emission Spectroscopy

As mentioned, a key characteristic in both of the systems analysed is the final lithium content in the generated pellets. In both cases this has been hypothesised to be the core issue resulting in the retention of lithium deficient species:  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  in the single phase samples and  $\text{Li}_2\text{SiO}_3$  in the biphasic samples.

Lithium is notoriously hard to detect using standard analytical techniques, a light atom with weak interactions and low characteristic X-ray energies, precluding its identification using X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDXA) respectively [171,172]. Hence, only very limited conclusions can be drawn from the X-ray diffraction (XRD) and EDXA experiments performed so far as potentially unreacted inclusions of  $\text{Li}_2\text{O}$  or  $\text{LiCl}$  may remain undetected under analysis using those techniques.

Neutron diffraction as a technique is conceptually similar to XRD and will provide the lithium sensitivity desired however, is much more involved, requiring a source of thermal neutrons — usually meaning a spallation source or a nuclear reactor — to interact with the sample, resulting in few research centres even having this capability. A more accessible technique which will still provide the empirical evidence required to confirm the hypotheses is Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES).

As mentioned in the methodology, this technique involves the ionisation *via* a plasma of an aqueous solution formed by dissolving the sample to be analysed. The ionised atoms repeatedly gain and lose electrons resulting in the emission of characteristic photons (hence optical emission spectroscopy) [173]. This allows for the detection and quantification of atomic proportions in the sample and, therefore, these can be compared to the expected proportions added when batching.

To extract as much information as possible a series of four samples were prepared for this technique: two main phase  $\text{Li}_2\text{TiO}_3$  powders synthesised at 730 °C and 1100 °C and two cold sintered bimodal pellets (chapter 3), one using stoichiometric proportions of  $\text{LiCl}$  and  $\text{TiO}_2$  and the other using double the stoichiometric amount of  $\text{LiCl}$ . These were designed to identify where the lithium deficiency arises in the method, by targeting

samples after firing during synthesis and then after firing during the final post-anneal.

The first group of pre-synthesised powders (synthesised at 730 °C and 1100 °C) aimed to assess the potential off-stoichiometry inherent to the initial powders used in the cold sintering process which may be introduced *via* lithium volatilisation during the heating regime [103, 104, 108]. Variance from the expected lithium to titanium ratio of 2:1 will show whether or not volatility is an issue, even in the low dwell times used in this work (4 hours).

The second group in context with the first will show if the added infill results in any variation from the measured lithium to titanium ratio found in the pre-synthesised powders and, therefore, the impact the extrusion observed during pressing has on the resultant stoichiometry. The aim behind analysing a sample with double the lithium concentration, is to work at a huge lithium excess (and therefore high partial pressure) to control for a potentially faster volatilisation rate in these samples due to the high vapour pressure (1.11 Pa at 575 °C) of pure LiCl [174] at post anneal temperatures (730 °C). The actual rate of LiCl volatilisation will be measured in section 5.3.1.3.2 using thermogravimetric analysis.

Table 5.1: Table showing sample description against measured Li:Ti ratio.

| Sample                | Li:Ti ratio |
|-----------------------|-------------|
| 730 °C powder         | 2.12:1      |
| 1100 °C powder        | 2.11:1      |
| Stoichiometric pellet | 1.77:1      |
| 100% Li excess pellet | 1.81:1      |

From these results (table 5.1) it is clear that there is no significant lithium evaporation occurring during synthesis of the solid state powders. The slight lithium richness leading to a Li/Ti ratio above 2 is perhaps unexpected, as these powders were batched aiming for a 2:1 ratio, however the value did not drop below 2, and was comparable between both powders. There is no meaningful difference between the Li/Ti ratio of the pre-synthesised powders, with both synthesised powders being measured as slightly lithium rich.

However, both the stoichiometric and the Li-excess cold sintered pellets show a significant lithium deficiency with the pellet sintered with double the available lithium showing just a 0.04 point improvement in the Li/Ti ratio compared to stoichiometric. This is an insignificant difference, especially considering the large excess added. Even if these values are somewhat inaccurate (measurements were performed by another lab with conditions not fully described), the qualitative assessment is clear: prior to RCS stoichiometry is slightly lithium rich and post-RCS the pellets are significantly lithium deficient, with the pellet made using double the available LiCl resulting in an improvement so slight it points to a necessary increase in Li content of 550% over stoichiometric to reach the desired 2:1 Li:Ti ratio.

This suggests that the mechanism by which the lithium is being lost is independent of initial LiCl concentration. The only two points in the procedure where lithium can be leached are: in the extruded material lost during pressing and any potential volatilised

material during firing. It is clear from the pre-synthesised powders that no significant volatilisation occurs in this system under normal circumstances, therefore, the lost lithium must be preferentially extruding out of the die leading to the off-stoichiometry observed. The higher the LiCl content the higher the mobility of the lithium species due to increased re-hydration.

To summarise, lithium loss has been confirmed in the system however, based on a qualitative assessment of the ICP data, it is unlikely to be due to volatilisation during post-anneal and may be due to poor equipment tolerances, leading to uncontrolled extrusion; as postulated in chapter 3.3.3.4.

### 5.3.1.3 High temperature analysis

Even though lithium deficiency is responsible for the presence of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_2\text{SiO}_3$  in the single and biphasic systems respectively, there is a key difference, and that is the affected component. In the single phase lithium metatitanate sample, the added infill is affected by the systemic off-stoichiometry, resulting in the formation of both  $\text{Li}_2\text{TiO}_3$  and the lithium deficient  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as it reacts during the post-anneal step. However, in the biphasic scenario, the infill has fully reacted to form single phase  $\text{Li}_2\text{TiO}_3$  and now, the impacted species is the pre-synthesised “main phase” powder, having been re-carbonated and orphaned as  $\text{Li}_4\text{SiO}_4$  and the lithium deficient  $\text{Li}_2\text{SiO}_3$ .

To identify the mechanism by which the  $\text{Li}_2\text{SiO}_3$  species is formed, the sample’s evolution throughout the post-anneal step must be understood. To this end, a series of high temperature analytical techniques were applied to both simulate the conditions in the furnace and measure the resultant changes to the pellet *in-situ*.

#### 5.3.1.3.1 High temperature X-ray diffraction

Firstly, to identify how phases develop within the system, high temperature X-ray diffraction (HT-XRD) was employed. In order to simulate as closely as possible the environment during post-anneal, the pre-sintered biphasic mixture was cold sintered as normal and then ground to allow for loading into the furnace module for the XRD equipment (refer to methodology section 2.4.1.1).

To simulate the conditions during post-anneal the furnace module was opened to air and a heating regime was designed to adhere to those conditions (same maximum temperature, 900 °C and dwell time, 4 hours) whilst allowing for the desired measurements (figure 5.7).

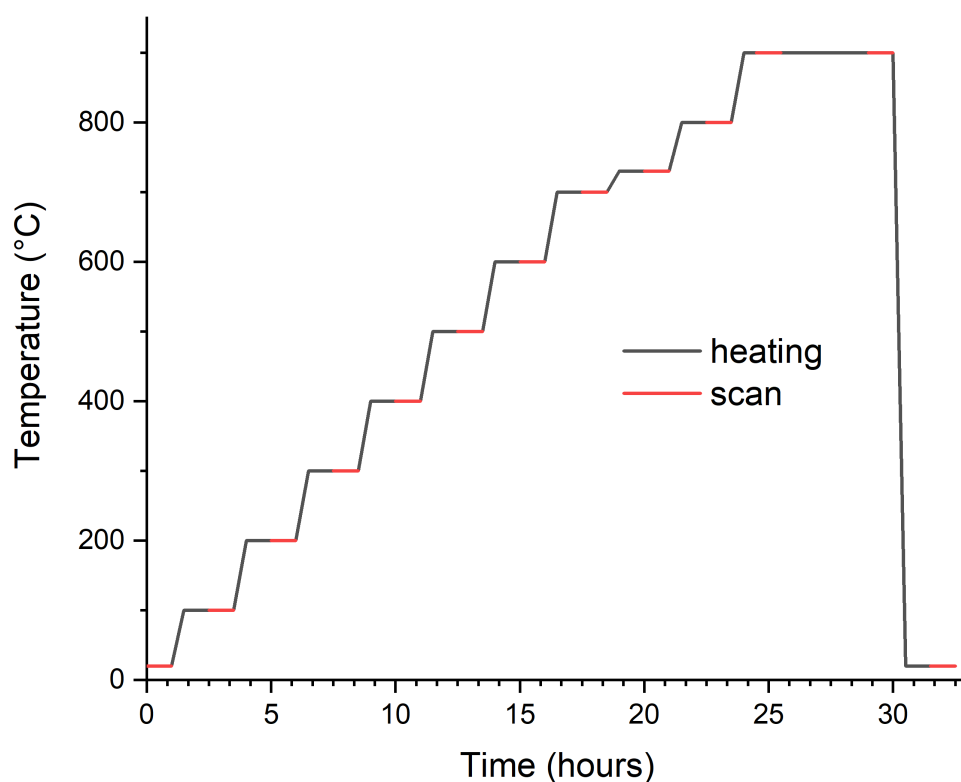


Figure 5.7: Heating regime used to simulate post-anneal conditions. An hour long scan was preceded by an hour at each temperature to allow for the sample to equilibrate. Initial scan at RT was carried out immediately. An additional step at 730 °C was added to avoid any potential  $\text{Li}_2\text{CO}_3$  melt which could damage the alumina holder.

It is inevitable that the overall heating regime will be slightly extended as the time required for a complete XRD pattern must be added, as well as the time required for the whole sample to equilibrate at the target temperature. These measurements were initially taken during short dwells at 100 °C intervals to identify where changes occur within the system.

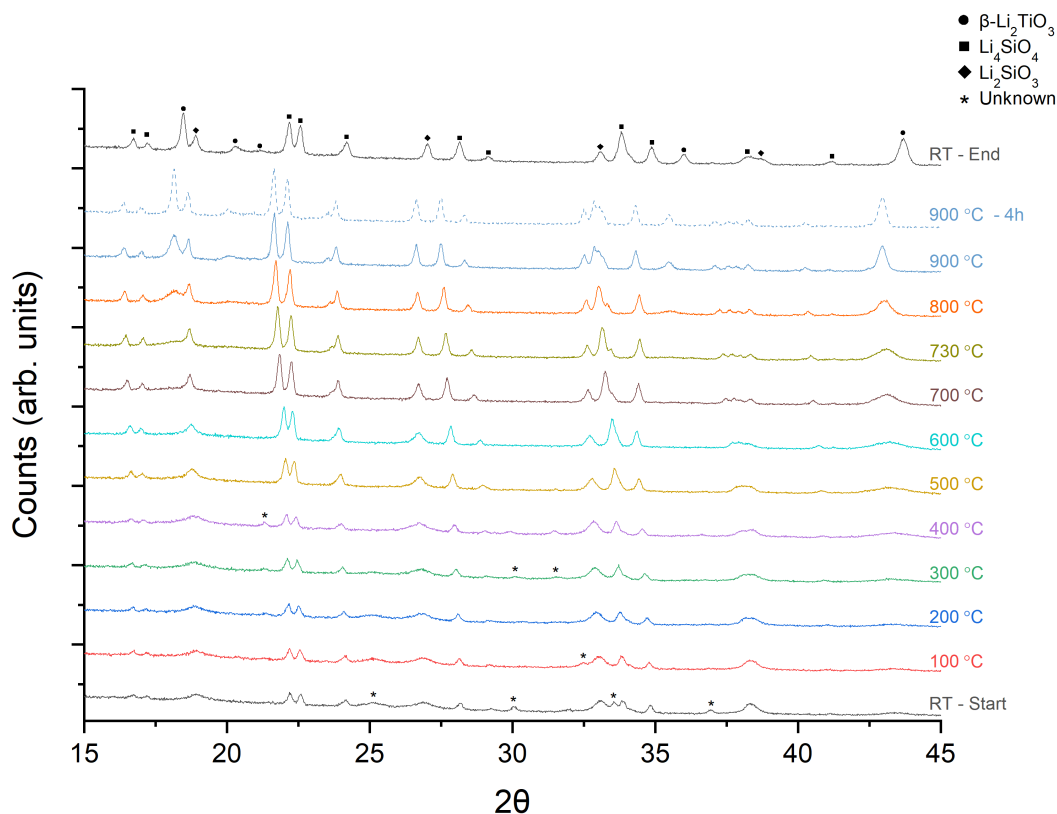


Figure 5.8: Stacked X-ray diffraction pattern of a post-anneal simulant. Temperature ramp is bookended with measurements at RT of both the initial material and the final, fully reacted sample. Sample post dwell at 900 °C is marked with a dashed line. Final sample is fully characterised and unknown phases are marked with \* as they arise.

The final sample is exactly as expected (figure 5.8), with no discernible change in peak ratios and, therefore, it may be concluded, that the experiment as-performed is an accurate simulant of the post-anneal process.

Both the  $\text{Li}_4\text{SiO}_4$  phase and the lithium deficient  $\text{Li}_2\text{SiO}_3$  phase can be observed throughout the entire procedure. Lithium orthosilicate was clearly identifiable even at low temperatures as the powder used was already fully crystalline and hence peak resolution is acceptable across all patterns, with sharpness of those peaks improving with increasing temperature.  $\text{Li}_2\text{SiO}_3$  however can be initially seen as broad peaks ( $18.9^\circ$ ,  $33^\circ$ ,  $26.9^\circ$ ) which slowly become more defined and increase in intensity as the temperature is increased.

This confirms the hypothesis that lithium metasilicate is being produced in large enough quantities to be detectable under XRD, even during the low temperature stages of the cold sintering process, therefore implying the simultaneous generation of  $\text{Li}_2\text{CO}_3$  as seen in equation 5. Another key detail is the clear retention of the  $\text{Li}_2\text{SiO}_3$  phase, even at temperatures above the theoretical regeneration temperature of  $\text{Li}_4\text{SiO}_4$ ; re-absorbed  $\text{CO}_2$  is what results in the formation of the metasilicate which, above  $650^\circ\text{C}$  [175], should

react back to form the orthosilicate. This reaction may only happen so far as the  $\text{Li}_2\text{CO}_3$  produced during re-carbonation is still present. Considering that this phase is not detectable on the XRD of the final pellet, it seems clear that the reason why regeneration does not occur is due to a loss of this carbonate, leading to the orphaning of  $\text{Li}_2\text{SiO}_3$  observed.

The appearance of peaks related to  $\text{Li}_2\text{TiO}_3$  phases can also be noted. The peak at  $43^\circ$  develops first, starting at around  $500^\circ\text{C}$ . This however doesn't happen concurrently with a peak at  $18.5^\circ$  which, as previously noted, suggests the initial formation of  $\alpha\text{-Li}_2\text{TiO}_3$ . This peak isn't detected until  $730^\circ\text{C}$ , when a slight hump can be observed at that angle, which becomes a clearly defined peak as  $800^\circ\text{C}$  is reached. Hence, it may be noted that in this system, formation of  $\beta\text{-Li}_2\text{TiO}_3$  requires temperatures well in excess of the reported  $\alpha\text{-}\beta$  transition temperature of  $300^\circ\text{C}$  [164]. The stabilisation of this low temperature phase was not observed in the single phase system, therefore some characteristic of the added lithium orthosilicate must be stabilising the  $\alpha$  phase well past this point. Knowing this, the post-anneal heating regime may be further tweaked to form  $\beta\text{-Li}_2\text{TiO}_3$  within the same dwell time at lower temperatures ( $730 - 800^\circ\text{C}$ ), however further analysis is needed to identify where within this range the lowest ideal temperature is.

From the appearance and disappearance of the unidentified species it can be surmised that there are two significant stages in the system:

Between RT and  $300^\circ\text{C}$  there are likely a series of species produced due to ambient processing conditions of the sample interacting with the rest of the sample, some of these species disappear in the first heating step – namely the peaks at  $30^\circ$ ,  $33.5^\circ$  and  $37^\circ$  – whilst others, such as the broad peak at  $25^\circ$  are retained until  $300^\circ\text{C}$ .

Between  $300^\circ\text{C}$  and  $600^\circ\text{C}$  another set of intermediate peaks appear and disappear. After this point the only significant change seems to be the aforementioned transition of the  $\alpha$  to  $\beta$   $\text{Li}_2\text{TiO}_3$ .

In order to deconvolute the contributions due to the interactions between the main phase powder and the added infill, the experiment was repeated on a sample of only  $\text{Li}_4\text{SiO}_4$  solid state powder. This will allow for the identification of the phase progression in a single phase scenario, the confirmation of the referenced lithium orthosilicate regeneration and if any residual  $\text{Li}_2\text{SiO}_3$  remains after heating.

This will also aid in the identification of the peaks that remain uncharacterised, and whether or not the events identified in the HT-XRD experiment are due to the presence of the infill or simply due to the relative instability of  $\text{Li}_4\text{SiO}_4$ .

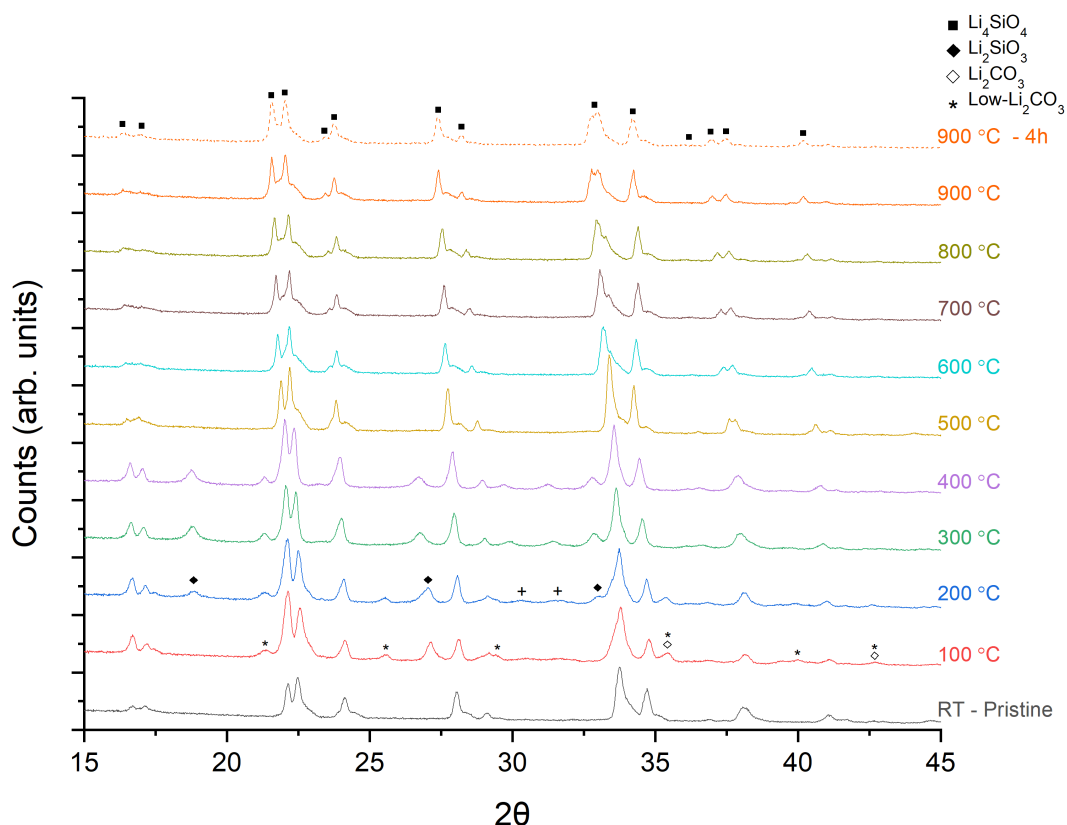


Figure 5.9: Stacked X-ray diffraction pattern of a  $\text{Li}_4\text{SiO}_4$  sample stored under Ar. Sample fully characterised after dwell at 900 °C (dashed line). Other phases added as they appear. Unknown phase labelled as +.

Initially, the bare lithium orthosilicate sample is single phase, confirming the storage conditions are sufficient to avoid significant re-carbonation or re-hydration of the orthosilicate. As the sample reaches 100 °C peaks related to  $\text{Li}_2\text{CO}_3$  start to become visible. These peaks match those observed from  $\text{Li}_2\text{CO}_3$  formed at the surface of the garnet type Li-ion batteries by Abdel-Bassett *et al.* [165], which seems to be a distorted low-temperature meta-stable form (ICSD 259172). Some of these peaks overlap with regular  $\text{Li}_2\text{CO}_3$  therefore both forms may exist simultaneously. All of the peaks related to this phase disappear by 300 °C with the notable exception of the peak at 21° which is retained until 500 °C. No other relevant phases match this peak; therefore, it may only be due to further distortion of the  $\text{Li}_2\text{CO}_3$  structure or an unidentified intermediate phase.

As temperature reaches 200 °C the appearance of peaks related to  $\text{Li}_2\text{SiO}_3$  can be identified as expected from the re-carbonation of the  $\text{Li}_4\text{SiO}_4$ . Simultaneously, two unidentified peaks appear at 30.3° and 31.5°. These are likely related to anhydrous  $\text{LiOH}$  which increases in intensity as it loses water of crystallisation.

All of these phases which have slowly appeared are completely gone when 500 °C is reached. This confirms that the lithium orthosilicate synthesised in this work re-carbonates and re-hydrates when in contact with air, and then reacts back to form single



phase lithium orthosilicate as described in equation 5 and by Quinn *et al.* [175]. Therefore, the presence of  $\text{Li}_2\text{SiO}_3$  after firing in the final biphasic pellets must be brought about by an interaction with added components in the infill ( $\text{LiCl}$ ,  $\text{TiO}_2$  and  $\text{H}_2\text{O}$ ).

Having analysed the phase transitions of the single phase  $\text{Li}_4\text{SiO}_4$  system, the progression in the biphasic system can now be approached in more detail with added context. Another post-anneal simulant sample was produced with scans every 25 °C between 300 °C and 600 °C.

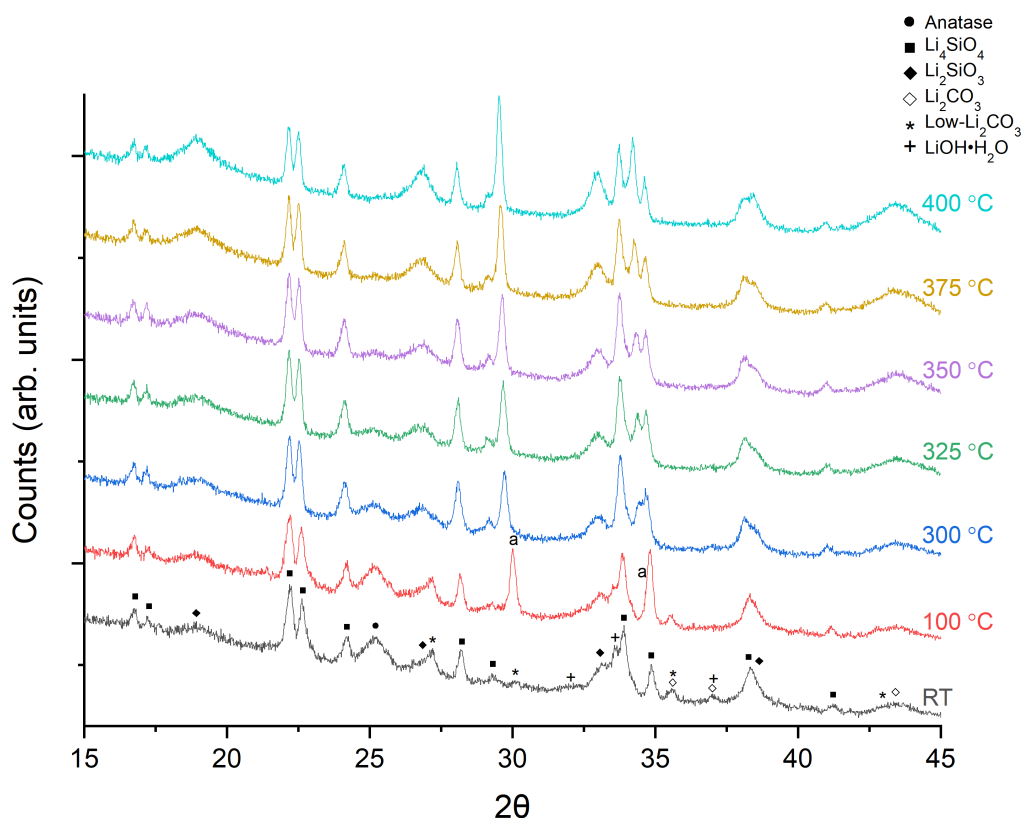


Figure 5.10: Stacked X-ray diffraction pattern of a post-anneal simulant from RT to 400 °C. Initial sample has been fully characterised. New unidentified intermediate phase has been labelled ‘a’.

Using the newly added context the initial state of the sample prior to post-anneal can now be fully characterised. Peaks related to  $\text{Li}_2\text{SiO}_3$  and both forms of  $\text{Li}_2\text{CO}_3$  previously identified can be clearly seen (white diamond and \*).  $\text{LiOH}\cdot\text{H}_2\text{O}$  (ICSD 9138) can also be observed (+ symbol), as well as a broad peak at 25° related to the anatase nanopowder added with the infill (black circle).

By the time 300 °C is reached, the  $\text{Li}_2\text{CO}_3$  phases as well as the  $\text{LiOH}\cdot\text{H}_2\text{O}$  are undetectable and the anatase signal is significantly subdued, implying some reaction between these lithium salts and the titania; any  $\text{Li}_2\text{TiO}_3$  produced through the interaction of these species will however be generated in the  $\alpha$  form as has been previously demonstrated. As the main peak at 43° overlaps with a  $\text{Li}_2\text{CO}_3$  peak it cannot be fully confirmed whether or

not the loss of the  $\text{Li}_2\text{CO}_3$  and the  $\text{LiOH}\cdot\text{H}_2\text{O}$  occurs simultaneously with the appearance of the  $\alpha$  lithium metatitanate.

A significant change can be spotted at the same time. Intermediate phase ‘a’ appears between room temperature and 300 °C which then increases in intensity as temperature is increased further. This phase aligns perfectly with anhydrous  $\text{LiCl}$  (PDF - 00-004-0664). It may be surmised that as temperature is increased  $\text{LiCl}$ , loses its water of crystallisation transitioning from an orthorhombic structure to a higher symmetry rock salt.

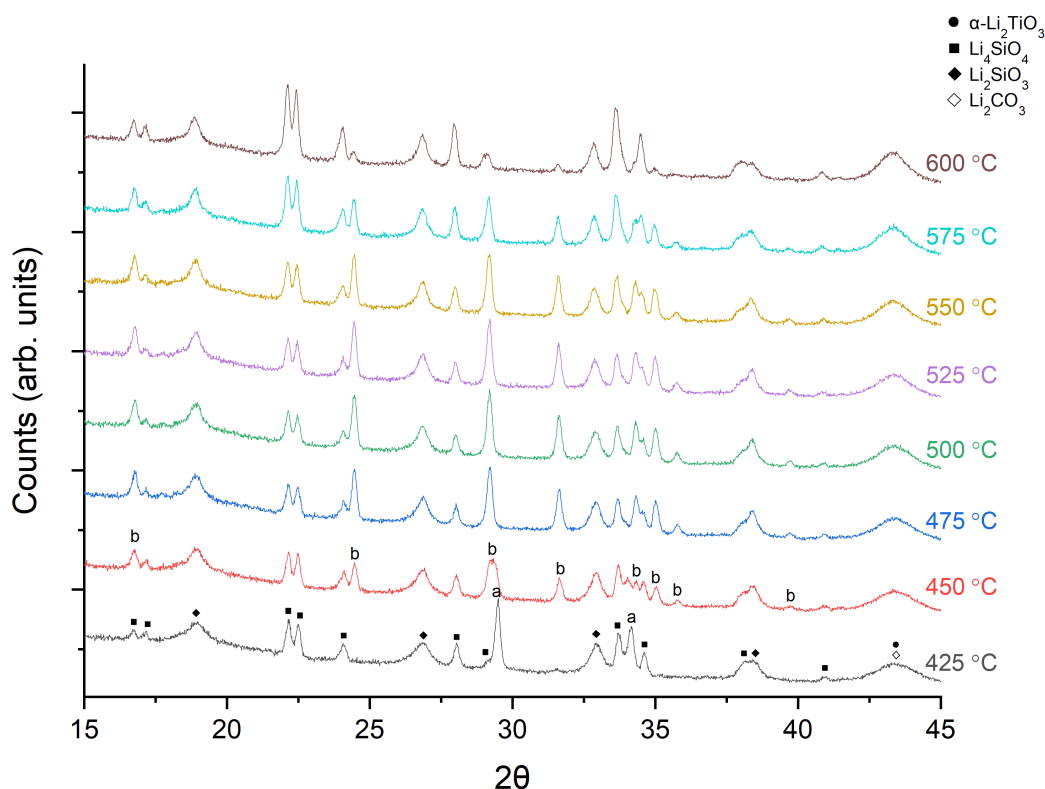


Figure 5.11: Stacked X-ray diffraction pattern of a post-anneal simulant from 425 °C to 600 °C. Initial sample has been fully characterised. Previously unidentified phase still labelled ‘a’ for consistency. New unidentified intermediate phase has been labelled ‘b’.

Continuing up in temperature,  $\text{LiCl}$  labelled ‘a’ is still present and it is now apparent the peak at 43° is increasing in size, suggesting the generation of  $\alpha\text{-Li}_2\text{TiO}_3$ . However, as 450 °C is reached,  $\text{LiCl}$  quickly reduces in intensity and a new intermediate phase, ‘b’, appears simultaneously. This phase cannot be detected in the final post-annealed sample and increases in intensity as temperature is increased until 550 °C is reached, after which it starts reducing in intensity.

All of these peaks can be described by a high temperature metastable phase:  $\text{Li}_6\text{SiO}_4\text{Cl}_2$  (PDF 01-091-2558). This phase has been previously identified and synthesised by Morscher *et al.* via the addition of  $\text{LiCl}$  to a pre-synthesised  $\text{Li}_4\text{SiO}_4$  powder (produced using the same precursors as in this work see section 2.1.1) under heat [176]. Not only does this

match exactly the conditions found in the simulant mixture but perfectly aligns with the sudden reduction in intensity of the anhydrous LiCl peaks identified.

To summarise, intermediate phase ‘a’ (anhydrous LiCl) reacts with the plentiful  $\text{Li}_4\text{SiO}_4$  to form intermediate phase ‘b’ ( $\text{Li}_6\text{SiO}_4\text{Cl}_2$ ). This reveals an additional LiCl sink, which combined with the increasing intensity of the  $43^\circ$  peak suggests that the titania present must be reacting with the lithium species which have dissociated from the lithium orthosilicate, rather than the LiCl, as this species has now been accepted into the lithium orthosilicate structure and, is therefore, inaccessible and unable to participate in the formation of lithium metatitanate.

The slow decrease in peak intensity of intermediate phase ‘b’ suggests that LiCl comes back out of the structure as the metastable  $\text{Li}_6\text{SiO}_4\text{Cl}_2$  decomposes. This re-introduces this species as a lithium source, however, as seen from the EDXA of the biphasic pellets (figure 4.5), significant chlorine peaks may still be observed, suggesting incomplete uptake of the LiCl. As no lithium deficient titanate can be observed in the final samples it may be reasoned that all the titania has reacted to form lithium metatitanate, leading to the conclusion that the accessible dissociated lithium salts (mainly  $\text{Li}_2\text{CO}_3$ ) are being used in the reaction as a supplemental lithium source, resulting in the presence of  $\text{Li}_2\text{SiO}_3$  under XRD and chlorine under EDXA.

#### 5.3.1.3.2 Differential scanning calorimetry/Thermogravimetric analysis

Although the sequence of reactions observed using HT-XRD has been identified, this technique is unable to elucidate all the potential issues and characteristics of the biphasic system: uptake/release of atmospheric gases, melt events, subtle transition events and lithium volatilisation to name a few. In order to aid in the identification and further analysis of the phase progression and physical state of the system, Differential Scanning Calorimetry in combination with Thermogravimetric Analysis (DSC/TGA) was used as an independent, high-temperature, analytical technique with analogous physical conditions to both the box furnace during sintering and the conditions in the HT chamber of the XRD equipment.

Firstly, concerns over the storage of LiCl stock were addressed. This was mostly due to the highly deliquescent nature of the salt potentially leading to the amplified ingress of water into the storage container. Large changes in mass may have resulted in a compounding effect on the seemingly random variation in stoichiometry observed in all final pellets in this work. DSC/TGA was used in order to quantify this and analyse the degree of re-hydration of the LiCl stock in air.

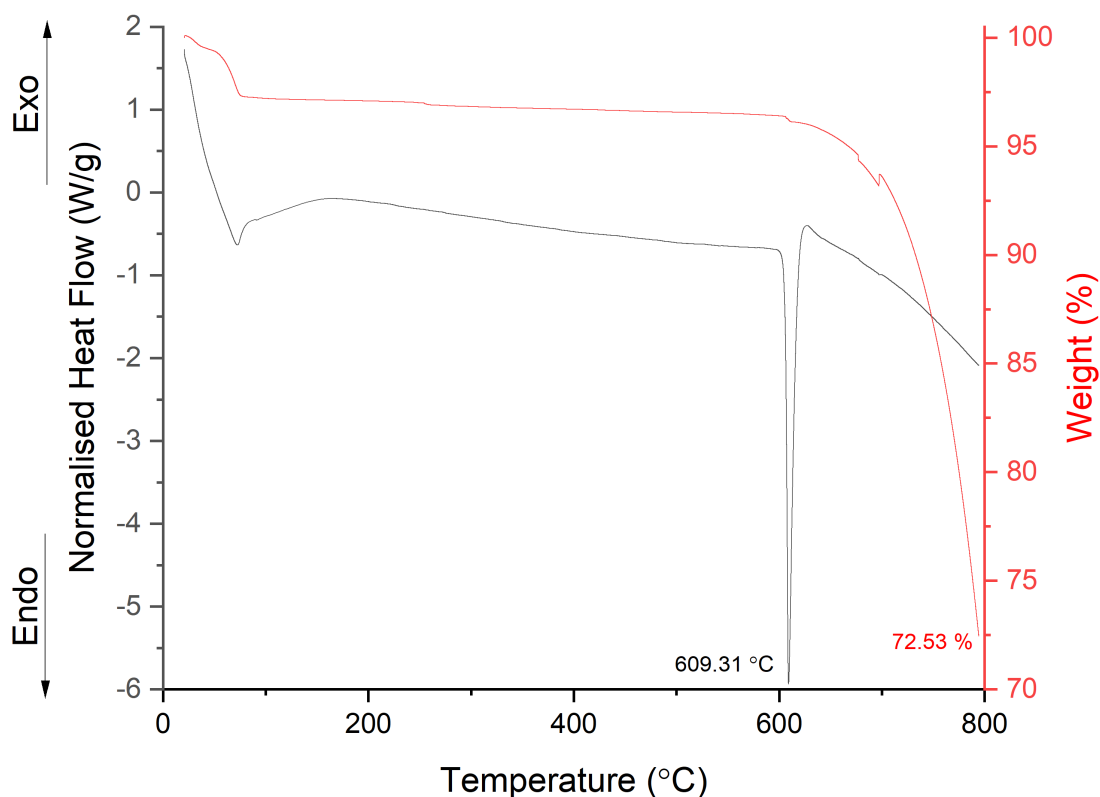


Figure 5.12: TGA (in red) and DSC (in black) of an as-removed sample of LiCl. Sample was run in air. Final mass loss as well as measured melting point added for clarity.

Analysis of the LiCl sample (figure 5.12) shows that current storage methods lead to little hydration, with only a 3% weight drop seen on the first 100 °C of the ramp. This was deemed a sufficiently low level of hydration to be incapable of leading to the results observed in the samples throughout the work. The melting point was sharp and around the expected temperature (604 - 614 °C) [177] therefore high purity as cited by the supplier.

Another observation is the sudden increase in rate of mass loss after melting occurs. It has already been established that LiCl has a high vapour pressure at temperatures below its melting point [174], transitioning from the solid to the liquid state will only lead to an increase to this vapour pressure which may be further exacerbated by the decomposition of the salt [178]. By the end of the test weight % had dropped from around 97% prior to melting to 72.5% by the end of the experiment at 800 °C. Rate of volatilisation seems to be increasing as temperature is increased, reaching a maximum of 2.25 %min<sup>-1</sup> at the end of the test from around 0.006 %min<sup>-1</sup> immediately prior to melting.

With this knowledge, analysis of the salt after exposure to water - as it would be added as a slurry to the die - can be carried out to observe how the LiCl evolves during firing.

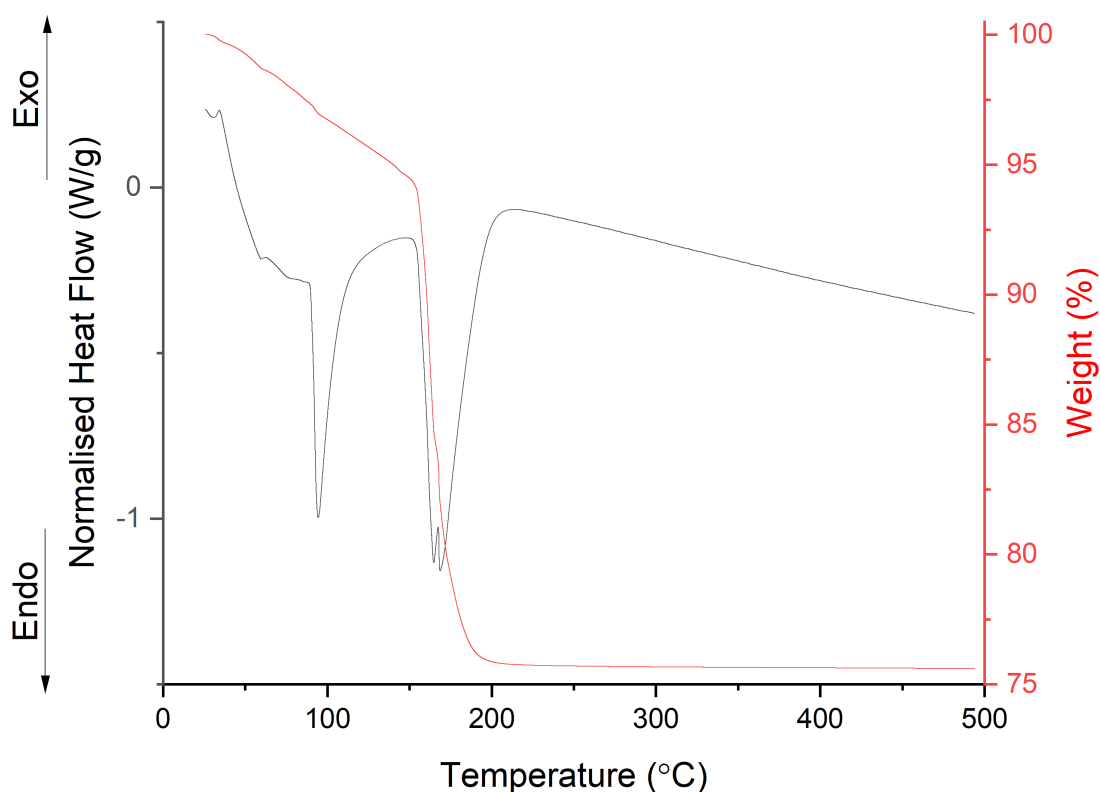


Figure 5.13: TGA (in red) and DSC (in black) of a sample of LiCl left in air for 4 hours. Sample was run in air.

Two clear endothermic events can be observed in the DSC trace of the LiCl left in air. The first occurs before 100 °C and can be attributed to absorbed water evaporating as the sample is ramped. This first loss of water leads to a weight loss of just 5% from the initial reading. The second and much more significant event occurs after 150 °C and is likely related to loss of water of crystallisation. LiCl can form a multitude of hydrates [179] and this double peak in the DSC curve seems to suggest two separate de-hydration events, implying that the LiCl is in a dihydrate form. After this dehydration event, weight drops by a further 20% and remains constant. Just as with the LiCl as-removed, weight loss remains negligible, likely maintaining this rate of volatilisation until after the melting point, after which significant volatilisation will occur.

Comparing figure 5.12 and figure 5.13 the deliquescence of LiCl can be clearly observed. In 4 hours of contact with moisture in the air the sample gained 25% extra weight and had formed a dihydrate from what initially seems to be a relatively anhydrous sample.

Having analysed the LiCl stock, it may be concluded that it is unlikely that the stoichiometric imbalance is due to an overly hydrated source of LiCl. However, the impact that volatilisation may have on the final sample may be large if indeed the salt

forms a melt during post-anneal.

Analysis of the generated pellets is the next step to assess the process and identify where the issues may be.

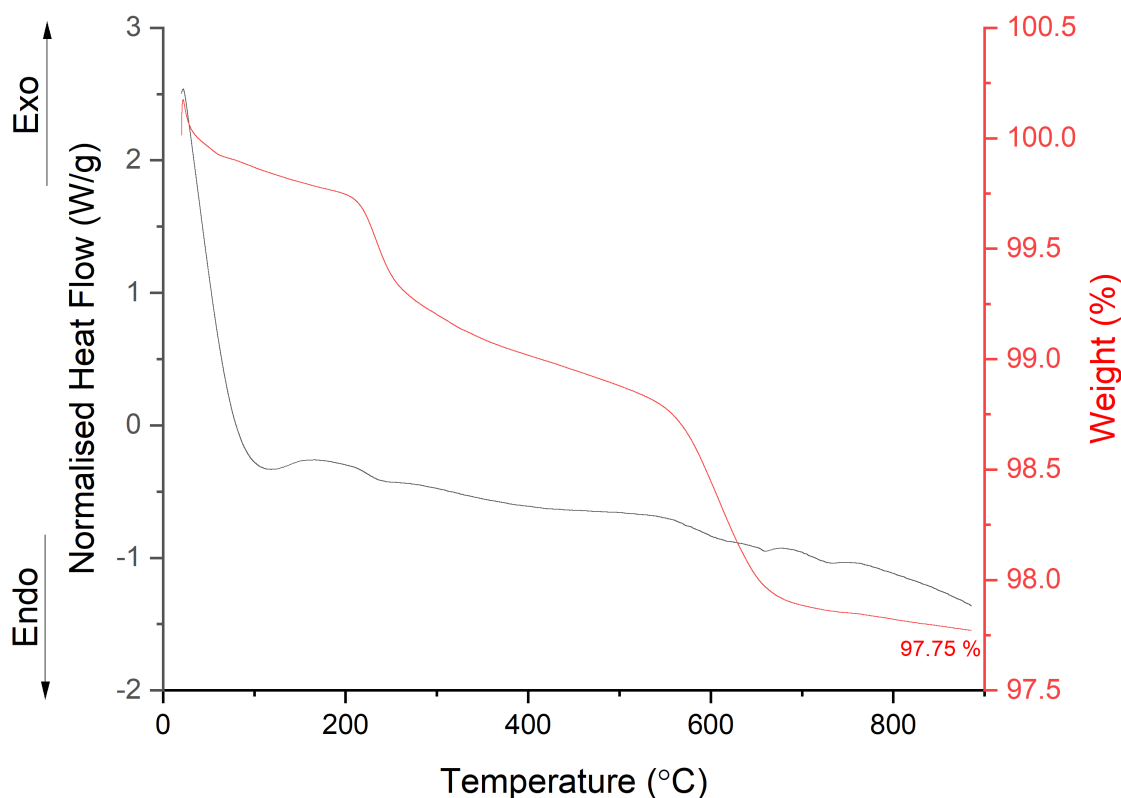


Figure 5.14: TGA (in red) and DSC (in black) of a biphasic (batched as 77% $\text{Li}_4\text{SiO}_4$  - 23% $\text{Li}_2\text{TiO}_3$  by mass) sample stored in air. Sample was run in air. Final weight % added in red for clarity.

Observing our final pellets after post-anneal (figure 5.14) we can see two main events which correspond with the dehydration and decarbonation of the lithium orthosilicate. A 1% drop in weight occurs at around 200 °C followed by a further 1.25% around 600 °C. As mentioned before and according to Quinn *et al.* [175] regeneration of lithium orthosilicate after  $\text{CO}_2$  absorption happens between 550 °C and 650 °C which is commensurate with the position of the second event.

As expected, final samples have no obvious further reactions, with all observed events explained by the known interactions of lithium orthosilicate with air. Weight seems to still be decreasing as the end of the test is reached, however rate of change is much lower than observed in the pure LiCl sample.

In order to further elucidate the post-anneal phase progression and mechanisms, the HT-XRD experiment was replicated in the TGA/DSC apparatus in an attempt to com-

pare and contrast.

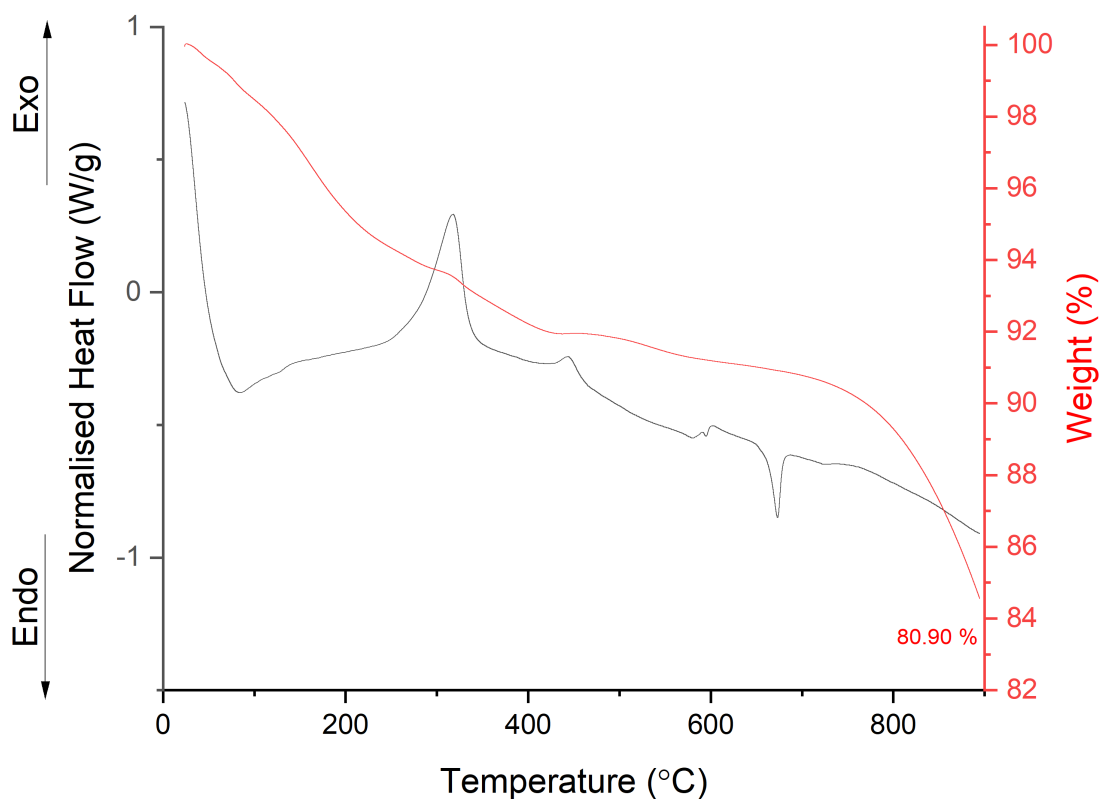


Figure 5.15: TGA (in red) and DSC (in black) of a biphasic simulant during post-anneal. Sample was run in air. Final weight % added in red for clarity.

TGA/DSC analysis was now performed on a biphasic post-anneal simulant (figure 5.15), essentially mirroring the conditions in the HT-XRD experiment. A large exothermic event occurs around 316 °C, this could potentially be related to a transformation of the metastable low temperature  $\text{Li}_2\text{CO}_3$  identified into a stable high temperature form. HT-XRD doesn't suggest this could be due to some other phase being formed, this could be further clarified by performing TGA/DSC analysis on a sample of bare lithium orthosilicate and see if this exotherm can still be observed.

A second exotherm at around 443 °C seems to align with the appearance of intermediate phase 'b' ( $\text{Li}_6\text{SiO}_4\text{Cl}_2$ ), as well as showing a slight increase in weight, likely due to the high  $\text{CO}_2$  absorbing capacity of the lithium orthosilicate at high temperatures [175]. The small endotherm at 590 °C matches the beginning of the  $\text{Li}_6\text{SiO}_4\text{Cl}_2$  decomposition, as  $\text{LiCl}$  begins to come back out of the orthosilicate structure. This happens concurrently with a change in rate of the TGA curve, around the regeneration temperature of  $\text{Li}_4\text{SiO}_4$ .

Finally, a large 'melting-like' endotherm can be observed at 672 °C. This is incongruous with the potential melting point of any of the components in the system.  $\text{LiCl}$  melts at

around 610 °C and  $\text{Li}_2\text{CO}_3$  melts at 723 °C. As the presence of  $\text{Li}_2\text{CO}_3$  has been confirmed in these samples, a potential explanation for this is the formation of a binary salt eutectic between the  $\text{LiCl}$  and the dissociated  $\text{Li}_2\text{CO}_3$ . This is further explored below.

Weight loss between the regeneration temperature (600 °C) and final post-anneal equates to about a 10% drop. Total Cl loss from the added  $\text{LiCl}$  should equate to around a 15% weight loss which, adds to the evidence that incomplete uptake of  $\text{LiCl}$  into the  $\text{Li}_2\text{TiO}_3$  structure is occurring, again confirming the single phase titanate is preferentially utilising lithium coming from the dissociated  $\text{Li}_2\text{CO}_3$ .

Just as with the HT-XRD experiment, a sample of only lithium orthosilicate powder was analysed in air.

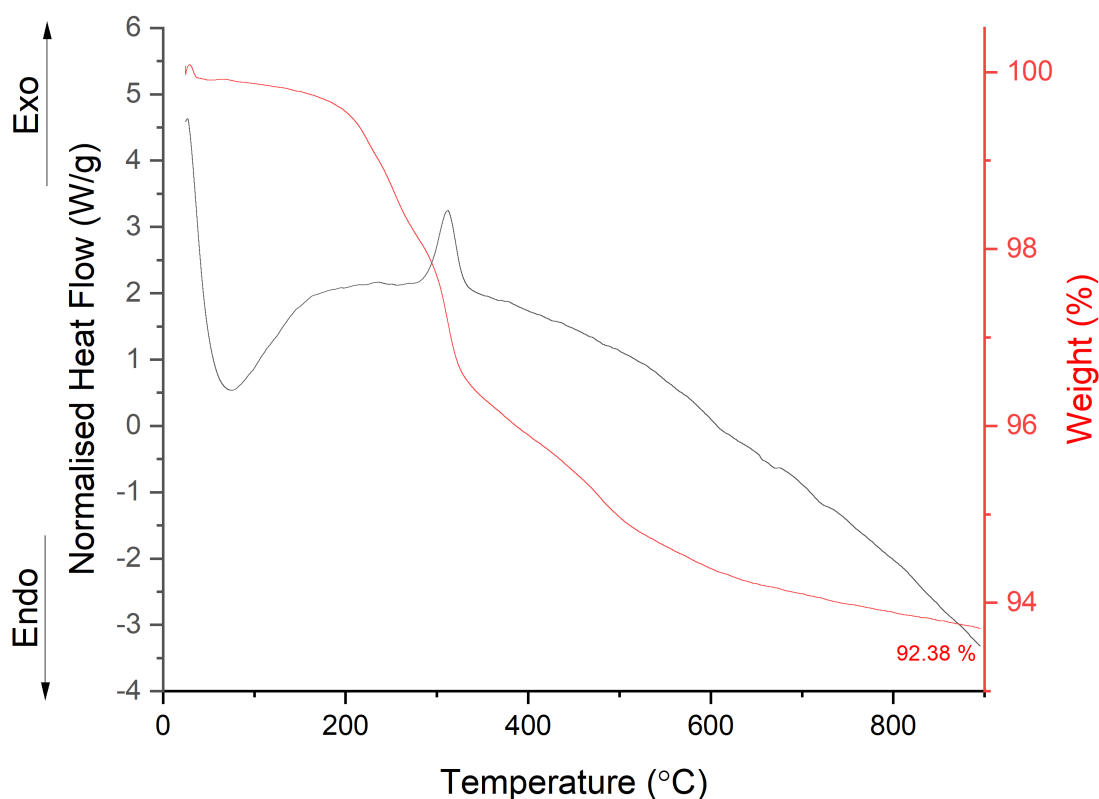


Figure 5.16: TGA (in red) and DSC (in black) of a  $\text{Li}_4\text{SiO}_4$  sample. Sample was run in air. Final weight % added in red for clarity.

TG/DSC of the lithium orthosilicate main phase powder shows that same large exotherm seen in the previous experiment with a large related loss of mass. Previously this exotherm was attributed to a transformation of the metastable low temperature  $\text{Li}_2\text{CO}_3$  identified into a stable high temperature form. However, conversely to the results in figure 5.15, this exotherm results in significant mass loss; the transformation of a phase should not directly result in this. One possible explanation is that this expected transformation occurs



concurrently with the dehydration of  $\text{LiOH}\cdot\text{H}_2\text{O}$ , as figure 5.10 shows the disappearance of this species between 100 and 300 °C and the appearance of anhydrous  $\text{LiOH}$  which persists until 500 °C in figure 5.11. Running the outgas through a mass spectrometer would elucidate this, by showing what species is resulting in this loss of mass, however no such piece of kit was available.

In order to characterise the melting event observed in figure 5.15 at 672 °C, the binary eutectic  $\text{LiCl} - \text{Li}_2\text{CO}_3$  system must be considered.

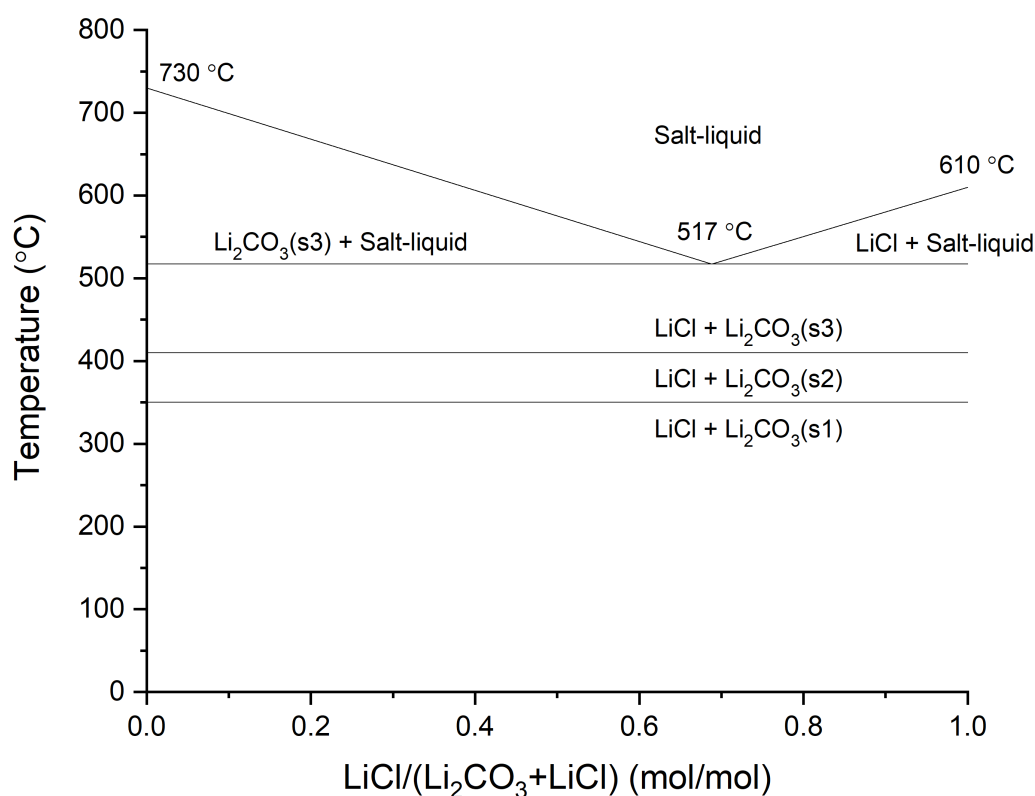


Figure 5.17: Phase diagram of the binary eutectic  $\text{LiCl} - \text{Li}_2\text{CO}_3$  system. Produced from FTsalt – FACT salt database.

Using figure 5.17 it can be noted that at 0.23  $\text{LiCl}$  the final melting point of mixture equates that found in the DSC curve of the post-anneal simulant. This melt occurs after the decomposition of  $\text{Li}_6\text{SiO}_4\text{Cl}_2$  therefore  $\text{LiCl}$  should be available to mix with the  $\text{Li}_2\text{CO}_3$  present to form this composition.

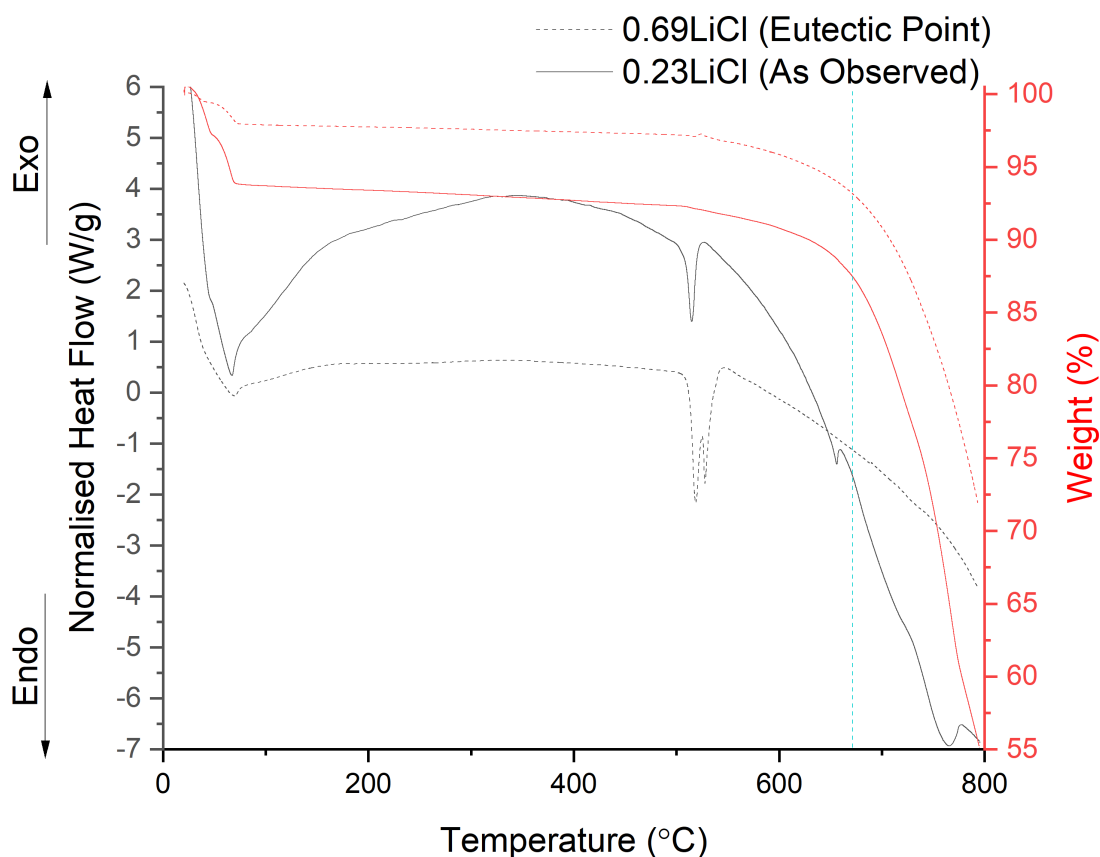


Figure 5.18: TGA (in red) and DSC (in black) of an  $\text{LiCl} - \text{Li}_2\text{CO}_3$  mixture at the eutectic point (solid line) and at the 0.23LiCl concentration (dashed line). Sample was run in air. Dashed blue line added at 672 °C (observed endotherm in figure 5.15).

Firstly, figure 5.18 confirms these salts combine to form a binary eutectic mixture as described in figure 5.17. An initial melting event at the eutectic temperature (517 °C) occurs in both compositions, as expected by following the phase diagram. The mixture theoretically at the eutectic point has a secondary melting event slightly out of phase with the first, suggesting either poor mixing or slight stoichiometric deviation. Similarly, the 0.23LiCl mixture shows the second melting event at much higher temperatures, if falling short of the expected 672 °C derived from the phase diagram. This deviance is minor and is still commensurate with the melting event observed in the post-anneal simulant.

The presence of such a salt mixture introduces the potential to extract information about the relative proportions of components in the system.

Using the endotherm assumed to be the second melting point of a  $\text{LiCl} - \text{Li}_2\text{CO}_3$  binary eutectic mixture, 672 °C in this case, a ratio between these salts can be derived using the phase diagram in figure 5.17, 23:77.

Now, assuming no  $\text{TiO}_2$  is lost *via* extrusion during the pressing step of CSP and  $\text{Li}_2\text{CO}_3$  is being used preferentially in the formation of  $\text{Li}_2\text{TiO}_3$ , the following can be

calculated:

- LiCl lost prior to post-anneal.
- $\text{Li}_4\text{SiO}_4$  lost due to re-carbonation.
- Final mass of  $\text{Li}_2\text{SiO}_3$  in sample.

This would mean that in a prototypical sample around 85% of the added LiCl is lost due to extrusion. Roughly 40% of the batched  $\text{Li}_4\text{SiO}_4$  is lost to re-carbonation and around 27% of the final sample by mass would be  $\text{Li}_2\text{SiO}_3$ . All of this is commensurate with the observations herein, however there are obvious limitations with these calculations. Firstly, there is likely loss of titania *via* extrusion, even if this is heavily subdued when compared to the LiCl loss. LiCl is also, likely still being used as a lithium source in the formation of  $\text{Li}_2\text{TiO}_3$  even if lithium carbonate is indeed being utilised preferentially. Another issue is due to the uncontrollable nature of the extrusion. As noted before, changes in ambient conditions result in wildly different amounts of extrusion, leading to differing degrees of overall mass loss, *i.e.* final pellet weight was inconsistent. The proportion of material loss is likely as postulated in chapter 3 and 4 ( $\text{LiCl} > \text{TiO}_2 > \text{Li}_4\text{SiO}_4$ ), however exact amounts lost of each component would be impossible to calculate without the use of mass spectrometry.

Therefore, even though this characteristic allows for a deeper understanding of the material analysed, the inconsistencies introduced through the equipment used lead to inaccuracies. However, if the equipment tolerances can be addressed such as to reduce extrusion down to a minimum, the temperature of the melt occurring during post-anneal can give detailed information about the degree of re-carbonation observed.

## 5.4 Conclusions

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) was performed in order to compare, a group of pre-synthesised powders (synthesised at 730 °C and 1100 °C) – aiming to assess the potential off-stoichiometry inherent to them due to their respective synthesis temperatures – a second group, aiming to show if the added infill and post-anneal results in any variation from the measured lithium to titanium ratio found in the first group of powders. This revealed that lithium was indeed being lost, however it was unlikely due to volatilisation.

High temperature X-ray diffraction led to the identification of the reaction pathway occurring within the biphasic pellets, leading to the retention of  $\text{Li}_2\text{SiO}_3$  in the final material. Anhydrous LiCl reacts with the  $\text{Li}_4\text{SiO}_4$ , forming an intermediate phase ( $\text{Li}_6\text{SiO}_4\text{Cl}_2$ ) which acts as an LiCl sink. The lack of chemically available lithium leads to the uptake of  $\text{Li}_2\text{CO}_3$  (formed due to re-carbonation of the orthosilicate) to form  $\text{Li}_2\text{TiO}_3$ . The LiCl comes back into play as the intermediate decomposes, however, now most of the titania has reacted to form  $\text{Li}_2\text{TiO}_3$ , leaving the re-introduced LiCl abandoned. This results in the issues identified, namely the large  $\text{Li}_2\text{SiO}_3$  presence in the final pellets and the persistent Cl presence in the EDXA.

Differential Scanning Calorimetry in combination with Thermogravimetric Analysis (DSC/TGA) was used as an independent experiment to confirm and further elucidate the findings. All the events identified in the HT-XRD experiment were observed and identified. Two additional events were noted. At low temperatures the simultaneous dehydration of  $\text{LiOH}\cdot\text{H}_2\text{O}$  with the transformation of  $\text{Li}_2\text{CO}_3$  into its stable, high temperature form could be observed. At higher temperatures an unknown melt event was observed and attributed to a  $\text{LiCl} - \text{Li}_2\text{CO}_3$  binary eutectic mixture, as this occurs at a temperature in agreement with the eutectic diagram, and after the  $\text{Li}_6\text{SiO}_4\text{Cl}_2$  has decomposed.

This eutectic was identified as a potential signifier of the degree of re-carbonation of the final sample. This would allow for an indirect way to measure a characteristic classically hard to estimate, and may be useful to analyse any future samples produced using the reactive cold sintering method.

## 6 Conclusions

Ceramic synthesis is still primarily done following classic solid state synthesis, commonly termed ‘shake and bake’. Ceramics particularly susceptible to temperature generally struggle and lead to off-stoichiometry after firing. This method is also significantly energy intensive and reducing method’s footprint was of concern.

In this work,  $\text{Li}_2\text{TiO}_3$  synthesis was demonstrated and refined using the deep eutectic solvent (DES) method. Synthesis temperature has been decreased from 730 °C (lowest commonly used in solid state synthesis) to 700 °C – although further decrease may still be possible, with 650 °C found to be insufficient for a complete reaction with a 4-hour dwell. Further research is needed to precisely determine the minimum synthesis temperature. A successful lithium metatitanate batch following this method was deemed to require the following: a fully dried eutectic mixture prior to the addition of the alkoxide (titanium isopropoxide stored under dry conditions and free of debris) and good sample-air contact during calcination. These are true with all DES synthesis methods, with the prior condition aiming to keep the alkoxide dissolved in the eutectic and not precipitate out into an aqueous phase, and the latter allowing for enough air recirculation to allow all of the organic eutectic to burn off during calcination.

As with synthesis, sintering of pellets generally requires high temperatures which, especially with lithium ceramics, may lead to vaporisation of said lithium hence reducing overall lithium content of the ceramic. High temperatures also preclude much control over the sample’s microstructure, an aspect considered to be very important for tritium generating ceramics, and yet seldom addressed due to this.

Here, a low temperature sintering technique, namely reactive cold sintering (RCS), was used to form seemingly dense  $\text{Li}_2\text{TiO}_3$  pellets at a sintering temperature 400 °C lower (700 °C) than required during solid state sintering of similar powders (1100 °C). This was achieved *via* the use of two independent components, an infill, aqueous phase and a main, powder phase. A lithium deficient species ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) was repeatedly identified during analysis of the final pellets. This was likely due to faults in the procedure arising from the use of LiCl as a lithium source in the infill. This reactant is extremely hygroscopic and dissolves itself rapidly in contact with the moisture in air. Due to this, replicability was severely affected as changes in atmospheric conditions led to disparate batching and processing results. Two key factors were identified as barriers towards consistency: poor moisture control and poor equipment condition, leading to unacceptable tolerances.

A main phase,  $\text{Li}_2\text{TiO}_3$  powder was produced at higher temperatures than needed (1100 °C), in order to exaggerate the grain size of this particle population. This larger grain size population allowed the identification of both RCS components within the samples, with particles coming from the main phase powder being on the order of a micron (comparable to those from the pre-sintered powder) and those from the infill material on the order of 100 - 400 nm. This demonstrates the capacity of the RCS method to produce pellets with two different, independent particle populations. Not only this, but as particle size is retained from the pre-sintered powder used, the morphology of this population can be determined pre-sintering.

X-ray diffraction of the surfaces of RCS pellets show a high degree of texture (Lotgering

factor of 0.79). This texture was shown to appear principally when pellets made with the powder synthesised at 1100 °C were pressed in any way. Green body pellets pressed using this powder still showed significant texture (LF of 0.71), this texture only reducing once the pellet was fired at regular sintering temperatures (1100 °C), showing that it did anneal once a temperature high enough was reached. This preferred orientation effect is clearly pressure induced and surface dependent. The effect is retained due to the low temperatures used during the RCS method. Even though RCS presents the perfect conditions for particle rearrangement (high deviatoric stress and presence of an interspersed fluid), the relative isotropy of the crystal makes this unlikely to lead to the high degree of texture observed, further confirmed by the lack of particle alignment observed in cross-sectional SEM. Pressure induced crystallographic distortion is therefore the more likely mechanism at play here.

The unexpected characteristics of the pellets produced, namely the overly exaggerated preferred orientation and the presence of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , can all be concluded to arise from intrinsically methodological issues. The pressures necessary for densification under RCS lead to the induction of texture and the subsequent retention of said texture due to the low processing temperatures involved. Similarly, the pressures used combined with the poor tolerances of the equipment, lead to material extrusion which, in turn, lead to a loss of stoichiometric control over the RCS mass. Due to the differences in mobility of the components of the RCS mixture, lithium happens to be lost preferentially.

No single lithium ceramic manages to combine all of the properties beneficial to a tritium generating material and arise as an ideal candidate. To this end, combinatory ceramics can help marry the properties of multiple different materials to form ceramic-ceramic composites, improving flexibility and efficiency. Formation of ceramic-ceramic composites, especially at low temperatures, heavily depends on the properties of each component and may require highly specialised techniques.

Single phase  $\text{Li}_4\text{SiO}_4$  was produced using conventional solid state synthesis. Other groups report incomplete reactions, with  $\text{Li}_2\text{SiO}_3$  and  $\text{Li}_2\text{CO}_3$  as main by-products. This was found to mainly be due to rapid re-carbonation of the powder under atmospheric conditions, and was addressed with a re-fire of the powder.

To demonstrate the capacity for the reactive cold sintering method to form cohesive ceramic-ceramic composite pellets, pellets were generated replacing the lithium metatitanate main phase powder with the aforementioned lithium orthosilicate.

The previous temperature used to post-anneal the cold sintered  $\text{Li}_2\text{TiO}_3$  pellets (700 °C) resulted in the persistence of  $\alpha\text{-Li}_2\text{TiO}_3$  in the final samples. This phase was likely stabilised by some unknown interaction between lithium metatitanate and lithium orthosilicate. The  $\alpha - \beta$  transition temperature occurs at 300 °C under normal conditions, here the transition doesn't occur until the post-anneal temperature is raised to 900 °C. Not only this but, similarly to the  $\text{Li}_2\text{TiO}_3$  pellets, hints of lithium deficiency were observed, namely a large proportion of both  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_2\text{SiO}_3$ , with a distinct lack of  $\text{Li}_2\text{CO}_3$  related peaks. This lack of carbonate implying the lithium metasilicate present was not generated *via* re-carbonation post-sintering.

A mechanism was proposed in order to explain these findings. It was postulated that,

aided by the inherent off-stoichiometry induced *via* extrusion, lithium carbonate generated *via* the re-carbonation of the main phase powder ( $\text{Li}_4\text{SiO}_4$ ) is being preferentially utilised by the titania present in the infill to form  $\text{Li}_2\text{TiO}_3$ , obscuring the fact that the system is still operating with a lithium deficiency.

A layer of material was seen to commonly obscure any SEM generated with  $\text{Li}_4\text{SiO}_4$  content. This had been seen in work by Abdel-Basset *et al.* [165] and was found to be a low temperature, meta-stable  $\text{Li}_2\text{CO}_3$  phase. Their garnet material produced this “patina” due to re-carbonation; the similarities leading to the consideration that this may also be the mechanism at play here. Raman Spectroscopy was performed to identify the appearance of this “patina” and characterise it as  $\text{Li}_2\text{CO}_3$ . Within 5 hours of exposure to air  $\text{Li}_2\text{CO}_3$  could be identified in the Raman spectra, confirming the obscuring material to be  $\text{Li}_2\text{CO}_3$ , produced *via* re-carbonation of the  $\text{Li}_4\text{SiO}_4$  at speed.

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) was performed in order to compare the Li:Ti ratio of: two starting, “main phase” powders (synthesised at 700 and 1100 °C) and two final RCS pellets, one sintered using stoichiometric amounts of initial reactants and another with double the necessary amount of LiCl. This was done in order to attempt to deconvolute the potential source of lithium off-stoichiometry observed in both, single phase and multi-phase, sample populations. Lithium loss was confirmed in the system, based on a qualitative assessment of the ICP data, this was deemed unlikely to be due to volatilisation during post-anneal – as both the pellets showed similar degrees of lithium loss even while working with vastly different initial amounts of LiCl. It was clear from the pre-sintered powders that no significant volatilisation occurs in this system under normal circumstances, therefore, the lost lithium must be preferentially extruding out of the die leading to the off-stoichiometry observed. The higher the LiCl content the higher the mobility of the lithium species due to increased re-hydration.

High temperature X-ray diffraction was performed on the  $\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{TiO}_3$  mixture directly after cold sintering to analyse phase development during the post-anneal step and understand the phase make-up of the pellets generated. The LiCl introduced in the infill loses its water of crystallisation, forming anhydrous LiCl which, subsequently, reacts at low temperatures (450 °C) with the plentiful  $\text{Li}_4\text{SiO}_4$  to form an intermediate, metastable phase:  $\text{Li}_6\text{SiO}_4\text{Cl}_2$ . This phase acts as a LiCl sink, preventing the unreacted  $\text{TiO}_2$  from utilising it as its intended lithium source. Any lithium metatitanate formed up to this point (mostly in  $\alpha\text{-Li}_2\text{TiO}_3$  form) therefore, has utilised any available  $\text{Li}_2\text{CO}_3$  generated *via* re-carbonation of the initial  $\text{Li}_4\text{SiO}_4$  powder as a supplemental lithium source. In turn, this results in the orphaning of the  $\text{Li}_2\text{SiO}_3$  – also produced through this carbonation – observed in the final pellets. As the  $\text{Li}_6\text{SiO}_4\text{Cl}_2$  phase decomposes (past 550 °C), the LiCl dissociates out, re-introducing it as a lithium source. However, energy-dispersive X-ray analysis (EDXA) shows a retention of Cl, implying that the accessible dissociated lithium salts (mainly  $\text{Li}_2\text{CO}_3$ ) are being used in the reaction as a supplemental lithium source, resulting in the presence of both  $\text{Li}_2\text{SiO}_3$  and Cl under EDXA.

Differential Scanning Calorimetry in combination with Thermogravimetric Analysis (DSC/TGA) was used as an independent, high-temperature, analytical technique in order

to confirm and further elucidate the findings derived from the HT-XRD experiments. All the events observed in HT-XRD could be matched to events in the DSC/TGA curve, with the exception of a melt event at high temperatures (672 °C) and an exotherm with related mass loss at 316 °C. The former was identified as the formation of a binary salt eutectic between the LiCl and the dissociated  $\text{Li}_2\text{CO}_3$ . The latter could not be fully characterised, with the best hypothesis being the simultaneous dehydration of  $\text{LiOH}\cdot\text{H}_2\text{O}$  with the transformation of  $\text{Li}_2\text{CO}_3$  into its stable, high temperature form. Running the gases through a mass spectrometer will confirm whether this hypothesis is correct.

The aforementioned eutectic was identified as potentially referable to extract further information from the system. With the temperature of the melt event and the phase diagram of the  $\text{LiCl} - \text{Li}_2\text{CO}_3$  binary eutectic mixture, the degree of re-carbonation of the sample could be estimated; a characteristic hard to measure but extremely impactful to the final composition.

To conclude, cohesive, single phase and multi-phase pellets were generated applying the reactive cold sintering method. The capacity for this method to introduce different morphologies and phases through the use of the infill as an independent means of phase introduction was demonstrated. Dense, single phase  $\text{Li}_2\text{TiO}_3$  pellets were produced with maximum temperatures 400 °C below those used in regular sintering of these ceramics. Biphasic,  $\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{TiO}_3$ , pellets were generated at temperatures below those used in regular sintering resulting in exceptionally well-consolidated composites. Incompatibilities between the equipment and the materials used led to unpredictable shifts in stoichiometry, which ultimately led to sub-stoichiometric lithium content in the final pellets. This, combined with the atmospheric instability of  $\text{Li}_4\text{SiO}_4$ , resulted in complex mechanisms leading to the sequestration and eventual retention of unreacted material.



## 7 Further Work

As mentioned throughout the work and as is hopefully apparent from the results obtained, many avenues exist to further expand the method and amend the issues identified herein. The research question has been answered and composite Li-based oxide ceramics have been generated but, as is true with all research, in attempting to answer it, more questions have emerged.

These ceramics are paramount in the pursuit of a clean, sustainable and reliable source of energy and hence, an informed assessment of future pathways is key in order to pave the way for future research to eventually arrive at a functional fusion device.

Cold sintering, let alone reactive cold sintering (RCS) are yet in their infancy and hence are still techniques approached in a per system basis, hence adding further phases into the system results in compounding complexity. However, this work demonstrates that careful analysis of these interrelated mechanisms results in an increase in understanding of the system as a whole and therefore a deeper awareness of further potential research avenues.

These further research avenues are abundant, yet may be organised under the following:

- Material selection; *i.e.* utilisation of different, target phase ceramics exploiting the flexibility demonstrated by RCS.
- Further method refinement; *i.e.* addressing issues identified *via* the adjustment of instruments and/or techniques.
- Analysis of performance in reactor-relevant conditions; *i.e.* irradiation experiments and potential future labs.
- Bulk properties and bigger picture; *i.e.* formation of useable pellets/pebbles and scalability.

### 7.1 Material selection

This work concentrates on two ternary lithium ceramics (lithium metatitanate and lithium orthosilicate) as a proof of concept and to demonstrate the capacity of RCS to act as a flexible combinatorial technique. Reactive cold sintering as a technique has been demonstrated to be capable of such, with composite generation *via* the use of two independent phase formation steps and occurring at temperatures markedly lower than the melting point of either material. Material selection on a practical level was somewhat irrelevant as demonstrating and applying the method took precedent.

However, re-assessing the research question with its intended industrial context leads to an obvious conclusion, why stop at lithium metatitanate and lithium orthosilicate, and what about varying proportions. It must be reiterated that the choice to adhere to these materials was made with the industrial context always in mind, as both  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{SiO}_4$  (as well as their combination) have recently been the most favoured ceramics to be implemented into an operational fusion device. The main objective behind their use was combining the beneficial properties of each individual material, however, realistically,

the principal issue to be addressed is the enrichment of  $\text{Li}_2\text{TiO}_3$  with more lithium in order to increase lithium density, increase tritium breeding ratio (TBR) and therefore decrease reliance on neutron multipliers. Lithium titanate only fails as a viable breeder due to this need for more multiplier.

These are far from being the only ceramics considered as potential breeder materials, some of which result in much larger TBRs than either lithium metatitanate and lithium orthosilicate. Lithium oxide is a logical candidate to use as an enriching phase and may be adapted into the RCS method relatively simply as an infill. An  $\text{LiOH}$  solution could be added in the mixing stage prior to pressing, and allowed to dry, leaving behind an  $\text{LiOH}$  matrix which will decompose to form  $\text{Li}_2\text{O}$  during a post anneal. Of course, the impact of a basic starting mixture on the pre-sintered mass as well as the release of  $\text{H}_2\text{O}$  during decomposition on the final pellet are to be determined. A key detail if following this line of inquiry is that lithium oxide is relatively unstable under atmospheric conditions and has a relatively high vapour pressure, hence volatilisation during reactor operation is likely. However, these are the reasons why  $\text{Li}_2\text{TiO}_3$  was chosen as a companion ceramic for  $\text{Li}_4\text{SiO}_4$  in the first place.

This relies on the demonstration that the lithium metatitanate presence acts as a stabiliser, increasing atmospheric resistance of the pellet as a whole. Lithium titanate has been shown to increase crush load strength of  $\text{Li}_2\text{TiO}_3 - \text{Li}_4\text{SiO}_4$  [77] pellets, however further work is required to prove if this extends to atmospheric stability.

Other potential enriching phases are octalithium compounds which have been of interest recently due to their high Li atom densities. They however are not well researched phases and many either decompose at fusion relevant temperatures ( $\text{Li}_8\text{SiO}_6$  and most probably  $\text{Li}_8\text{PbO}_6$ ) or are an activation concern (namely  $\text{Li}_8\text{ZrO}_6$ ) [27]. To reiterate, low radiation daughter products of applied materials is one of the key characteristics that attempts to minimise the waste management issues ubiquitous with other nuclear technologies; hence the need for low activation materials (*i.e.* materials which result in weakly radioactive waste). Of course as they are not as well researched as the other ceramics mentioned, their synthesis, melting points as well as their interactions with other phases are relative unknowns and hence may propose a complicated research question, but their potential use as an enriching phase is intriguing and worthy of further research.

Another characteristic of the reactive cold sintering method that has not been thoroughly examined in this work, and related to its flexibility as a fabrication technique, is the potential to adapt to a variety of phase ratios, unbound by incompatible physical characteristics. This would mean the tailoring of phase proportions to maximise the benefit of a bi or multiphase system. Other sintering or pellet fabrication methods run into issues when combining phases either due to issues introduced due to co-synthesis of the materials in question [40] or due to temperature incompatibilities, limiting the useable phase proportions accessible through those techniques [85]. This work concentrates on a  $\text{Li}_4\text{SiO}_4$  rich composite ceramic but using RCS all of the available proportions should be accessible *via* the use of a different main phase powder to infill ratio. This would necessitate the design of an  $\text{Li}_4\text{SiO}_4$  infill; a good starting point would be imitating the successful  $\text{Li}_2\text{TiO}_3$  infill, hence using a  $\text{LiCl} - \text{SiO}_2$  mixture. Considering the relative atmospheric instability of a lithium orthosilicate powder, the generation of this material

during post-anneal may aid in the formation of the expected phases as it would avoid the re-carbonation which has led to the leaching of lithium from the main phase powder in the work presented. Different amounts of starting powder and infill concentration should lead to the formation of solid pellets with controllable proportions of each phase, the low temperature of the post-anneal allowing for this flexibility. This of course could be replicated for any biphasic system.

Multiphase systems (*i.e.* more than two component ceramics) may prove challenging although may be accessible using RCS. Co-firing of lithium orthosilicate and lithium metatitanate is known to be problematic [67] mainly due to the latter's capacity to dissolve lithium, hence leading to the formation of lithium metasilicate, but other compatible phases could be added within the infill mixture. This could be done using a starting main phase powder, say  $\text{Li}_2\text{TiO}_3$ , and an added infill composed of an  $\text{LiCl}$  solution, acting as a general lithium source, and a mixture of both  $\text{SiO}_2$  and  $\text{ZrO}_2$ , with the expected result being the co-synthesis of  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{ZrO}_3$  during the post-anneal step. Considering the complexity of the biphasic system studied herein, this may prove impossible to successfully balance, however, improving stability under atmospheric conditions as well as improving equipment tolerances may lead to a much more predictable outcome than expected based on this work.

A secondary approach, and perhaps less promising, is the formation of ceramic-ceramic composites consisting of a lithium-containing ceramic and a neutron multiplier. The principal neutron multiplier candidate for such a combination would be beryllia and has been previously attempted [40]. This however results in significant safety concerns with beryllium being highly toxic and its oxide powder causing cancer and berylliosis [90] on inhalation. This combined breeder-multiplier simplifies breeder blanket design, as now all pebbles within the blanket would essentially be composed of the same composite material, however, a more pragmatic assessment would lead to questioning the practicality of using such a material. Respirators and other safety equipment would only be needed when handling the multiplier under normal circumstances, however, this combined ceramic now necessitates increased safety considerations when dealing with the totality of the breeder material, as well as complicating its recycling. As such, although the design and formation of composite, breeder-multiplier pellets using RCS is likely achievable (and perhaps scientifically engaging) it is practically unviable as a material concept for use in a breeder blanket.

Of course, all of this further material selection can happen concurrently with alterations to the microstructure of the pellets generated. Again, the independence of the phases utilised should allow for the separate grain size addressment of the starting powder and the added infill.

Further, in order to ascertain the source of the lithium in the final phases identified, isotopic labelling could be done. Replacing the Li in the main phase powder (as it is the most heavily monitored phase) with  $^6\text{Li}$  would introduce the capacity to analyse isotopic ratios in any phases formed in the sintered samples. This will confirm if the mechanism suggested in chapter 4 is correct and how much each lithium source contributes to the final phases observed.

## 7.2 Methods

A multitude of the issues identified in this work led back to the same core problem, the equipment used. Poor tolerances are acceptable in systems where the infill material used in reactive cold sintering dries readily, leading to a dry, free-flowing powder. This “dry” powder (not actually dry as moisture is required for the process to lead to fully sintered pellets) usually leads to little to no extrusion of material out of the die, hence resulting in minimal material loss. Not only little material is lost, but the relative dryness of the mixture leads to mostly non-preferential extrusion, therefore leading to a small enough stoichiometric imbalance to be undetectable. The use of LiCl however, complicates matters. Other groups have talked about the issues identified throughout this work when working with LiCl [67, 178, 180, 181], and in general it precludes its use as a solid. Its highly hygroscopic nature leads to rapid moisture draw from that available in air, resulting in a hard-to-weigh, hard-to-manipulate paste, which continues to hydrate until fully dissolved.

As LiCl is the most flexible lithium salt to use in this application it would be beneficial to find a way to permit its use whilst stopping the material loss which is resulting in loss of control of the samples herein. An obvious first course of action would be the machining of a set of die and plunger with extremely tight tolerances. This may introduce a series of new challenges, such as increase the force needed to separate the pieces once cold sintering has occurred, as any extruded material which may have been lodged in between the die and the plunger will harden and act as binder between them. This is observed using the equipment available, it may result in an unreasonable amount of force needed to fully dislodge the plunger in this higher tolerance scenario. Another issue may be the time required for the water to fully evaporate during the cold sintering pressing step. Here, the presence of water and pressure are expected to allow for densification of the body, whilst heat will eventually result in complete evaporation of the water, leaving a fully dry, fully dense pellet. With tighter tolerances, water vapour will struggle to escape at the same rate and perhaps at all if enough material is lodged between the die and the plunger. This will need to be assessed and pressing time may have to be increased in order to account for it.

Introducing some method to allow for the grains to align with the *ab* plane perpendicular to the surface could aid in the formation of ceramics with enhanced characteristics, as the RCS method would allow (as demonstrated in chapter 3) for the retention of said texture post-sintering. This plane has enhanced thermal conductivity as well as tritium diffusivity, both properties extremely beneficial to fusion breeder ceramics. Biotemplating is one technique with which grains could be coerced to grow in a particular direction. Further research into other methods to achieve this should be conducted.

## 7.3 Further analysis techniques

Aside from this, further analysis of the materials generated would be beneficial when further considering the application of these ceramics in a fusion device.

Lithium partial pressure of the ceramics in question may be high, as suggested by the TGA curves shown in chapter 5.3.1.3.2, however, accurate lithium off-gassing at

temperatures of interest (900 °C), as well as through multiple temperature cycles is hard to quantify. TGA shows a general trend towards mass loss, however analysis of the exhaust would be necessary to conclude if this is due to lithium species. To this end, mass spectrometry (MS) of the exhaust would help elucidate the evolution of gaseous species and, therefore, help in both further understanding the reaction pathways leading to a final pellet, as well as the lithium volatility of said pellets. MS could be used in combination with isotopic labelling as well, to identify which component is most susceptible to lithium volatilisation during a simulated post-anneal by analysing said exhaust and identifying the lithium isotopic ratio.

MS can help detail how the pellet evolves in fusion relevant conditions, however, to assess the condition of the pellet after post-anneal (in the case of pellets generated *via* RCS) the current stoichiometry needs to be fully understood. Inductively coupled plasma (ICP) experiments were used in this work to this end, however the equipment was hard to access and often unavailable. Further analysis of the final pellets using ICP would aid in understanding how changes in the methodology affect atomic ratios and, therefore will help elucidate where lithium is being lost, and if the attempts to alleviate this are successful.

Further TEM should be performed to elucidate and build upon the findings reported. Unusual behaviour could be observed, however not enough repeats were performed to either confirm if these effects were widespread or indeed what they were showing.

## 7.4 Radiation performance

Even if the issues identified cannot be addressed, radiation performance of the pellets generated is of import.

In this instance radiation performance relates to experiments which attempt to simulate the conditions the pellets will experience within a functioning fusion device. Several experiments exist around the world that very closely simulate the conditions within a fusion device and several more are due to come online in the near future [42]. However, accessibility is limited due to their small number and high demand. As such simulant experiments are the next step forwards for these materials.

Simulant experiments mainly attempt to simulate radiation damage and tritium generation due to lithium transmutation, *via* ion implantation. As an example, in  $\text{Li}_2\text{TiO}_3$ , titanium is commonly used as an ion source to simulate displacements per atom resulting from radiation exposure during operation. This allows for an estimation of the radiation performance of the material inside the fusion device, by analysing and comparing the material pre and post-implantation. Titanium is used as it generally will not affect the chemistry of the sample. This kind of experiment has been done in  $\text{Li}_2\text{TiO}_3$  sintered using solid state techniques [79], however no comparative analysis of differing microstructures has been done on implanted samples. The impact of microstructural adjustments (using reactive cold sintering) on radiation resistance could be significant, and may aid in the identification of an ideal morphology – a search convoluted by the simultaneous aim to maximise density. Additional phases complicate ion beam choice and may result in unforeseen effects which could obfuscate any real results.

Tritium or, more commonly hydrogen or deuterium, can be implanted as a simulant of the products of lithium transmutation within the samples. Tritium implantation experiments are the most accurate, however due to the inherent radioactivity of tritium, very few experiments actually utilise it and in most cases hydrogen and deuterium are used as simulants. Bubble formation and tritium retention are key aspects to study for any prospect breeder material.

Simultaneous ion and tritium implantation is likely the most accurate simulant of an in-reactor profile, however experiments where both can be performed concurrently are rare.

## 7.5 Bulk properties and scaling

Contextualisation of the ceramics produced in this work against those generated *via* different methods, and with different compositions, is paramount considering the difficulties associated with fusion. Every component must operate as efficiently as possible to increase the viability and future prospects of this technology, and hence generating a comprehensive and truly cross-comparative assessment of properties between materials is necessary to make an informed selection of an ideal material. These include but may not be limited to: moisture sensitivity, lithium density and crush load.

Firstly, a more in-depth assessment of moisture stability would aid in understanding the processing requirements for these materials as-generated. Salt solutions have been used to assess the stability of these ceramics under specific, and well controlled, moisture levels; this however, has only been attempted with single phase ceramics and the improvement in stability introduced by the addition of a strengthening phase (as done in this work with  $\text{Li}_2\text{TiO}_3$ ) has remained unquantified so far. Knowing the degree to which this additional phase improves or worsens atmospheric stability of the generated pellets is key to inform further study of the reactive cold sintering (RCS) method, specifically when applied to the formation of ceramic-ceramic composites for this purpose.

Lithium density of the pellets is directly related to sample density and the crystal structure of the ceramic in question. Addressing the methodological issues identified should refine the composition of the pellets generated, allowing for the crystal structure of the phases involved to be fully characterised. After this, sample density needs to be accurately measured. In most cases this is a simple matter, these ceramics tend to form with significant surface porosity which causes density to fluctuate significantly. A combination of values extracted from the Archimedes method, geometrical density and SEM can be used to ensure the results obtained are an accurate representation of reality. As mentioned in the work herein, the Archimedes method can be altered to increase the accuracy and repeatability of the values extracted (following ASTM standard B962-17 for example). This adjusted method needs to be applied to pellets produced using different sintering methods as well using different particle morphologies to generate a well contextualised picture of the available material and method selection.

As these ceramics are being generated with a pebble bed design in mind, the pellets produced must survive loading, operation and resist crushing under the weight of the bed itself. To this end crush load needs to be high. The difficulty here lies in the necessity for

pellets of a consistent shape to generate comparable values. Pellets generated in the work generally vary in height due to differing degrees of material loss during processing and many of the results in literature have been produced using spherical pellets; the difference in force propagation through the pellets giving incomparable results. A complete series of identical pellets needs to be produced, with all compositions of interest and of suitable size to generate comparable values and assess if the RCS method and/or the formation of ceramic-ceramic composites has any impact (as expected) on the crush load of the pellets.

Scaling of the RCS method may be challenging, as currently pellets need to be prepared and pressed individually. Not only this but currently, this method is highly system specific and requires a degree of trial and error to fine tune the specific conditions required for the formation of a successful pellet. Other die geometries may enhance scaling, by introducing more sample loading zones and therefore generate more pellets per pressing stage but, this method will likely struggle to match the throughput of other methods such as melt spray for example [85].

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