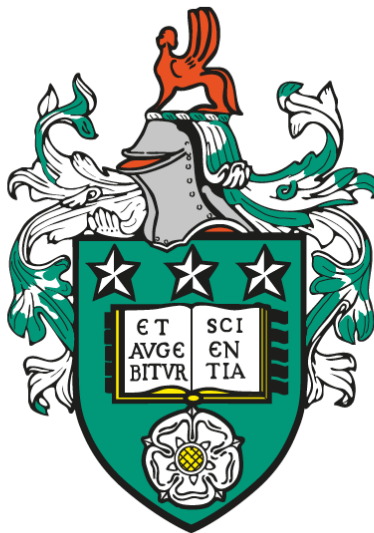


Structure – Dielectric Property Relationships in Filled and Unfilled Strontium Niobate based Tetragonal Tungsten Bronze Ceramics for Temperature Stable Electronic Applications

Submitted in accordance with the requirements for the
degree of
Doctor of Philosophy



The University of Leeds
School of Chemical and Process Engineering

Supervisors
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Parts of this thesis (Chapter 1 – Introduction, Chapter – 3 Experimental Methods, and Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) have been included in a manuscript published in *Acta Materialia*.

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“¡que viva los llanis!”

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Abstract

Tetragonal tungsten bronzes (TTBs) have emerged as a promising structure type for Pb- and Bi- free ferroelectrics for temperature stable ceramic capacitors, with filled $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN1) and unfilled $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ (SBN) attracting recent interest. In this work, A and B site co-doped $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ (with $z = 0$; SNN1 to 0.075) and Na^+ vacancy containing $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ ($w = 0$, $[y = 1]$; SNN1 to $w = 0.15$, $[y = 0.7]$) ceramics were synthesized, and shown to exhibit a flattening of relative permittivity (ϵ_r) across a wide temperature range covering two dielectric anomalies: a relaxor ferroelectric peak at T_1 , between -8°C and -70°C and a ferroelectric to paraelectric transition at T_2 , between 229°C and 297°C .

Rietveld refinement of variable temperature synchrotron X-ray powder diffraction of the SNN ceramics was performed using an orthorhombic *Ama2* structural model. Doping smaller A site cations (Ca^{2+} , Y^{3+}) for Sr^{2+} and less polarisable B site cations (Zr^{4+}) for Nb^{5+} in SNN reduces the c lattice parameter, reducing negative thermal expansion below the ferroelectric to paraelectric transition temperature, T_2 . The reduction of c destabilises the ferroelectric polar mode, lowering the temperature at which the amplitude of this polar distortion mode rises above zero, ultimately decreasing T_2 and ϵ_r at T_2 with doping. Doping also reduces the negative thermal expansion of the a lattice parameter below the low temperature, relaxor-like peak (T_1), onset to which there is sufficient orthorhombic strain to drive the *Ama2* to *Aa* phase transition, ultimately decreasing T_1 with doping. Transmission electron microscopy shows that increased doping, increased octahedral tilt, leading to a higher density of stacking faults to accommodate the associated strain increase. Thus, the ferroelastic domain structure is disrupted, contributing to a relaxor ferroelectric (RFE)-like frequency dispersion at T_1 and flattening the permittivity (ϵ_r) – temperature profile. A flattening of permittivity with addition of Na^+ vacancies in $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$, was attributed to similar effects. Na^+ vacancies can be considered to have an effective size at the A-site and thus play a similar role to A-site dopants, which facilitate tilting of the octahedral framework, through an incommensurate modulation. In turn, this breaks

down the ferroelastic domain structure, disrupting long-range ferroelectric ordering decreasing T_2 and by extension contributing to the relaxor-like nature of T_1 .

Introduction of A- and B-site co-dopants into $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) to form $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} = \text{Y}^{3+}, \text{Dy}^{3+}, \text{Gd}^{3+}, \text{Sm}^{3+}, \text{Nd}^{3+}$, and La^{3+} is also reported here because this lowers and broadens the relaxor ferroelectric permittivity anomaly T_m . A large decrease in tetragonality (c/a) with R^{3+} and Ta^{5+} doping, is followed by a minor decrease in tetragonality with increasing R^{3+} cationic radii, coinciding with little change of T_m and $P_{\max}$ from SBYTN to SBLTN. The expansion of the a lattice parameter reflects that reported in A- and B-site co-doped SNN1 ($\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) and Na^+ A-site vacancy containing SNN1 ($\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$).

Taken together, the work in this thesis demonstrates that an A- and B-site co-doping strategy for an unfilled TTB can lead to a flattened, high and wide temperature ranging permittivity (ϵ_r) – temperature response ideal for capacitor applications

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Abbreviations and Symbols

$A_{12}A_{24}C_4B_{12}B_{28}O_{30}$	Tungsten bronze oxide general formula
ABO_3	Perovskite formula
AC	Alternating current
BNN	Barium sodium niobate, $Ba_2NaNb_5O_{15}$
BSE	Backscattered electron
CBN	Calcium barium niobate, $Ca_xBa_{1-x}Nb_2O_6$
CN	Coordination number
CW	Curie-Weiss law
DC	Direct current
E_c	Coercive field
E	Applied field
EDX	Energy Dispersive X-ray spectroscopy
EIA	Electronics Industries Alliance
ϵ''_r	Imaginary relative permittivity
ϵ_r or ϵ'_r	Real relative permittivity
ICDD	International Centre for Diffraction Data
$K_n^{+/-}$	Bradley-Cracknell notation
MLCC	Multilayer ceramic capacitor
η	Energy efficiency
OM	Optical microscopy
P	Polarization
P - E	Polarisation (P) versus Field (E) hysteresis loop.
P_{max}	Maximum polarisation

PNR	Polar nanoregion
P_{rem}	Remanent polarisation
Pseudo-TTB	Tetragonal tungsten bronze with an orthorhombic setting
PXRD	Powder X-ray diffraction
R_{A1}	Radii of A1 site cation
R_{A2}	Radii of A2 site cation
R_{O}	Radii of oxygen anion
R_{wp}	Weighted R-factor
SBN	Strontium barium niobate, $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$
SE	Secondary electron
SEM	Scanning electron microscopy
SNN	Strontium sodium niobate, $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$
SNN1	Strontium sodium niobate, where Na^+ stoichiometry = 1, $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$
SNNy	Na^+ deficient strontium sodium niobate, $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$, where $y = \text{Na}^+$ stoichiometry
T_1	Low temperature, relaxor like, dielectric anomaly
T_2/T_c	Curie temperature
t_{A1}	Tolerance factor of A1 site
t_{A2}	Tolerance factor of A2 site
$\tan\delta$	Dielectric loss
T_{B}	Burns temperature
TEM	Transmission electron microscopy
T_{m}	Temperature of permittivity maxima
TTB	Tetragonal tungsten bronze
t_{TTB}	Tolerance factor of tetragonal tungsten bronze

W_{loss}	Energy loss density energy efficiency
W_{rec}	Recoverable energy density
γ	Modified Curie-Weiss law coefficient
3-D	Three dimensions

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Chapter 1 – Introduction

1.1 Dielectric Multilayer Ceramic Capacitors (MLCCs)

Accelerating the energy transition from fossil fuels to renewable energy sources presents challenges and exciting opportunities for the functional ceramics industry [1]. Power electronics play a paramount role in expediting this transition [2]. Multilayer ceramic capacitors (MLCCs) are a core component in all electrical circuits for a wide range of functions: *e.g.* coupling and decoupling, blocking, filtering, alternating current (AC) – direct current (DC) separation and ultimately, capacitance (energy storage) [3]. Thus, capacitors are the keystone passive component in electrical circuitry, and their advancement is of crucial importance for temperature stable power electronics [4]. Current research is in pursuit of expanding the Class II MLCC application space, which faces a growing demand for operational temperatures $> 300\text{ }^{\circ}\text{C}$ [5, 6].

BaTiO₃ lies at the heart of class II MLCCs manufacturing, with more than 3 trillion MLCCs produced yearly [7-12]. 80 % of compositions are BaTiO₃ perovskite-based ceramics [13] and presently $> 50\%$ of MLCC products use nickel electrodes [14]. According to standards established by the Electrical Industries Alliance (EIA), BaTiO₃ based MLCCs operate between $-55\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$, with a maximum capacitance variability from that at room temperature (R.T.) of $\pm 22\%$ [8]. Commercial interest has evolved beyond BaTiO₃ to PbZr_xTi_{1-x}O₃ (PZT), BiFeO₃ (BF), and Na_{0.5}Bi_{0.5}TiO₃ (NBT), owing to greater relative permittivities (ϵ_r) and Curie point temperatures (T_c) [7].

In addition to the environmental obstacles associated with lead containing perovskites, MLCCs employing nickel or copper base metal electrodes (BMEs) are also compositionally incompatible with bismuth and lead based ceramics due to redox reactions when cofiring with BMEs at high temperature within a reducing atmosphere during manufacturing [15]. Research perspectives have extended beyond perovskites to the more complex and compositionally flexible, yet relatively poorly understood, bismuth and lead-free tetragonal tungsten bronzes (TTBs) [16].

1.2 Research Problem

TTBs present an exciting opportunity for application as dielectric capacitor materials, owing to their promising energy storage capability, dielectric performance *and* temperature stability [17]. $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN) has shown promise for class II MLCCs and X9R performance or better [15]. However, an in-depth understanding of the thermal, dielectric stability and phase transitions SNN undergoes on heating beyond the X8R temperature range has only recently emerged [15, 18]. The presence of volatile Na^+ in SNN [19], however, paves the way for a structurally similar but alternative system, $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN). SBN has also been proposed as a temperature stable material for temperature stable capacitors [20].

Extensive research on SNN and SBN has focused on maximising recoverable energy densities (W_{rec}) and energy efficiencies (η); *i.e.* by increasing maximum polarisation (P_{max}) and breakdown strength (E_{B}), whilst reducing remnant polarisation, (P_{rem}) [21]. Despite encouraging results regarding the electrical performance characteristics, the outlook of current research is principally focused on further optimising electrical performance (*e.g.* maximising energy storage/capacitive performance) *via* crystal-site doping (A and/or B site co-doping).

1.3 Aim and Objectives

This research aims to pursue an understanding of the structure - dielectric property relationships of $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ (SNN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBN) TTBs for applications in temperature stable capacitors. The role of A- and B-site co-doping, and the introduction of A-site vacancies on the dielectric properties of SNN and SBN based TTBs will be examined.

1.3.1 Objectives

The objectives of this research are as follows:

- O1.** Synthesise a range SNN and SBNs, namely A- and B-site co-doped, A-site deficient (containing Na^+ vacancies) $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN), in addition to A+B-site co-doped and A-site deficient $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ (SBN).

- O2.** Understand SNN and SBN's structure-dielectric property relationships with respect to A- and B-site co-dopants and/or A-site vacancy content for use in wide temperature, temperature stable, high permittivity (ϵ_r) capacitors.
- O3.** Undertake in-depth structural studies (specifically variable temperature synchrotron X-ray diffraction) on A- and B-site co-doped and A-site vacancy containing SNN to illustrate the structural mechanisms that drive changes in SNN's dielectric anomalies, namely the relaxor ferroelectric peak (T_1) and the ferroelectric to paraelectric transition (T_2).
- O4.** Use scanning electron microscopy to investigate microstructure, Raman spectroscopy to examine lattice vibrations related to structural distortions of the TTB octahedral framework.
- O5.** Use dielectric spectroscopy to measure ϵ_r and dielectric loss ($\tan\delta$) temperature evolution, and dielectric hysteresis to measure ferroelectric properties (maximum polarisation [$P_{\max}$], remnant polarisation [P_{rem}], and coercive field [E_c]).
- O6.** Investigate A- and B-site co-doped *and* A-site vacancy containing SBN as a possible alternative to SNN, probing the role of cationic rare earth radii (for Y^{3+} to La^{3+}) in modulating relaxor behaviour and the subsequent effect on the temperature of permittivity maxima (T_m).

1.4 Thesis Outline

This thesis contains 7 chapters and 5 appendices. The first being this chapter, Chapter 1 – Introduction. The second chapter, Chapter 2 – Background Science and Literature Review, contains two major sections. The opening sections of this chapter will concentrate on the rich scientific background and theoretical concepts underpinning dielectric ceramics. Topics treated here begin with fundamental crystal chemistry, ferroelectrics/relaxor ferroelectrics, to ultimately, the complex TTB structured ceramics. The latter section of Chapter 2 – Background Science and Literature Review will proceed with an extensive review of current published research, concentrating on the specific TTB materials of study in this thesis, SNN and SBN.

Chapter 3 – Experimental Methods will encompass the ceramic processing, electrical and structural characterisation techniques underpinning the results chapters of this thesis (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$, and Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$). The chemical stoichiometric calculations and processing steps to form dense ceramic pellets of SNN and SBN will be described. This is followed by sample preparation, instrument parameters, and theoretical background of the structural and electrical experimental techniques used to characterise SBN and SNN.

The three results chapters of this thesis are centred on structure - dielectric property determination for: Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ (objectives O1 – O5), Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$ (objectives O1 – O5), and Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (objectives O1, O2, O4 – O6). Chapters 4 and 5 are focused on SNN, whereas Chapter 6 concentrates on SBN.

The final chapter, Chapter 7 – Conclusions and Future Work, will conclude this thesis and provide future research directions guided by the results and perspectives reported in Chapter 4, 5 and 6. The Appendices contain supplementary data not central to the main results chapters of this thesis but provide additional information that may be of interest to the reader. Appendices A contains Shannon ionic radii [22] and polarizabilities [23] used throughout this thesis. Appendices B – Visualisation of Irreducible representations (irreps) are a visual guide of density functional theory (DFT) derived irreps discussed in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$. Appendices B – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Appendices C – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$, and Appendices D – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ contain supplemental data (microstructure, electrical, and diffraction data) to results Chapters 4, 5 and 6.

Chapter 2 – Background Science and Literature Review

2.1 Introduction

This chapter comprises two major sections, background science and literature review. The first section (background science), will concentrate on crystal structure, dielectric properties, and polarisation mechanisms, followed by provision of the groundworks of ferroelectrics and relaxor-ferroelectrics. The second section (literature review) will describe tetragonal tungsten bronze (TTB) structured ceramics, followed by a review of published research, with a focus on the materials of study in this thesis: $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN1) and $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ (SBN).

2.2 Fundamentals of Crystallography

2.2.1 Unit Cells

Crystalline solids are composed of a repeating atomic arrangement that extends in 3 dimensions (3-D) such that the crystal lattice can be represented by the smallest repeating unit, denoted as the unit cell [24]. Unit cells that can make up a crystalline solid are interrelated by translational symmetry in 3-D [25]. Unit cells are mathematically expressed by their geometry and can be defined by lattice parameters [26]. Lattice parameters represent the geometric dimensions (lengths a , b , and c) and angles (α , β , and γ) that define a unit cell [26]. A diagram illustrating the lattice parameters defining a triclinic unit cell are shown in Figure 2.1.

A crystalline solid may also be described by a crystal lattice, a mathematical construct [27]. A 3-D array of lattice points summate to produce the crystal lattice, embodying a motif (e.g. an asymmetric molecule) [28]. Convoluting the crystal lattice and motif characterizes the unit cell of a given crystal system [26, 28]. A crystalline solid may also be described by a crystal lattice, a mathematical construct [27]. A 3-D array of lattice points summate to produce the crystal lattice, embodying a motif (e.g. an asymmetric molecule) [28]. Convoluting the crystal lattice and motif characterizes the unit cell of a given crystal system [26, 28]. A schematic diagram showing the

convolution of a motif and lattice points to form a crystal lattice to define a unit cell is shown in Figure 2.2.

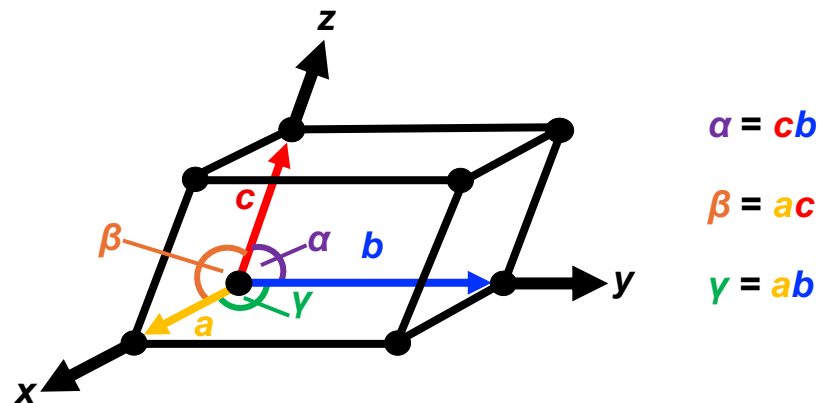


Figure 2.1: A unit cell showing the lattice parameters used to geometrically define a unit cell and the associated lattice lengths (a , b , and c) and angles (α , β , and γ), taken and reformatted after Cullity *et al.* [27].

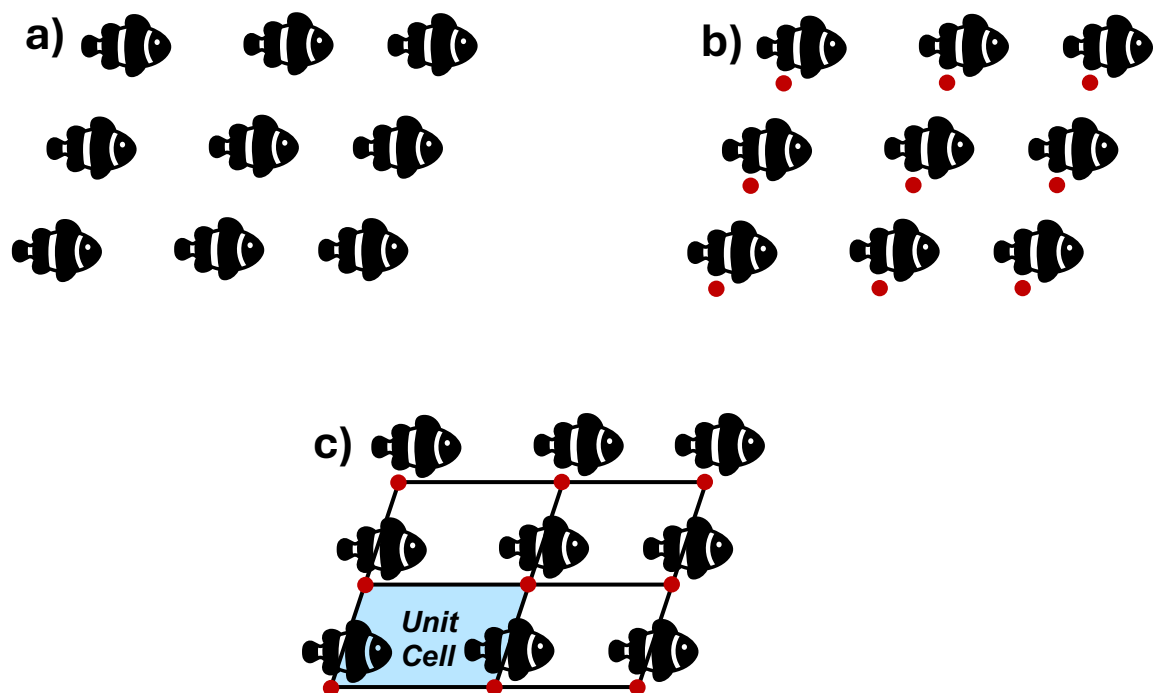


Figure 2.2: Diagram showing a) a motif (*i.e.* an asymmetrical shape), alongside b) a motif and corresponding lattice points, and c) the crystal lattice and unit cell, for a two dimensional (2D) system, reformatted after Hammond [28].

2.3 Lattice Types and the Reciprocal Lattice

Unit cell geometries are quantified by lattice parameters, summarised by the seven crystal systems (Table 2.1). Lattice points solely at the corners of the unit cell are categorised as primitive unit cells [26, 27]. However, instances of non-primitive (centered) lattice points in combination with the seven primitive crystal systems, culminates in fourteen Bravais lattices [26]. The fourteen Bravais lattices are shown in Figure 2.3. So called centring of non-primitive lattice points in unit cells are considered as being base centered (*S*: *A*, *B* or *C*), body centered (*I*), or face centered (*F*) [29].

Table 2.1: The seven crystal systems.

Bravais Lattice System	Lattice Parameters	
	Lengths	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ, < 120^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Trigonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta > 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$

A point group characterises the symmetry of a given crystal [29]. Point symmetry is defined as symmetry operations around a given lattice point, leaving at least one lattice point unaltered [29]. Combining symmetry planes and centres ultimately leads to the thirty-two crystallographic point groups [29]. Unique combinations of the thirty-two crystallographic point groups in conjunction with the 3-D translational symmetry of the fourteen Bravais lattices, results in two-hundred and thirty space groups [29]. The space group of a given unit cell gives full information on lattice centring and symmetry elements [26]. In this thesis, Hermann-Mauguin space group notation is used, as is the convention for the International Union of Crystallography (IUCr) [30] where a) a capital letter indicates the lattice centering of the unit cell and b) lower case letters and numbers indicate the symmetry elements [31].

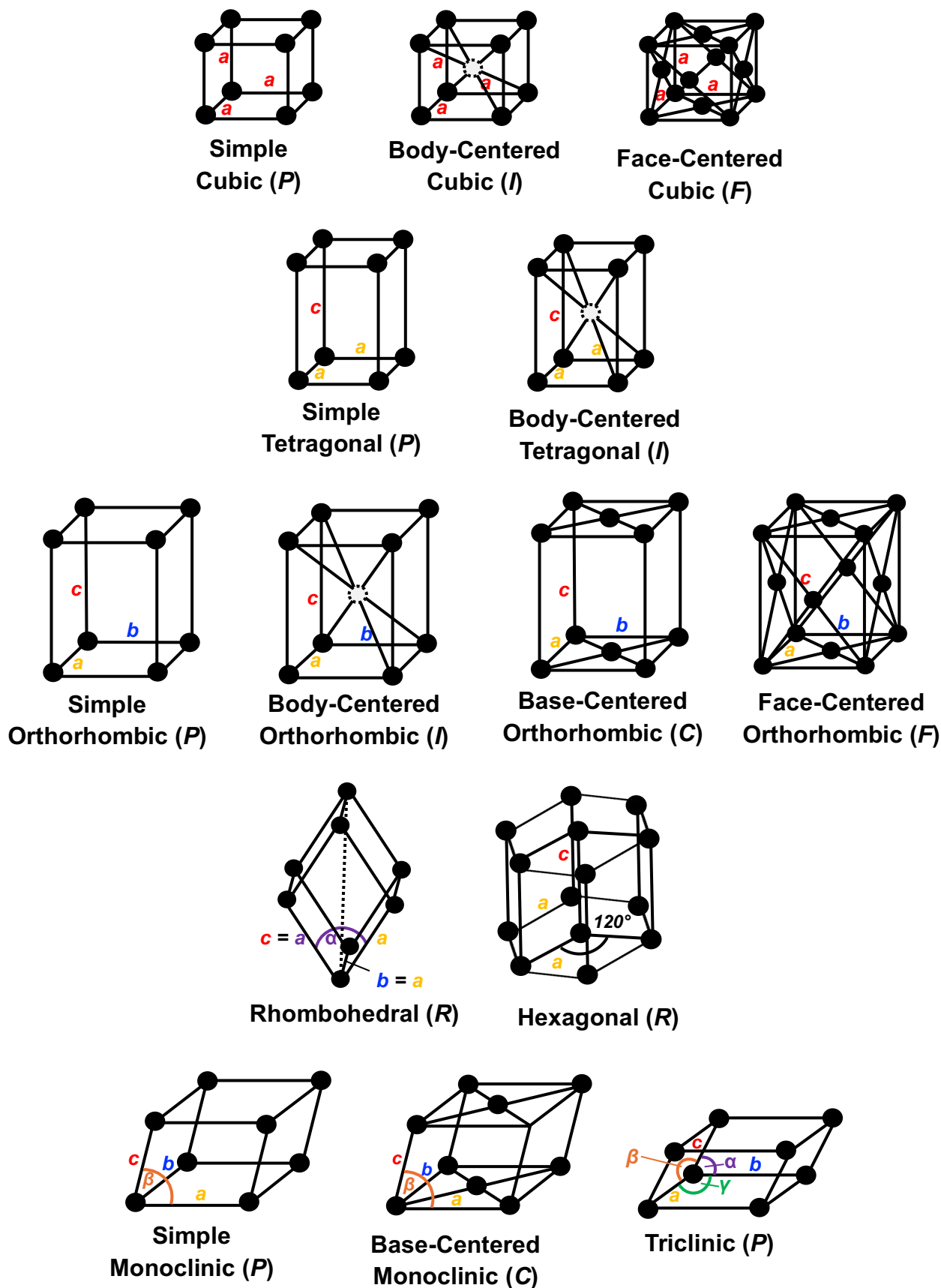


Figure 2.3: The 14 Bravais lattices taken and adapted after Hammond [28].

Chapter 2 – Background Science and Literature Review

The reciprocal lattice may be mathematically derived from the direct lattice (*i.e.* the ‘real’ lattice) [27]. X-ray diffraction (XRD) is typically treated with respect to reciprocal space [32]. For every lattice plane, there is an equivalent point in reciprocal lattice [33]. This point can be represented by Miller indices (h,k,l), which define the lattice planes from which diffraction could occur [34]. The diffraction of X-rays is therefore defined by Bragg’s law¹ where the direct lattice is related to the reciprocal lattice [32]. The reciprocal lattice, together with the Ewald sphere [35, 36] is used as a mathematical construct to define points where diffracted planes satisfy the Bragg law, constituting diffraction possibilities [37, 38].

2.4 Polarisation, Dielectrics, and Capacitors

Dielectric materials are electrical insulators, which are capable of being polarised upon the application of an electric field (E) [3]; this involves generation of a dipole (charge separation). The charge separation from one end of the material to the other, allows for the exploitation of the material to store charge, *i.e.* for capacitor applications [3]. If two oppositely charged species (*i.e.* Na^+ and Cl^-) are separated by a distance, d , a dipole moment, μ , is defined by Equation 2.1 [39].

$$\mu = qd$$

$\mu = \text{Dipole moment}$
 $q = \text{Charge}$
 $d = \text{Distance between charges}$
Equation 2.1

The polarisation (P) from a point negative charge to the point positive charge is defined by μ , a vector quantity [39]. μ can be expressed as a vector summation ($\Sigma\mu$) of all dipole moments for a given volume of dielectric material shown in Equation 2.2 [40].

$$P = \frac{\Sigma\mu}{V}$$

$P = \text{Polarisation}$
 $\mu = \text{Dipole moment}$
 $V = \text{Unit volume}$
Equation 2.2

The induced dipole moment, μ , can be expressed in terms of polarisability, α , and the applied electric field, E (Equation 2.3). Polarisability, α , is a quantity measuring the

¹For more details, see Chapter 3 – Experimental Methods, section 3.3.1.

Chapter 2 – Background Science and Literature Review

degree to which a dipole moment is induced per unit of the applied electric field, E [3, 32].

$$\mu = \alpha E$$

Equation 2.3

μ = Dipole moment
 α = Polarisability
 E = Electric field

Polarisation, P , is a summation of all individually induced dipole moments (with a polarisability, α) [32] and is directly related to the applied electric field, E , by Equation 2.4 [3].

$$P = \epsilon_0 \chi_E E$$

Equation 2.4

P = Polarisation
 ϵ_0 = Permittivity of a vacuum ($8.85 \times 10^{-12} \text{ Fm}^{-1}$)
 χ_E = Electric susceptibility
 E = Electric field

Positively charged species will shift in the direction of the applied electric field, while negatively charged species will shift away from said electric field direction, leading to a dipole, μ ; in order words, a separation of charge and thus polarisation, P [41]. Hence, it is useful to discuss dielectric materials in the context of storing electrical charge, namely capacitors [41]. The ability of the dielectric material to store charge can be quantified by the relative permittivity, ϵ_r (Equation 2.5) [3].

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

Equation 2.5

ϵ_r = Relative permittivity
 ϵ = Permittivity
 ϵ_0 = Permittivity of free space ($8.85 \times 10^{-12} \text{ Fm}^{-1}$)

If a dielectric between charged plates has a susceptibility of χ_E , then its capacitance increases by $1 + \chi_E$ shown by Equation 2.6 and Equation 2.7 [3].

$$\epsilon = \epsilon_0 (1 + \chi_E)$$

Equation 2.6

ϵ = Permittivity
 χ_E = Electric susceptibility
 ϵ_0 = Permittivity of free space ($8.85 \times 10^{-12} \text{ Fm}^{-1}$)
 ϵ_r = Relative permittivity

where

$$\frac{\epsilon}{\epsilon_0} = 1 + \chi_E = \epsilon_r$$

Equation 2.7

The relative permittivity, ϵ_r , is related to the charge stored, and thus capacitance, C , of a dielectric material, illustrated by parallel plate capacitor (Figure 2.4). In an empty

Chapter 2 – Background Science and Literature Review

parallel plate capacitor (Figure 2.4, left), capacitance, C_0 , is defined by Equation 2.8, where ϵ_0 is constant, so C_0 is solely dependent on the area, A , and distance, d , of the parallel plates [32]. Applying a voltage, V , through the plates, sees a build-up of charge, Q_0 , on the plate surfaces (Equation 2.9) [32]. The ϵ_r is therefore related to the overall capacitance (Equation 2.10) [32].

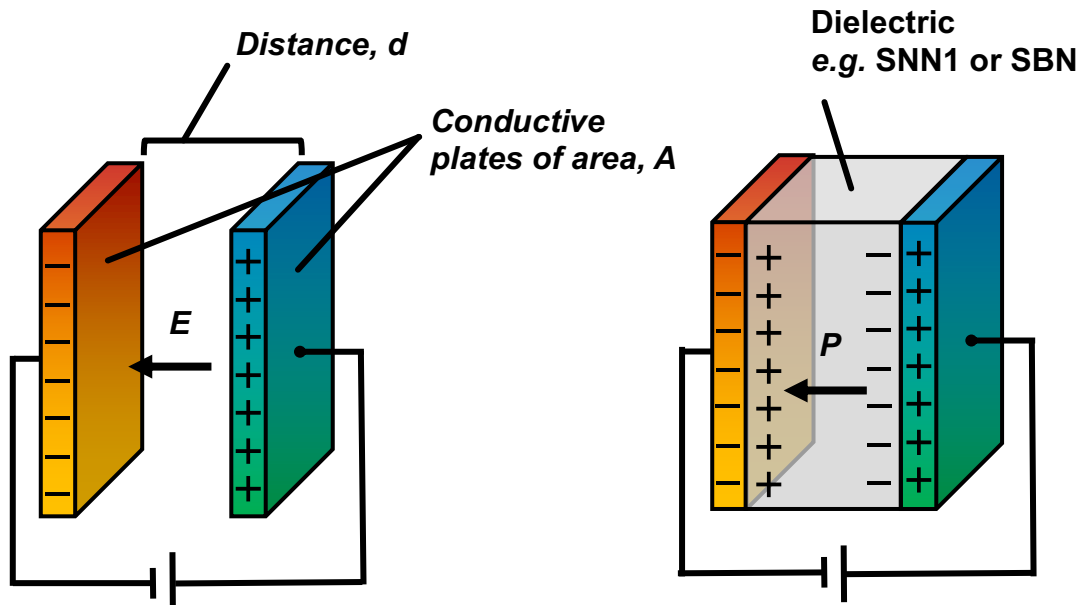


Figure 2.4: A schematic diagram of an empty (vacuum) parallel plate capacitor (left) and a parallel plate capacitor with a dielectric material (which stores more charge than that of the vacuum) between the conductive plates (right) taken and adapted after Moulson [3].

$$C_0 = \frac{\epsilon_0 A}{d} \quad \text{Equation 2.8}$$

$$Q_0 = C_0 V \quad \text{Equation 2.9}$$

$$\epsilon_r = \frac{C}{C_0} \quad \text{Equation 2.10}$$

If a dielectric material is placed between the plates (Figure 2.4, right), the stored charge, Q , is increased along with capacitance, C , [32] and so capacitance of a parallel plate capacitor with a dielectric material can be expressed by Equation 2.11 [3].

Chapter 2 – Background Science and Literature Review

$$C = \frac{Q}{V}$$

$C =$ Capacitance of parallel plate capacitor
 $Q =$ Charge stored in parallel plate capacitor
 $V =$ Applied voltage

Equation 2.11

Subsequently, capacitance, C , can be expressed by Equation 2.12 [3].

$$C = \epsilon_r \epsilon_0 \frac{A}{d}$$

$C =$ Capacitance of parallel plate capacitor
 $\epsilon_r =$ Area of plates
 $\epsilon_0 =$ Relative permittivity
 $A =$ Area of plates
 $d =$ Diameter of plates

Equation 2.12

For a dielectric in a capacitor to be effective, the dielectric must be able to withstand fluctuating charge, yet curtail the amount of energy dissipation (*i.e.* heat) [41]. In an ideal dielectric capacitor, the 90° phase relationship between current, I , and voltage, V , rotating counterclockwise at angular frequency, ω , can be depicted using a phasor diagram (Figure 2.5 [left]) [3, 42]. In reality, real dielectric capacitors have a capacitive *and* lossy component, where current, I , and voltage, V , are out of, or in phase, respectively [43].

This is shown by phase components, δ ($< 90^\circ$) and Φ ($90^\circ - \delta$) respectively in Figure 2.5 (right). That is to say, the lead voltage, V , in a real dielectric capacitor ‘lags’ behind the current, I , by Φ ($90^\circ - \delta$) under an applied alternating current (AC) field [42]. Hence, ϵ_r is a complex quantity, expressed by Equation 2.13 [44-46], where the ratio of energy dissipated to energy (in the form of charge) stored may be expressed by the dielectric loss tangent, $\tan\delta$ (Equation 2.14) [46, 47].

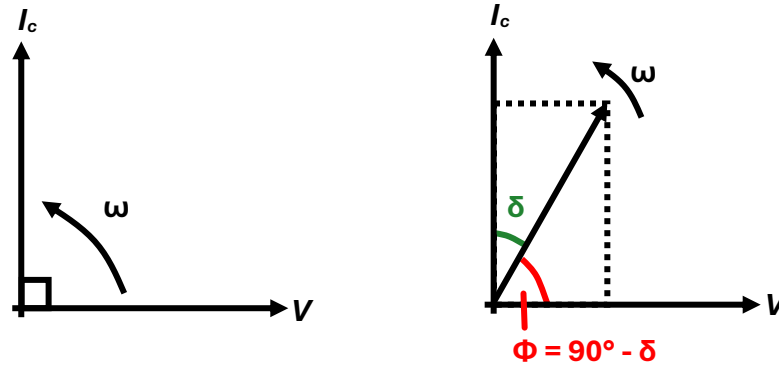


Figure 2.5: A phasor diagram for an ideal dielectric capacitor (left) and a real capacitor (right) taken and reformatted after Moulson [3] where ω is the angular frequency, δ is the capacitive and Φ is the lossy component phases respectively.

$$\varepsilon_r = \varepsilon'_r - i\varepsilon''_r \quad \varepsilon'_r = \text{Real relative permittivity}^* \quad \text{Equation 2.13}$$

$$\tan \delta = \frac{\varepsilon''_r}{\varepsilon'_r} \quad \varepsilon''_r = \text{Imaginary relative permittivity}^* \quad \text{Equation 2.14}$$

$$i = \sqrt{-1}, \text{ imaginary unit}$$

$$\tan \delta = \text{Dielectric loss tangent}$$

*Where ε'_r is the capacitive component and ε''_r is the lossy component.

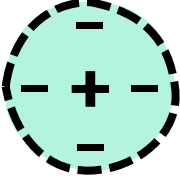
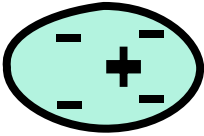
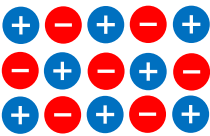
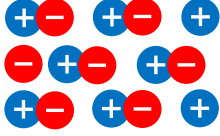
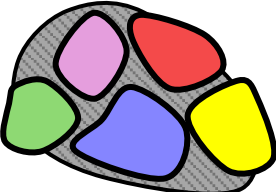
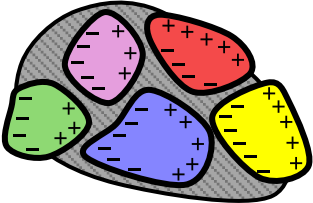
2.4.1 Polarisation Mechanisms

The quantities α , ε_r , and thus χ_E are dependent on the measured frequency of the applied AC field [32]. In dielectric materials, there are four polarisation mechanisms contributing to the magnitude of ε_r ; namely electronic, ionic, dipolar and space charge polarisation [3]. The four polarisation mechanisms are summarised in Figure 2.6². Such polarisation mechanisms occur at differing relaxation times [32] and so are frequency dependent [46]. The relationship between real (ε'_r), imaginary permittivity (ε''_r) and onset polarisation mechanism frequencies are shown in Figure 2.7.

²In some literature, dipolar polarisation is referred to as orientation polarisation, while space charge polarisation is referred to as interfacial polarisation.

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Figure 2.6: Different types of polarisation mechanisms observed in dielectric materials taken and reformatted after Moulson [3].

Polarisation Mechanism	Unpolarised State	Polarised State $E \longrightarrow$
Electronic		
Ionic		
Dipolar		
Space Charge		

At high frequency (10^{15} Hz) [32], electronic polarisation refers to a displacement of electrons away from the nucleus [3]. At a slightly lower frequency (10^{13} Hz), ionic displacement (*i.e.* in an ionic solid such as NaCl) occurs when the cation and anions sublattices displace, relative to one and other [3]. Both mechanisms are thought to be relaxation processes [48] and temperature independent [3]. Dipolar polarisation refers to materials that have a permanent dipole and occurs at 10^{10} Hz [3]. Here, randomly oriented dipoles are reoriented in the direction of the applied electric field [3]. Space charge polarisation occurs at the lowest frequency (10^4 Hz) comprises the movement of charged defects until they are halted by a potential barrier (*i.e.* a phase or grain boundary), which facilitates the separation of charge [3].

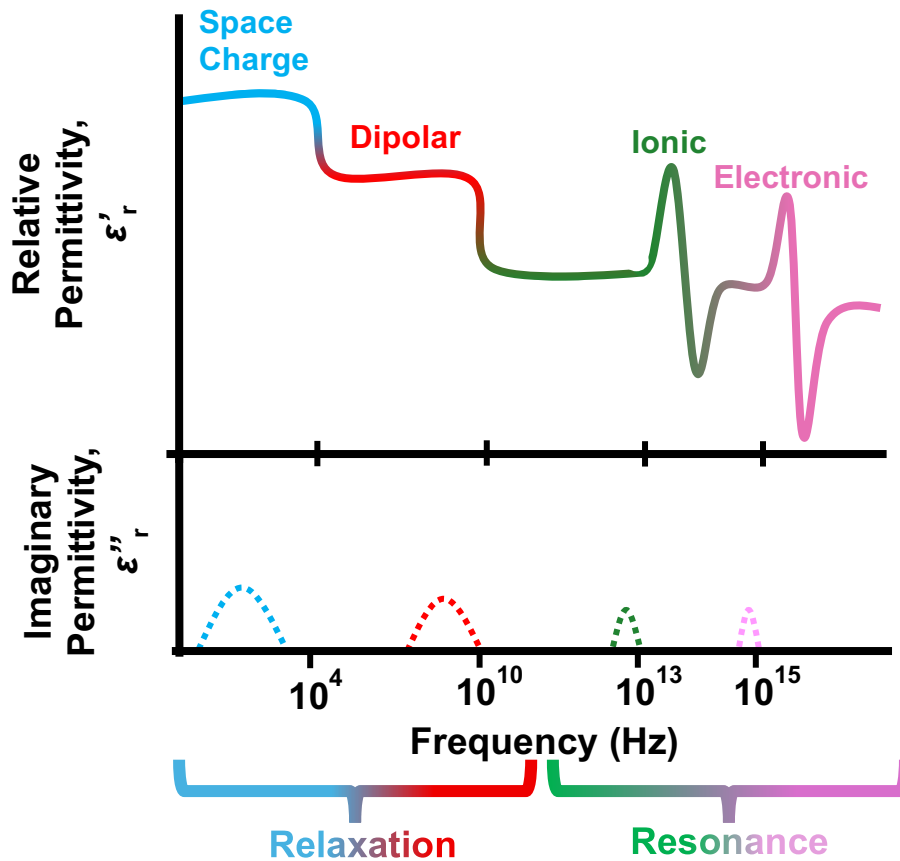


Figure 2.7: Different types of polarisation mechanisms and their relationship to relaxation frequencies of real (ϵ'_r), imaginary permittivity (ϵ''_r), observed in dielectric materials taken and reformatted after Moulson [3].

The real (ϵ'_r) and imaginary (ϵ''_r) permittivities (see Equation 2.13 in section 2.4 above) are frequency dependent due to each polarisation mechanism not responding beyond particular frequencies (critical frequency [48]). It is at these specific frequencies that the contribution to the real permittivity, ϵ_r , subsides, and is reflected in peaks of the imaginary permittivity, ϵ''_r [3, 49] shown in Figure 2.7. Dipolar and space charge polarisation are considered relaxational processes (Figure 2.7.) [48], and are temperature dependent [3] and thus considered to be affected by extrinsic contributions (*i.e.* frictional forces [48]) [50]. Conversely, ionic and electronic (displacive) polarisation is resonance-type in nature (Figure 2.7) [48]. The maximum phase shift between polarisation, P , and applied field, E , is related to the critical frequency (*i.e.* 10^{15} Hz for electronic polarisation) and corresponds to a dielectric loss, $\tan\delta$ maximum (see Equation 2.14 in section 2.4 above) [48].

2.5 Polar Dielectrics

The thirty-two crystal classes described in section 2.3 can be distinguished by whether they contain a centre of inversion and are mapped out in Figure 2.8. Polar crystals are distinguishable from non-polar crystals due to their unique polar axis (the direction to which spontaneous polarisation occurs) in which an ion can be displaced to generate a dipole moment [3]. Eleven are centrosymmetric (no centre of inversion) and thus are considered non-piezoelectric, where structural symmetry prevents ionic displacement [3].

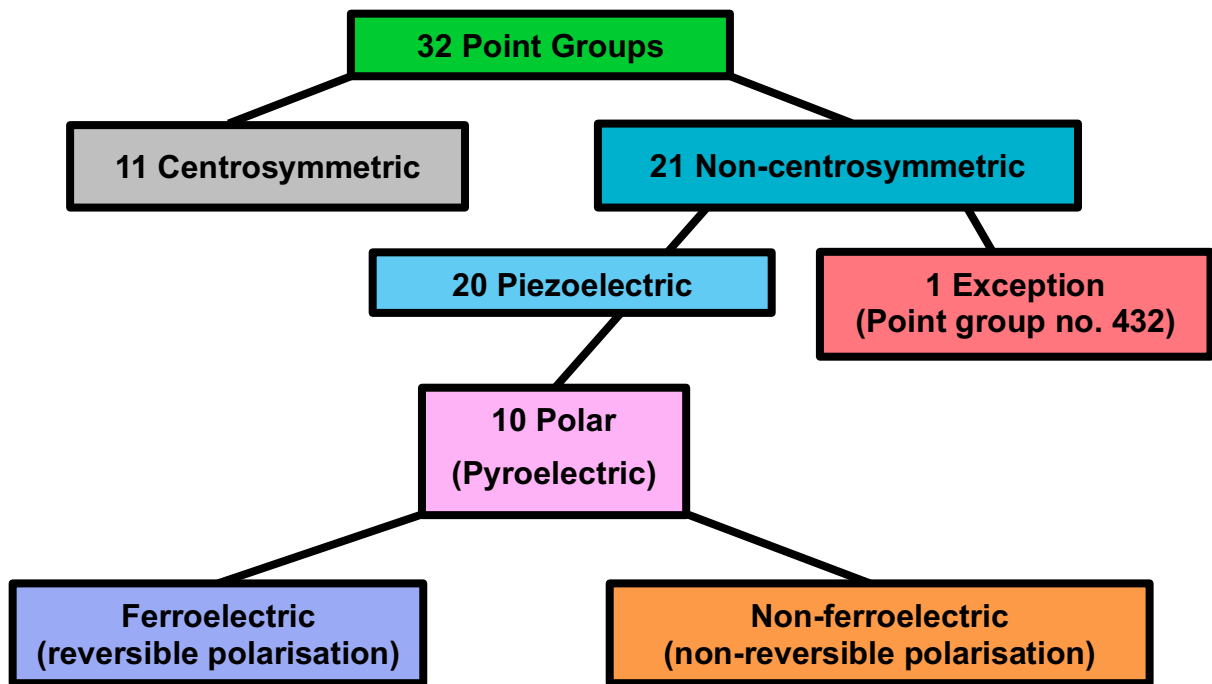


Figure 2.8: Schematic of the 32-point groups and the relationship between the crystal symmetry driven dependence of piezoelectricity, pyroelectricity, and ferroelectricity taken and reformatted after [51, 52].

The outstanding twenty-one are non-centrosymmetric, twenty of which are piezoelectric and ten are polar [3]. Piezoelectric crystals exhibit the so-called piezoelectric effect; where stress and strain are electromechanically coupled and strain in the crystal is directly proportional to the applied electric field [3]. The pyroelectrics subgroup within the piezoelectric group undergo temperature dependent spontaneous polarisation [53]. The piezoelectric, pyroelectric and ferroelectric point

groups within the thirty-two point groups (Figure 2.8) will be discussed in the next section.

2.5.1 Ferroelectrics

Ferroelectrics are a subgroup of pyroelectrics, where spontaneous polarisation is reversible upon application of an applied electric field [54]. A ferroelectric typically has two (or more) dipole orientational states which can be aligned by applying an electric field [53]. The two orientational states however, can be switched from one to the other by applying an electric field [53]. Such orientational states are stable because they sit in potential energy wells (*i.e.* energy minima), the potential (energy) barrier of which can be surmounted by an applied electric field [55]. Residual electrical polarisation can be retained in a ferroelectric after the removal of an applied electric field [32]. The reversal of polarisation, P , once subjected to an applied electric field in the opposite direction (coercive field, E_c), gives rise to a polarisation (P) versus field (E) hysteresis loop [32], shown in Figure 2.9.

For ferroelectricity to occur, one must consider the crystallographic constraints for ferroelectrics, *i.e.* polymorphism as a function of temperature [50]. A change in the crystal structure, such as through a phase transition, may affect the degree of, or even total loss of spontaneous polarisation [50]. A classic example is a phase transition from a ferroelectric structure to a high symmetry and non-polar, paraelectric structure, the temperature at which this occurs is termed the Curie temperature, T_c [50]. The origin of ferroelectricity is illustrated by BaTiO_3 perovskite, widely considered as the prototype ferroelectric ceramic [56]. Perovskites, like BaTiO_3 , have a general ABO_3 structure [57]. A diagram of a unit cell of BaTiO_3 perovskite is shown in Figure 2.10 with a ferroelectric effect shown in Figure 2.11.

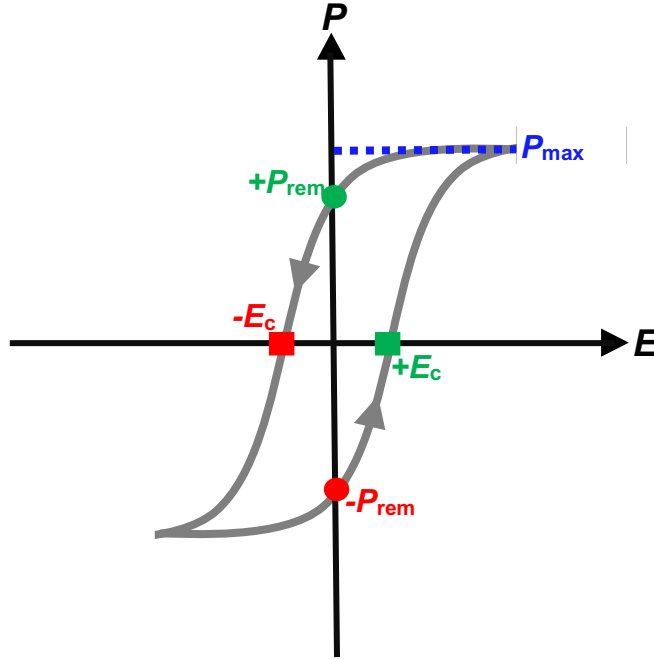


Figure 2.9: A typical ferroelectric hysteresis loop with maximum polarisation ($P_{\max}$), remanent polarisation (P_{rem}) and coercive field (E_c) labelled, taken and reformatted after Liao [58].

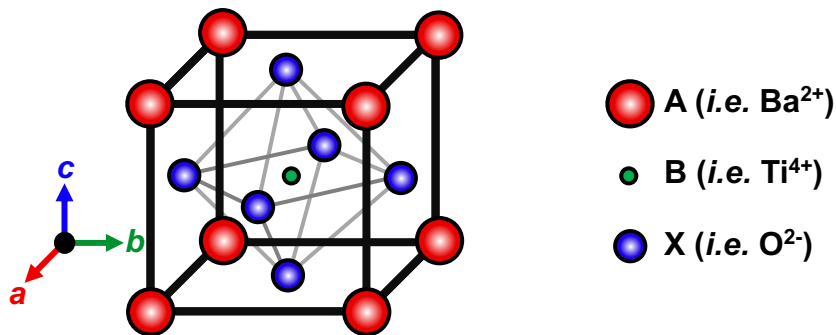


Figure 2.10: A cubic aristotype perovskite structure of BaTiO_3 taken and adapted after Moulson [3].

A-site cations are located at the corners of the unit cell, while B cations are situated at the body centred position, enclosed by an octahedral cage of, typically, oxygen anions, present at each face of the unit cell [57]. Cooling through T_c ($\sim 130^\circ\text{C}$) from the high symmetry cubic paraelectric phase to the lower symmetry tetragonal ferroelectric phase, the B site cation in the octahedral cage is displaced along the c axis (Figure

2.11) [3]. Further cooling sees additional phase transitions to orthorhombic and rhombohedral phases varying the direction of the unique polar axis [3].

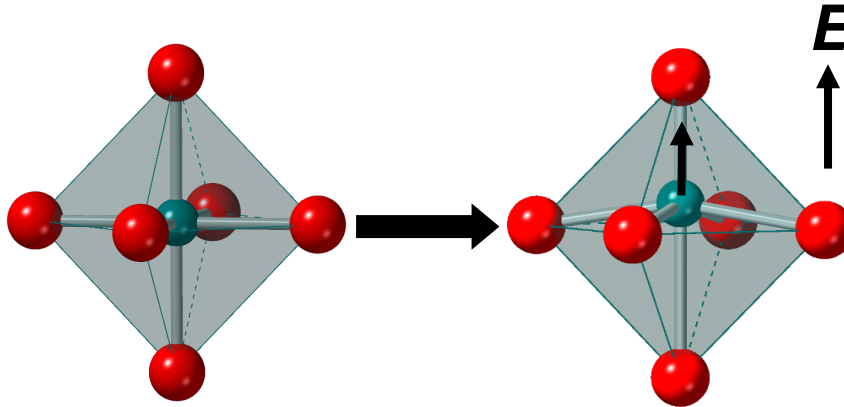


Figure 2.11: A dipole occurring *via* ionic displacement of the B cation in the octahedral cage, subjected to the applied field, E , reformatted after Gardner [50].

2.5.2 Relaxor-Ferroelectrics (RFEs)

Ferroelectric materials can be categorized into 3 sub-classes with respect to the character of the transition, a) classical ferroelectrics, b) relaxor ferroelectrics (RFEs), and c) canonical relaxors [59]. Classical ferroelectrics show a sharp, frequency-independent permittivity peak, at the Curie temperature, T_c which is associated with a ferroelectric to paraelectric transition [60]. Relaxor-ferroelectrics (RFEs) and canonical relaxors, show a broad, high value ϵ_r peak (relative to classical ferroelectrics) when plotted against temperature, accompanied by frequency dispersion [3]. The temperature of maximum ϵ_r , T_m , becomes smeared with increasing frequency, the temperature of which increases with frequency [61, 62]. A schematic diagram distinguishing classical ferroelectrics, RFEs and canonical relaxors is shown in Figure 2.12a – c. The relatively high ϵ_r , $P_{\max}$, in addition to a low P_{rem} and E_c , compared to classical ferroelectrics, make RFEs promising candidates for capacitive (energy storage) applications (Figure 2.13a – b).

Much like classical ferroelectrics, RFEs are paraelectric at high temperature (*i.e.* $> T_c$ [classical ferroelectrics] or $> T_m$ [RFEs]). Upon cooling however, a paraelectric-RFE transition occurs, where clusters of aligned dipoles, namely polar nanoregions (PNRs) embedded in a non-polar environment develop (Figure 2.12b) [63]. This transition is termed the Burns Temperature (T_B) [63]. PNRs are highly mobile and dynamic, and

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are said to be ergodic (fluctuating [64, 65]) in nature when cooling from the paraelectric phase [66]. Therefore, no long range ferroelectric order (as in classical ferroelectrics) is present, contributing to the lower E_c and therefore larger $P_{\max}$ - P_{rem} (*i.e.* slimmer P - E hysteresis loops [67]) making RFEs materials of interest for capacitive (energy storage) applications [68]. Disorder, in conjunction with charge and cationic radii variances are suggested to be the underlying mechanism behind the fluctuation of stress and electrostatic fields that disrupt long range ferroelectric order giving rise to PNRs in RFEs [69]. Compositional disorder of A- and/or B-site cations is therefore commonplace in RFEs [63].

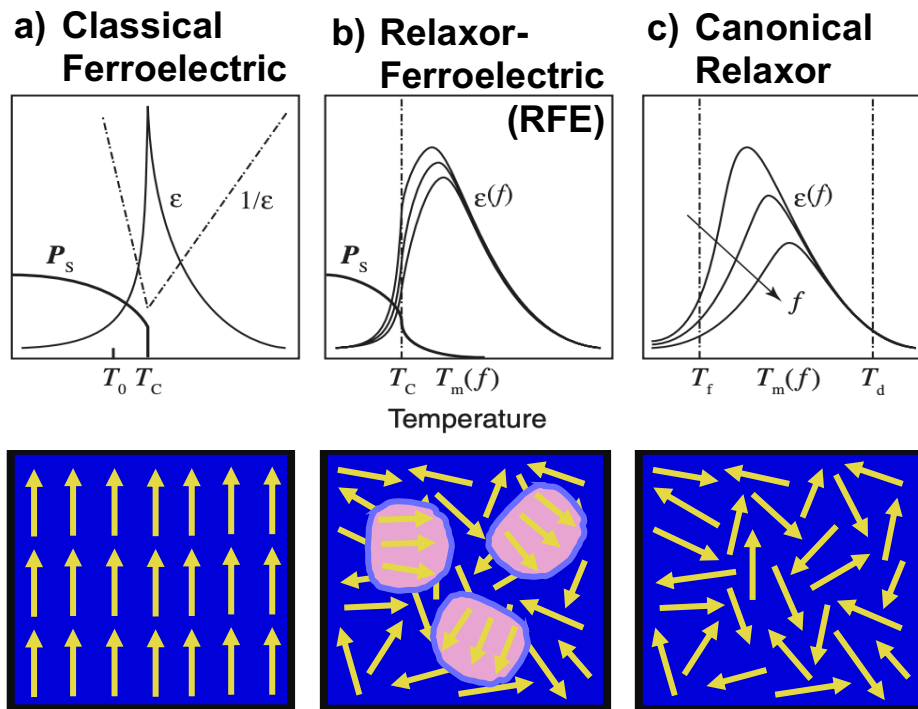


Figure 2.12a – c: Schematic diagram showing the dielectric property-temperature dependency of a) a classical ferroelectric and corresponding domain structure, b) a relaxor ferroelectric (RFE) and equivalent domain structure showing polar nanoregions (PNRs) and c) a canonical relaxor with the related dipolar-glass domain structure. Temperature dependency plots (top) and reproduced from Hirota *et al.* [59] with permission of The Physical Society of Japan, and domain structure diagrams taken and adapted after Rotaru [70].

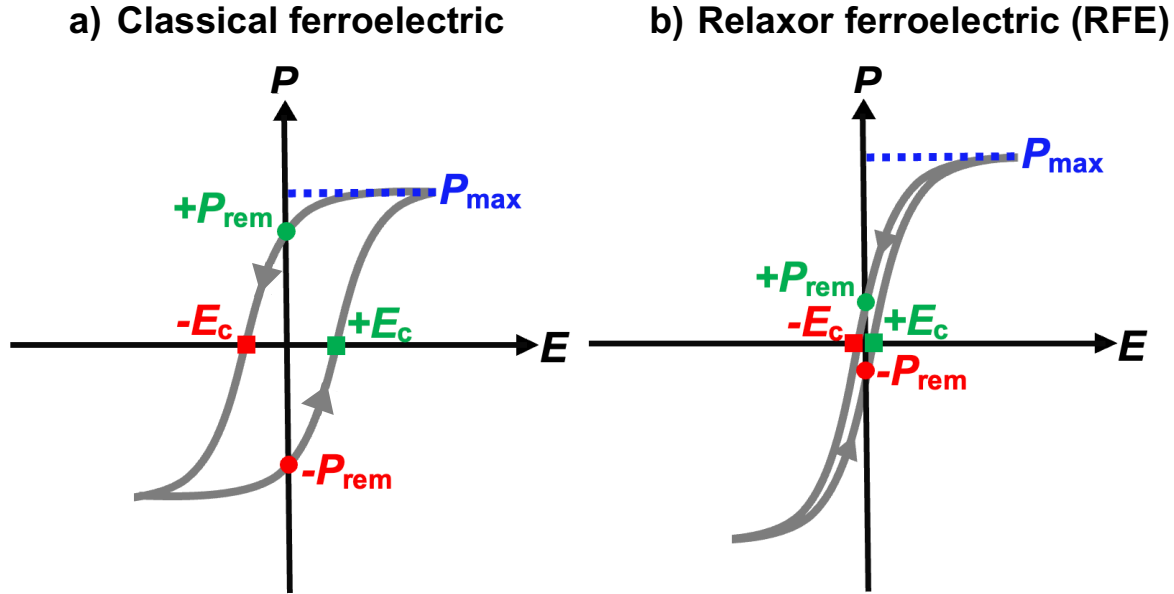


Figure 2.13a – b: Polarisation (P) versus field (E) hysteresis loops of a) classical ferroelectric and b) a relaxor ferroelectric (RFE) showing a larger $P_{\max}$ and lower P_{rem} of the RFE in b) leading to desirable capacitive (energy storage) performance.

A prototypical RFE is the perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), which exhibits B- site disorder of Mg^{2+} and Nb^{5+} , which in conjunction with the valence difference between both cations, drives relaxor behaviour [71]. Other perovskites, like $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$, exhibit relaxor behaviour only when Sc^{5+} and Ta^{5+} where disordered on the B-site [72]. Upon application of a sufficiently high electric field, the random orientation of the PNRs is thought to irreversibly align, akin to that of a classical ferroelectric [63, 66]. Well below T_B , the RFE becomes non-ergodic (*i.e.* the dynamism and mobility of PNRs are ‘frozen’), analogous to that of a dipolar glass, occurring at transition temperature T_f [63]. Both “relaxor” and “RFE” nomenclature are used interchangeably in the literature, with relaxors referring to canonical relaxors [70]. Canonical relaxors exhibit dipolar glass-like behaviour [73], distinguishable from RFEs in that they don’t form a characteristic P - E hysteresis loop under an appropriately strong applied field [50, 59, 70].

Above the ferroelectric-paraelectric transition (T_c), ϵ_r is linear well above T_c , adhering to Curie-Weiss (CW) law [74], shown in Equation 2.15. As previously mentioned, RFEs exhibit diffuse phase transitions [75] and deviate from CW law near T_c resulting in a

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difference between T_C and T_0 [75]. The extent of the difference between T_C and T_0 (*i.e.* $T_C - T_0$) has been suggested to be related to the order of the phase transition [75, 76].

$$\varepsilon_r = \frac{C}{T_C - T_0}$$

Equation 2.15

ε_r = Relative permittivity
 C = Curie-Weiss constant
 T_C = Curie temperature
 T_0 = Curie-Weiss temperature

When $T_C - T_0 > 0$, the phase transition is first order with a corresponding sharp $\varepsilon_r - T$ phase transition [75, 76]. On the other hand, second order transitions are characterised by $T_C - T_0 \approx 0$, accompanied by a broad $\varepsilon_r - T$ phase transition [75, 76]. Deviation from CW law can be described by a quadratic equation shown by Equation 2.16 [76].

$$\frac{1}{\varepsilon_r} = A + B (T_0 - T_C)^2$$

Equation 2.16

ε_r = Relative permittivity
 $A = 1/\varepsilon_{r,max}$
 $B = 1/2\varepsilon_{r,max}$
 δ = Parametrised diffuseness of the phase transition
 T_C = Curie temperature
 T_0 = Curie-Weiss temperature

However, phase transitions often do not follow a quadratic relationship and may be better generalised by Equation 2.17 [77].

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{r,max}} = \frac{(T_0 - T_C)^\gamma}{C}$$

Equation 2.17

T_0 = Curie-Weiss temperature
 T_C = Curie temperature
 C = Curie-Weiss constant
 ε_r = Relative permittivity
 γ = Curie-Weiss coefficient

The CW coefficient, γ , is typically within the range of $1 \leq \gamma \leq 2$ [75]. When $\gamma = 1$ the phase transition abides by Equation 2.15 (*i.e.* ferroelectric, obeys CW law) while when $\gamma = 2$ the phase transition abides by Equation 2.16 (*i.e.* RFE, deviates from CW law) [77-79]. The degree of relaxor behaviour may this be quantified by plotting $\ln(1/\varepsilon_r - 1/\varepsilon_{r,max})$ versus $\ln(T - T_C)$ at some temperature above T_C to obtain a straight line, the gradient of which is γ . Equation 2.17 may be rewritten in the form of $y = mx + c$ as shown by Equation 2.18 [68].

$$\log\left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_{r, \max}}\right) = \gamma \log(T_0 - T_C) + \log G$$

Equation 2.18

T = Curie-Weiss Temperature

$\epsilon_{r, \max}$ = Maximum relative permittivity

T_c = Curie temperature

γ = Curie-Weiss coefficient

C = Curie-Weiss constant

G = Fitting coefficient

ϵ_r = Relative permittivity

It should be noted diffuse phase transitions and corresponding $\epsilon_{r, \max}$ are not typically associated with macroscopic, coherent long-range polarisation associated with ferroelectricity [68]. To better represent this fact, T_C is more appropriately labelled as T_m for RFEs with respect to CW law and associated equations described above [68]. The identification of a diffuse T_m and a deviation from CW law are critical in the classification of RFEs to a) identify the presence of PNRs and b) quantify the degree of disorder (diffuseness) that give RFEs their strong capacitive (energy storage) and piezoelectric properties.

Commercial interest has progressed beyond perovskite-based classical ferroelectrics and RFEs such as BaTiO_3 to $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), BiFeO_3 (BF), and $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT), owing to their higher relative permittivities (ϵ_r) and transition temperatures (T_c or T_m) [7]. However, besides environmental obstacles associated with lead and bismuth containing perovskites, they are also compositionally incompatible with MLCCs employing nickel or copper base metal electrodes (BMEs) due to redox reactions during manufacturing when cofiring with BMEs at high temperature within a reducing atmosphere [15]. Consequently, interest has now extended beyond perovskites to the more complex and compositionally versatile, yet relatively poorly understood, bismuth- and lead-free tetragonal tungsten bronzes (TTBs) [16].

2.6 Tetragonal Tungsten Bronze (TTBs) Structure and Stoichiometry

The TTB structure can be derived by transforming a layer or perovskite units (*i.e.* a layer of multiple perovskite cubic structures shown in section 2.5.1, Figure 2.10) [50, 80], illustrated in schematic diagram by Gardner [50] and Ngai *et al.* [80] shown in Figure 2.14a – d. Four octahedral units (purple in Figure 2.14a) are rotated about 45° (Figure 2.14b), leading to the formation squared, pentagonal and trigonal channels characteristic to the TTB structure (Figure 2.14c), ultimately leading to the $P4/mbm$ tetragonal aristotype (Figure 2.14d). The TTB structure is described in further detail below.

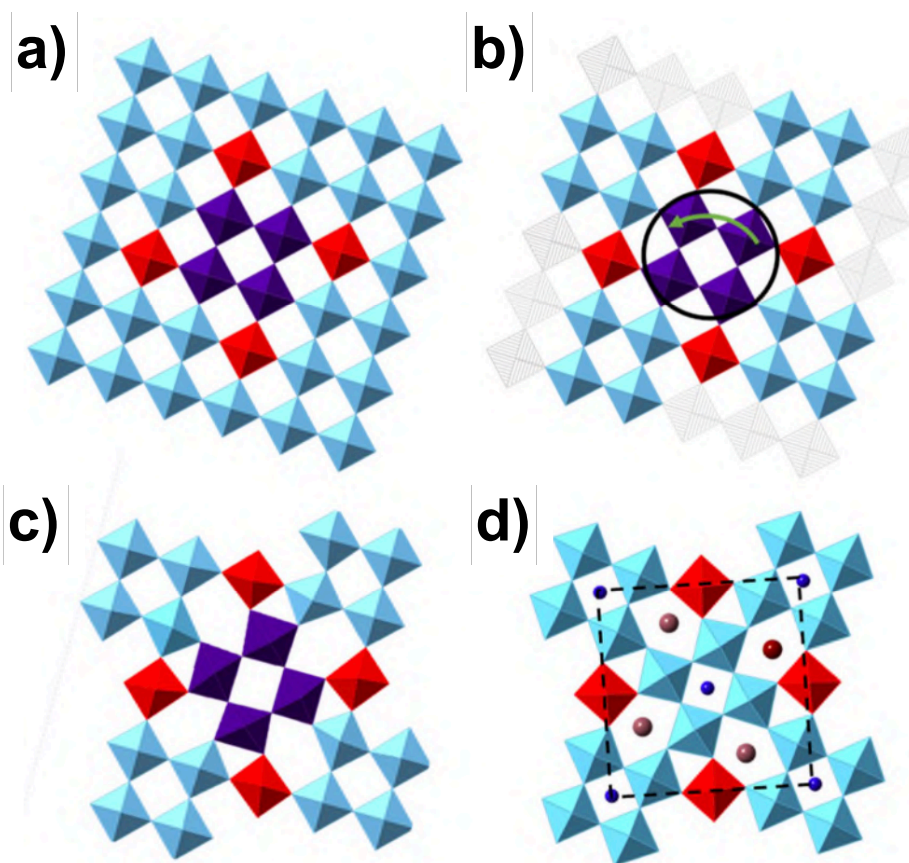


Figure 2.14a – d: The structural evolution to form the a) $P4/mbm$ tetragonal aristotype from a layer of cubic perovskite units, starting from b) an anticlockwise rotation of the central four octahedra leading to c) the TTB structure and d) the outlined $P4/mbm$ aristotype taken from Gardner [50] (adapted from Ngai *et al.* [80]).

Tetragonal tungsten bronzes (TTBs) have a general formula of $(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$, where there is a main framework comprising of corner sharing BO_6 octahedra [81-85]. Such octahedra are tilted about the c direction, interconnected at their apex in this direction and by their corners in the ab plane [86, 87], reducing overall symmetry relative to perovskites [88]. The aristotype high symmetry TTB parent structure is shown in Figure 2.15a – b [50, 89].

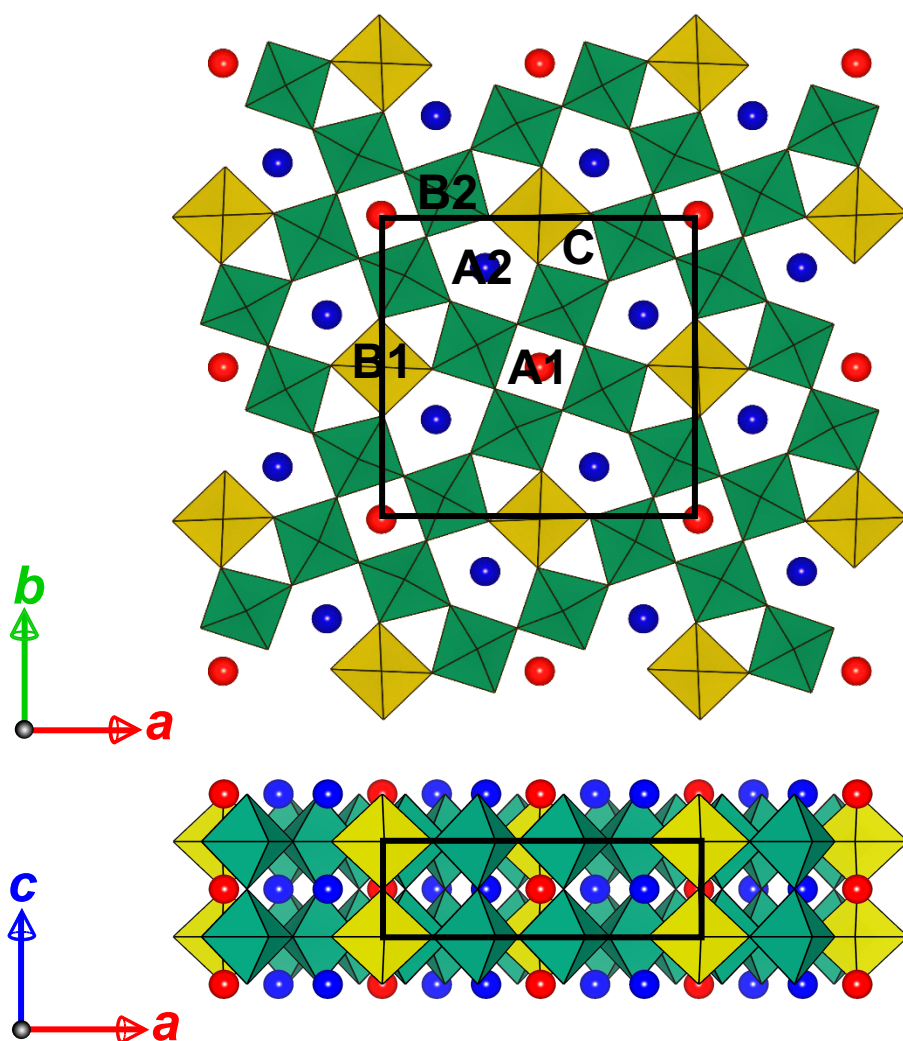


Figure 2.15a – b: Tetragonal tungsten bronze (TTB) aristotype space group $P4/mbm$: a) viewed along the c direction and; b) viewed along the b direction with A1 (red), A2 (blue) sites labelled alongside B1 (yellow) and B2 (green) oxygen octahedra, reproduced after Gardner [50, 89].

The octahedral framework gives rise to of the square 12 – coordinated (A1), pentagonal 15 – coordinated (A2) and trigonal 9 – coordinated (C) sites [90], alongside non-equivalent B sites, B1 and B2 [3]. B2 sites are perovskite like units $[(B2)O_6]$, four of which are arranged corner to corner to form the square A1 site in between, *i.e.* $A1(B2)O_6$ [50]. These units are linked by crystallographically distinct $(B1)O_6$ octahedra, which pack with the $(B2)O_6$ octahedra to form the A2 site in between [50]. TTBs can be categorized as having three stoichiometries; “stuffed”, “filled” or “unfilled”. Stuffed TTBs have all A, B and C cation sites fully occupied (*e.g.* $K_3Li_2Nb_5O_{15}$). Filled TTBs and unfilled TTBs both have fully occupied B cation sites and vacant C cation sites [91].

A distinction can be drawn between filled and unfilled TTBs, where all A cation sites are fully occupied in filled TTBs (*e.g.* $Sr_2NaNb_5O_{15}$ [SNN1]), while 5 out of 6 are A sites occupied in unfilled TTBs (*e.g.* $Sr_xBa_{1-x}Nb_2O_6$ [SBN]) [91]. The A1 site is perovskite-like [92], and is crystallographically distinct from the larger A2 site which can accommodate larger cations with the presence of differently sized ionic radii [89]. The *c* directional open channels (A1 and A2) in the *ab* plane allow for a variety of metal cations to be doped into the A sites [90]. Non-equivalent A and B sites in TTBs contribute to enhanced levels of flexibility when modifying composition by doping [93, 94].

2.6.1 Superstructures, Commensurate, and Incommensurate Modulations of Pseudo – Tetragonal Tungsten Bronzes (Pseudo – TTBs)

TTBs have a tetragonal centrosymmetric $P4/mbm$ aristotype structure where $a = b \approx 12.5 \text{ \AA}$ and $c \approx 4 \text{ \AA}$ [89, 95]. Orthorhombic distortion of TTBs presents as an expansion of the *ab* plane (where $\sqrt{2} a_{tet} = a_{ortho}$ and $2\sqrt{2} b_{tet} = b_{ortho}$), though *a*, *b* and/or *c* can also double further [89, 96]. The doubling of *a*, *b* and/or *c* in TTBs have resulted in various orthorhombic space groups being reported, expressed with respect to the $P4/mbm$ tetragonal (TTB) aristotype, where the most reported orthorhombic space groups are:

<i>Ama2</i> [18, 97, 98] where	$\sqrt{2} a_{\text{tet}} = a_{\text{ortho}}, 2\sqrt{2} b_{\text{tet}} = b_{\text{ortho}}, 2c_{\text{TTB}} = c_{\text{ortho}}$
<i>Ima2</i> [82, 99, 100] where	$\sqrt{2} a_{\text{tet}} = a_{\text{ortho}}, \sqrt{2} b_{\text{tet}} = b_{\text{ortho}}, 2c_{\text{TTB}} = c_{\text{ortho}}$
<i>Cmm2</i> [101-103] where	$2\sqrt{2} a_{\text{tet}} = a_{\text{ortho}}, 2\sqrt{2} b_{\text{tet}} = b_{\text{ortho}}, c_{\text{TTB}} = c_{\text{ortho}}$

The expansion of the *P4/mbm* TTB aristotype (Figure 2.16a) to such orthorhombic structures are shown in Figure 2.16b, which result from a $\sqrt{2}$ expansion of *a* and *b* and a rotation about 45° [85].

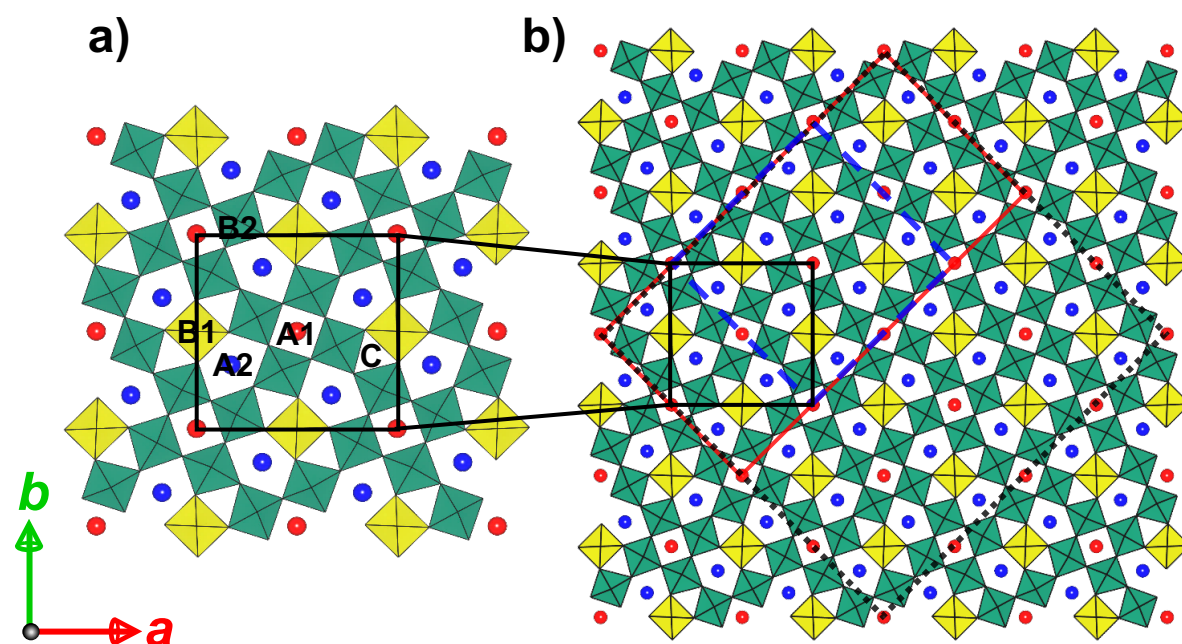
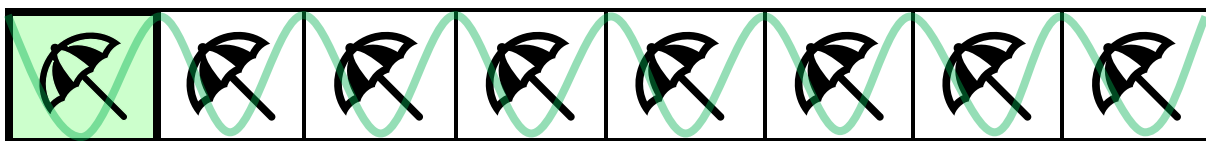


Figure 2.16a – c: Tetragonal tungsten bronze (TTB) aristotype space group *P4/mbm*: a) viewed along the [001] direction with A1 (red), A2 (blue) sites labelled alongside B1 (yellow) and B2 (green) oxygen octahedra, reproduced after Gardner [50, 89] and; b) an expanded view along [001] with possible pseudo-TTB orthorhombic space groups, *Ima2* (blue, dashed), *Ama2* (red) and *Cmm2* (black dotted) viewed along the *c* axis.

A distortion from a tetragonal (point group *4mm*) to orthorhombic (point group *mm2*) space group is relatively subtle owing to the rigidity of the octahedral framework in TTBs [85, 104, 105]. High-resolution diffraction patterns obtained from synchrotron X-ray radiation sources can help elucidate such distortions [85, 89, 104-106]. Orthorhombic TTBs occurring from the expansion of *a*, *b*, and/or *c* with respect to the aristotype *P4/mbm* unit cell (*i.e.* an orthorhombic distortion) arise from octahedral

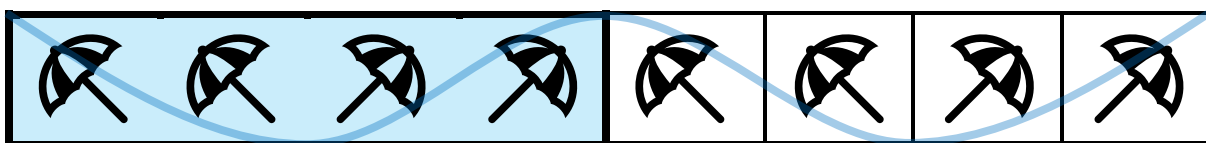
tilting out of the ab plane [85, 107-117], where the oxygen anions show the most significant displacement [113]. The tilting of octahedra contributes to orthorhombic distortion, leading to implications on the coherence of the long-range ferroelectric polarisation along c (the polar axis), ultimately affecting ϵ_r at T_c (or T_m). A schematic of a periodic crystal is illustrated in Figure 2.17a, where a singular unit cell represents the variation of the asymmetric unit (umbrella in Figure 2.17a) [118].

a) Periodic



b) Commensurate Modulation

(i.e. $q = 0.25a^*$)



c) Incommensurate Modulation

(i.e. $q = 0.29a^*$)

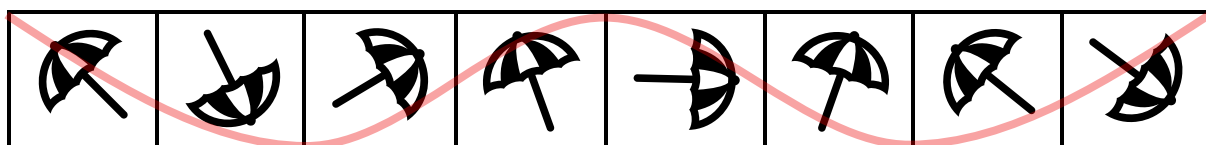


Figure 2.17a – c: A schematic representation of a) periodic crystal lattice and the two types of modulated crystal lattice where b) a commensurate modulation and b) an incommensurate modulation, where the umbrella illustration represents the asymmetric unit (i.e. octahedra in perovskites or TTBs). The boldened box represents the unit cell where the unit cell in b) is a supercell. This was reformatted and reproduced with permission of the International Union of Crystallography after Lovelace *et al.* [118].

Commensurately and incommensurately modulated crystals can be differentiated by wave vector, q , through the spacing of the satellite reflection with regard to the main reflection [118]. In commensurate modulations, all q vector components are rational (i.e. $q = 0.25a^*$ or $\frac{1}{4}a^*$ in Figure 2.17b). Here, the commensurately modulated crystal

system exhibits translational symmetry (varying through four unit cells, boldened box, Figure 2.17b) akin to that of an ideal crystal system, represented by a supercell (boldened box, Figure 2.17b) [119]. However, in the incommensurate case, at least one component is irrational (*i.e.* $q = 0.29a^*$ in Figure 2.17c) [118] and thus has no translational symmetry or long-range periodicity and therefore is unable to be described by a superlattice [119]. There is no repetition of the asymmetric unit (umbrella in Figure 2.17c) in adjacent unit cells and a superlattice can't be defined [118].

2.6.2 Ferroelectricity in TTBs

The origin of ferroelectricity in TTBs resembles that of the classic case of BaTiO_3 perovskite, described in section 2.5.1. Crucially, for a material and indeed a TTB, to be ferroelectric, the structure must be non-centrosymmetric with a polar space group [50]. In TTBs, the aristotype space group ($P4/mbm$) is paraelectric, centrosymmetric and non-polar [18]. Synonymous with BaTiO_3 , the off-centering of B cations along the c -axis is the driver for the ferroelectric effect in TTBs [18]. The loss of the mirror plane of the $P4/mbm$ aristotype perpendicular to the polar c -axis at the T_c phase transition is a result of such B-site cation displacements [50]. In this sense, TTBs are examples of displacive ferroelectrics solely along c [18]. However, A site cation displacements in the ab plane have also been reported for Pb-based TTBs such as PbNb_2O_6 [18, 120-122]. Cooling through T_c leads to a phase transition from the paraelectric centrosymmetric $P4/mbm$ space group (point group $4/mmm$) to the ferroelectric non-centrosymmetric $P4bm$ space group (point group $4mm$), or perhaps even an orthorhombic space group (point group $mm2$) [123].

2.7 Literature Review

2.7.1 Materials of Study: $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN1) and $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN)

In this thesis, two strontium niobate-based TTBs have been studied. The first is the filled TTB; strontium sodium niobate ($\text{Sr}_2\text{NaNb}_5\text{O}_{15}$), abbreviated to SNN1 herein, where the “1” denotes the stoichiometry of sodium (Na). In the ideal

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$(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$ filled TTB structure described in section 2.6., Sr^{2+} (1.44 Å, CN = XII [22]) occupies the larger A2-sites, Na^+ (1.39 Å, CN = XII [22]) occupies the A1-sites, and Nb^{5+} (0.64 Å, CN = VI [22]) occupies the B-sites, where cationic radii used here, are taken after Shannon [22] and CN denotes coordination number. However, mixed occupancy of Sr^{2+} and Na^+ in both A1 and A2-sites is likely probable due to their similar ionic radii [82]. SNN1 has attracted recent interest, owing to its high relative ϵ_r and P_{max} combined with a low $\tan\delta$ over a wide temperature range [124] for temperature stable capacitor applications. SNN1 is characterised by two distinct dielectric anomalies: a) a ferroelastic to ferroelectric transition temperature (T_1) and b) a ferroelectric to paraelectric transition at higher temperature (T_2 or the Curie temperature, T_c) [125].

The second material of study is the unfilled TTB strontium barium niobate ($Sr_{0.53}Ba_{0.47}Nb_2O_6$ or $Sr_{1-x}Ba_xNb_2O_6$) abbreviated to SBN herein. The key difference compared to SNN1 is the lack of volatile Na^+ ; the absence of which can significantly improve sample density during high-temperature ceramic processing [126], offering a structurally related alternative to SNN1. In SBN, 5/6 of the A sites are occupied (1/6 A-site vacancies), where Ba^{2+} (1.61 Å, CN = XII [22]) solely occupies the A2-sites and Sr^{2+} (1.44 Å, CN = XII [22]) occupies *both* the A2-sites and A1-sites [127-129]. Indeed, SBN is an example of a RFE, characterised by a singular, diffuse, frequency dependent dielectric anomaly, at the temperature of ϵ_r maximum, T_m . SBN has been proposed as viable temperature stable capacitor material [126].

A large body of literature is dedicated to SNN1 and SBN, with an emphasis on A-site, B-site, and A- and B-site co-doping structure-dielectric property relationships. Indeed, TTBS like SNN1 and SBN present an exciting opportunity for application as temperature stable MLCC dielectric ceramic materials, owing to their promising capacitance (*e.g.* energy storage), dielectric performance, *and* temperature stability [17]. Several studies have principally focused on maximising high recoverable energy densities (W_{rec}) and energy efficiencies (η); by increasing the maximum polarisation (P_{max}) and breakdown strength (E_b), whilst reducing remnant polarisation, (P_{rem}) [21].

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Despite encouraging results regarding dielectric performance characteristics of SNN1 and SBN (described below), current research continues to focus primarily on their empirical optimisation by maximising capacitance/energy storage capabilities experimentally *via* A and/or B site co-doping. However, the vital underlying structure-dielectric property relationships remain descriptive in nature and a richer crystallographic understanding of the role of minor A- and B-site dopant substitution remains to be realised.

The dielectric properties affected by the doping of SNN1 are the relative permittivity (ϵ_r) values at the low temperature relaxor transition temperature (T_1) and the ferroelectric to paraelectric transition at higher temperature (T_2) (*i.e.* ϵ_r at T_1 and T_2) and its behaviour in between, as well as the transition temperatures themselves. Likewise, the dielectric properties affected for doped SBN are the temperature of permittivity maxima (T_m) and ϵ_r at T_m . Doping presents an opportunity to establish control over the temperature of transition temperatures (*i.e.* T_1 , T_2 [SNN1] and T_m [SBN]) and the value of ϵ_r at such transition temperatures.

Compositions with a sharp T_c (as is the case with SNN1, *i.e.* T_2) typically present one (or more) low temperature relaxor-like dielectric anomalies (*i.e.* T_1 in SNN1). Through increasing disorder [130] *via* doping, T_c may evolve to more relaxor-like and ultimately convolute with the low temperature relaxor-like peak to form a large frequency dispersed ϵ_r at T_m becoming a strong RFE [82, 85, 108, 130, 131]. The implications of the transition to an RFE contributes to the stability of the ϵ_r temperature profile, improving capacitive performance *and* temperature stability for use in temperature stable capacitors. Developing an understanding of the structure-property relationships that drive the dielectric performance characteristics of SNN1 and SBN will set a basis for facilitating the application of doped SNN1 and SBN for MLCCs. This literature review will draw upon recent published research on B-site, A-site, and A- and B-site co-doping effects on the structure-property relationships of SNN1, SBN and closely related TTBs.

2.7.2 A-site Doping

A-site doping forms a large part of the TTB literature and has been discussed at great length. The Goldschmidt tolerance factor, t , [132] is used in perovskite systems to quantify their structural stability [133]. Likewise, this has been applied to TTBs by Wakiya *et al.* [133] to account for the distinct A1 (Equation 2.19) and A2 (Equation 2.20) tolerance factors, t_{A1} and t_{A2} , respectively on TTB structural stability. The two equations (t_{A1} [Equation 2.19] and t_{A2} [Equation 2.20]) are combined to form a modified TTB tolerance factor, t_{TTB} (Equation 2.21). Notably, t_{A1} is the same as that proposed by Goldschmidt [132] for perovskites. However, TTBs are more structurally complex than perovskites due to their enhanced compositional versatility [89]. A consequence of such versatility is the resultant commensurate/incommensurate structural modulations of the TTB octahedral framework, driving different degrees of polar ordering length scales (e.g. short range PNRs for RFEs or long range, coherent polarisation for classical ferroelectrics) [106].

$$t_{A1} = \frac{(R_{A1} + R_O)}{\sqrt{2} (R_B + R_O)} \quad \text{Equation 2.19}$$

$$t_{A2} = \frac{(R_{A2} + R_O)}{\sqrt{23-12\sqrt{3}} (R_B + R_O)} \quad \text{Equation 2.20}$$

t_{A1} = A1-site tolerance factor
 t_{A2} = A2-site tolerance factor
 t_{TTB} = TTB tolerance factor
 R_{A1} = Cationic radii of A1 ions
 R_{A2} = Cationic radii of A2 ions
 R_O = Anionic radii of O ions

$$t_{TTB} = \frac{(R_{A1} + 2R_{A2})}{3} \quad \text{Equation 2.21}$$

Meanwhile Zhu *et al.* [107] report a crystal-chemical framework for relaxor versus normal ferroelectric behaviour in TTBs, achieved by plotting the average A site ionic radii ($[A1+A2]/2$) versus the A1 site tolerance factor. The A1 tolerance factor (t_{A1}) has been previously reported as being the driving force for octahedral tilting in Sr/Ba-based complex perovskites by Reaney *et al.* [134]. If the ionic radii of the A site species are too small to occupy the available volume, it is suggested that the octahedra tilt and

rotate to reduce the cuboctahedra interstices within the oxygen sub-lattice. Zhu *et al.* [107] also state that a low A1 tolerance factor promotes commensurate tilting and normal ferroelectric behaviour. Meanwhile, they propose that an increase in the average A site ionic radius ($[A1+A2]/2$) stretches the O-B-O bond length, increases dielectric polarizability and promotes long-range ferroelectric coupling. In between these two competing crystal-chemical factors, they predict that relaxor behaviour dominates through an incommensurate modulation.

Stennett and co-workers [135, 136] investigated the $Ba_2MTi_2Nb_3O_{15}$ (where $M = Bi^{3+}$, La^{3+} , Nd^{3+} , Sm^{3+} , and Gd^{3+}) and $Ba_2MTi_2X_3O_{15}$ (where $M = Bi^{3+}$, La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , and Dy^{3+} ; $X = Nb^{5+}$, Ta^{5+}) systems, where T_c increased with decreasing A1-site M^{3+} cation radii. Larger Bi^{3+} and La^{3+} dopants ($> 1.3 \text{ \AA}$), had an incommensurate modulation of the octahedral framework, exhibiting RFE behaviour [135, 136]. Smaller rare earth dopants ($< 1.3 \text{ \AA}$), however, were commensurate, showing classical ferroelectric character [135, 136]. For the unfilled TTB, $Ba_4R_{0.67}\square_{1.33}Nb_{10}O_{30}$ (where $R = La^{3+}$, Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , and Y^{3+}) system, studied by Gardner *et al.* [89], increasing R^{3+} cation radii, decreased tetragonality and thus increased T_c . Levin *et al.* [108] reported that RFE behaviour couples to the incommensurate modulation, while classical ferroelectric behaviour couples to the commensurate modulation, both of which are driven by the average A1-site rare earth cation radius in agreement with Zhu *et al.* [107].

For the unfilled TTB $Sr_{1-x}Ba_xNb_2O_6$ (SBN), Sr-rich compositions ($x < 0.5$) are relaxor-ferroelectrics whilst Ba-rich compositions are classical ferroelectrics [60, 107, 137, 138]. $Ba_xSr_{1-x}Nd_2Ti_4Nb_6O_{30}$ (where $x=0, 0.2, 0.4, 0.6$, and 1) reported by Zhu *et al.* [139] suggested a larger A1/A2 site size difference (*i.e.* increased amounts of larger Ba^{2+} cations), facilitated incommensurate octahedral tilting, stabilising PNRs and driving RFE behaviour [139]. Similarly, Gardner *et al.* [106] reported a gradual onset of RFE character for $x \geq 2$ in the $Ba_{4-x}Sr_xDy_{0.67}\square_{1.33}Nb_{10}O_{30}$ “empty” TTB system (where $x = 0, 0.25, 0.5, 1, 2$, and 3) where T_c decreased with x . Other A-site dopants have been introduced into the TTB system, such as Bi^{3+} [140, 141], Ag^{2+} [142] and varying singular rare earths, primarily in the context of optical properties [143-145].

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The most popular A-site dopant in SNN1 is the smaller Ca^{2+} (1.34 Å, CN = XII [22]) cation for Sr^{2+} (1.44 Å, CN = XII [22]), with early studies dedicated to the synthesis and characterisation of Ca^{2+} doped SNN1 [146-148]. $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$ (where $x = 0.05, 0.1, 0.2, 0.25, \text{ and } 0.3$) reported by Wei *et al.* [149] showed a decrease in tetragonality (c/a ratio), and a decrease in the unit cell volume with increasing Ca^{2+} content. This same study also reported an increase in the low temperature relaxor-like transition temperature (labelled as T_e in this publication where $T_e \sim -10^\circ\text{C}$, [$x = 0.05$] to $T_e \sim 36^\circ\text{C}$ [$x = 0.3$]) and T_c ($T_c \sim 285^\circ\text{C}$ [$x = 0.05$] to $T_c \sim 305^\circ\text{C}$ [$x = 0.3$]) with increasing Ca^{2+} content [149] at 1 kHz. Relative permittivity values were highest at $x = 0.15$ for both ϵ_{me} (ϵ_r at T_e) and ϵ_m (ϵ_r at T_c) at 1650 and 1954 at 1 kHz respectively, decreasing with increasing x , however ϵ_r at T_c drastically decreased relative to ϵ_r at T_e [149].

These observations are supported by Xie *et al.* [150] in the $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$ ($x = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, \text{ and } 0.35$) system. The relaxor-like low temperature anomaly (T_e) and T_c increased with x where $T_e \sim -11^\circ\text{C}$ ($x = 0.05$) and $T_s \sim 2^\circ\text{C}$ ($x = 0.35$), whilst $T_c \sim 279^\circ\text{C}$ ($x = 0.05$) and $T_c \sim 297^\circ\text{C}$ ($x = 0.35$) with ϵ_r at T_c decreasing by 60 % (ϵ_r at $T_c \sim 1353$ [$x = 0.05$] to 543 [$x = 0.35$]) at 1 kHz. A similar study on the $(1-x)\text{Sr}_2\text{NaNb}_5\text{O}_{15}-x\text{Ca}_2\text{NaNb}_5\text{O}_{15}$ by the same author [151] also reported identical trends in T_s ($T_s \sim -11^\circ\text{C}$ [$x = 0.05$] and $T_s \sim 2^\circ\text{C}$ [$x = 0.35$]), T_c ($T_c \sim 279^\circ\text{C}$ [$x = 0.05$] and $T_c \sim 297^\circ\text{C}$ [$x = 0.35$]) with ϵ_r at T_c reduced by 60 % from $x = 0.05$ to $x = 0.35$ at 1 kHz. In both these studies [150, 151], ϵ_r at T_s varies minimally relative to ϵ_r at T_c , suggesting Ca^{2+} doping primarily affects the ferroelectric-paraelectric transition, T_c . This is attributed to a reduced unit cell volume limiting the degree to which the B cation can shift along c . That is to say, the degree of spontaneous polarisation is limited by the compression of c in the unit cell(s) induced by the presence of Ca, reducing ϵ_r at T_c [152].

Doping Na^+ in the $(\text{Sr}_{0.925}\text{Ca}_{0.075})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ($x = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, \text{ and } 1.0$, *i.e.* going from unfilled to filled TTB) system increased T_c and the low temperature dielectric anomaly (labelled T_s in this publication) with increasing x ($T_s \sim -67^\circ\text{C}$ [$x = 0.4$] and $T_s \sim 51^\circ\text{C}$ [$x = 1.0$] whilst $T_c \sim 260^\circ\text{C}$ [$x = 0.4$] and $T_c \sim 306^\circ\text{C}$ [$x = 1.0$])

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[153]. ϵ_r at T_c increased with x up to $x = 0.8$ (ϵ_r at $T_c \sim 1300$) while ϵ_r at T_s steadily increased from $x = 0.4$ (ϵ_r at $T_s \sim 1196$) to $x = 1.0$ (ϵ_r at $T_s \sim 1748$) at 10 kHz. This suggests a transition from an unfilled to filled TTB facilitates the structural distortion of the octahedral framework by reducing A-site vacancies [153]. The depreciation of the dielectric properties $x > 0.8$ was attributed to the formation of a $\text{Na}_{0.5}\text{Sr}_{0.25}\text{NbO}_3$ secondary perovskite phase [153].

Major A-site doping (e.g. $x = > 0.05$ in $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$) increases both the relaxor-like low temperature dielectric anomaly (labelled as T_1 in this thesis) and T_c . This insight, however, becomes more nuanced when evaluating T_c between larger (La^{3+} [$> 1.3 \text{ \AA}$]) and smaller (Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} and Dy^{3+}) rare earths A-site dopants. The crystal-chemical framework proposed by Zhu *et al.* [107] rationalises the effect of A-site cation dopant size with two key parameters ($([A1+A2]/2)$ and t_{A1}):

- i. average A-site cationic radii, $([A1+A2]/2)$, where an increase stretches the O-B-O bond length, favouring commensurate tilting (classical ferroelectric behaviour).
- ii. A1-site tolerance factor, t_{A1} , where a low tolerance factor promotes commensurate tilting (classical ferroelectric behaviour).

When neither $(A1+A2)/2$ and t_{A1} dominate, incommensurate tilting is facilitated, associated with RFE behaviour arising from chemical disorder and ultimately a frequency dependent dielectric anomaly, T_m . The crystal chemical framework of Zhu *et al.* [107], whilst relevant to a broad range of TTB systems, does not consider vacancies in calculations of R_{A1} and R_{A2} . Moreover, the role of minor A-site doping is an area of emerging interest greatly affecting dielectric properties, and using the framework of Zhu *et al.* [107] it is unlikely significant changes in $(A1+A2)/2$ versus t_{A1} will be observed, hence presenting an alternative avenue to induce RFE-behaviour which is lesser understood. Taken together, this suggests A-site doping does not directly affect B cation polarisation but affects the coherence of the ferroelectric ordering *via* octahedral tilting, which is facilitated by disorder, hence affecting transition

temperatures T_1 , T_c (or T_m in the case of RFEs) and ultimately their suppression for a temperature stable response.

2.7.3 B-site Doping

Sole B-site doping and its effect on ferroelectric properties in TTBs is a lesser explored avenue in the literature [154]. T_c is typically associated with classical ferroelectrics, while T_m is concomitant with RFEs, however for the similar systems (see below) T_c and T_m are, unfortunately, interchangeably used (*i.e.* T_c [T_m] in reference [154]). For the $\text{Ba}_3\text{M}^{4+}\text{Nb}_4\text{O}_{15}$ system ($\text{M} = \text{Ti}^{4+}$ [0.61 Å, CN = VI], Sn^{4+} [0.69 Å, CN = VI], or Zr^{4+} [0.72 Å, CN = VI], radii taken after Shannon [22]), T_c was shown to decrease with increasing M^{4+} ionic radius (Ti^{4+} [$T_c \sim 180^\circ\text{C}$], Sn^{4+} [$T_c \sim 10^\circ\text{C}$], Zr^{4+} [$T_c \sim -30^\circ\text{C}$]) whilst also increasing the unit cell volume [104]. Likewise, for the $\text{Ba}_3\text{M}^{4+}\text{Nb}_4\text{O}_{15}$ system (where $\text{M} = \text{Ti}^{4+}$, or Zr^{4+} or Hf^{4+}) studied by Chi *et al.* [155] the same trend in decreased T_c with increasing ionic radii was reported (Ti^{4+} [$T_c \sim 230^\circ\text{C}$], Zr^{4+} [$T_c \sim 70^\circ\text{C}$], Hf^{4+} [$T_c \sim 25^\circ\text{C}$]). Conflictingly, for the $3+$ B-site cation analogue, $\text{Ba}_3\text{M}^{3+}\text{Nb}_{4.5}\text{O}_{15}$ (where $\text{M} = \text{Ga}^{3+}$, Sc^{3+} , or In^{3+}), T_m decreased with decreasing M^{3+} ionic radii (Ga^{3+} [$T_m \sim -193^\circ\text{C}$] to In^{3+} [$T_m \sim 37^\circ\text{C}$]) [154].

The conflicting trends from M^{3+} and M^{4+} cation radii is rationalised by considering the degree of tetragonal distortion, namely tetragonality (c/a) [104, 154]. Increased tetragonal distortion stabilises the ferroelectric displacement of the central metal B-site (*e.g.* M^{3+} and M^{4+} in $\text{Ba}_3\text{M}^{4+}\text{Nb}_4\text{O}_{15}$ and $\text{Ba}_3\text{M}^{3+}\text{Nb}_4\text{O}_{15}$ respectively [104, 154]) along the c axis, lowering T_c (T_m) [154]. Both systems exhibit relaxor behaviour due to the disordered distribution of $\text{M}^{3+}/\text{M}^{4+}$ and Nb^{5+} on the B-sites, leading to local compositional inhomogeneity, disrupting long range ferroelectric polar ordering [154]. Likewise, in the similar $\text{Ba}_2\text{RTi}_2\text{Nb}_3\text{O}_{15}$ system ($\text{R} = \text{Bi}^{3+}$, La^{3+} , Nd^{3+} , Sm^{3+} , and Gd^{3+}) reported by Stennett *et al.* [136] the disorder of Ti^{4+} and Nb^{5+} on the B-sites has been reported to possibly contribute to relaxor-like behaviour [136, 156].

Based on the above observations, recent studies have exploited the use of chemical doping (*e.g.* Zr^{4+} for Nb^{5+} on the B-sites) to tune dielectric properties in pursuit of high

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energy density MLCCs. Successful doping of isovalent Sb^{5+} (0.60 Å, CN = VI [22]) for Nb^{5+} (0.64 Å, CN = VI [22]) to invoke B-site disorder, has been shown to induce relaxor behaviour [157, 158]. Increasing Sb^{5+} content in $(\text{Ca}_{0.28}\text{Ba}_{0.72})_{2.1}\text{Na}_{0.8}\text{Nb}_{5-x}\text{Sb}_x\text{O}_{15}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$, and 1.0), $\text{Sr}_2\text{NaNb}_{5-x}\text{Sb}_x\text{O}_{15}$ ($x = 0.0, 0.3, 0.5$, and 1.0), and $\text{Sr}_2\text{Ag}_{0.2}\text{Na}_{0.8}\text{Nb}_{5-x}\text{Sb}_x\text{O}_{15}$ ($0, 0.1, 0.2, 0.3, 0.4$, and 0.5) decreased T_c , and reduced the unit cell volume [157-159]. For $(\text{Ca}_{0.28}\text{Ba}_{0.72})_{2.1}\text{Na}_{0.8}\text{Nb}_{5-x}\text{Sb}_x\text{O}_{15}$, T_c decreased from 350 °C (ϵ_r at $T_c \sim 2500$) when $x = 0$, to 60 °C (ϵ_r at $T_c \sim 920$) when $x = 1.0$ [157]. T_c in $\text{Sr}_2\text{NaNb}_{5-x}\text{Sb}_x\text{O}_{15}$ decreased from 302 °C (ϵ_r at $T_c \sim 1200$) when $x = 0$, to -73 °C (ϵ_r at $T_c \sim 650$) when $x = 1.0$ [158]. Finally, for the $\text{Sr}_2\text{Ag}_{0.2}\text{Na}_{0.8}\text{Nb}_{5-x}\text{Sb}_x\text{O}_{15}$, T_c decreased from 291 °C ($x = 0$) to -49 °C ($x = 0.4$) [159].

In the case of $\text{Sr}_2\text{NaNb}_{5-x}\text{Sb}_x\text{O}_{15}$ ($x = 0.0, 0.3, 0.5$, and 1.0), and $\text{Sr}_2\text{Ag}_{0.2}\text{Na}_{0.8}\text{Nb}_{5-x}\text{Sb}_x\text{O}_{15}$ ($0, 0.1, 0.2, 0.3, 0.4$, and 0.5) the low temperature dielectric anomaly (labelled T_m and T_s in each study respectively), namely the low temperature, RFE-like transition temperature, labelled T_1 throughout this thesis, shifts to lower temperatures [158, 159]. Similarly, aliovalent Zr^{4+} doping in the $(\text{Sr}_{0.485}\text{Gd}_{0.03}\text{Ba}_{0.47})\text{Nb}_{2-x}\text{Zr}_x\text{O}_6$ system (where $x = 0, 0.1, 0.2$, and 0.3) decreased tetragonality, reducing T_m [160]. Indeed, for the single Zr^{4+} doped SNN1 system $(\text{Sr}_2\text{NaNb}_{5-4y}\text{Zr}_{5y}\text{O}_{15})$ where $y = 0.01$ and 0.02) reported by Brown [49], T_c (or T_2 as reported by Brown [49])³ decreases ($T_c \sim 285$ °C, ϵ_r at $T_c \sim 1743$ [$x = 0.01$] and $T_c \sim 257$ °C, ϵ_r at $T_c \sim 1743$ [$x = 0.02$]) but the unit cell volume exhibits no change.

Besides Zr^{4+} , another B-site dopant attracting recent interest is Ta^{5+} , with the motivation remaining true to recent trends in the literature – inducing relaxor behaviour to boost energy density performance of MLCCs. The disordered distribution of Ta^{5+} and Nb^{5+} increases disorder on the B-site, breaking long range ferroelectric polar ordering, and inducing relaxor behaviour [17]. Relevant compositions studied include: $\text{Sr}_2\text{Na}(\text{Nb}_{1-x}\text{Ta}_x)_5\text{O}_{15}$ (where $x = 0, 0.1, 0.2, 0.25$, and 0.5) [161], $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (where $x = 0, 0.05, 0.1, 0.15, 0.2, 0.3$, and 0.4) [17], $\text{Sr}_{1.88}\text{La}_{0.12}\text{NaNb}_{4.88-x}\text{Ta}_x\text{Ti}_{0.12}\text{O}_{15}$

³ It should be reiterated here that in some SNN1 literature, T_c is labelled as T_2 (ferroelectric to paraelectric transition temperature) to distinguish it from the second, low temperature RFE-like dielectric anomaly, T_1 , which, as seen in section 2.5.2 - 2.5.3, has been labelled T_s , T_e or confusingly, T_m .

(where $x = 0, 0.4, 0.6, 0.8$, and 1.0) [125] $\text{Sr}_{0.475}\text{Ba}_{0.475}\text{La}_{0.1}\text{Hf}_{0.1}\text{Ti}_{0.1}\text{Sb}_{0.2}\text{Ta}_x\text{Nb}_{1.6-x}\text{O}_6$ (where $x = 0, 0.1, 0.2$, and 0.3) [162], and $\text{Ba}_4\text{Sm}_2\text{Zr}_4(\text{Nb}_x\text{Ta}_{1-x})_6\text{O}_{30}$ ($x = 0, 0.3, 0.5, 0.7, 0.9$, and 1.0) [163]. In some compositions such as $\text{Sr}_{1.88}\text{La}_{0.12}\text{NaNb}_{4.88-x}\text{Ta}_x\text{Ti}_{0.12}\text{O}_{15}$ studied by Cao *et al.* [125], beyond $x = 0.4$ the T_c peak is lost, leaving solely a low temperature RFE-like dielectric anomaly, which may better be represented by T_m . These studies, however, all reach similar conclusions, where T_c (or T_m), tetragonality, and grain size decrease with increasing Ta^{5+} content. The identical cationic radii yet differing electronic configuration of Ta^{5+} ($0.64 \text{ \AA}$, CN = VI [22]) relative to Nb^{5+} ($0.64 \text{ \AA}$, CN = VI [22]) has led to discussions on the effects of the differing polarisability of the Ta – O bond weakening the octahedral framework [17, 161, 162]. Other studies reported by Zhu *et al.* [107] suggest the lowering of T_c (or T_m) to be caused by the lower polarizability of Ta^{5+} relative to Nb^{5+} [164, 165].

Hence, the role of B site dopants is two-fold in their effect on T_c (or T_m) and ϵ_r at T_c (or T_m). First, is a size effect where B site doping with cations of varying sizes, have been shown to affect the degree of tetragonality (c/a), where a large tetragonal distortion lowers T_c (T_m). As such, the ferroelectric polarisation along the polar axis (c axis), despite conflicting trends in M^{3+} and M^{4+} cationic radii, is stabilised. The introduction of differing sized cations also contributes to B-site disorder (*i.e.* Zr^{4+} [$0.72 \text{ \AA}$, CN = VI [22]] for Nb^{5+} [$0.64 \text{ \AA}$, CN = VI] [22]), which facilitates RFE behaviour. Secondly, there is also the consideration of polarizability, where despite size effects, a lower polarizability (*i.e.* Ta^{5+} or Zr^{4+} relative to Nb^{5+} [23]) of the B-site cation contributes to a lowering of ϵ_r at T_c (or T_m) and ultimately T_c (or T_m). Like the case of A-site dopants however, studies focus on major doping strategies, with minor doping effects receiving considerably less attention.

2.7.4 A- and B-site Co-doping

In the previous two sections, A-site doping was found to affect the degree of octahedral tilt and by extension the coherence of polar ordering along the polar axis (c axis) by using two parameters (average A-site cation radii $([A1+A2]/2)$ and t_{A1} proposed by Zhu *et al.* [107]). Incommensurate tilting was associated with RFE behaviour and commensurate tilting with classical ferroelectric behaviour. On the other hand, B-site

doping has a more direct role in ferroelectric polarisation *via* modulating tetragonality (c/a), facilitating the stabilisation of the ferroelectric polar mode along the polar axis (c axis), lowering T_c (or T_m). Moreover, lower polarizability of the B-site cation itself is also instrumental in reducing ϵ_r at T_c (or T_m) and ultimately T_c (or T_m). In both A- and B-site doping, A- or B-site disorder also contributed to the disturbance of long-range polar ordering, ultimately inducing RFE-behaviour. In the case of materials with both T_1 and T_c (as in SNN1) the facilitation of RFE-behaviour would allow for the control of T_1 and T_c and suppress their corresponding ϵ_r maxima to form a flat ϵ_r temperature response, which is beneficial for temperature stable capacitors. Combined, A- and B-site co-doping provides an opportunity to unify the above A- and B-site effects to further leverage RFE-behaviour.

Cao *et al.* [166] reported a $\text{Sr}_{2-x}\text{Gd}_x\text{NaNb}_{5-x}\text{Ti}_x\text{O}_{15}$ system (where $x = 0.05, 0.08, 0.12$, and 0.15) where ϵ_r at T_c was suppressed when $x \geq 0.08$, while the low temperature ferroelastic to ferroelectric transition temperature (not labelled in this publication, labelled as T_1 here for convenience) and T_c , increased with x ($T_1 \sim -50^\circ\text{C}$ [$x = 0.05$] to -100°C [$x = 0.15$] and $T_c \sim 275^\circ\text{C}$ [$x = 0.05$] to 150°C [$x = 0.15$] at 1 kHz). Similarly, the same author reported a $\text{Sr}_{2-x}\text{M}_x\text{NaNb}_{5-x}\text{Ti}_x\text{O}_{15}$ system (where $\text{M} = \text{La}^{3+}$ and Ho^{3+} and $x = 0.05, 0.08, 0.12$, and 0.15) which also showed a decrease in ϵ_r at T_c and T_c for both La^{3+} ($T_c \sim 200^\circ\text{C}$ [$x = 0.05$] to 150°C [$x = 0.15$] at 1 kHz) and Ho^{3+} doped ($T_c \sim 275^\circ\text{C}$ [$x = 0.05$] to 180°C [$x = 0.08$] at 1 kHz) compositions. However, the smaller dopant (Ho^{3+}) exhibited a complete suppression, and ultimately the disappearance of a distinct T_c peak, leaving solely the relaxor-like T_m peak.

Likewise the disappearance of T_c , was reported for the similar $\text{Sr}_{2-x}\text{Ho}_x\text{Na}_{0.8}\text{Ag}_{0.2}\text{Nb}_{5-x}\text{Ti}_x\text{O}_{15}$ ($x = 0.00, 0.10, 0.15, 0.20, 0.25$) system by Han *et al.* [167]. In these studies, the introduction of smaller Gd^{3+} ($1.107\text{ \AA}$, CN = IX [22]), La^{3+} ($1.36\text{ \AA}$, CN = XII [22]) or Ho^{3+} ($1.12\text{ \AA}$, CN = X [22]) for Sr^{2+} ($1.44\text{ \AA}$, CN = XII [22]) on the A sites, with Ti^{4+} ($0.605\text{ \AA}$, CN = VI [22]) doped for Nb^{5+} ($0.64\text{ \AA}$, CN = VI [22]) on the B sites led to the onset of RFE behaviour, evidenced by a reduction in P_{rem} and E_c from P - E hysteresis loops. Likewise the disappearance of T_c , was reported for the similar $\text{Sr}_{2-x}\text{Ho}_x\text{Na}_{0.8}\text{Ag}_{0.2}\text{Nb}_{5-x}\text{Ti}_x\text{O}_{15}$ ($x = 0.00, 0.10, 0.15, 0.20, 0.25$) system by Han *et al.* [167].

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In these studies, the introduction of smaller Gd^{3+} (1.107 Å, CN = IX [22]), La^{3+} (1.36 Å, CN = XII [22]) or Ho^{3+} (1.12 Å, CN = X [22]) for Sr^{2+} (1.44 Å, CN = XII [22]) on the A sites, with Ti^{4+} (0.605, CN = VI Å [22]) doped for Nb^{5+} (0.64 Å, CN = VI [22]) on the B sites led to the onset of RFE behaviour, evidenced by a reduction in P_{rem} and E_c from P - E hysteresis loops.

Other works on $\text{Sr}_{1.85-2x}\text{Ba}_{0.15+x}\text{Sm}_x\text{NaNb}_x\text{Nb}_{5-x}\text{O}_{15}$ (where $x = 0.005, 0.01, 0.015$, and 0.02), $\text{Sr}_{1.85-2x}\text{Ca}_{0.15+x}\text{Sm}_x\text{NaNb}_{5-x}\text{Hf}_x\text{O}_{15}$ ($x = 0, 0.02, 0.04$, and 0.05) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{Gd}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (where $x = 0, 0.1, 0.2, 0.3$, and 0.5) systems, have also demonstrated similar trends in T_c (or T_m) [20, 168, 169]. This is also true for the low temperature ferroelectric-ferroelastic transition (labelled T_s in [169]) in the aforementioned SNN1 based compositions [168, 169]. Doping with Bi^{3+} into the A-sites has also attracted recent attention, owing to the Bi $6s^2$ lone pair electron facilitating polarisation, akin to that of Pb^{2+} based TTBs [170, 171]. Compositions include $\text{Sr}_{2-x}\text{Bi}_x\text{NaNb}_{5-x}\text{Ti}_x\text{O}_{15}$ ($x = 0, 0.05, 0.1, 0.15, 0.2$, and 0.25), and $(\text{Sr}_{0.7}\text{Ba}_{0.3})_{2-x}\text{Bi}_x\text{NaNb}_{5-x}\text{Ti}_x\text{O}_{15}$ ceramics (where $x = 0.00, 0.10, 0.15, 0.20, 0.25$) which showed a decrease in T_c (or T_m) and increased RFE behaviour attributed to PNRs [172, 173]. However, the use of Bi^{3+} based (albeit lightly doped) TTBs is rendered moot due to performance-degrading redox reactions when co-fired with base metal electrodes (BMEs) in multilayer ceramic capacitor (MLCC) manufacturing as stated in Chapter 1 – Introduction [15].

Much of the literature has focused on compositionally tuning RFEs to maximise capacitive performance, typically termed energy storage in these works, through measurement of room temperature P - E hysteresis loops and subsequent charge-discharge analysis (*i.e.* W_{rec} , η). Few studies however, have gone beyond the permittivity temperature evolution to consider the temperature stability of energy storage properties. Yang *et al.* [20] reported a Gd^{3+} and Ta^{5+} co-doped SBN system ($\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{Gd}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$) with a W_{rec} 5 J cm^{-3} with $\eta > 85\%$ between 20 to 140 °C. Riaz *et al.* [174] reported a variation of W_{rec} and η is $\leq 6.5\%$ and 7.4% where $\eta < 82\%$ between 30 to 150 °C for the $\text{Sr}_2\text{Na}_{(1-x)}\text{Bi}_{(x)}\text{Nb}_{(5-x)}\text{Fe}_{(x)}\text{O}_{15}$

system ($x = 0.15$). Likewise, Xu *et al.* [175] reported a $\text{Sr}_2\text{Ag}_{0.2}\text{Na}_{0.8}\text{Nb}_{5-x}\text{Ta}_x\text{O}_{15}$ system showing a W_{rec} of 1.44 Jcm^{-3} , η is 82 % when $x = 0.3$ between -9.6 to 232.7°C .

Brown *et al.* [15] reported a reduction of T_1 (relaxor-like low temperature transition) and T_2 (ferroelectric $\rightarrow$ paraelectric transition) transition temperatures and relative permittivities (ϵ_r) at T_1 and T_2 with increasing dopant level in $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, where $z = 0, 0.025$, and 0.05 . Markedly, $z = 0.025$ showed promising X9R Class II capacitor performance where $\epsilon_{r,\text{median}} = 1565 (\pm 15 \%)$ from -65°C to 325°C at 1 kHz . However, this study did not include energy storage performance metrics beyond the measured room temperature P - E hysteresis loops. Taken together, the above literature suggests that minor A- and B-site co-doping has a significant effect on T_c (or T_m) and ϵ_r at T_c (or T_m) yet has received considerably less attention.

2.7.5 A-site Vacancies

The above three sections focused on A- and/or B-site doping in SNN1 and SBN based TTBs. Average A-site cation radii ($[A1+A2]/2$) and t_{A1} has been suggested to play a crucial role in determining the commensurate/incommensurate modulation of the octahedral framework and the resultant ferroelectric/RFE behaviour of TTBs [107]. In this respect, Zhu *et al.* [107] noted more research is needed to understand the impact of A1-site vacancies on dielectric performance.

A-site vacancies in perovskites have been shown to expand the A-site, more so than the equivalent cation occupied A-site in $\text{Sr}_{1-3x}\text{R}_{2x}\text{TiO}_3$ ($R = \text{La}^{3+}$, Nd^{3+} , or Ce^{3+}) [176]. To date, only one study has closely examined the role of A-site vacancies in TTBs [177]. A crystallographic and density functional theory (DFT) guided study by Zeiger *et al.* [178] reported vacant A1 sites to be 13% and 6 % larger than the equivalent site occupied by a cation for $\text{Sr}_{5-5x}\text{Ba}_{5x}\text{Nb}_{10}\text{O}_{30}$ where $x = 0.1, 0.2, 0.3, 0.4, 0.6, 0.7$, and 0.8 and $\text{Ba}_{5-1.5x}\text{R}_x\text{Nb}_{10}\text{O}_{30}$ (where $R = \text{Bi}^{3+}$, La^{3+} , Sm^{3+} , Y^{3+} , or Dy^{3+} and $x = 0.67, 1, 2$, and 3) respectively.

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Gardner *et al.* [89] highlighted the size of the A-site vacancy is difficult to quantify but that they could possibly lower the size difference ratio between the A1 and A2 sites of unfilled TTBs relative to filled TTBs, favouring classical ferroelectric behaviour [139]. However, later work by the same author suggests classical ferroelectric behaviour is perturbed with sufficient A-site vacancy concentration, in favour of RFE behaviour [85]. It has been suggested that A1-site vacancies allow for a greater degree of flexibility (*i.e.* relaxation [85]) in the octahedral framework [178], facilitating disorder, and stabilising the incommensurate modulation, enabling RFE behaviour [107]. This is supported by Cao *et al.* [166] who reported a $\text{Sr}_{2-1.5x}\text{Gd}_x\Box_{0.5x}\text{NaNb}_5\text{O}_{15}$ system (where $x = 0.05, 0.08, 0.12$, and 0.15 and $\Box$ = vacancy) which exhibited a complete broadening and disappearance of a distinct T_c peak, in favour of a singular low temperature RFE-like dielectric anomaly T_m , which shifted to lower temperatures with increasing Gd^{3+} (x) and A-site vacancies ($T_1 \sim -80^\circ\text{C}$ [$x = 0.05$] to -100°C [$x = 0.15$] at 1 kHz).

Vacancies can also play a role in TTB phase stability and the potential formation of a second phase. The SrNb_2O_6 – NaNbO_3 phase diagram was constructed in the 1970s [179, 180], with SNN1 typically showing evidence of a secondary Sr-modified NaNbO_3 perovskite phase through XRD analysis [82, 181]. These phase diagrams [179, 180] indicate that single phase SNN1 is only possible with A site vacancy containing SNN1, *i.e.* unfilled SNN1 [152]. The metastable phase diagram constructed by Tang *et al.* [180] is shown in Figure 2.18. Successful synthesis from a filled TTB to an unfilled TTB to produce a single phase has been reported by Xu *et al.* [140], who synthesised a series of $\text{Sr}_2\text{Na}_{1-3x}\text{Bi}_x\Box_{2x}\text{Nb}_5\text{O}_{15}$ ceramics ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07$, and 0.08). This study reported a single phase when $x > 0.02$ and a fall in T_c and minor variation in ϵ_r at T_c ($T_c \sim 300^\circ\text{C}$ [$x = 0.01$] to $T_c \sim 260^\circ\text{C}$ [$x = 0.08$] at 10 kHz), while the ferroelectric-ferroelastic low temperature transition temperature increased across the reported compositional range [140]. Yang *et al.* [182] reported single phase $(\text{Sr}_{0.53}\text{Ba}_{0.47})_{2.5-0.5x}\text{Na}_x\Box_{0.5x}\text{Nb}_5\text{O}_{15}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0$, and 2.5) when

$x \leq 1.0$, which saw an increase in T_c from ($T_c \sim 75^\circ\text{C}$ [$x = 0$] to $T_c \sim 290^\circ\text{C}$ [$x = 2.5$] at 10 kHz), with a low temperature dielectric anomaly emerging beyond $x = 0.8$.

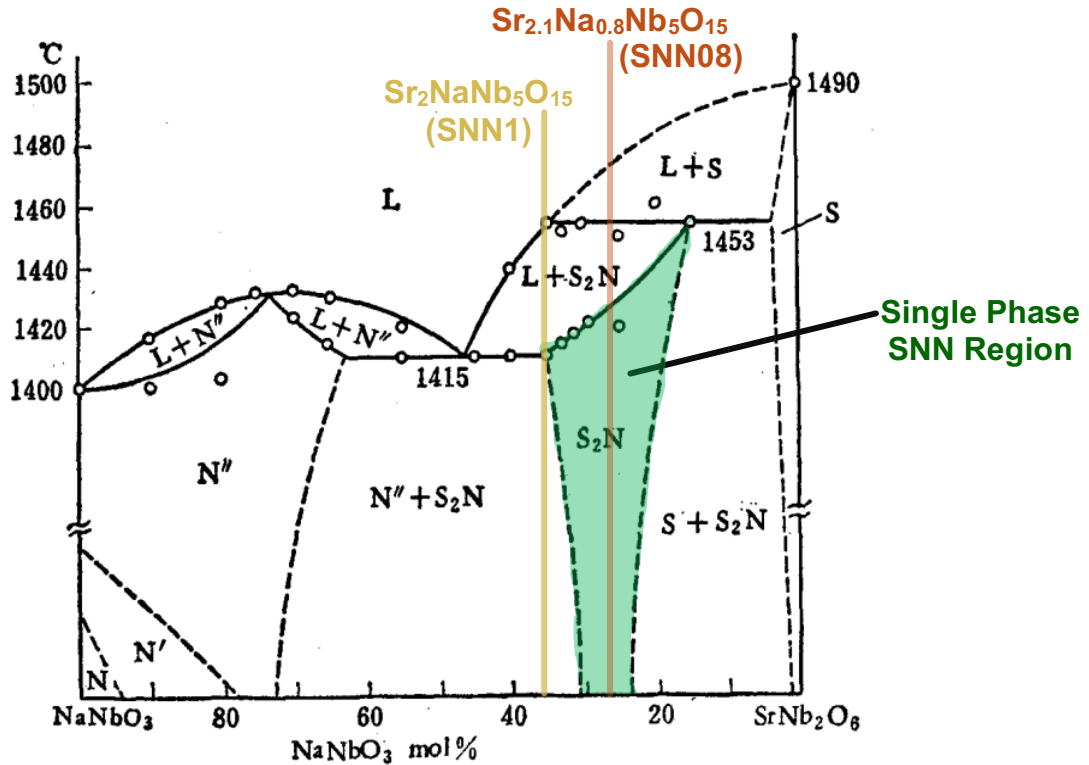


Figure 2.18: Metastable SrNb₂O₆-NaNbO₃ phase diagram constructed by Tang *et al.* [180] showing the single phase SNN1 region (green shaded area). SNN1 and sodium deficient Sr_{2.1}Na_{0.8}Nb₅O₁₅ (SNN08) plot points are taken from Brown [49].

The similar compositional series (Sr_{0.925}Ca_{0.075})_{2.5-0.5x}Na_x□_{0.5x}Nb₅O₁₅ ($x = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$, and 1.0) reported by Yang *et al.* [153] showed an increase of T_c and ϵ_r at T_c with increasing Na⁺ content from ($T_c \sim 270^\circ\text{C}$ [$x = 0.4$] to $T_c \sim 310^\circ\text{C}$ [$x = 1.0$] at 10 kHz) which were single phase when $x \leq 0.8$. Yang *et al.* [183] likewise reported single phase (Ca_{0.28}Ba_{0.72})_{2.5-0.5x}Na_x□_{0.5x}Nb₅O₁₅ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$, and 1.0) which showed an increase in T_c ($T_c \sim 230^\circ\text{C}$ [$x = 0$] to $T_c \sim 340^\circ\text{C}$ [$x = 1.0$] at 10 kHz). For the similar (Ca_{0.28}Ba_{0.72})_{2.5-0.5x}□_{0.5x}K_xNb₅O₁₅ composition, Yang *et al.* [184] reported all compositions to be single phase with an increase in T_c and ϵ_r at T_c (from $T_c \sim 245^\circ\text{C}$, ϵ_r at $T_c \sim 1660$ [$x = 0$] to $T_c \sim 300^\circ\text{C}$, ϵ_r at $T_c \sim 1880$ [$x = 0.6$] at 10 kHz).

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Brown [49] reported a single-phase $\text{Sr}_{2.1}\text{Na}_{0.8}\text{Nb}_5\text{O}_{15}$ (SNN08) system with a flat temperature stable, high permittivity response ($T_1 \sim -42^\circ\text{C}$, ϵ_r at $T_1 \sim 1990$, $T_2 \sim 280^\circ\text{C}$, ϵ_r at $T_2 \sim 1976$ at 1 kHz) highlighting sodium deficient SNN1 as a viable candidate for temperature stable capacitors. However, it should be noted that thermal stability studies on SNN08 by Brown [49] did suggest thermal cycling at 300°C (9 runs) reduced ϵ_r by approximately 1.5 %, with powder X-ray diffraction suggesting decomposition into NaNbO_3 , SNN, and SrNb_2O_6 (which has been subsequently confirmed by in-situ heating in an XRD stage, data not published yet). Additionally, an equilibrium phase diagram constructed by Tang *et al.* [180] (Figure 2.19) also highlights that below approximately 1180°C , SNN1 is metastable (*i.e.* thermodynamically unstable below 1180°C [49]).

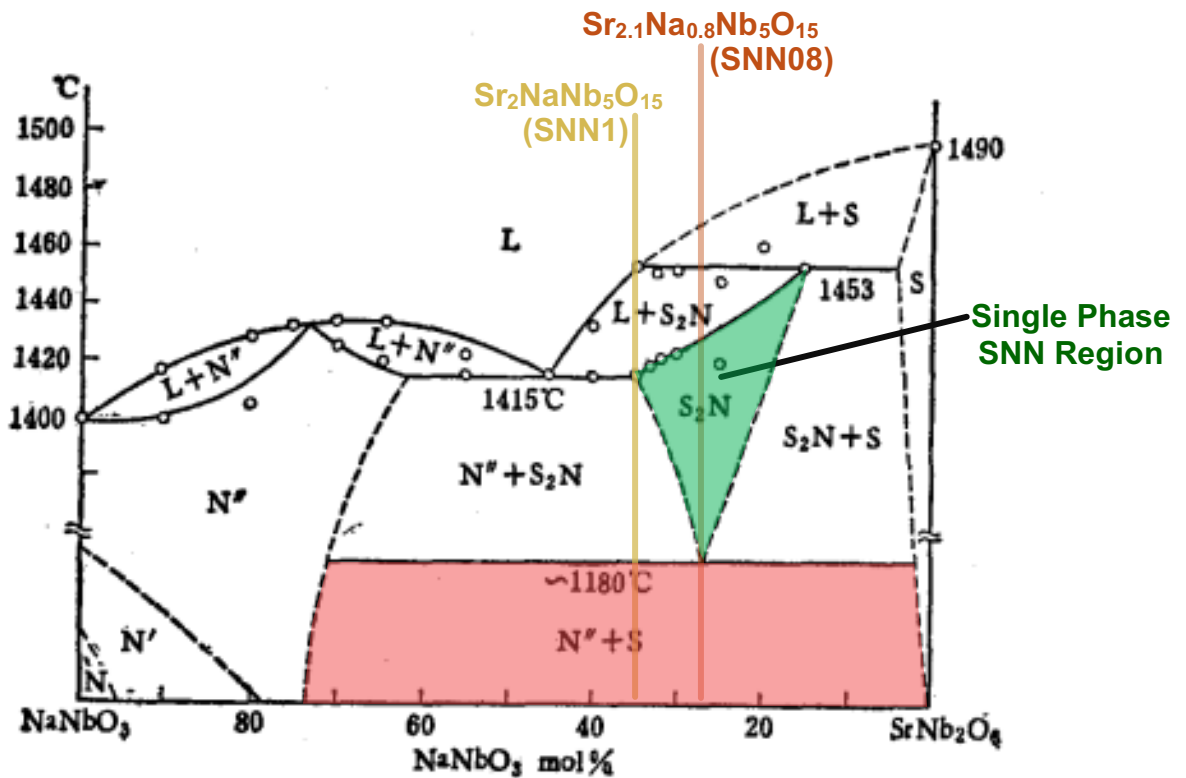


Figure 2.19: Equilibrium SrNb_2O_6 - NaNbO_3 phase diagram constructed by Tang *et al.* [180] showing the single phase SNN1 region (green shaded area). SNN1 and sodium deficient $\text{Sr}_{2.1}\text{Na}_{0.8}\text{Nb}_5\text{O}_{15}$ (SNN08) plot points are taken from Brown [49] showing SNN1 is metastable below 1180°C (red shaded area).

This puts into question the reliability and longevity of both SNN1 and sodium deficient counterparts (*i.e.* SNN08) for temperature stable MLCCs, setting a precedent for the

investigation of structurally related non-volatile containing TTBs, such as SBN. However, the above literature suggests minor A-site vacancies introduced into SNN1 permit the formation of a single phase SNN (shown in Figure 2.18 and Figure 2.19). Major vacancy concentrations however, much like A- and B-site co-doping strategies, reduce T_c and ϵ_r at T_c , such that low temperature transitions, like T_1 , play a critical role in a temperature stable, flat, permittivity temperature response.

2.7.6 Structural Characterisation of SNN1 and SBN

The studies discussed above on SNN and its doped counterparts have seen contradictory reports on the room temperature structure assignment [18], ranging from tetragonal $P4bm$ [15, 166, 169, 172, 181, 185-187] to orthorhombic $Im2a$ [166, 181, 186, 187]. Unit cells for the proposed room temperature structures and corresponding space groups are illustrated in Figure 2.16b. The assignment of structure in TTBs is challenging because, in addition to the displacement of cations with relatively high atomic number, a significant contribution to the lowering of symmetry that takes the structure from tetragonal to lower symmetries is due to relatively subtle distortions of the highly rigid, but weakly scattering oxygen octahedral framework [166, 181, 186, 187]. High-resolution diffraction patterns obtained from synchrotron X-ray radiation sources can help elucidate such distortions [85, 89, 104-106], but are not always sufficient.

Tidey *et al.* [18] recently reported SNN1 as being incommensurate at room temperature but well-approximated as a commensurate orthorhombic $Ama2$ phase, using density functional theory (DFT) for total energy predictions and group theoretical analysis, alongside high-resolution X-ray and neutron powder diffraction as well as transmission electron microscopy (TEM) and electron diffraction. The evidence that SNN1 is incommensurate is associated principally with the presence of octahedral tilting revealed by TEM electron diffraction.

Upon cooling from high temperature, Tidey *et al.* [18] describe consecutive symmetry-lowering phase transitions, derived from combined DFT, electron, X-ray and neutron

diffraction analyses on SNN. When cooling below T_2 (the paraelectric to ferroelectric transition), the non-polar $Amam$ phase transitions to the ferroelectric $Ama2$ phase (with an out-of-(ab)plane polar distortion mode of the $Ama2$ structure. At T_1 (the ferroelectric to ferroelastic transition), the $Ama2$ phase transitions to a lower symmetry monoclinic Aa phase. Critically, on cooling from T_2 , Tidey *et al.* [18] details a positive thermal expansion of the c lattice parameter up to T_1 , followed by a contraction of c on cooling through T_1 , accompanied by an expansion of the ab -plane on further cooling. The ferroelectric nature of the $Ama2$ phase used for the refinements allows for a direct analysis of the doping-induced structural changes that drive the permittivity anomalies/maxima at T_1 and T_2 in SNN1.

2.8 Summary and Outlook

The first half of this chapter focused on the fundamental background science of dielectric ceramics, including crystal chemistry, polarisation mechanisms, dielectric properties and lastly, the TTB structural family. The latter half introduced the materials of study in this thesis: filled SNN1 and unfilled SBN TTBs. This was followed by a literature review on SNN1 and SBN, assessing the effect of: a) A- and/or B-site doping and b) A-site vacancies on dielectric properties, namely T_1 and T_c (or T_m) and their corresponding ϵ_r maxima (ϵ_r at T_1 and/or ϵ_r at T_c [or T_m]). A significant body of the literature is focused on maximising RFE behaviour through A- and/or B-site co-doping strategies to improve capacitive performance (*i.e.* energy storage) at room temperature.

The existing literature, however, does little to disentangle the individual impact of A-, B-site dopants and A-site vacancies in TTBs, particularly at minor levels. Overall, while the crystal chemical framework of Zhu *et al.* [107] (orange box, Figure 2.20), is relevant to a broad range of TTB systems, it is not applicable to minor levels of A-, B-site doping and A-site vacancy containing TTBs (*e.g.* unfilled TTBs). The effect of minor doping on dielectric properties, however, is evident for minor A-site doped CBN (green box, Figure 2.20), B-site doped SNN1 (red box, Figure 2.20), and A- and B-site co-doped SNN1 (blue box, Figure 2.20). The crystal structure-dielectric property reasoning behind the dielectric property improvement in *via* A-, B-site doping in TTBs remains

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largely interpretive in nature, especially with respect to the temperature evolution of T_1 , T_c (or T_m) and their corresponding ϵ_r maxima, which have received considerably less interest.

The first two results chapters of this thesis (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$) aim to build on the unambiguous *Ama2* assignment of the room temperature structure of SNN1, and the approximating method for sequential Rietveld refinements of variable temperature high resolution X-ray diffraction data reported by Tidey *et al.* [18]. Here, the analysis extends to an expanded series of A and B site, co-doped, $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and A1-site vacancy containing $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ ceramics originally reported by Brown, T. [15, 49]. Variable temperature Rietveld refinement and careful analysis of the lattice parameters and symmetry-adapted mode temperature evolution using solely the orthorhombic *Ama2* structural model will be undertaken to show how temperature stability of permittivity is achieved.

This thesis will illustrate the crucial interplay between A and B-site co-dopants, A-site vacancy levels and the symmetry-driven distortion modes that occur during the temperature evolution of lattice parameters and how, together, these affect the temperature stability of the permittivity of SNN1. The dielectric characteristics affected by the co-doping and vacancies are the relative permittivity (ϵ_r) values at the relaxor like transition temperature (T_1) and the ferroelectric to paraelectric transition at higher temperature (T_2) (ϵ_r at T_1 and T_2) and its behaviour in between, as well as the transition temperatures themselves. Developing an understanding of the structure-property relationships that drive the dielectric performance characteristics of $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ will set a basis to exploit doped and vacancy containing SNN1 for their application as temperature stable capacitors. The final results chapter of this thesis, Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ will focus on A- and B-site co-doped SBN, building on insight from Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$.

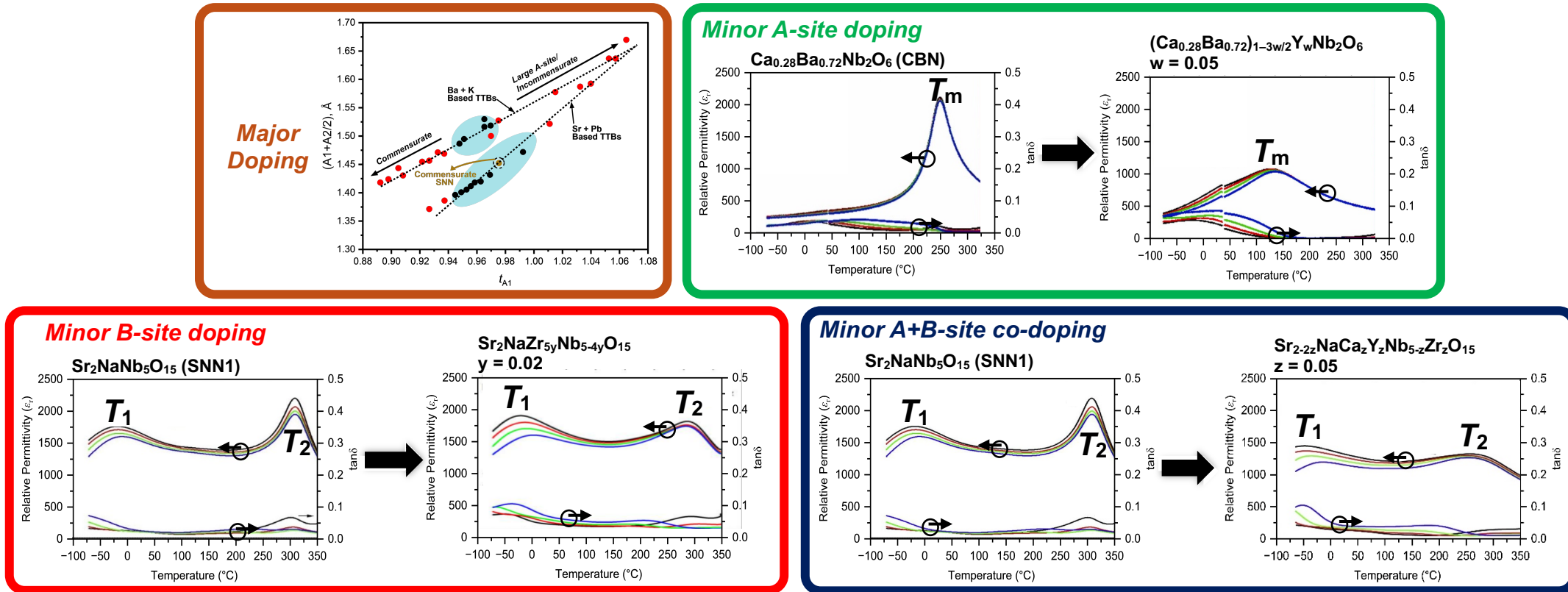


Figure 2.20: A summary of literature review findings from section 2.7, subsection 2.7.1 – 2.7.6. The effects of major doping (orange box) is described by the crystal framework ($[A1 + A2]/2$ versus t_{A1}) proposed by Zhu *et al.* [107], while the effects of minor A-site doping (green box [188]), minor B-site doping (red box [49]), and minor A- and B-site doping (blue box [15]) are evident, despite not being fully applicable to the framework set by Zhu *et al.* [107].

Chapter 2 – Background Science and Literature Review

These compositions are based on the $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{Gd}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (where $x = 0.2$) system reported by Yang *et al.* [20] where rare earths (R^{3+}) of varying cationic radii will be introduced into the A-site (in place of Gd^{3+} in the aforementioned ceramic system), alongside the popular energy storage focused B-site dopant Ta^{5+} .

SNN1 is extensively studied owing to its high permittivity over a wide temperature range, but the presence of volatile Na^+ makes the case for alternative, structurally related TTBs, such as SBN. The volatile loss of cations, such as Na^+ , forms oxygen vacancies as a charge compensating mechanism [189-192], leading to elevated dielectric losses at room temperature [189, 193]. Moreover, faltering thermal stability of permittivity at 300 °C (and phase at higher temperature) upon thermal cycling of SNN1 and its sodium deficient counterpart, SNN08 has been highlighted by Brown [49]. This chapter seeks to uncover the structural reasoning for the selection of certain rare earth dopants (*i.e.* Gd^{3+} in the report by Yang *et al.* [20]), disseminating the role of both R^{3+} and Ta^{5+} co-dopants on the RFE dielectric anomaly T_m . These compositions will be assessed as possible, thermally stable (volatile free) alternatives for SNN1 as materials for temperature stable capacitor materials.

Chapter 3 – Experimental Methods

3.1 Introduction

The foundations of materials science are epitomised by the materials tetrahedron [194], shown in Figure 3.1. Ceramic processing determines composition and structure, structure determines properties, properties determine performance, and characterisation interrelates crystal (and microstructure) structure, processing, properties, and performance [194]. Structure, properties and performance of $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN1) and $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) based ceramics will be interpreted using a range of structural and electrical characterisation techniques.

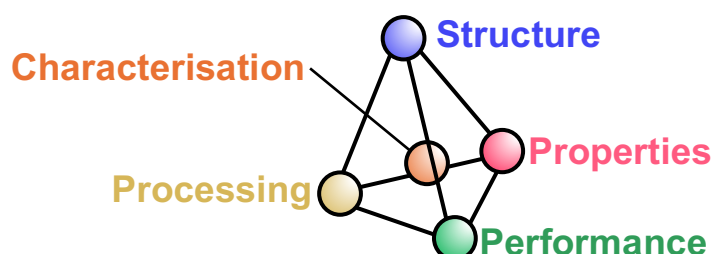


Figure 3.1: The materials tetrahedron showing the relationship between structure, properties, processing, characterisation, and performance, taken and reformatted after Callister *et al.* [194].

This chapter will firstly cover the ceramic processing stages to form dense, homogenous ceramic pellets. Structural and electrical characterisation techniques used for this research will be outlined, with additional details on background theory, instrumentation set-up, and sample preparation.

3.2 Ceramic Processing

All compositions were synthesised *via* a conventional mixed oxide route using oxide and carbonate reagent powders of high purity (> 99 %). Powder reagent purity, suppliers, and CAS codes are listed in Table 3.1. The processing steps for the conventional mixed oxide route used in this research are shown in Figure 3.2. and will be described in more detail in the sections below.

Table 3.1: Oxide and carbonate reagents, purity, supplier name, and CAS Codes.

Raw Reagent Powder	Purity (%)	Supplier	CAS Code
SrCO_3	≥ 99.9	Sigma Aldrich (Merck)	1633-05-2
Na_2CO_3	$> = 99.5$	Sigma Aldrich (Merck)	497-19-8
BaCO_3	99.95	Alfa Aesar	513-77-9
CaCO_3	99	Sigma Aldrich (Merck)	471-34-1
Y_2O_3	99.99	Sigma Aldrich (Merck)	1314-36-9
Dy_2O_3	99.99	BioServ	1308-87-8
Gd_2O_3	99.9	Alfa Aesar	12064-62-9
Sm_2O_3	99.9	BioServ	12060-58-1
Nd_2O_3	99.99	BioServ	1313-97-9
La_2O_3	99.99	Alfa Aesar	1312-81-9
Nb_2O_5	99.9	Alfa Aesar	1313-96-8
ZrO_2	99	Sigma Aldrich (Merck)	1314-23-4
Ta_2O_5	99.85	Alfa Aesar	1314-61-0

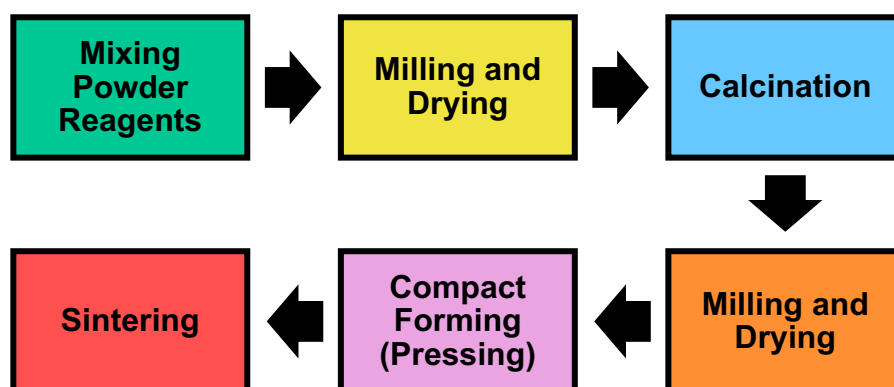


Figure 3.2: Processing steps of the conventional mixed oxide route used to process SNN and SBN ceramics in this thesis, based on Figure 1.2 from Kang [195].

Powders were preserved in furnaces set at 100 °C, while hygroscopic Na_2CO_3 was kept at 300 °C. Prior to weighing, the powders were cooled in a vacuum desiccator containing silica gel desiccant beads (indicating water saturation). Stoichiometric

Chapter 3 – Experimental Methods

ratios of powders for a given composition were weighed to a precision of ± 0.001 g using an electronic balance (Sartorius, Göttingen, Germany).

Stoichiometric ratios of powder masses were combined to make a 50 g batch. $\text{Sr}_{1.95}\text{NaCa}_{0.025}\text{Y}_{0.025}\text{Nb}_{4.975}\text{Zr}_{0.025}\text{O}_{15}$ (abbreviated to $z = 0.025$) will be used as an example herein. The formula mass of $z = 0.025$ is the total of the atomic mass of the elements multiplied by their atomic fraction (z):

Sr	→	1.950	×	87.620	g mol ⁻¹	=	170.859	g mol ⁻¹
Ca	→	0.025	×	40.078	g mol ⁻¹	=	0.575	g mol ⁻¹
Y	→	0.025	×	88.905	g mol ⁻¹	=	2.223	g mol ⁻¹
Na	→	1.000	×	22.989	g mol ⁻¹	=	40.076	g mol ⁻¹
Nb	→	4.975	×	92.906	g mol ⁻¹	=	462.207	g mol ⁻¹
Zr	→	0.025	×	91.224	g mol ⁻¹	=	2.281	g mol ⁻¹

$$\text{Formula Mass} = 901.546 \text{ g mol}^{-1}$$

The moles of $z = 0.025$ to make a 50 g sample are found by dividing 50 g by the formula mass ($901.546 \text{ g mol}^{-1}$) of $z = 0.025$:

$$\begin{aligned} \text{Moles (z = 0.025)} &= \frac{50 \text{ g}}{901.546 \text{ g mol}^{-1}} \\ &= 0.055 \text{ mol} \end{aligned}$$

The formula mass of the powder reagents (*i.e.* $147.628 \text{ g mol}^{-1}$ for SrCO_3) was multiplied by their molar ratio:

Chapter 3 – Experimental Methods

SrCO₃	→	147.628	g mol ⁻¹	×	(1.95 × 0.055)	mol	=	15.966	g
CaCO₃	→	100.086	g mol ⁻¹	×	(0.025 × 0.055)	mol	=	0.139	g
Y₂O₃	→	225.809	g mol ⁻¹	×	(0.025 × 0.055/2)	mol	=	0.157	g
Na₂CO₃	→	105.988	g mol ⁻¹	×	(0.055/2)	mol	=	2.939	g
Nb₂O₅	→	265.807	g mol ⁻¹	×	(4.975 × 0.055/2)	mol	=	36.670	g
ZrO₂	→	123.222	g mol ⁻¹	×	(0.025 × 0.055)	mol	=	0.171	g

$$\text{Total Mass of Powder Reagents} = 56.041 \text{ g}$$

The loss of carbon dioxide (CO₂) to make 50 g of z = 0.025 is taken into consideration. The total mass of all powder reagents (56.041 g) to form z = 0.025 was subtracted from the sum of the moles of carbonates (SrCO₃, CaCO₃, and Na₂CO₃) and multiplied by the formula mass of CO₂ (44.009 g mol⁻¹):

$$50 \text{ (z = 0.025)} \text{ g} = 56.041 \text{ g mol}^{-1} - \sum \left[\begin{array}{l} 0.108 \text{ mol} \times 44.009 \text{ g mol}^{-1} \\ 0.028 \text{ mol} \times 44.009 \text{ g mol}^{-1} \\ 0.001 \text{ mol} \times 44.009 \text{ g mol}^{-1} \end{array} \right]$$

$$50 \text{ (z = 0.025)} \text{ g} = 56.041 \text{ g mol}^{-1} - \sum \left[\begin{array}{l} 4.753 \text{ g} \\ 1.232 \text{ g} \\ 4.401 \text{ g} \end{array} \right]$$

The resulting 50 g batches were placed in 1 L cylindrical polypropylene screw top bottles (12 cm height by 5 cm diameter). The bottles were approximately filled two thirds full of cylindrical stabilized zirconia (Y₂O₃) grinding bead media (6.35 mm height by 6.35 mm diameter) with approximately 80 mL of propan-2-ol (> 99.9 %, Sigma

Aldrich, United States of America). For a homogenous and agglomerate free mixture, the white-coloured slurries were mechanically ball milled horizontally for 24 hours at 150 rpm (Capco Test Equipment, Ball Mill Model 12 Variable Speed, Suffolk, United Kingdom).

The slurries were dried at 90 °C in an induction stand mixer (Kenwood Cooking Chef Major KM096, Havant, United Kingdom) and were continually stirred until the propan-2-ol was evaporated to obtain a dry white powder. The white powder was filtered through a 300 µm mesh, nylon sieve to further eliminate any remaining agglomerates. The sieved powder was tightly packed into an alumina crucible of 0.5 L capacity. SNN powders to be calcinated were covered by an alumina tile to reduce Na₂O losses.

Calcination was carried out for the thermal decomposition (*i.e.* reduction) of metal carbonates to metal oxides. Here, the interdiffusion of metal cations also facilitates a phase transition to the desired TTB phase (Figure 3.3a). Calcination heating and cooling rates were 5 °C/min up to a temperature of 1100 – 1200 °C for a dwell time of 4 – 6 hours in a conventional box furnace (Figure 3.3b). Calcination temperatures and dwell times vary between SNN and SBN compositions and thus will be specified in the experimental section of results Chapter 4 – Sr_{2-2z}NaCa_zY_zNb_{5-z}Zr_zO₁₅, Chapter 5 – Sr_{2+w}Na_y□_wNb₅O₁₅ and Chapter 6 – Sr_(0.53-0.15x)Ba_{0.47}R_{0.1x}Nb_{2-x}Ta_xO₆.

The cooled, calcined powders were horizontally mechanically ball milled (Ball Mill Model 12 Variable Speed, Capco, Suffolk, United Kingdom) with deionised water for 23 hours at 150 rpm. This was followed by the addition of 1 wt% binder (Optapix AC112, Zwimmer & Schwartz, Lahnstein, Germany) and milling for an additional 1 hour. Approximately 0.4 g of the dried and sieved powders (using same methodology as above) were uniaxially pressed into cylindrical shaped pellets using a 10 mm diameter steel die with a force of 1 tonne for 1 minute and 30 seconds.

Pellets were then isostatically cold pressed for 5 minutes to a pressure of 200 MPa (Stanstead Fluid Power, Essex, United Kingdom).

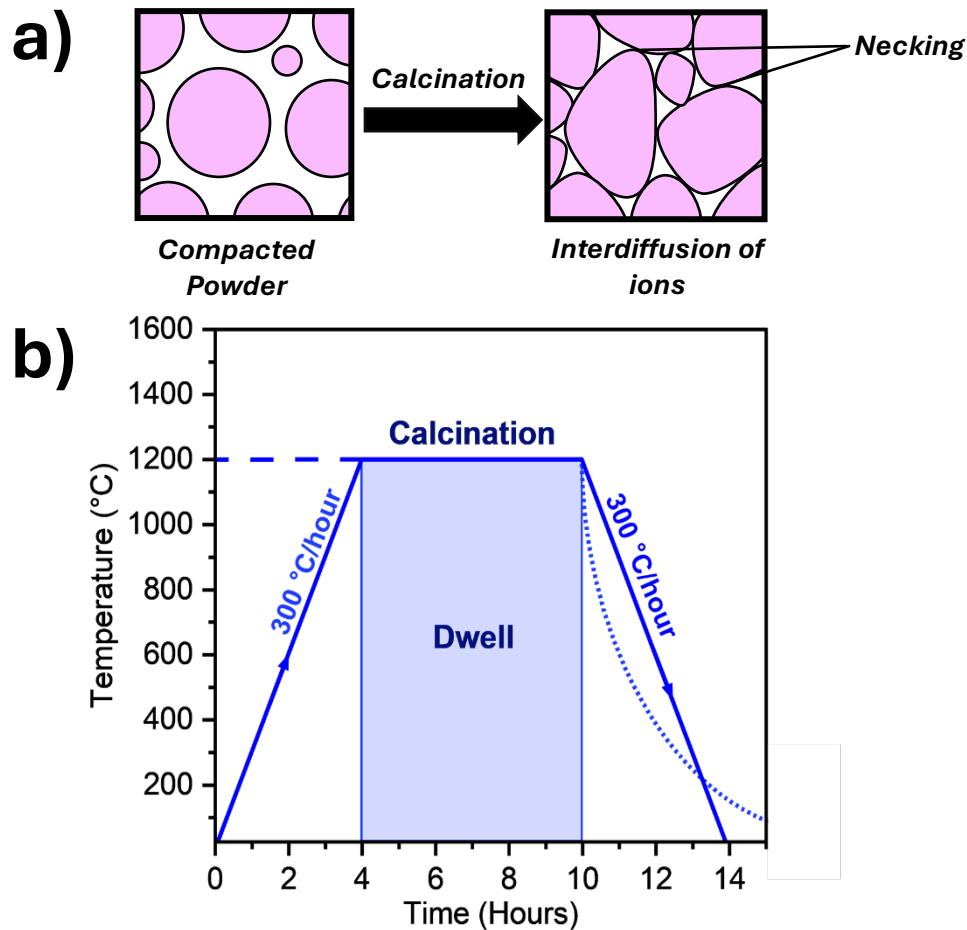


Figure 3.3a – b: Schematic diagram illustrating a) the calcination process and b) temperature – time plot showing a typical calcination profile used throughout this research, where the dotted line signifies the furnace natural cooling rate.

Sintering is a thermal densification process[3], illustrated in Figure 3.4a. It is described by Malič *et al.* [196] as

“...an irreversible thermodynamic process in which powder compacts are consolidated using thermal energy to obtain dense, polycrystalline ceramics”.

Here, all pelletised compositions were covered and embedded in atmospheric powder⁴

⁴ Atmospheric powder is loose (non-compacted) calcined powder that is used to embed and cover the shaped pellets prior to sintering to reduce volatile losses, such as loss of Na₂O from SNN.

and enclosed with a round shallow alumina crucible prior to sintering. Sintering was undertaken in two stages.

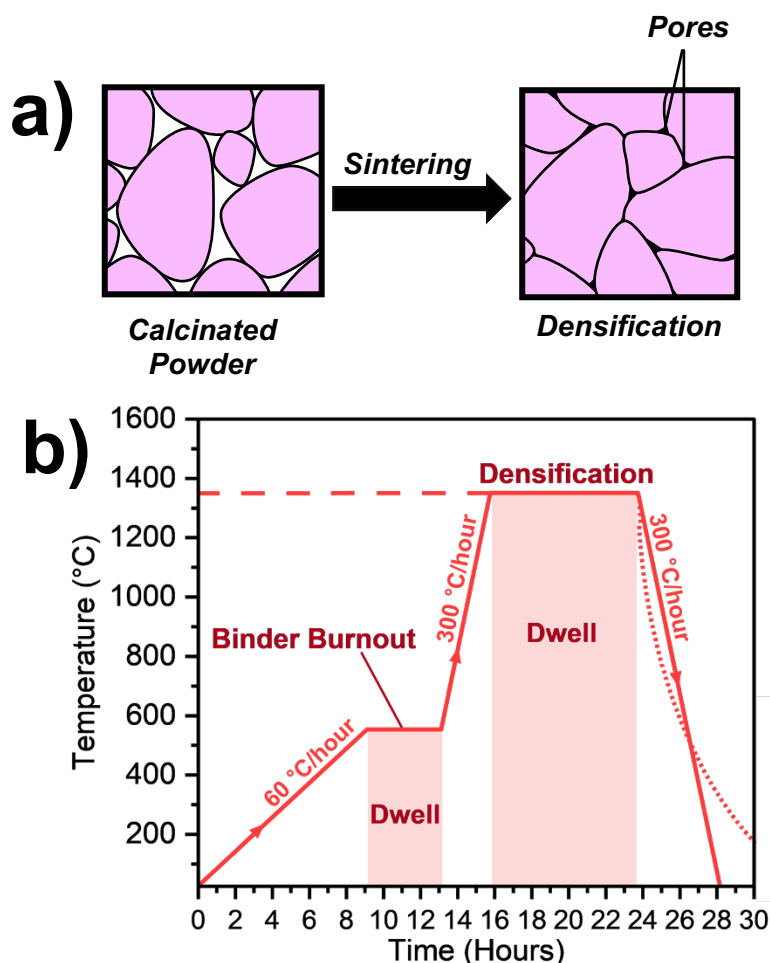


Figure 3.4a – b: Schematic diagram illustrating a) the sintering process and b) temperature – time plot showing a typical sintering profile used throughout this research, where the dotted line signifies the furnace natural cooling rate.

First, a binder burnout stage with a heating rate of 60 °C/hour up to 550 °C and held for 5 hours. Maximum densities (92 – 97 %) were then obtained at a sintering temperature of 1300-1350 °C, held for 4-5 hours with a heating and cooling rate of 300 °C/hour. A plot showing a typical sintering regime is shown in Figure 3.4b. Sintering temperatures and dwell times also vary between SNN and SBN compositions and will be specified in the experimental section of results Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ and Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$.

3.2.1 Ceramic Density Measurements

After sintering, pellets were ground with P600 silicon carbide paper (CarbiMet®, Buehler Leinfelden-Echterdingen, Germany) to remove residual agglomerates of atmospheric powder on pellet surfaces and edges. Experimental pellet densities (ρ_{exp}) were obtained from measured volumes (V) and masses (m) of the cylindrical shaped pellets, determined using Equation 3.1 and Equation 3.2. The pellet thicknesses and diameters were measured by a micrometer screw gauge (RS Pro, External Micrometer, Northants, United Kingdom), while masses were acquired using a precision (± 0.001 g) electronic balance (Sartorius, Göttingen, Germany).

$$\rho_{exp} = \frac{m \text{ (g)}}{V \text{ (cm}^3\text{)}} \quad \begin{array}{l} m = \text{Mass (g)} \\ V = \text{Volume (cm}^3\text{)} \end{array} \quad \text{Equation 3.1}$$

$$\rho_{exp} = \frac{m \text{ (g)}}{\pi \left(\frac{d \text{ (cm)}}{2} \right)^2 t \text{ (cm)}} \quad \begin{array}{l} m = \text{Mass (g)} \\ d = \text{Pellet diameter (cm)} \\ t = \text{Pellet thickness (cm)} \end{array} \quad \text{Equation 3.2}$$

Theoretical pellet densities were calculated from Rietveld refined lattice parameters (for more detail see 3.3.4 Rietveld Refinement), obtained from laboratory powder X-ray diffraction patterns (PXRD patterns). The theoretical pellet density is reached on the basis that the pellet is single crystal with no imperfections [194]. In the tetragonal unit cell (*i.e.* $P4bm$) lattice parameters $a = b \neq c$ [31], so theoretical density is calculated by Equation 3.3. Alternatively, the orthorhombic unit cell (*i.e.* $Ama2$) lattice parameters $a \neq b \neq c$ [31] are calculated by Equation 3.4.

$$\rho_{theo} \text{ (tetragonal)} = \frac{\Sigma(A_r)}{a^2 c N_A} \quad \text{Equation 3.3}$$

$$\begin{array}{l} A_r = \text{Relative atomic mass} \\ N_A = \text{Avogadro's number} \\ a, b, c = \text{lattice parameters} \end{array}$$

$$\rho_{theo} \text{ (orthorhombic)} = \frac{\Sigma(A_r)}{a b c N_A} \quad \text{Equation 3.4}$$

The percentage experimental pellet density is therefore calculated as a percentage of the theoretical density, calculated by Equation 3.5.

$$\rho_{\%} = \left(\frac{\rho_{exp}}{\rho_{theo}} \right) \times 100$$

$\rho_{\%}$
 ρ_{exp}
 ρ_{theo}

$=$ *Percent pellet density*
 $=$ *Experimental pellet density*
 $=$ *Theoretical pellet density*

Equation 3.5

3.3 Structural Characterisation

Many of the structural characterisation techniques ever-present to materials chemistry research today, depend on the interaction between electromagnetic radiation and matter [197]. The structural techniques used in this thesis are both laboratory and synchrotron powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and Raman spectroscopy. PXRD was used to examine phase identity, purity, and crystal structure. SEM and EDX will be used to investigate microstructure and elemental distribution, while Raman spectroscopy will be utilised to investigate changes in vibrational modes. A brief theoretical background on each technique will be given, followed by the respective sample preparation methodology.

3.3.1 Principles of Powder X-ray Diffraction (PXRD)

The properties of materials are significantly dependent on the arrangement of atoms in a material's crystal structure [194]. The wavelength of X-rays used to probe this arrangement are of a comparable magnitude to lattice planes in crystal structures distances ($\sim 1 \text{ \AA}$, *i.e.* 10^{-10} m [198]), and so incident X-rays are diffracted by the crystal lattice [199]. This makes PXRD a valuable, non-destructive technique for phase identification, purity and crystal structure analysis [200]. X-rays are diffracted in a crystalline material when the reflection of the incident X-ray beams from adjacent lattice planes scatter and constructively interfere [33, 201].

Parallel and monochromatic X-ray beams (labelled 1 and 2 in Figure 3.5) of wavelength, λ , are incident on lattice plane pairs A–A' and B–B' with spacing, d , at angle θ [194]. The incident beams are reflected and scattered by atoms C and D in lattice plane pairs A–A' and B–B' respectively [194]. If the path length difference between 1–C–1' ($\overline{ED}$) and 2–D–2' ($\overline{DF}$) is an integer, n , of wavelengths, λ , then scattered X-ray beams (labelled 1' and 2' in Figure 3.5) will constructively interfere

[194]. Hence the conditions to be satisfied for X-ray diffraction are expressed by Equation 3.6, which can be written in terms of $d_{hkl}\sin\theta$ (Equation 3.7) and ultimately simplified to Bragg's Law (Equation 3.8). Bragg's law expresses the relationship between X-ray wavelength, interatomic (lattice plane) spacing, and angle of diffraction, assuming constructive interference of the scattered beams [194].

A diffraction pattern of intensity versus 2θ allows for the interpretation of space group symmetry, peak position (lattice parameters, *i.e.* unit cell geometry), peak intensity (atomic positions, occupancies) and peak width plus shape (crystallinity, strain, defects, and disorder) [202]. Notably in polycrystalline materials, it is not unusual for peaks with reflections close in 2θ position to be convoluted, hence structural refinement methods are used on experimental diffraction patterns (see section 3.3.4 Rietveld Refinement). In the sections to follow, X-ray generation from laboratory and synchrotron diffractometers will be outlined, followed by a summary of Rietveld structural refinement.

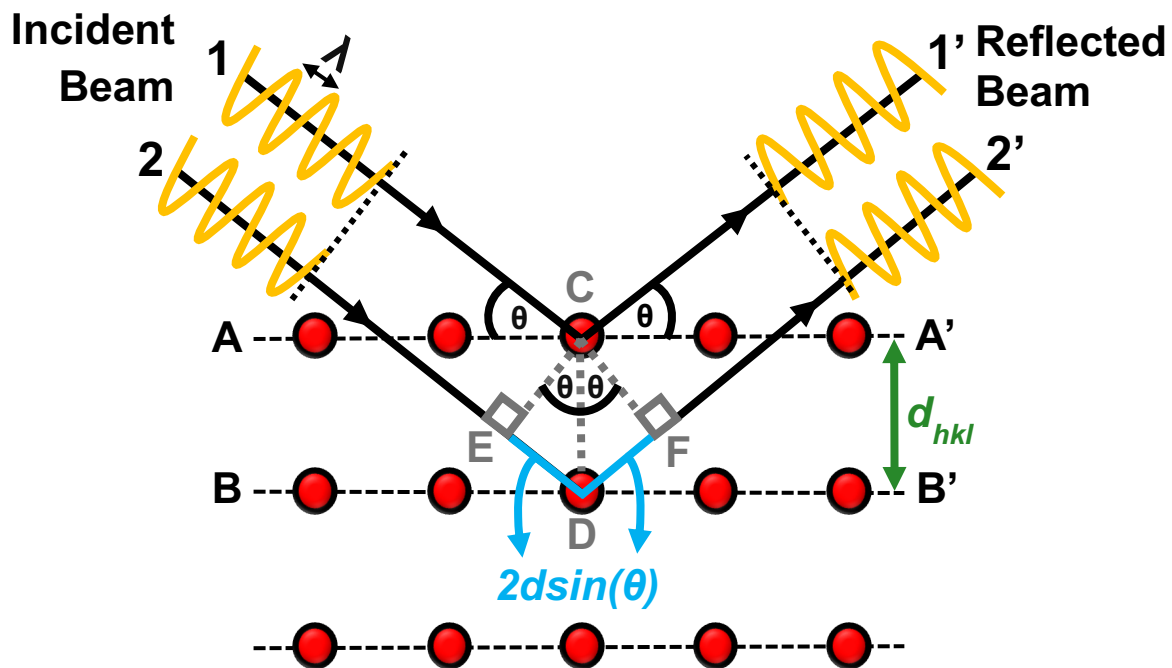


Figure 3.5: A geometric diagram of Bragg's law, taken and adapted after Callister *et al.* [194].

$$n\lambda = \overline{ED} + \overline{DF} \quad \text{Equation 3.6}$$

$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta \quad \text{Equation 3.7}$$

$$\text{Bragg's Law} \longrightarrow n\lambda = 2d_{hkl}\sin\theta \quad \text{Equation 3.8}$$

3.3.2 Laboratory Powder X-Ray Diffraction (Laboratory PXRD)

The thermionic emission of a tungsten filament produces a beam of electrons that can be accelerated towards a metal target by an electric field [27]. The metal target is then ionised, thus an inner orbital electron is struck by the electron beam and ejected [203]. The transition of an atomic electron in the metal from a higher energy orbital to a lower energy orbital (*i.e.* $L \rightarrow K$) will produce characteristic X-rays of wavelength, λ , shown in Equation 3.9.

$$\lambda = \frac{hc}{E_1 - E_2} \quad \begin{array}{l} h = \text{Planck's constant } (6.63 \times 10^{-34} \text{ m}^2 \text{ kg/s}) \\ c = \text{Speed of light } (2.99792458 \times 10^8 \text{ m/s}) \\ E_1 = \text{Energy of electron in higher energy orbital } i.e. L \\ E_2 = \text{Energy of electron in lower energy orbital, } i.e. K \end{array} \quad \text{Equation 3.9}$$

A diagram of the ionisation processes upon an electron beam striking a copper (Cu) metal target is shown in Figure 3.6.

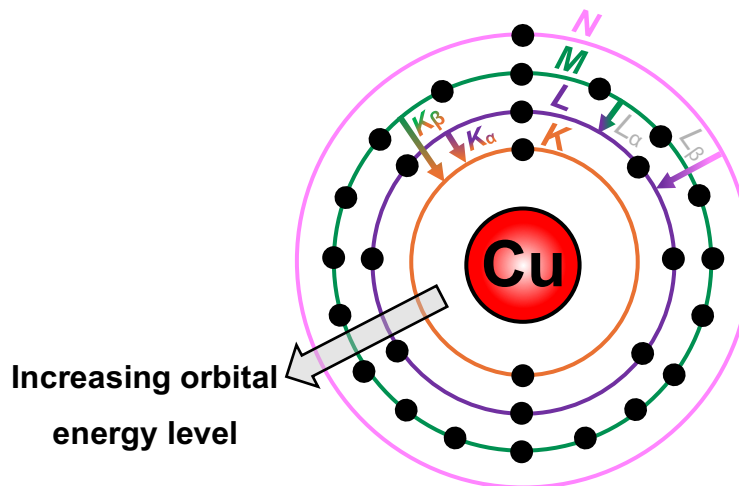


Figure 3.6: A schematic diagram of the subatomic orbital structure of a Copper (Cu) atom, showing the electronic emissions (arrows) from to *L* and *K* energy levels, taken and reformatted after Cullity *et al.* [27].

Laboratory PXRD diffractometers typically use Bragg-Brentano focusing geometry [204], which leverages circle theorem within a focusing circle (grey dashed line, Figure 3.7) [28]. A simplified schematic of a Bragg-Brentano geometry focused laboratory diffractometer is shown in Figure 3.7. Here, the sample lies horizontally on the tangent of the focusing circle at the center of the goniometer [28]. The X-ray detector and generator are located at the intersects of the focusing circle and goniometer, where the angle of the goniometer controls the focusing circle radius [204]. Thus, the incident and reflected beams are at equal angles and lengths with respect to the horizontal sample [28]. The goniometer is commonly configured in a Bragg-Brentano θ/θ setting [205], where X-ray generator and X-ray detector move in a synchronised fashion, while the (powdered) sample remains horizontal [28].

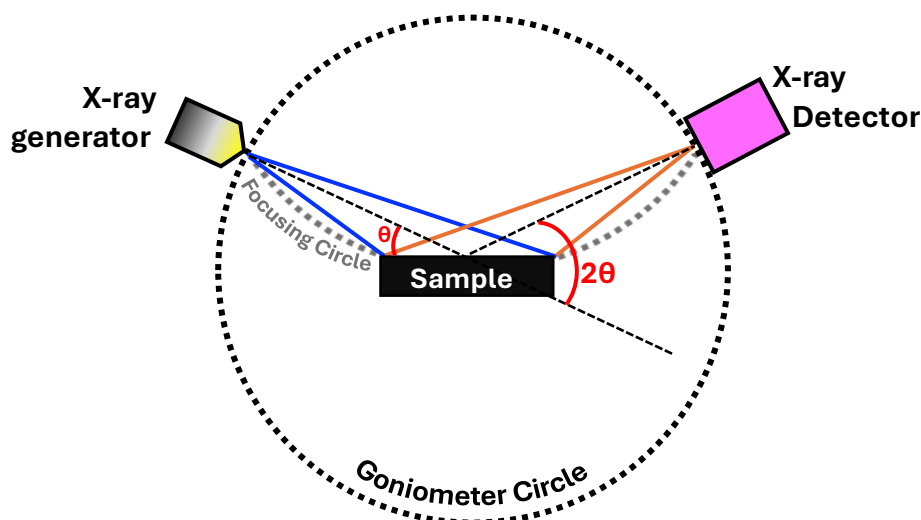


Figure 3.7: A schematic of a laboratory PXRD diffractometer which uses Bragg-Brentano geometry, taken and adapted after Doménech-Carbó *et al.* [206].

Room temperature (R.T.) laboratory PXRD was undertaken on a Bragg-Brentano focused Bruker D8 Advance (Massachusetts, United States of America) diffractometer (radiation source, Cu- K_α [$\lambda = 1.541 \text{ \AA}$]) with the goniometer configured to operate in θ/θ . Sintered pellets were crushed into a fine powder using a pestle and mortar and tightly compressed onto a 10 mm diameter silicon disc sample holder. Room temperature scan conditions used were a 2θ angle scan range of $20\text{--}80^\circ$ with a step size of 0.02° for a 12-hour scan duration.

3.3.3 Synchrotron Powder X-Ray Diffraction (Synchrotron PXRD)

Electromagnetic radiation (X-rays) are emitted when high-energy electrons are wiggled and undulated by magnetic fields on a curved trajectory, causing a change in acceleration, defined as synchrotron radiation [207]. A typical synchrotron configuration is shown in Figure 3.8. The radiation emitted is extremely bright (intensity per unit area of source [201]), covering a wide array of wavelengths, typically orders of magnitude smaller compared to laboratory PXRD X-ray sources [203, 207].

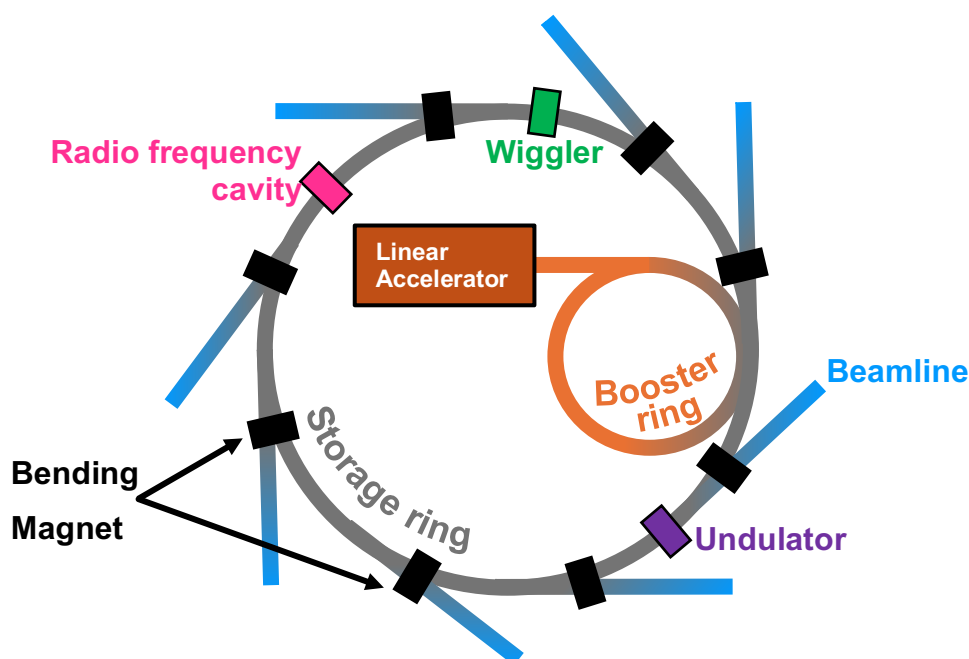


Figure 3.8: A schematic of a typical synchrotron configuration adapted from Woolfson [203], Cullity *et al.* [201], and Hwu *et al.* [208].

An electron gun produces a low energy electron beam through thermionic emission to a linear accelerator, increasing the beam's kinetic energy, *i.e.* acceleration to mega electron volts (MeV, 10^6 eV) [201]. The booster ring augments the acceleration of electrons to an energy of giga electron volts (GeV, 10^9 eV) and proceed into the storage ring [201]. The electrons are forced to accelerate around the ring on a circular trajectory by bending magnets located periodically around the ring [201]. Upon interacting with the bending magnets, the electrons decelerate, lose energy, and emit radiation [201]. This is termed *Bremsstrahlung* radiation (German for braking radiation) [42].

The acceleration of the electrons around the storage ring is sustained and compensated for by passing through a radio frequency cavity [201]. It should be noted that electrons travel on interconnected chords (straight lines) separated by the bending magnets around the ring and it is in these sections there is the radio frequency cavity [201]. In these sections, magnetic insertion devices, namely wigglers and undulators, are also placed to generate synchrotron radiation [209].

In this thesis, variable temperature crystal structure analysis was carried out by high resolution synchrotron powder X-ray diffraction (abbreviated to synchrotron PXRD hereafter) at beamline I11 (Diamond Light Source, Didcot, United Kingdom) [210]. Pellets were crushed into a fine powder and tightly packed into quartz capillaries (0.3 mm internal diameter and 0.1 mm wall thickness) and sealed. Diffraction patterns at variable temperatures were measured using a Mythen-2 position sensitive detector (Dectris, Baden-Daettwil, Switzerland) using 15 keV radiation (where $\lambda \sim 0.8 \text{ \AA}$)⁵ with a heating rate of 3 °C/min from -173 °C to 350 °C. Low temperature measurements were attained by using an Oxford Cryosystems Cryostream Plus (Oxford Instruments, Oxford, United Kingdom) from -173 °C to R.T. High temperatures were controlled by a Cyberstar hot air blower (ECM Lab Solutions, Grenoble, France) from R.T. to 350 °C.

3.3.4 Rietveld Refinement

All laboratory and synchrotron PXRD experimental diffraction patterns were analysed using the Rietveld refinement method [211] within the refinement software *TOPAS Academic* (Version 7.1.0) [212] and the Java-based text editor software *jEdit* (Version 5.7.0). As previously mentioned in section 3.3.3. Synchrotron Powder X-Ray Diffraction (Synchrotron PXRD), synchrotron PXRD data was collected using two separate temperature control systems: i) an Oxford Cryosystems Cryostream Plus (low temperature, -173 °C to R.T.) and ii) a Cyberstar hot air blower (high temperature, R.T. to 350 °C). Rietveld refinement was performed on the R.T. data sets gathered using the low and high temperature control systems, setting the starting point for

⁵The precise wavelength, λ , used is reported in the experimental sections of Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$.

sequential variable temperature Rietveld refinement on cooling or heating. Sequential Rietveld refinement was carried out using *Python*, which performed Rietveld refinements on PXRD patterns acquired at increasing temperature and decreasing temperature (from R.T.) for the hot and cold temperature control system data sets respectively. In consequence of the two separate temperature control systems, a discontinuity in the lattice parameter and symmetry-symmetry adapted mode temperature evolution is sometimes evident in results Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$.

At its core, Rietveld refinement is a least squares method which fits a theoretical (calculated) diffraction pattern to the experimental (observed) diffraction pattern [213]. The quality of the calculated diffraction pattern is largely dependent on a structural model specified by the user [28], *i.e.* an approximation. The user-specified structural model includes space group symmetry, peak position, lattice parameters (a , b , c , α , β , and γ), peak intensity (atomic positions/occupancies x , y , and z), and peak shape (crystallinity, strain, defects, and disorder) [202, 213]. The least squares method minimises the residual, S_y , which is the weighted sum of the difference between the calculated pattern profile from the observed pattern profile and is shown in Equation 3.10 [213].

$$S_y = \sum_i w_i (Y_i^{\text{calc}} - Y_i^{\text{obs}})^2$$

Equation 3.10

$S_y = \text{Residual}$
 $i = 2\theta \text{ point in diffraction pattern}$
 $w_i = \text{Weight factor of intensity}$
 $Y_i^{\text{obs}} = \text{Observed pattern intensity}$
 $Y_i^{\text{calc}} = \text{Calculated pattern intensity}$

The weight factor, w_i , measured at data point, i , (*i.e.* data point at 2θ) measures the standard error of Y_i^{obs} based on the standard deviation, σ , defined in Equation 3.11 [214].

$$w_i = \frac{1}{\sigma_i^2(Y_i^{\text{obs}})}$$

Equation 3.11

$w_i = \text{Weight factor of intensity}$
 $i = 2\theta \text{ point in diffraction pattern}$
 $\sigma = \text{Standard deviation}$

The shapes of the peaks must also be accounted for in a refinement, namely by a peak function [215]. The peak function is typically a combination of Lorentz and Gaussian profiles, usually a pseudo-Voigt function [215]. Additionally, the background in the observed peak profile is modelled using a high order polynomial [215], which considers the contribution of unconstructively interfering scattered X-rays and those scattered from the atmospheric sample environment [213]. Instrumental-dependent parameters such as wavelength, axial divergence, and zero point are calibrated with a standard [215], typically NIST 640 silicon powder [216].

The quality of the Rietveld refinement fit can qualitatively be examined by a difference plot, but can also be quantitatively evaluated using discrepancy values, namely residual (or simply R) factors. These include the R-factor, R_p (Equation 3.12), weighted R-factor, R_{wp} (Equation 3.13), and expected R factor, R_{exp} (Equation 3.14). The R_{wp} over the R_{exp} is defined as chi squared, χ^2 (Equation 3.15) [217].

$$R_p = \frac{\sum_i w_i (Y_i^{calc} - Y_i^{obs})}{\sum_i w_i (Y_i^{calc})} \quad \text{Equation 3.12}$$

$$R_{wp} = \sqrt{\frac{\sum_i w_i (Y_i^{calc} - Y_i^{obs})^2}{\sum_i w_i (Y_i^{calc})^2}} \quad \text{Equation 3.13}$$

$$R_{exp} = N / \sum_i w_i (Y_i^{obs})^2 \quad \text{Equation 3.14}$$

$R_p =$ *R-factor*
 $R_{wp} =$ *Weighted R-factor*
 $R_{exp} =$ *Expected R-factor*
 $N =$ *Number of 2θ points*
 $\chi^2 =$ *Chi squared*

$$\chi^2 = \frac{R_{wp}}{R_{exp}} \quad \text{Equation 3.15}$$

3.3.5 Representation Analysis, Group Theory, and Notation

Representation analysis is an arm of group theory in mathematics [218]. The section to follow will give a brief overview of the methodology used in the first two results chapters of this thesis (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$). The mathematical constructs that underpin representation

analysis and group theory are complex, and a more in-depth overview can be found in fundamental textbooks [219-221].

Refinements were undertaken in the basis of symmetry-adapted irreducible representations (irreps) and associated nomenclature, and output through the web-based software *ISODISTORT* [222]. As stated in the previous chapter, Tidey *et al.* [18] reported SNN1 as being incommensurate but appropriately described at room temperature as a commensurate, orthorhombic *Ama2* phase. Structural distortions of the *Ama2* structure are characterised as irreducible representations (irreps) of the higher symmetry parent structure aristotype, *P4/mbm*. Representation analysis used here uses Bradley-Cracknell notation [219], tabulated by Miller and Love [223], and generalised by:

$$K_n^{+/-}$$

K = High symmetry point in the Brillouin zone
n = Integer (used to distinguish irreps with same *K*)
 + = Maintained inversion symmetry
 – = Lost inversion symmetry

Symmetry-mode analysis provides fertile ground to breakdown collective distortions into singular parameters (transforming as irreps) enabling the ability to monitor their evolution as a function of temperature, pressure and/or composition [224]. Amplitudes of a given distortion are reported here as absolute (A_p) values, which are given with respect to normalised distortion amplitudes (in Angstroms, Å) of the aristotype *P4/mbm* unit cell [224]. Structural distortions transform as eight unique irreps with respect to the aristotype, high symmetry, *P4/mbm* structure, $\Gamma_1^+(a)$, $\Gamma_4^+(a)$, $\Gamma_2^-(a)$, $\Gamma_3^-(a)$, $S_1(0,a;0,0)$, $S_3(0,a;0,0)$, $M_5^+(a,a)$, and $M_5^-(a,a)$ [18]. Visualisations of the modes refined in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ are shown in Appendix B – Visualisation of Strain and Distortion Mode Irreducible Representations (Irreps).

The order parameter directions (OPDs, written in brackets *i.e.* $\Gamma_1^+(a)$) will be written as Γ_1^+). define the direction of such distortions but are omitted from irrep labels for clarity herein. Macroscopic strains transforming as irrep Γ_1^+ represent the volumetric

symmetry strain, while Γ_4^+ denotes the orthorhombic strain in the ab plane [18]. Atomic displacements along c , transforming as irrep Γ_2^- , correspond to the antiferroelectric antipolar modes, while irrep Γ_3^- represents the ferroelectric polar mode. Inclusion of modes transforming as irreps representing octahedral tilts (S_1), and shears (M_5^+ and M_5^-) in Rietveld refinements offered no improvement to the quality of the fit and were all constrained to zero [18].

3.3.6 Raman Spectroscopy

Raman spectroscopy is a type of spectroscopic technique used to study vibrational modes of materials [198]. A beam of monochromatic photons strikes the sample [198], where majority of the incident photons will scatter elastically (*i.e.* no change in scattered photon energies), this is termed Rayleigh scattering [198]. However, 1 in 10^7 photons will scatter inelastically (*i.e.* change in scattered photon energies) [198]. The scattering phenomenon where photons lose energy (reduced frequency) due to vibrational scattering upon striking the sample is termed Stokes scattering [24]. Conversely, anti-Stokes scattering occurs when photons gain energy (increase frequency) [24]. A summary of the Rayleigh, Stokes and anti-Stokes scattering phenomena are shown in Figure 3.9, showing the excitation of a material from its ground state to its virtual (excited) state.

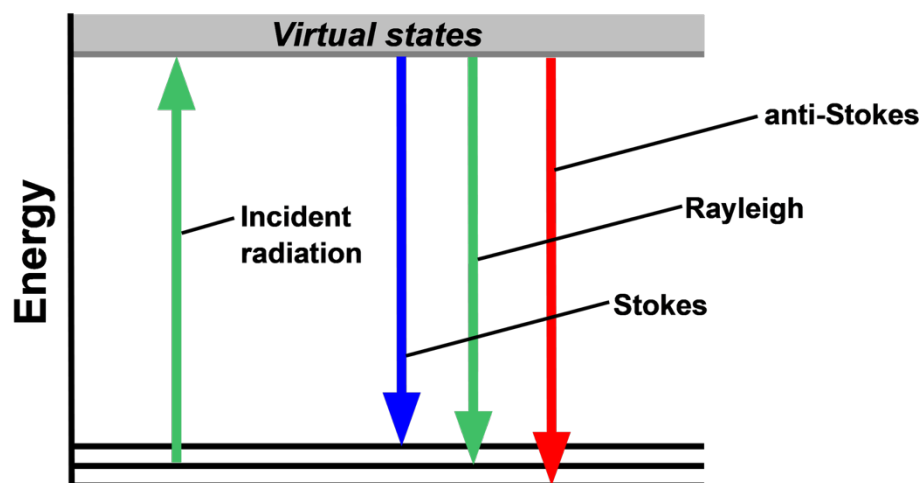


Figure 3.9: A photon energy level diagram showing the excitation of photons from the ground state to the virtual (excited) state (grey shaded area) and the three types of scattering back, namely Stokes (blue), Rayleigh (green), anti-Stokes (red), taken and adapted after Atkins *et al.* [198].

The energy difference here allows for a direct comparison of the Raman shift (frequency/wavenumber in units of cm^{-1}) of the scattered photons to lower or higher energy levels relative to the incident beam [24]. Raman offers sensitivity to local crystal structure symmetries by correlating to variation of soft vibrational modes arising from structural transitions [225]. Consequently, the technique has been used to quantify how A and B site substitutions in TTBs may affect the B1 – O stretching (ν_2), B1 – O bending (ν_1) and O – B1 – O bending (ν_5), or B2 equivalent vibrational modes [84, 166]. Additionally, external vibrational modes of A cation motion relative to the octahedral framework below 200 cm^{-1} in TTBs are reported [226].

Raman spectra of powders of crushed, sintered pellets were measured on a Renishaw inVia Raman Microscope (Wotton-under-Edge, England, United Kingdom) with a 532 nm solid-state laser at 0.5 mW power. Measurements were taken at room temperature and the microscope focused at 20x magnification. Peaks output from intensity versus Raman shift plots were integrated using *Origin 2024b* (Massachusetts, United States of America) data analysis and graphing software to find peak positions and full width at half maxima (FWHM) of ν_2 , ν_1 , and ν_5 , vibrational modes.

3.3.7 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was utilised to obtain microstructural information, including grain size, morphology, and porosity (*i.e.* density of the ceramic pellets). The maximum theoretical resolution⁶ in optical microscopes (OMs) adheres to the Rayleigh criterion (Equation 3.16) for visible light, being proportional to the wavelength of the incident radiation [227]. The wavelength of visible light ranges between 400 – 700 nm (median = 550 nm). Therefore, the maximum theoretical resolution of an OM is $\sim 200 \text{ nm}$.

⁶ Resolution is defined as the minimum distance between two distinct points on a sample which can be observed as distinct objects.

$$\delta = \frac{0.61\lambda}{\mu \sin \beta}$$

Equation 3.16

δ = Resolution
 λ = Incident radiation wavelength
 μ = Refractive index of viewing medium
 β = Semi-angle of microscope aperture

Optical microscopy is consequently limited by the wavelength of the incident light. On the other hand, electrons can have a significantly smaller wavelength which is dependent on the accelerating voltage applied in the electron microscope [227], as shown by the de Broglie relationship (Equation 3.17). For instance, for a given applied electron accelerating voltage of 10 keV, the De Broglie wavelength is ~ 0.001 nm. This significantly smaller wavelength of accelerated electrons (~ 0.001 nm at 10 keV) compared to the wavelength of light (~ 200 nm) permits a vastly better resolution and magnification capability to observe ceramic microstructure.

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Equation 3.17

λ = de Broglie wavelength
 h = Planck's constant ($6.626 \times 10^{-34} \text{ m}^2\text{kg/s}$)
 m = mass of electron ($9.109 \times 10^{-31} \text{ kg}$)
 e = Electron charge ($1.60 \times 10^{-19} \text{ C}$)
 V = Accelerating voltage

The discovery that electrons were able to be deflected by a magnetic field further paved the way for the replacement of light radiation by a high energy electron beam [228, 229]. A schematic of a typical SEM is shown in Figure 3.10.

When the electron beam strikes the sample, detectors are used to differentiate the generation of secondary electrons (SE), backscattered electrons (BSE) or characteristic X-rays (Figure 3.10). SEs are emitted from close to the surface of the sample, through the inelastic scattering of the incident electrons [230]. Since these electrons are inelastically scattered, they will always be lower in energy than the incident beam [234]. SEs are easily re-absorbed by the specimen and so contrast in SE mode is dependent on specimen topography. BSEs originate from deeper within the sample and are a product of high angle elastic scattering, thus they are much higher in energy relative to SEs and are of similar energy to the incident beam [234]. Contrast in BSE images is largely dependent on atomic number, Z . Hence, in a sample region with a higher average value of Z , a larger number of BSEs will be detected, providing increased contrast [230].

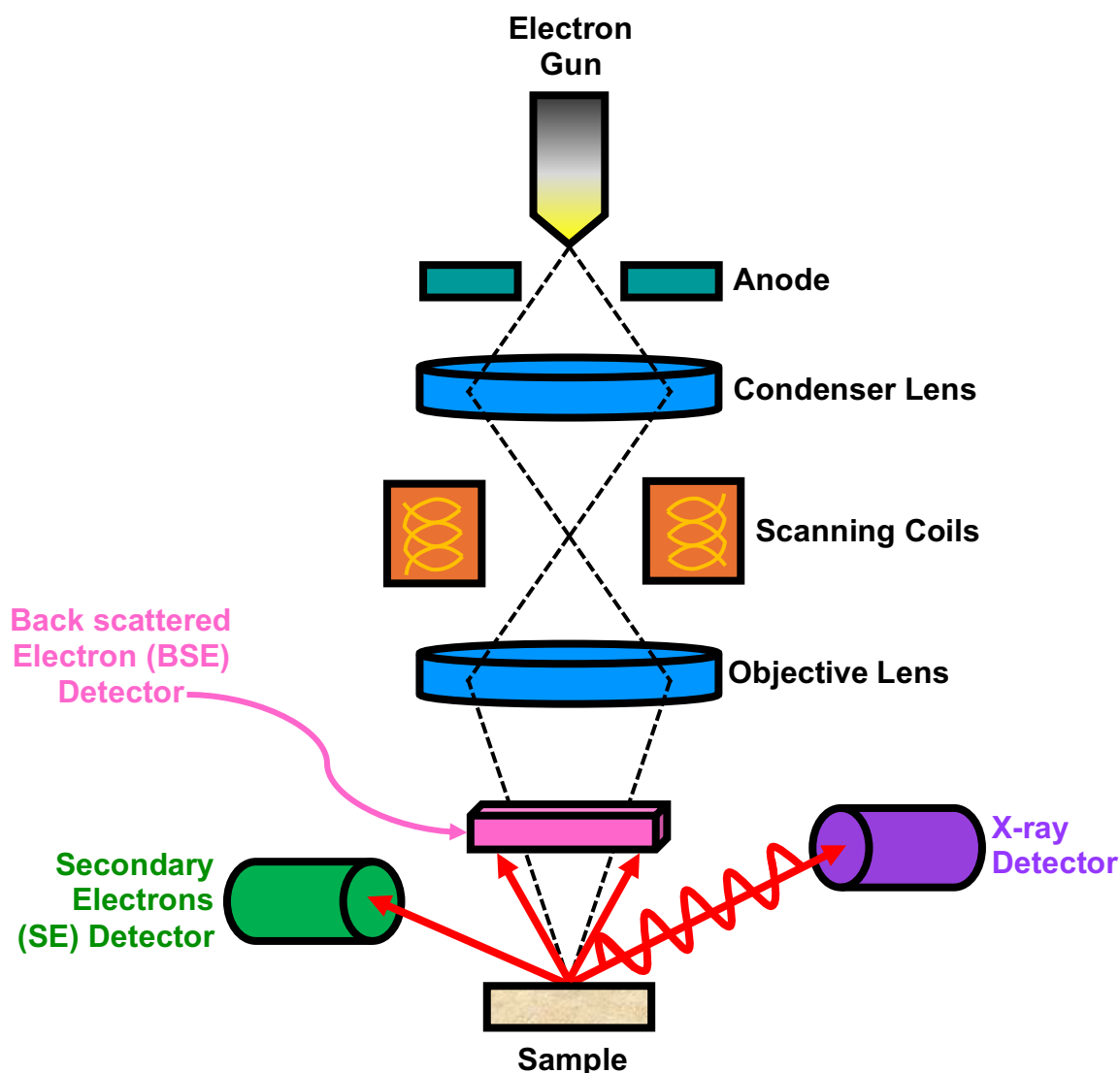


Figure 3.10: A schematic of a typical SEM taken and adapted after references [230, 231].

3.3.8 Energy Dispersive X-Ray Spectroscopy (EDX)

In addition to SEs and BSEs, characteristic X-rays arising from characteristic energy de-excitation of ionised atoms in the sample allow for elemental identification and mapping. When the incident electron beam strikes the sample, a core orbital electron will be ejected (ionised), akin to that discussed for the copper (Cu) target in section 3.3.2 Laboratory Powder X-Ray Diffraction (Laboratory PXRD). Likewise, a higher energy outer orbital electron will relocate in place of the lower energy emitted electron in the sample [230]. The difference in energy, and the consequent emission of X-rays are termed characteristic X-rays because they are energetically unique to each element in the specimen allowing for both qualitative and quantitative elemental

analysis [230]. For a visual diagram of the ionisation process in copper metal orbitals, the reader is referred to Figure 3.6.

3.3.9 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) Sample Preparation

One pellet face of each sample was mounted on a 1:2 ratio mixture of epoxy resin hardener (EpoxiCure[®] 2, Buehler, Leinfelden-Echterdingen, Germany) to epoxy resin (EpoThin[™] 2, Buehler, Leinfelden-Echterdingen, Germany). The mounted pellet was left to cure in a 1.5 cm height by 3 cm diameter cylindrical mould (SamplKup[®] Buehler, Leinfelden-Echterdingen, Germany). The cured, mounted samples were manually ground using increasingly finer P240, P600 (CarbiMet[®], Buehler Leinfelden-Echterdingen, Germany) and P2500 (MicroCut[®], Buehler Leinfelden-Echterdingen, Germany) silicon carbide papers.

Subsequent polishing was carried out using TexMet[®] C microcloths (Buehler, Leinfelden-Echterdingen, Germany) with applied MetaDi[®] 2 diamond pastes (Buehler, Leinfelden-Echterdingen, Germany) of decreasing particle size (9 µm, 3 µm, 1 µm), lubricated with MetaDi[®] fluid (Buehler, Leinfelden-Echterdingen, Germany). A final 10-minute polish was carried out with a ChemoMet[®] (Buehler, Leinfelden-Echterdingen, Germany) polishing pad using MasterMet[®] 0.06 µm colloidal silica (Buehler, Leinfelden-Echterdingen, Germany) on an EcoMet[®] 300 automatic polisher (Buehler, Leinfelden-Echterdingen, Germany). SNN-based resin mounted samples were chemically etched using a 2:1 ratio of hydrofluoric acid and concentrated nitric acid for 1 minute and 30 seconds. SBN-based resin mounted samples were thermally etched at approximately 100 °C below the sintering temperature with a rapid heating/cooling rate of 900 °C/hour, dwelling for 15 minutes.

Back scattered scanning electron micrographs were obtained using a SU8230 (Hitachi, Tokyo, Japan) high performance cold field emission SEM. EDX analysis was carried out using an 80 mm² X-Max silicon drift detector (Oxford Instruments,

Abingdon, United Kingdom). EDX mapping was obtained and analysed using the AZtec software interface (Oxford Instruments, Abingdon, United Kingdom).

3.4 Electrical Characterisation

Electrical characterisation undertaken in this research combines ferroelectric hysteresis loops and dielectric spectroscopy measurements. Ferroelectric hysteresis can be quantified due to the reversible spontaneous polarisation exhibited by ferroelectrics upon application of an electric field [235]. Here, maximum polarisation ($P_{\max}$), remnant polarisation (P_{rem}), and coercive field (E_c) can be directly measured [236].

Dielectric spectroscopy is a widely used technique to measure electrical properties of electroceramics [237]. This technique uses variable temperature, fixed frequency sweeps of relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) [237]. This technique allows for the interpretation of the coupling between structural phase transitions and electrical properties (*i.e.* macroscopic polarisation). For example, the Curie temperature (T_c) and the corresponding relative permittivity (ϵ_r at T_c). SNN-based composition dielectric spectroscopy data were used to evaluate the temperature relaxor-like transition, T_1 , the ferroelectric $\rightarrow$ paraelectric transition, T_2 (*i.e.* T_c) and the corresponding ϵ_r value at T_1 and T_2 . SBN based compositions were evaluated in terms of T_m (temperature of ϵ_r maxima) and ϵ_r at T_m .

3.4.1 Sample Preparation for Dielectric and Ferroelectric Characterisation

Pellets were ground and polished using P400 silicon carbide paper (CarbiMet®, Buehler Leinfelden-Echterdingen, Germany) to ~ 1 mm thickness. Silver electrode paint (Sun Chemical, Gwent Electronic Materials, Pontypool, United Kingdom) was applied onto each side of the pellet face and heated to 550 °C and held for 30 minutes with a heating and cooling rate of 300 °C/hour.

3.4.2 Sample Preparation for Dielectric and Ferroelectric Characterisation

Dielectric properties, ϵ_r and $\tan\delta$, were measured as a function of temperature (R.T. to 350 °C) at frequencies of 1 kHz, 10 kHz, 100 kHz and 1 MHz (Hewlett Packard, HP4284 LCR, California, United States of America) at low field. A conventional box furnace was used for high temperature measurements (R.T. – 350 °C). An environmental chamber (Tenney Jr, Tenney Environmental-SPX, California, United States of America) was used for low temperature counterpart measurements (-75 °C – R.T.). Dielectric property data (SNN; T_1 , T_2 and ϵ_r at T_1 and T_2 , SBN; T_m and ϵ_r at T_m) were extracted between -75 °C to 350 °C.

3.4.3 Ferroelectric Polarisation – Electric Field (*P-E*) Hysteresis Loops Measurements

R.T. polarisation-electric field (*P-E*) hysteresis loops were obtained using a modified Sawyer-Tower circuit equipped with a function generator (HP33120A, Keysight Technologies, Berkshire, United Kingdom) and attached high voltage amplifier (HVA1B, Chevin Research, Otley, United Kingdom). A quadrupled cycle of a sinusoidal alternating current (AC) with an electric field waveform with a frequency of ~ 2 Hz was applied to sample pellets from 5 kV/cm, 10 kV/cm, 20 kV/cm, 30 kV/cm and to 40 kV/cm.

Pellets were submerged in a silicone oil dielectric liquid medium, increasing dielectric breakdown voltage to reduce arcing. A modified Sawyer-Tower circuit using a 5 kV amplifier source (Model 5/80, Trek Inc., Medina, New York, United States of America) was used to apply an electric field to induce a current at room temperature in the sample pellets. To increase the applied field, the voltage was increased in increments. Data were collected on the Vision software (Radiant Technologies, Albuquerque, New Mexico, United States of America).

Correlating A and B Site Co-Doping Effects on the Dielectric Properties and Crystallographic Structure of $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN) Tetragonal Tungsten Bronze (TTB)

4.1 Introduction

This chapter reports the ceramic processing and characterisation of $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (abbreviated to SNN1 herein, where 1 denotes sodium $[\text{Na}^+]$ stoichiometry) and an expanded series of A- and B-site co-doped equivalents of the nominal formula $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ proposed by Brown *et al.* [15]. Based on the comparable Shannon cationic radii [22] of dopants to their substituents, the nominal formula $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ postulates Y^{3+} (1.08 Å) and Ca^{2+} (1.34 Å) replace Sr^{2+} (1.44 Å) on the A1/A2 sites, while Zr^{4+} (0.72 Å) replaces Nb^{5+} (0.64 Å) on the B sites. Taken together, the selection of Y^{3+} and Zr^{4+} co-dopants by Brown *et al.* [15] preserves electrical charge neutrality in the nominal formula [49].

The Y^{3+} and Ca^{2+} dopants should introduce additional structural disorder at the A sites, potentially influencing both the cation-site occupancy, the strain and tilt across the network of interconnected NbO_6 octahedra and the in and out of plane polarization. Tidey *et al.* [18] undertook refinement of the Na:Sr site occupancy in undoped SNN1 and suggested ratios of 0.48:0.52 at A1 sites and 0.26:0.74 at A2 sites in agreement with previous work [18]. Hence, in doped SNN1, it is likely that A-site dopants are distributed on both A1 and A2 sites. B site doping by Zr^{4+} , which has a lower dielectric polarizability in BO_6 (3.25 Å³) than Nb^{5+} (3.97 Å³) [23], should decrease the off-centre displacement of the B cation, leading to a decrease in long range ferroelectric coupling as well as potentially facilitating the compression of the *c* lattice parameter due to the lower charge density of Zr^{4+} (relative to Nb^{5+}) and weakening electrostatic interactions within the octahedral framework. For a tabulated list of all cations, their charges, Shannon cationic radii [22] and polarizabilities [23] present in compositions studied in this thesis see Appendix A – Shannon Radii and Polarizabilities.

Brown *et al.* [15] reported a reduction of T_1 (relaxor ferroelectric peak) and T_2 (ferroelectric $\rightarrow$ paraelectric transition) transition temperatures and relative permittivities (ϵ_r) at T_1 and T_2 with increasing dopant level (z , in $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$). Dopant levels investigated by Brown *et al.* [15] were $z = 0$ ($T_1 = -14^\circ\text{C}$ where $\epsilon_r = 1714$, $T_2 = 305^\circ\text{C}$ where $\epsilon_r = 2146$), $z = 0.025$ ($T_1 = -18^\circ\text{C}$ where $\epsilon_r = 1549$, $T_2 = 345^\circ\text{C}$ where $\epsilon_r = 1580$), and $z = 0.05$ ($T_1 = -49^\circ\text{C}$ where $\epsilon_r = 1433$, $T_2 = 255^\circ\text{C}$ where $\epsilon_r = 1308$). Markedly, $z = 0.025$ showed promising X9R Class II capacitor performance where $\epsilon_{r, \text{median}} = 1565 (\pm 15 \%)$ from -65°C to 325°C at 1 kHz. Fundamental crystallographic structure and dielectric property relationships in SNN and TTBs in general, however, remain largely descriptive in nature.

Using density functional theory total energy predictions and group theoretical analysis in conjunction with high resolution X-ray, neutron, and electron diffraction, Tidey *et al.* [18] recently reported SNN1 as unambiguously having an incommensurate crystal structure across a wide temperature range, arising from the presence of concerted octahedral tilting, using density functional theory for total energy predictions and group theoretical analysis, alongside high-resolution X-ray and neutron powder diffraction. They proceeded to demonstrate that it can be closely approximated by a commensurate, orthorhombic, $Ama2$ phase, allowing accessible means by which to analyse the structural evolution of the material with temperature. In TTBs, the rigidity assumed by the octahedral framework leads to structural distortion from tetragonal (point group $4mm$) to orthorhombic (point group $mm2$) at room temperature [85, 104, 105]. High-resolution diffraction patterns obtained through synchrotron X-ray radiation sources can allow for the study of such tenuous structural distortions [85, 89, 104-106].

This chapter will build on the orthorhombic $Ama2$ room temperature structural assignment of SNN1 and sequential Rietveld refinements of variable temperature synchrotron powder X-ray diffraction (PXRD) patterns reported by Tidey *et al.* [18]. The synergistic interplay between dielectric performance, lattice parameters, and symmetry – adapted mode temperature evolution will be correlated to dopant level, z . The analysis herein is applied to an extended series of A- and B-site co-doped $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ ceramics originally reported by Brown *et al.* [15]. Understanding

the crystallographic structure and phase transitions that drive the dielectric performance characteristics of $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ (e.g. T_1 , T_2 , ϵ_r at T_1 and T_2) will lay the groundwork in facilitating the application of doped SNN1 or related TTBs for Pb-/Bi-free multilayer ceramic capacitors (MLCCs).

4.2 Experimental Methods

4.2.1 Ceramic Processing

$\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ (where $z = 0$ [SNN1], $z = 0.0125$, $z = 0.025$, $z = 0.037$, $z = 0.05$, and $z = 0.075$) ceramics were processed by the conventional mixed oxide route as outlined in Chapter 3 – Experimental Methods, using SrCO_3 (Sigma-Aldrich, > 99.9 %), Na_2CO_3 (Sigma-Aldrich, > 99 %), CaCO_3 (Alfa Aesar, 99%), Y_2O_3 (Sigma-Aldrich, 99.99%), ZrO_2 (Sigma-Aldrich, 99%), and Nb_2O_5 (Alfa Aesar, 99.9 %) chemical reagent powders. CAS codes of chemical reagent powders used in this chapter are shown in Table 3.1, Chapter 3 – Experimental Methods. Complete information of calcination, sintering temperatures, and dwell times for each composition are given in Table 4.1. Calcination was carried out at 1200 °C for 6 hours with a heating/cooling rate of 300 °C/hour. Maximum densities (93 – 96 %) were obtained with a sintering temperature of 1300-1350 °C whilst being held for 4-5 hours with a heating/cooling rate of 300 °C/hour.

4.2.2 Structural and Electrical Characterisation

Using measured pellet volumes and masses, experimental pellet densities were obtained, as described in Chapter 3 – Experimental Methods. Rietveld refinements using a DFT-derived *Ama2* structural model for $z = 0$ (SNN1) [18] and second phase tetragonal *I4/mcm* structural model for Sr-modified NaNbO_3 [18, 238] were undertaken on room temperature (R.T.) laboratory PXRD diffraction patterns to verify phase identity, purity and densities of SNN1 and all 5 $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ z -compositions. The second phase Sr-modified NaNbO_3 was fitted using a tetragonal *I4/mcm* structural model that corresponds to the high temperature phase of NaNbO_3 (> 570 °C). However, it is more likely the true phase of Sr-modified NaNbO_3 is orthorhombic as reported in the literature [239-241]. It should be noted that the

estimated phase fraction of Sr modified NaNbO_3 never exceeds ~5 wt.%. Theoretical pellet densities for all compositions were extracted from R.T. laboratory PXRD Rietveld refined lattice parameters.

Rietveld refinement analysis on variable temperature synchrotron PXRD diffraction patterns was conducted on $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ ($z = 0$ [SNN1], 0.0125, 0.025, 0.037, 0.05, and 0.075) from -173 °C to 350 °C using the orthorhombic *Ama2* structural model for SNN1 [18]. Peak shape contributions, including instrument, zero-point error, and wavelength ($\lambda = 0.824993(3)$ Å), were calibrated against a NIST® 640 silicon standard. Variable temperature sequential refinements were performed using the least squares refinement program *TOPAS Academic* (Version 7.1.0) [212] in conjunction with *jEdit* (Version 5.7.0) text editor software to run sequential refinements across the measured temperature range (-173 °C – 350 °C). Irreducible representations (irreps) using symmetry – adapted distortion mode and strain nomenclature by Miller *et al.* [223] were used as refinement parameters and refined together with lattice parameters. Irrep nomenclature is detailed in Chapter 2 – Background Science & Literature Review.

Transmission electron microscopy (TEM) sample preparation and analysis was undertaken by Dr. Robin Sjökvist and Professor Richard Beanland (University of Warwick), with figures and captions produced by Dr. Robin Sjökvist. TEM samples were prepared as reported by Sjökvist *et al.* [242]. Pellets were ground alongside fine (<10 µm) aluminium powder, at a 1:10 ratio and placed in aluminium foil. The folded foil was next pressed using cold rollers, to produce a thin solid aluminium sheet containing particles of ceramic which was thinned through mechanical grinding and polishing. The specimen was mounted to a Cu TEM support using epoxy resin and thinned to transparency using Ar^+ ion milling (Gatan PIPS II, California, United States of America). Electron diffraction and dark field TEM was carried out using a JEOL 2100 LaB_6 (JEOL, Tokyo, Japan) TEM operated at 200 keV.

Table 4.1: Nominal composition, composition code, calcination and sintering temperatures, respective dwell times for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$, $z = 0.0125$, $z = 0.025$, $z = 0.037$, $z = 0.05$, and $z = 0.075$.

Nominal Formula $z(\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15})$	Composition Code	Calcination		Sintering	
		Temperature (°C)	Time (hours)	Temperature (°C)	Time (hours)
$\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN1)	$z = 0$	1200	12	1300	5
$\text{Sr}_{1.975}\text{NaCa}_{0.0125}\text{Y}_{0.0125}\text{Nb}_{4.9875}\text{Zr}_{0.0125}\text{O}_{15}$	$z = 0.0125$	1200	12	1350	5
$\text{Sr}_{1.95}\text{NaCa}_{0.025}\text{Y}_{0.025}\text{Nb}_{4.975}\text{Zr}_{0.025}\text{O}_{15}$	$z = 0.025$	1200	12	1350	5
$\text{Sr}_{1.926}\text{NaCa}_{0.037}\text{Y}_{0.037}\text{Nb}_{4.963}\text{Zr}_{0.037}\text{O}_{15}$	$z = 0.037$	1200	12	1350	5
$\text{Sr}_{1.9}\text{NaCa}_{0.05}\text{Y}_{0.05}\text{Nb}_{4.975}\text{Zr}_{0.05}\text{O}_{15}$	$z = 0.05$	1200	12	1350	5
$\text{Sr}_{1.85}\text{NaCa}_{0.075}\text{Y}_{0.075}\text{Nb}_{4.925}\text{Zr}_{0.075}\text{O}_{15}$	$z = 0.075$	1200	12	1350	4

SEM-EDX, Raman spectroscopy, electrical characterisation measurements and sample preparation were conducted as described in Chapter 3 – Experimental Methods.

4.3 Results and Discussion

4.3.1 Room Temperature Laboratory X-ray Powder Diffraction (PXRD)

The work in this section presents an expanded series of the $\text{Sr}_{2-2z}\text{Ca}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ system reported by Brown *et al.* [15] to intermediary and higher dopant levels. Laboratory powder X-ray diffraction was used to determine the phase purity and densities of $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ samples (where $z = 0$ [SNN1], 0.0125, 0.025, 0.037, 0.05, and 0.075). Weight percentages of the orthorhombic *Ama2* TTB phase across all compositions were $\sim 95\%$, while the secondary perovskite tetragonal *I4/mcm* NaNbO_3 phase was $< 5 \text{ wt.}\%$, and all residual (R_{wp}) values for the fit were $< 10\%$. Calculated pellet densities were $\geq 93\%$, where the theoretical density did not account for the presence of the secondary phase. Sample codes and corresponding weight percentages of each phase, in addition to the refinement R_{wp} values, are shown in Table 4.2. Here, the *Ama2* structural model assigned to SNN1 and $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ is orthorhombic. Hence, in this chapter compositions will collectively be referred to as pseudo – TTBs.

Rietveld refinement fits, based on the DFT-derived *Ama2* structural model [18], of diffraction patterns obtained from laboratory PXRD at room temperature (R.T.) are shown in Figure 4.1a – f. The secondary NaNbO_3 phase is a common by-product in the synthesis of $z = 0$ (SNN1) [166, 181, 186]. However, the exact stoichiometry of the secondary phase of NaNbO_3 cannot be ascertained as the complex polymorphism of NaNbO_3 [243] circumvents the ability to determine accurately the room temperature phase with certainty when it is doped with Sr (50). The likely presence of $\text{Na}_{1-x}\text{Sr}_{x/2}\text{NbO}_3$ has been proposed by Garcia-Gonzalez *et al.* [186] and Torres-Pardo *et al.* [181]. The presence of only the TTB and perovskite Sr-modified NaNbO_3 phases suggests that the dopants have integrated into the parent $z = 0$ (SNN1) phase to form $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ ($z = 0.0125, 0.025, 0.037, 0.05, \text{ and } 0.075$) as intended in

the nominal formula. The secondary NaNbO_3 phase is a common by-product in the synthesis of $z = 0$ (SNN) [166, 181, 186]. The presence of only the TTB and perovskite Sr-modified NaNbO_3 phases suggests that the dopants have integrated into the parent $z = 0$ (SNN) phase to form $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ ($z = 0.0125, 0.025, 0.037, 0.05$, and 0.075) as intended in the nominal formula. Changes in lattice parameters, particularly the c lattice parameter, and unit cell volumes (see later - Figure 4.13a – d) support this view, however, a low-level of dopants within the Sr-modified NaNbO_3 cannot be discounted.

Table 4.2: Room temperature laboratory PXRD crystallographic information highlighting pseudo – TTB and perovskite weight percentages (wt.%), weighted R - factors (R_{wp}), theoretical pellet densities, geometric pellet densities, and pellet density (%) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$, $z = 0.0125$, $z = 0.025$, $z = 0.037$, $z = 0.05$, and $z = 0.075$.

Composition Code	Pseudo — TTB Phase (wt. %)	Perovskite Sr-modified NaNbO_3 Phase (wt. %)	R_{wp} (%)	Theoretical Pellet Density (g cm^{-3})	Geometric Pellet Density (g cm^{-3})	Pellet Density (%)
$z = 0$ (SNN1)	95.52	4.48	6.41	5.03	4.68	93
$z = 0.0125$	95.20	4.80	6.58	5.04	4.79	95
$z = 0.025$	95.91	5.09	5.49	5.04	4.79	95
$z = 0.037$	95.03	4.97	6.13	5.04	4.79	95
$z = 0.05$	95.91	5.09	8.61	5.05	4.85	96
$z = 0.075$	95.19	4.81	5.48	5.05	4.75	94

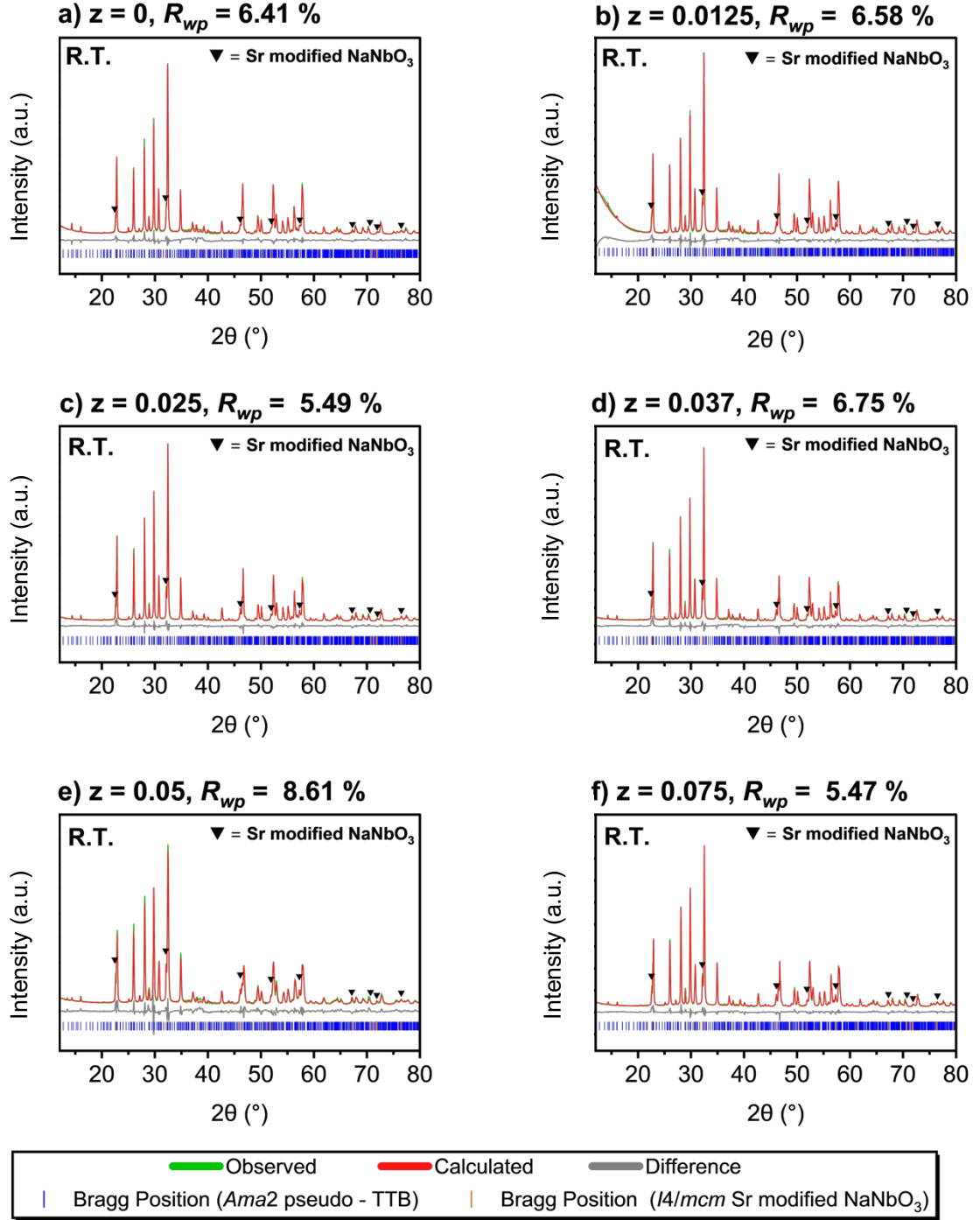


Figure 4.1: Rietveld refinement plots of the *Ama2* structural model against diffraction patterns obtained from laboratory PXRD at room temperature (R.T) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$. Tick marks indicate Bragg positions for the structural models of the main orthorhombic *Ama2* pseudo – TTB phase (blue) and tetragonal *I4/mcm* perovskite Sr-modified NaNbO_3 phase (orange), marked by ∇ .

4.3.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX)

Scanning electron microscopy (SEM) micrographs, grain size distribution plots and EDX elemental mapping for all $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ compositions are shown in Figure 4.2 – Figure 4.7, while superimposed grain size distribution plots are shown in Appendix C – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Figure C1. Full grain size data are summarised in Table 4.3. All compositions show the presence of uniformly distributed minor, dark grains of Sr-modified NaNbO_3 , corroborated by laboratory PXRD (Table 4.2 and Figure 4.1a – f). The presence of Sr within the NaNbO_3 phase is validated by SEM-EDX elemental mapping, which shows Na^+ rich and Sr^{2+} deficient grains consistently observed across all dopant levels (Figure 4.2 – Figure 4.7).

A homogenous distribution of Y^{3+} , Ca^{2+} and Zr^{4+} in the main pseudo –TTB phase is demonstrated across all z by EDX elemental mapping. This observation, supported by laboratory PXRD (Table 4.2 and Figure 4.1a – f), emphasises that the dopants have integrated into the desired TTB structure and that the only secondary phase present is Sr-modified NaNbO_3 . However, the specific stoichiometry of Sr and indeed, dopants in NaNbO_3 remains difficult to establish, particularly at such low total concentrations in all compositions (< 5 wt. %). Porosity and microcracks were evident for all dopant levels, despite high apparent densities (93 – 95%); porosity may have arisen from mechanical grinding and grain pull-out during SEM sample preparation.

The average grain size in the $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ samples increased from 7.8 μm ($z = 0$ [SNN]) to 12.7 μm ($z = 0.0125$). From $z = 0.0125$ to $z = 0.075$ the average grain size remained relatively constant at 11.3 and 14.3 μm respectively, within a standard error of 0.2 – 0.4 μm . The minimum grain size remained approximately constant in the range of 3.7 – 5.7 μm across all dopant levels. The maximum grain size increased from 9 μm ($z = 0$) to 22.4 μm ($z = 0.0125$) and remained constant thereafter within the range of 21.1 to 27.3 μm . This indicates a uniform distribution of grain sizes from $z = 0$ to $z = 0.075$ in $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ samples, with no evidence of abnormal grain growth (grains $> 50 \mu\text{m}$).

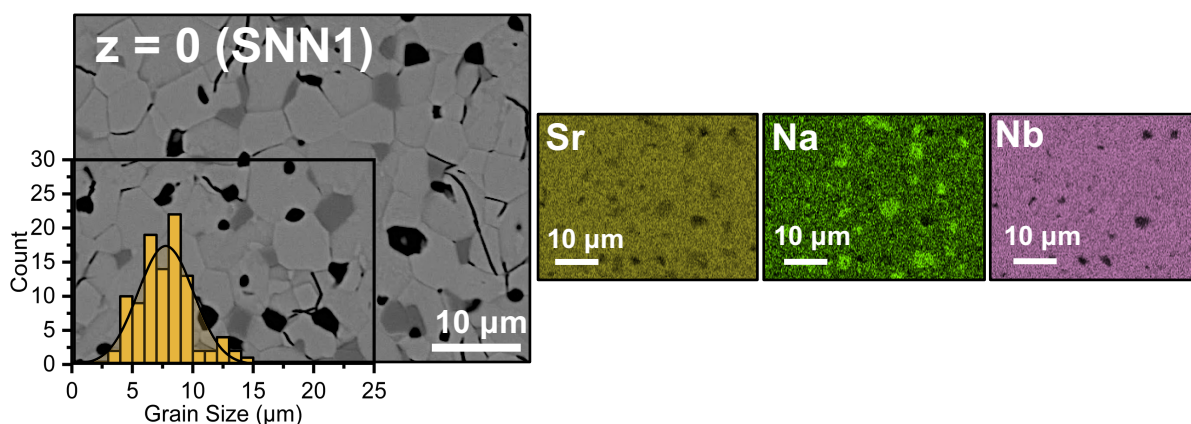


Figure 4.2: Back scattered SEM micrograph with corresponding grain size distribution plot (left), and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac) cations for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$ (SNN1).

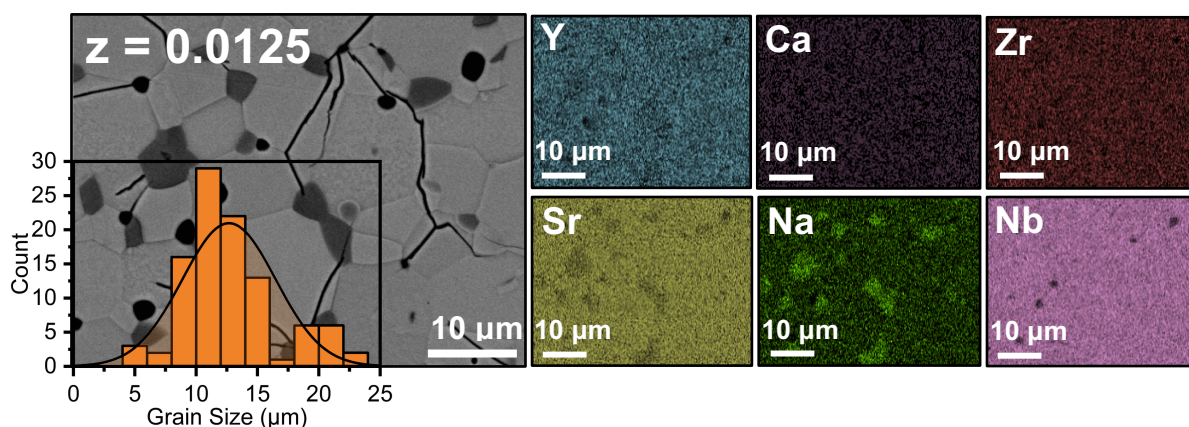


Figure 4.3: Back scattered SEM micrograph with corresponding grain size distribution plot (left), and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac), Y^{3+} (blue), Ca^{2+} (purple), and Zr^{4+} (red) cations for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0.0125$.

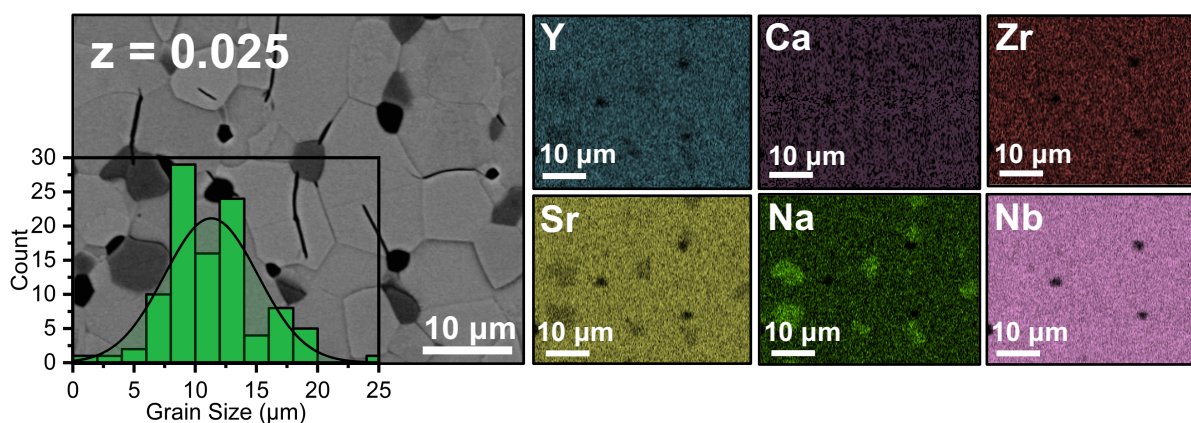


Figure 4.4: Back scattered SEM micrograph with corresponding grain size distribution plot (left), and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac), Y^{3+} (blue), Ca^{2+} (purple), and Zr^{4+} (red) cations for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0.025$.

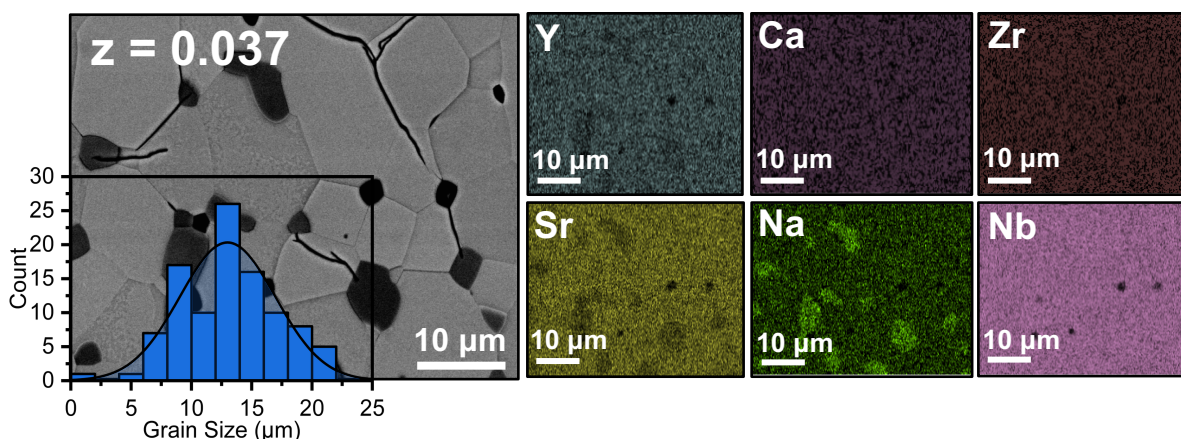


Figure 4.5: Back scattered SEM micrograph with corresponding grain size distribution plot (left), and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac), Y^{3+} (blue), Ca^{2+} (purple), and Zr^{4+} (red) cations for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0.037$.

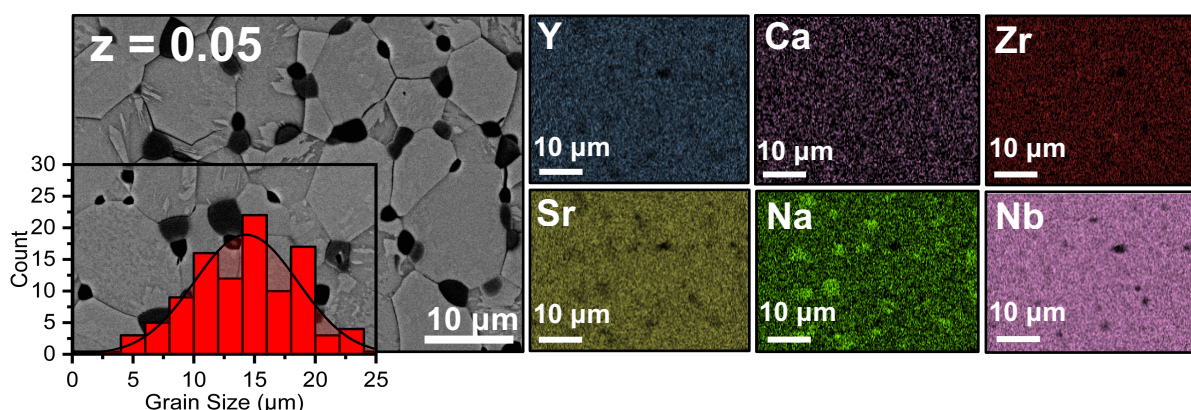


Figure 4.6: Back scattered SEM micrograph with corresponding grain size distribution plot (left), and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac), Y^{3+} (blue), Ca^{2+} (purple), and Zr^{4+} (red) cations for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0.05$.

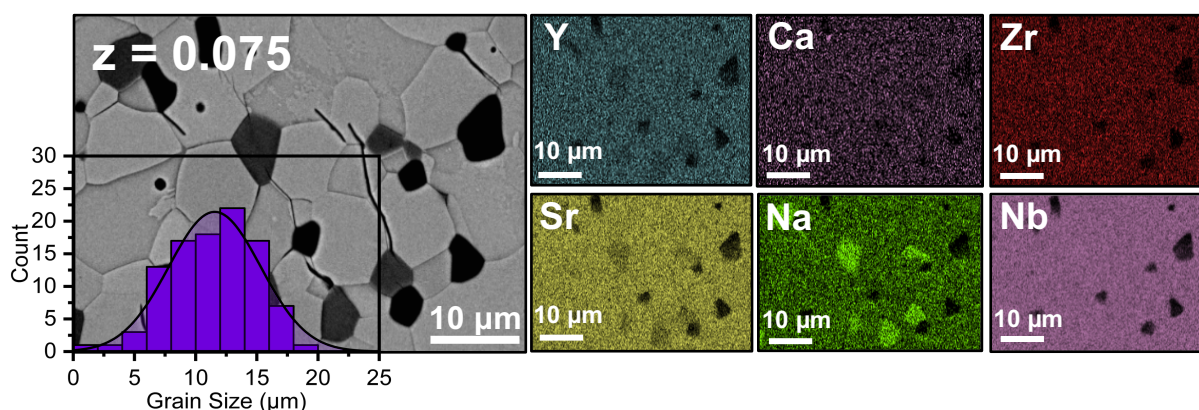


Figure 4.7: Back scattered SEM micrograph with corresponding grain size distribution plot (left), and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac), Y^{3+} (blue), Ca^{2+} (purple), and Zr^{4+} (red) cations for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0.075$.

Table 4.3: Quantified grain size data summary for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$, $z = 0.0125$, $z = 0.025$, $z = 0.037$, $z = 0.05$, and $z = 0.075$. Underestimation of grain sizes from cross-sectional imaging was considered *via* multiplication of a factor of 1.56 as proposed by Mendelson [244].

Composition Code	Average Grain Size (μm)	Standard Error (μm)	Minimum Grain Size (μm)	Maximum Grain Size (μm)
$z = 0$	7.8	0.2	3.8	14.8
$z = 0.0125$	12.7	0.4	4.7	22.4
$z = 0.025$	11.4	0.4	3.7	25.5
$z = 0.037$	13.1	0.4	5.2	21.1
$z = 0.05$	14.3	0.4	5.7	23.6
$z = 0.075$	11.7	0.4	3.8	27.3

Perhaps most notably, $z = 0.05$ (Figure 4.6) features jagged domain-like topography within SNN1 grains and ranging from 0.1 – 1 μm in size, which may point to possible domain pinning by accumulated defects [245, 246]. However, surface charges from the presence of charged defects (*i.e.* Na^+ or O^{2-} vacancies) may also contribute to the observed contrast in Figure 4.6 [247]. Repercussions of possible pinned domains from charged defects on dielectric performance (notably ϵ_r at T_2), will be discussed further in section 4.3.4 Dielectric and Ferroelectric Characterisation [247].

4.3.3 Raman Spectroscopy

Raman spectroscopy was used as a complementary technique to synchrotron PXRD to illustrate intrinsic, short range, local structural distortions of the Nb/ZrO_6 octahedral framework with respect to doping. Extrinsic lattice vibrations ($< 200 \text{ cm}^{-1}$) are a product of A site cation motion relative to the Nb/ZrO_6 octahedral framework [248]. Here, peaks $< 200 \text{ cm}^{-1}$ become less well-defined with doping, indicating increased disorder. For

$\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, vibrations related to B-site motion are observed at $\sim 250 \text{ cm}^{-1}$ (v_5 , O-Nb/Zr-O bend), $\sim 630 \text{ cm}^{-1}$ (v_2 , Nb/Zr-O stretch) and $\sim 850 \text{ cm}^{-1}$ (v_1 , Nb/ZrO₆ deformation), as highlighted in Figure 4.8a. Crucially, the v_2 and v_5 modes comprise normal vibrations related to cationic motion parallel to the ferroelectric mode along the *c*-axis [19, 249]. Raman peak shifts and full widths at half maxima (FWHMs) extracted from peak fitting of the v_2 and v_5 modes are shown in Figure 4.8b and Figure 4.8c respectively.

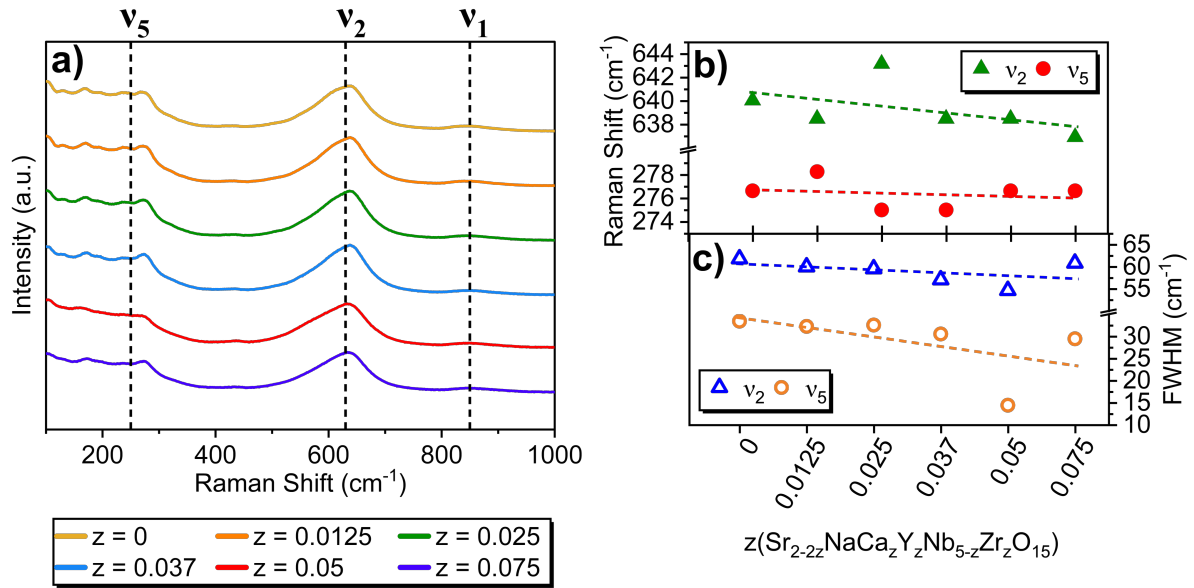


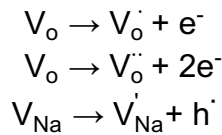
Figure 4.8a – c: Room temperature normalised intensity plots as a function of Raman shift for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$ (yellow), $z = 0.0125$ (orange), $z = 0.025$ (green), $z = 0.037$ (blue), $z = 0.05$ (red), and $z = 0.075$ (purple) between a) Raman shift spectral range of 100 -1000 cm^{-1} alongside plots of the b) Raman shift (peak position), and c) full width at half maximum (FWHM) of v_5 and v_2 vibrational modes.

The v_1 vibrational mode shows negligible variation of both peak position and FWHM with dopant level, reflecting the collective rigidity of the oxygen octahedral framework. Both v_5 and v_2 peak positions show a minor red Raman shift (Figure 4.8b). The FWHM of v_5 and v_2 , however, remain effectively constant, within error, with increasing dopant level (Figure 4.8c). The red shift of peak positions (*i.e.* a shift to lower frequency) with z , is indicative of a softening of the $\text{Nb}^{5+}/\text{Zr}^{4+}$ cation and O^{2-} anion electrostatic interaction within the Nb/ZrO₆ octahedral framework (*i.e.* weakening of the B–O–B linkages between octahedra), possibly leading to increased rigid unit mode (RUM)

octahedral tilt. The red shift of ν_2 has been previously attributed to the doping of smaller radii A site cations, increasing the B–O stretching vibration at $\sim 640 \text{ cm}^{-1}$ and weakening B–O bonds [187]. A weakening of the Nb/ZrO₆ octahedral framework, was also reported in the similar $\text{Sr}_{0.485}\text{Ba}_{0.47}\text{Gd}_{0.03}\text{Nb}_{2-x}\text{Zr}_x\text{O}_6$ ($x = 0, 0.1, 0.2, 0.3$) system by Yang *et al.* [160].

4.3.4 Dielectric and Ferroelectric Characterisation

Multi-frequency ϵ_r and $\tan\delta$ — temperature response plots with added low temperature $\tan\delta$ response plots inset are shown in Figure 4.9a – f. The extension of z in $\text{Sr}_{2-2z}\text{Ca}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ from Brown *et al.* [15] here, illustrates a flattening of dielectric anomalies (T_1 and T_2) from $z = 0$ to $z = 0.075$ (Figure 4.9a – f). Comparative plots of pellets from the same synthesis batch and differing batches, in addition to their heating and cooling profiles using compositions $z = 0$ (SNN1) and $z = 0.025$ as examples are shown in Appendix C – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Figure C2, to illustrate the consistency and reproducibility of the dielectric response at T_2 . Minor frequency dispersion is noted at T_2 for $z = 0$, $z = 0.0125$, $z = 0.025$ and, most noticeably, $z = 0.037$, at 1 kHz (marked by * in Figure 4.9d), which corresponds to an accompanied increase in $\tan\delta$ in these compositions (Figure 4.9a – d). This observation is consistent with that of Hooper *et al.* [152] for CaSnO_3 doped $\text{Sr}_{2.1}\text{Na}_{0.8}\text{Nb}_5\text{O}_{15}$. This phenomenon may be a product of space charge contributions (*i.e.* ionic conduction), such as oxygen vacancies ($V_o^\bullet$ or $V_o^{\bullet\bullet}$) and/or sodium vacancies ($V_{\text{Na}}^\bullet$) [19, 188, 250] such as:



which occur up to $\sim 1 \text{ kHz}$ [3, 152]. Additionally, the frequency dispersion at T_1 suggests increasingly relaxor-like behaviour with doping. A third, yet subtle, dielectric anomaly is observed in $z = 0$ (SNN1) (labelled as T_3 in which occur up to $\sim 1 \text{ kHz}$ [3, 152]. Additionally, the frequency dispersion at T_1 suggests increasingly relaxor-like behaviour with doping. A third, yet subtle, dielectric anomaly is observed in $z = 0$ (SNN1) (labelled as T_3 in Figure 4.9a – d) at $\sim 125^\circ\text{C}$. This aligns with observations of a T_3 by Cao *et al.* [166] and Cao *et al.* [251] featuring at $\sim 70^\circ\text{C}$ in $\text{Sr}_{2-x}\text{Gd}_x\text{NaNb}_{5-x}\text{Ti}_x\text{O}_{15}$, (where $x = 0.12$ and 0.15) and at $\sim 80^\circ\text{C}$ in $\text{Sr}_{2-x}\text{La}_x\text{NaNb}_{5-x}\text{Ti}_x\text{O}_{15}$ (where $x = 0.08$ and 0.12) respectively. These studies likewise suggest a relationship between T_3

and space charge contributions [152, 158]. a – d) at $\sim 125^\circ\text{C}$. A subtle distortion from an orthorhombic phase (*i.e.* $Cmm2$, $Im2a$, $Ama2$) to the non-centrosymmetric ferroelectric tetragonal phase ($P4bm$) followed by the centrosymmetric paraelectric phase ($P4/mbm$) at T_2 has also been proposed [152, 158].

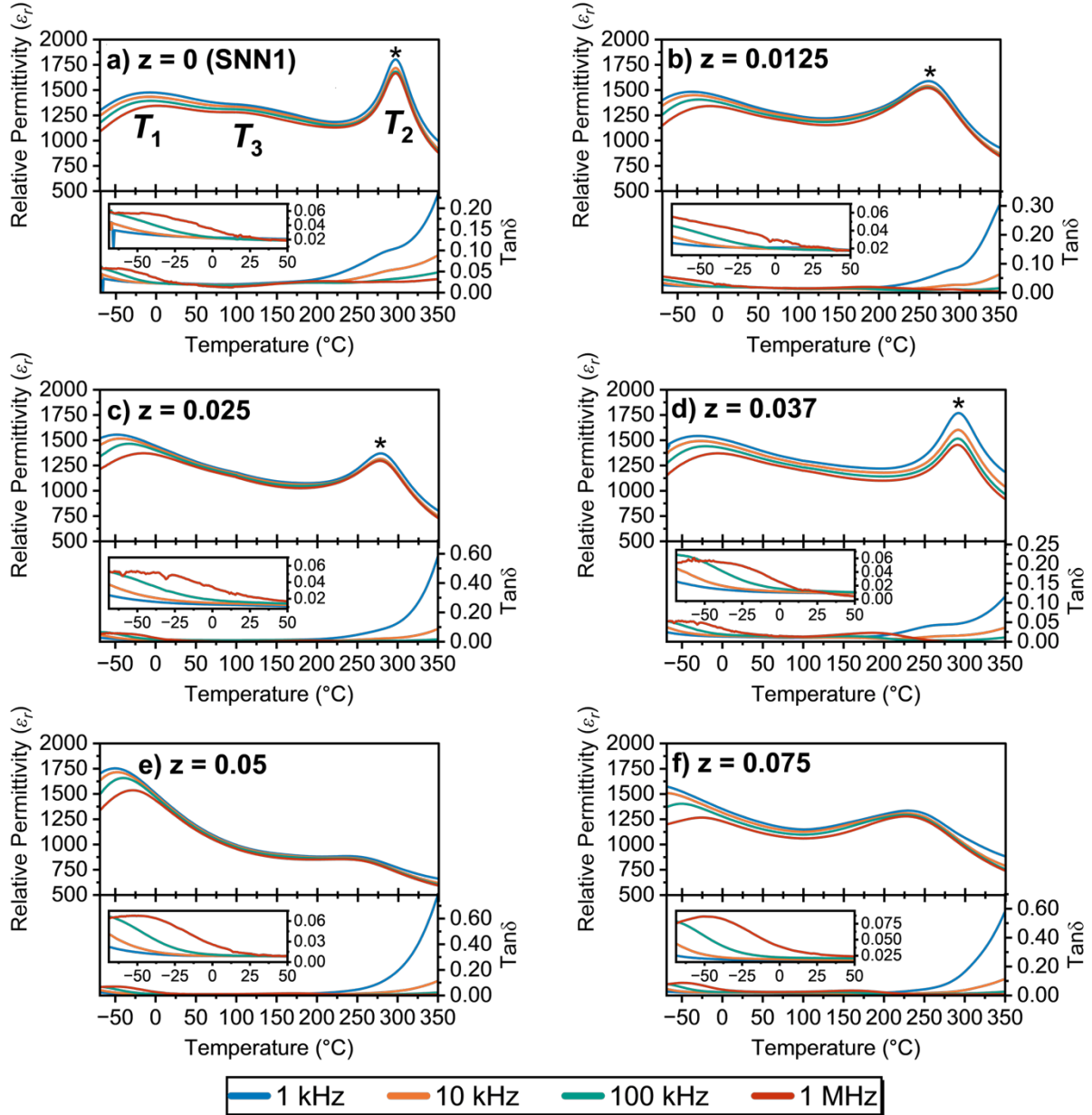


Figure 4.9– f: Multi-frequency relative permittivity (ϵ_r) and dielectric loss tangent ($\tan\delta$) response temperature evolution plots with additional low temperature $\tan\delta$ response inset plots for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$. Minor frequency dispersions at T_2 at 1 kHz are marked by an *.

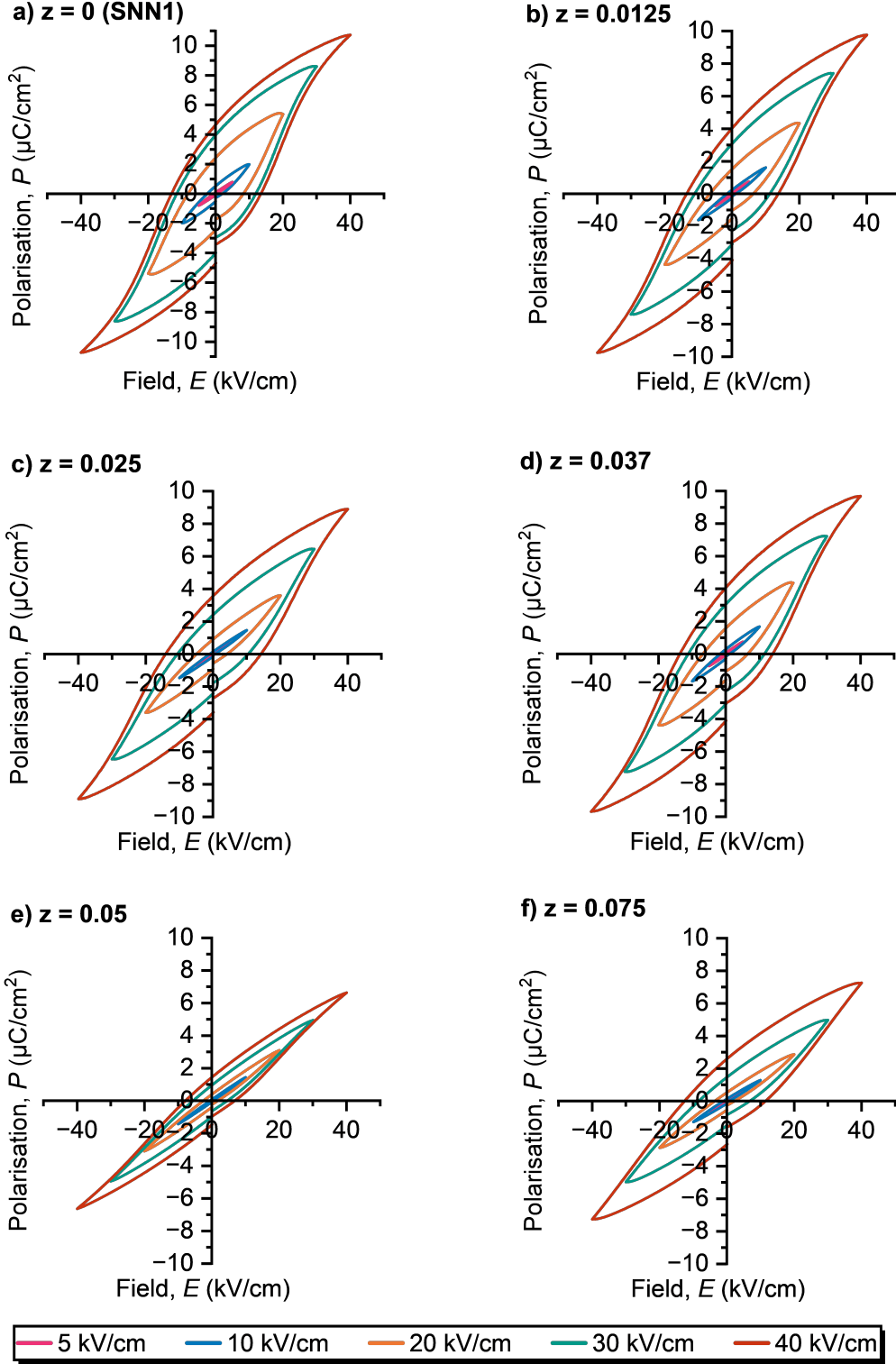


Figure 4.10a – f: Multi-field polarisation (P) versus field (E) measured at incremental fields of 5 kV/cm, 10 kV/cm, 20 kV/cm, 30 kV/cm, 40 kV/cm for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$.

Polarisation versus field hysteresis loops measured in increments up to 40 kV/cm are shown for $\text{Sr}_{2-2z}\text{Ca}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ in Figure 4.10a — f. All compositions exhibit ferroelectric behaviour, demonstrated by saturation nearing maximum polarisation, P_{max} . SNN1 displays a slightly more notable polarisation saturation relative to doped compositions, where P_{max} decreases with z . This emphasises the decrease in ϵ_r across all frequencies [250] illustrated in multi-frequency ϵ_r and $\tan\delta$ — temperature response plots (Figure 4.9a — f) adhering to the relationship $P = (\epsilon_r - 1)E\epsilon_0$ [252].

A comparative plot of ϵ_r and $\tan\delta$ — temperature profiles at 1 kHz are shown in Figure 4.11a. Corresponding extracted values of T_1 , T_2 , ϵ_r at T_1 and at T_2 at 1 kHz are plotted against doping level, z in Figure 4.11b. As the content of z increases, there is a gradual decrease in the T_1 ferroelectric relaxor peak from $z = 0$ (-8°C , $\epsilon_r = 1476$ at 1 kHz) to $z = 0.075$ ($>-75^\circ\text{C}$, $\epsilon_r = 1582$ at 1 kHz). At T_1 , $z = 0$ (-8°C , $\epsilon_r = 1476$ at 1 kHz) and $z = 0.0125$ (-31°C , $\epsilon_r = 1474$ at 1 kHz) showed similar ϵ_r values at T_1 . Increasing doping level from $z = 0.0125$ ($T_1 = -31^\circ\text{C}$, $\epsilon_r = 1474$ at 1 kHz) to $z = 0.075$ ($T_1 = >-75^\circ\text{C}$, $\epsilon_r = 1582$ at 1 kHz) showed a minor increase in ϵ_r at T_1 . Dopant levels $z = 0.025$ ($T_1 = -51^\circ\text{C}$, $\epsilon_r = 1714$ at 1 kHz) and $z = 0.05$ ($T_1 = -50^\circ\text{C}$, $\epsilon_r = 1751$ at 1 kHz) stand out with marginally higher ϵ_r values in comparison. The T_2 (ferroelectric $\rightarrow$ paraelectric) transition temperature reduced with doping, from $z = 0$ (297°C , $\epsilon_r = 1803$ at 1 kHz) to $z = 0.075$ ($T_2 = 229^\circ\text{C}$, $\epsilon_r = 1333$ at 1 kHz). ϵ_r at T_2 generally decreases from $z = 0$ ($T_2 = 297^\circ\text{C}$, $\epsilon_r = 1803$ at 1 kHz) to $z = 0.075$ ($T_2 = 229^\circ\text{C}$, $\epsilon_r = 1333$ at 1 kHz), with a rise from $z = 0.025$ ($T_2 = 279^\circ\text{C}$, $\epsilon_r = 1439$ at 1 kHz) to $z = 0.037$ ($T_2 = 292^\circ\text{C}$, $\epsilon_r = 1768$ at 1 kHz). A substantial drop in ϵ_r at T_2 is observed for $z = 0.05$ ($T_2 = 235^\circ\text{C}$, $\epsilon_r = 882$ at 1 kHz).

Polarisation versus field loops measured at 40 kV/cm are shown in Figure 4.11c, with P_{max} , remnant polarisation (P_{rem}) and coercive field (E_c) presented as a function of z in Figure 4.11d. P_{max} and P_{rem} show a decrease with doping level with a distinct maximum at $z = 0.037$ ($P_{\text{max}} = 9.8 \mu\text{C}/\text{cm}^2$ and $P_{\text{rem}} = 4.1 \mu\text{C}/\text{cm}^2$ at 40 kV/cm). E_c fluctuates minimally from $z = 0$ to $z = 0.037$ ($E_c = 13 - 14 \text{ kV}/\text{cm}$ at 40 kV/cm), falling thereafter to $z = 0.075$ ($E_c = 12 \text{ kV}/\text{cm}$ at 40 kV/cm). Notably, $z = 0.05$ showed a significant reduction in P_{max} ($P_{\text{max}} = 6.7 \mu\text{C}/\text{cm}^2$ at 40 kV/cm), P_{rem} ($P_{\text{rem}} = 1.4 \mu\text{C}/\text{cm}^2$

at 40 kV/cm) and E_c ($E_c = 7$ kV/cm at 40 kV/cm), coinciding with the reduced ϵ_r at T_2 relative to other z values.

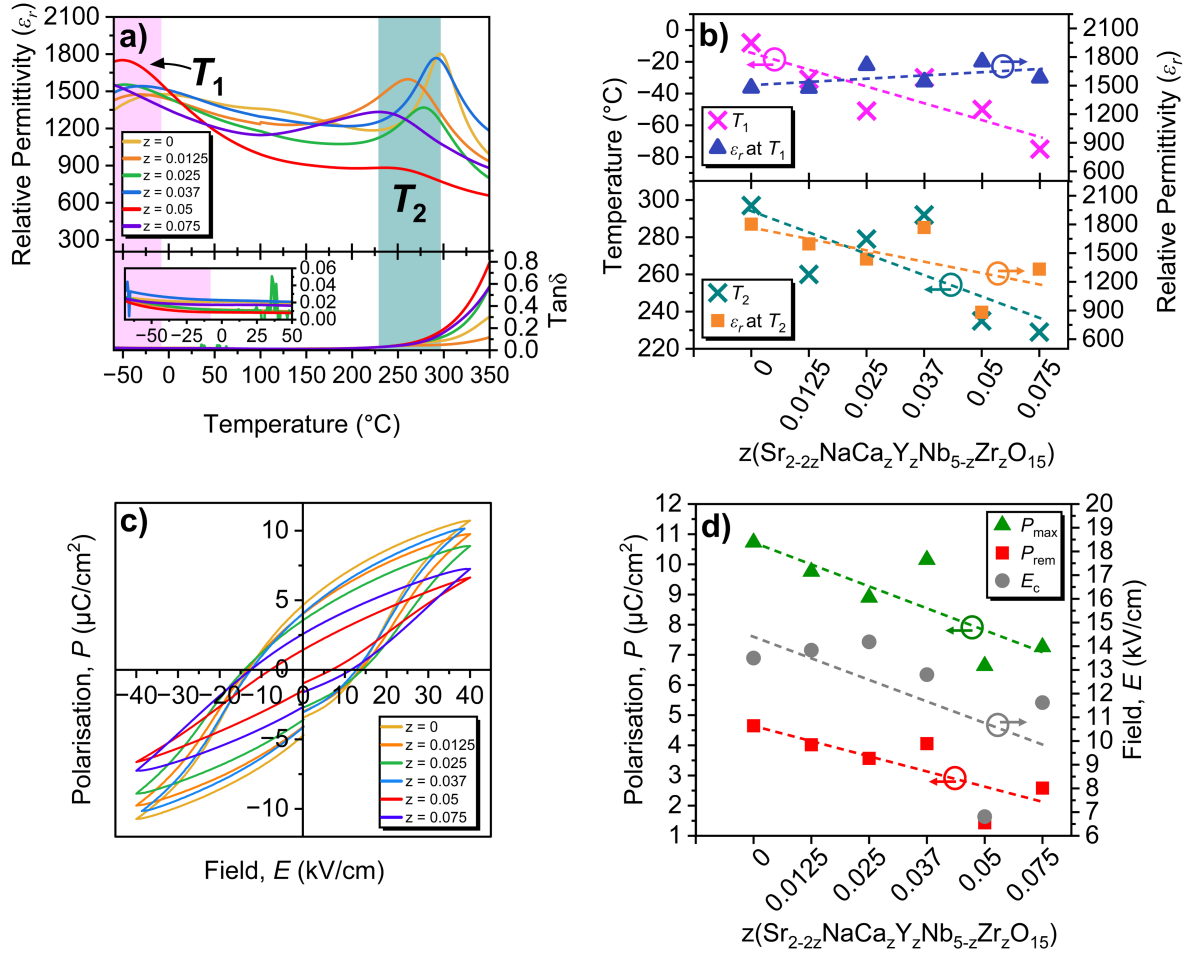


Figure 4.11a – d: Plots showing a) Relative permittivity (ϵ_r) and dielectric loss tangent ($\tan\delta$) response temperature evolution plots measured at 1 kHz for $z = 0$ (SNN1, yellow), $z = 0.0125$ (orange), $z = 0.025$ (green), $z = 0.037$ (blue), $z = 0.05$ (red), and $z = 0.075$ (purple) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, b) T_1 , ϵ_r at T_1 (top) and T_2 , ϵ_r at T_2 (bottom), c) polarisation, P versus field, E hysteresis loops for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ d) maximum, remnant polarisation ($P_{\max}$ and P_{rem}) and coercive field (E_c) versus z .

Composition $z = 0.05$ ($T_1 = -50$ $^{\circ}\text{C}$ where $\epsilon_r = 1751$, $T_2 = 235$ $^{\circ}\text{C}$ where $\epsilon_r = 882$) significantly deviates from the T_2 value reported by Brown *et al.* [15] for $z = 0.05$ ($T_1 = -49$ $^{\circ}\text{C}$ where $\epsilon_r = 1433$, $T_2 = 255$ $^{\circ}\text{C}$ where $\epsilon_r = 1308$). Repeated attempts at varying calcination and sintering conditions, offered no resolve to the consistently lower (1.5 times) ϵ_r at T_2 reported for $z = 0.05$ compared to Brown *et al.* [15]. Laboratory PXRD

showed no evidence of an unidentified tertiary phase, while SEM – EDX showed no evidence of grain segregation and/or chemical inhomogeneity.

Previously, in section 4.3.2, jagged domain-like topography seen in SEM micrographs for $z = 0.05$ (Figure 4.6) was attributed to accumulated charged defects. Indeed, $V_{\text{O}}^{\cdot}$ (or $V_{\text{O}}^{\cdot\cdot}$) and/or $V_{\text{Na}}^{\cdot}$ are known contributors to domain pinning [253]. These defects may have a part to play in hindering domain reorientation and effectively clamping polarisation [245, 246] contributing to the relatively lower ϵ_r at T_2 , P_{max} and P_{rem} for $z = 0.05$. Conversely, E_c is lower than expected, an unusual result, given a high E_c would be necessary to reorient what are assumed to be pinned domains by charged defects. Alternatively, dislocations have also been reported to have pinning effects [254]. The possible role of charged defects, ($V_{\text{O}}^{\cdot}$ [or $V_{\text{O}}^{\cdot\cdot}$] and/or $V_{\text{Na}}^{\cdot}$) or dislocations, remains speculative. Indeed, an open-ended question remains as to why this is only evident with solely $z = 0.05$ here. The use of *in situ* variable temperature transmission electron microscopy (TEM) could perhaps give insight into temperature-dependent defect-domain dynamics, possibly contributing to the unexpected ϵ_r at T_2 for $z = 0.05$ [255].

4.3.5 Variable Temperature Synchrotron X-ray Powder Diffraction (PXRD)

Variable temperature Rietveld refinement of variable temperature synchrotron PXRD diffraction patterns were based on the DFT-derived *Ama2* structural model [18]. Rietveld refinement plots of SNN1 and all $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ compositions at room temperature are shown in Figure 4.1a – f. Rietveld refinement fits at -173 °C (Figure C3) and 350 °C (Figure C4) are shown in Appendix C – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, demonstrating the variation of fit over the measured temperature range (-173 °C – 350 °C).

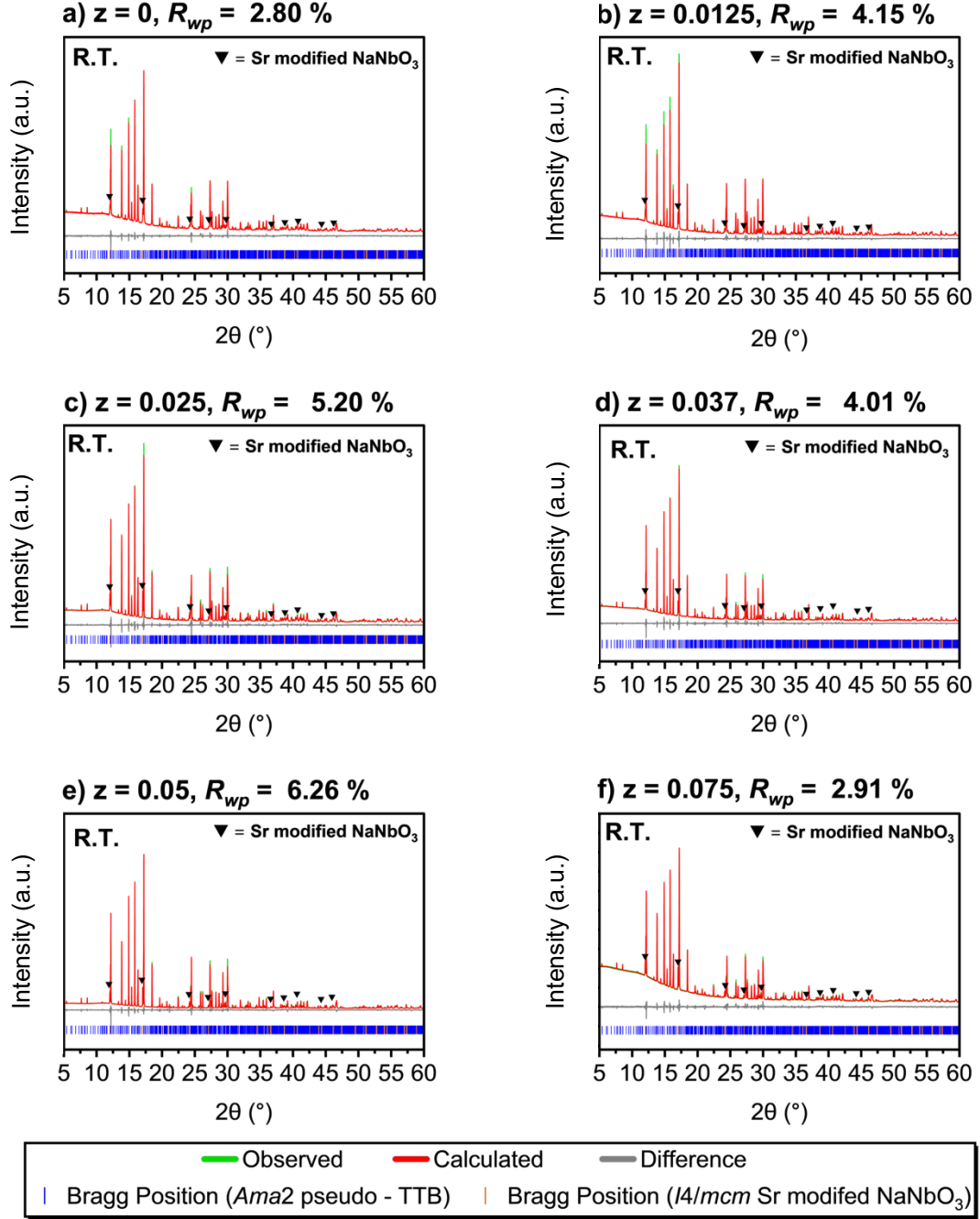


Figure 4. 12a – f: Rietveld refinement plots of the *Ama2* structural model against diffraction patterns obtained from synchrotron PXRD at room temperature (R.T.) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$. Tick marks indicate Bragg positions for the structural models of the main orthorhombic *Ama2* pseudo – TTB phase (blue) and tetragonal *I4/mcm* perovskite Sr-modified NaNbO_3 phase (orange), marked by ▼.

Lattice parameter lengths a , $b/2$, c , and unit cell volumes obtained from sequential variable temperature Rietveld refinements are shown in Figure 4.13a – d, while orthorhombic strain $\left(\frac{2(a - \frac{b}{2})}{(a + \frac{b}{2})}\right)$ versus temperature is shown in Figure 4.14.

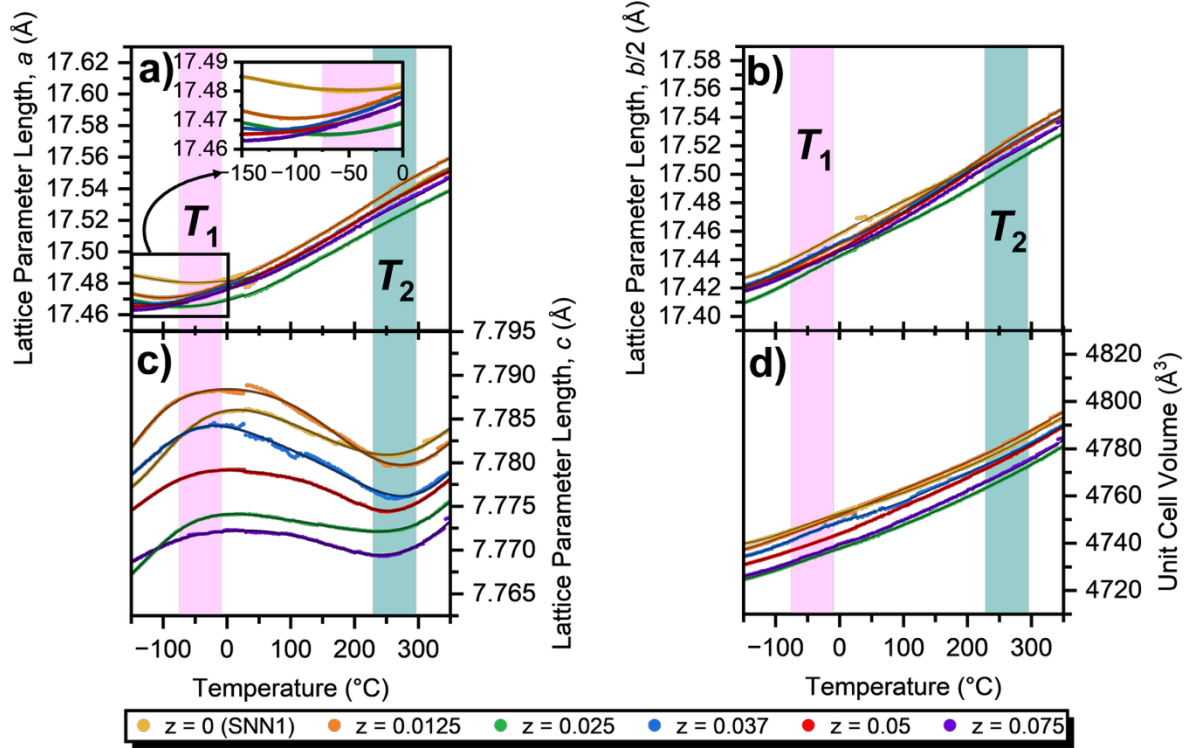


Figure 4.13a – d: Lattice parameter evolution with temperature where a) lattice parameters a , b) lattice parameter b , c) lattice parameter c , and d) unit cell volume, and corresponding high order polynomial fit (solid lines), where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$ for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ extracted from Rietveld refined synchrotron PXRD diffraction patterns.

Distortions of the $Ama2$ structure are characterised as irreducible representations (irreps) of the higher symmetry parent structure aristotype, $P4/mbm$. Distortion mode amplitudes are reported here as absolute A_p values (Å), which are given with respect to the $P4/mbm$ normalised amplitude of a given distortion [224]. Irreps are also labelled by an order parameter direction (OPD), which describes the direction of an active distortion [224]. Macroscopic strains transforming as irrep Γ_1^+ represent the volumetric symmetry strain, while Γ_4^+ denotes the orthorhombic strain in the ab plane (*i.e.* the deviation from tetragonal lattice parameters). Atomic displacements along c , transforming as irrep Γ_2^- , correspond to the antiferroelectric antipolar modes, while

irrep Γ_3^- represents the ferroelectric polar mode. The temperature variation of all refined irreps of Γ are shown in Figure 4.15a – d. It is important to note that lattice parameter determination is obtained exclusively from fitting to peak position. Whereas symmetry-adapted distortion modes are dependent on the accurate determination of atomic coordinates (*i.e.* the initial approximation used in the refinement model) and fitting to peak displacement, correlation between distortion modes, diffraction coherence length, and more broadly, peak intensity. Moreover, laboratory and synchrotron PXRD are not sensitive to displacements of light atoms (such as that of oxygen in the octahedral framework in the TTBs studied here). Consequently, the temperature evolution of the symmetry-adapted distortion modes does not perfectly marry that of the lattice parameters. Hence structure-property relationships discussed herein place more confidence in the lattice parameter temperature evolution.

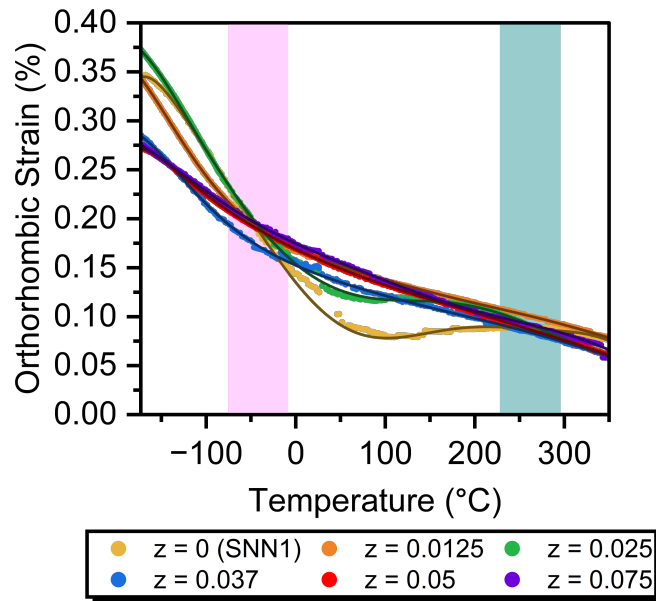


Figure 4.14: Symmetry adapted orthorhombic strain, transforming as irrep Γ_4^+ , as a function of temperature for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$, $z = 0.0125$, $z = 0.025$, $z = 0.037$, $z = 0.05$, and $z = 0.075$. Orthorhombic strain (%) is calculated by $\left(\frac{2(a - \frac{b}{2})}{(a + \frac{b}{2})}\right) \times 100$ where a and b are lattice parameters.

Inclusion of modes transforming as irreps representing octahedral tilts [$S_1(0,a;0,0)$], and shears [$M_5^+(a,a)$ and $M_5^-(a,a)$] in Rietveld refinements offered no improvement to

the quality of the fit and were all constrained to zero as in previous work [18]. Indeed, S_1 , M_5^+ and M_5^- distortion modes should be structurally and energetically unfavourable, due to the excessive strain induced upon the rigid TTB oxygen octahedral framework, as shown by the group theoretical symmetry analysis of Whittle *et al.* [256]. This led to the structural assignment of space group $Ama2$ to $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ by Whittle *et al.* [257] and more recently to SNN by Tidey *et al.* [18]. The evolution of S_3 amplitude with temperature is plotted in Figure 4.16. For visualisations of irreps refined in this work see Appendix B – Visualisation of Strain and Distortion Mode Irreducible Representations (Irreps).

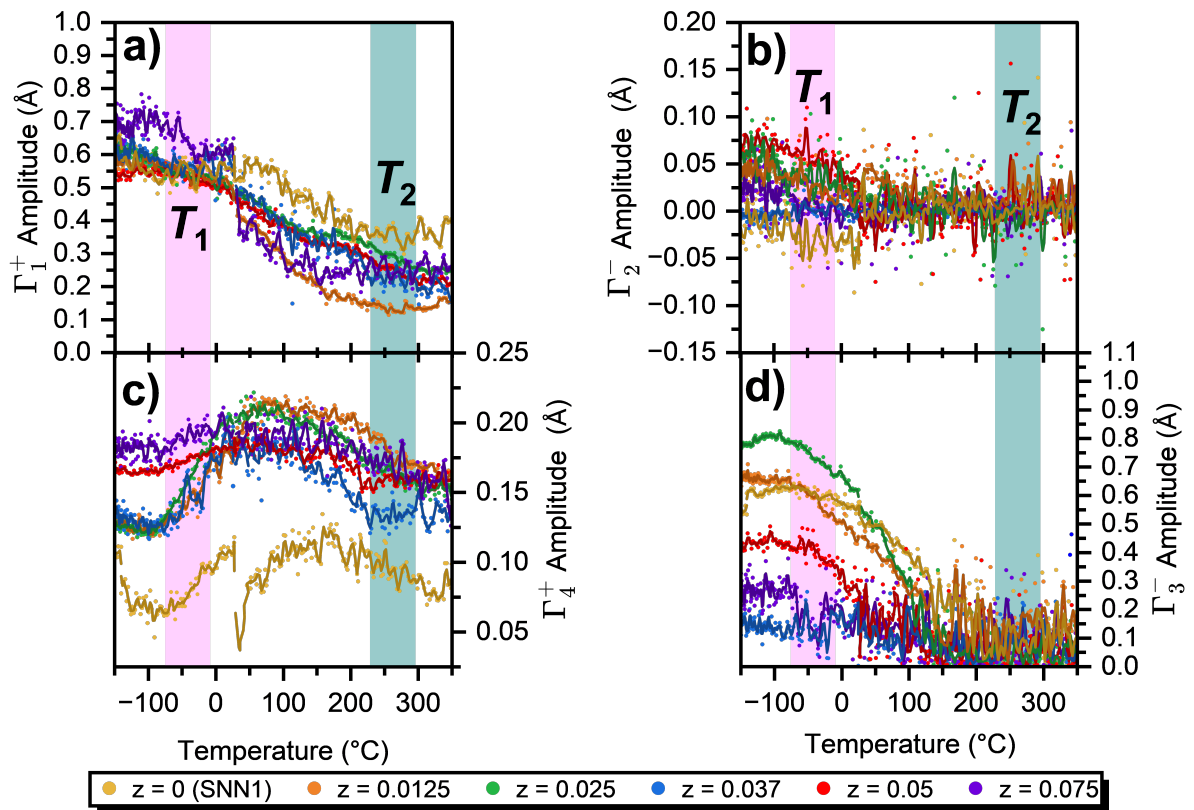


Figure 4.15a – d: Rietveld refined Γ modes ($k = 0$) evolution with temperature where a) the volumetric symmetry strain (Γ_1^+), b) antiferroelectric Γ_2^- distortion amplitude, c) orthorhombic strain (Γ_4^+), and d) the ferroelectric distortion Γ_3^- amplitude, where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$ for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$.

Upon cooling from high temperature, Tidey *et al.* [18] detail consecutive symmetry-lowering phase transitions for SNN. When cooling below T_2 (the paraelectric to ferroelectric transition), the non-polar Amm phase transitions to the ferroelectric

Ama2 phase (with an out-of-(*ab*)plane polar distortion mode of the *Ama2* structure transforming as irrep Γ_3^-). At T_1 (the relaxor ferroelectric peak), the *Ama2* phase transitions to a lower symmetry monoclinic *Aa* phase (with an in-(*ab*)plane polar distortion mode of the *Aa* structure transforming as irrep Γ_5^-). Here, the focus turns to the variable temperature Rietveld refinement of lattice parameters and symmetry-adapted modes using solely the orthorhombic *Ama2* structural model. The ferroelectric nature of the *Ama2* phase allows for a direct analysis of the doping-induced structural changes that drive the permittivity anomalies/maxima at T_1 and T_2 in SNN.

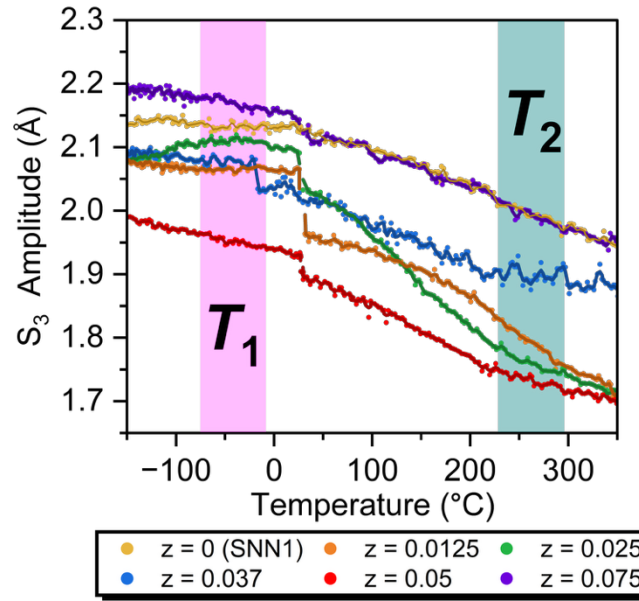


Figure 4.16: Rietveld refined irrep S_3 symmetry-motivated displacement mode evolution with temperature, where a) shows the S_3 amplitude variation with temperature for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$ (SNN1 [yellow]), $z = 0.0125$ (orange), $z = 0.025$ (green), $z = 0.037$ (blue), $z = 0.05$ (red), and d) $z = 0.075$ (purple). T_1 (pink) and T_2 (teal) ranges are extracted from 1 kHz dielectric data (Figure 4.11a).

Above T_2 , the a , b , and c lattice parameters all contract with decreasing temperature (Figure 4.13a – c). On cooling below T_2 , $z = 0$ (SNN) lattice parameters a (Figure 4.13a) and b (Figure 4.13b) continue to contract, whereas the c lattice parameter (Figure 4.13c) elongates with cooling. Correspondingly the polar mode transforming as the irrep, Γ_3^- , rises above zero amplitude approximately 50 °C below T_2 (Figure 4.15d). Tidey *et al.* [18] attribute the lag in temperature between the rise in Γ_3^- amplitude and T_2 to a gradual softening of this mode as temperature increases, with

local fluctuations continuing to drive the negative thermal expansion (NTE) of c , but before the correlation length of these distortions becomes sufficiently large for a phase transition (at T_2) to be observed in the diffraction intensities. Overall, the unit cell volume contracts with cooling (Figure 4.13d). Below T_2 , the symmetry adapted orthorhombic strain in the ab plane, transforming as irrep Γ_4^+ , is relatively constant at ca. 0.1%, as shown in Figure 4.14.

As cooling continues the ferroelectric polar mode, Γ_3^- , saturates at T_1 (Figure 4.15d). Over this temperature range, the antiferroelectric polar mode, Γ_2^- , is inactive (Figure 4.15c). The importance of competition arising from the coexistence of antiferroelectric Γ_2^- and ferroelectric Γ_3^- modes has been discussed for the paraelectric to ferroelectric transition in unfilled $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ [258] and filled $\text{R}^{3+}\text{K}_2\text{Nb}_5\text{O}_{15}$ (where R^{3+} = Rare Earth) [259] TTBs. At T_1 , the NTE-driven elongation of the c lattice parameter upon cooling reaches a local maximum while the contraction of a is a minimum. Upon further cooling below T_1 , a elongates (Figure 4.13a), whilst b continues to contract (Figure 4.13b), and c again resumes contracting (Figure 4.13b) in $z = 0$ (SNN). As the temperature approaches T_1 , this is accompanied by a sharp increase in the symmetry adapted orthorhombic strain in the ab plane, transforming as irrep Γ_4^+ , as shown in Figure 4.14c. This increasing strain drives the phase transition and permittivity anomaly/maxima at T_1 [18].

Tidey *et al.* [18] identify the low temperature phase below T_1 as a monoclinic Aa phase which exhibits an in- (ab) plane polar distortion mode of the $Ama2$ structure transforming as irrep Γ_5^- . This represents a polar displacement of atoms along $[110]$ of the parent tetragonal cell (and hence along the a direction of the $Ama2$ supercell), together with c -axis rotations of NbO_6 octahedra. This leads to particularly large displacements of cations in the A2 sites whose longer axis lies along the a direction. This in-plane polar instability is manifested as a soft phonon mode at temperatures above the phase transition to the Aa structure, with the associated atomic vibrations "freezing" out and becoming static when cooled through the crystallographic phase transition. Both above and below the phase transition, these in-plane polar distortions

may contribute to thermal expansion, driving the increase in orthorhombic strain at lower temperatures and giving rise to some NTE.

The in-plane domain structure described in Tidey *et al.* [18] arises from the in-plane polar distortion (Γ_5^-) and the ferroelastic domain structure, which may be disrupted by chemical disorder introduced by doping (and possibly the high density of stacking faults that manifest as a result of incommensurate distortion of the network of rigid unit-like tilted NbO_6 octahedra (S_3)) [242]. These may both be expected to reduce Γ_5^- domain sizes to the nanoscale, imparting relaxor-like behaviour for T_1 . Thus overall, between T_1 and T_2 the crystallographic and dielectric response of undoped SNN can be understood as arising from the competition between the in-plane (Γ_5^-) and out-of-plane (Γ_3^-) polar modes, alongside the presence of octahedral tilt (S_3).

Attention will now be turned to the effect of doping on SNN1. Ca^{2+} and Y^{3+} are doped on the A sites for Sr^{2+} , while Zr^{4+} is doped on the B sites for Nb^{5+} [15]. Correlations between dopant levels and T_2 , $\Gamma_3^- = 0$ (Γ_3^- saturation temperature), c lattice parameter length above T_2 , T_1 , and inflection point temperatures $\left.\frac{da}{dT}\right|_{T_1}$ and $\left.\frac{dc}{dT}\right|_{T_1}$ are shown in Figure 4.17a – b. Co-doping Ca^{2+} , Y^{3+} and Zr^{4+} significantly reduces the c lattice parameter (Figure 4.13c) with little alteration to a and b above T_2 (Figure 4.13a). The reduction in c lattice parameter correlates well with doping level (z) (Figure 4.17a). T_2 also seems to have a negative correlation with doping level as observed by dielectric spectroscopy and through refinement of the Γ_3^- polar distortions (Figure 4.17b). Furthermore, the temperature variation of lattice parameter c between T_2 and T_1 is progressively reduced with doping until it becomes almost flat at $z = 0.025$ and $z = 0.075$ (Figure 4.15c).

The analysis of the undoped material, SNN, suggests that the paraelectric to ferroelectric transition that causes a permittivity anomaly at T_2 has a strong coupling to out-of-plane thermal expansion and is driven by c elongation on cooling (*i.e.* NTE). Doping decreases the c -lattice parameter, inhibiting this cooling-driven elongation. The reduction of c is expected to destabilise the out-of-plane polar mode, since it will have a negative Grueneisen parameter (*i.e.* a vibrational mode which decreases in

frequency, and hence energy, as the volume decreases) [260]. Indeed, increased doping levels lower the temperature at which long-range ferroelectric ordering emerges, *i.e.* when the Γ_3^- distortion along c rises above zero [260] and the onset of the ferroelectric distortion moves closer to T_1 (Figure 4.15c and Figure 4.17a). This coincides with a decrease in T_2 and a lowering of ϵ_r at T_2 with doping (Figure 4.11a – b).

Tidey *et al.* [18] suggest that T_2 should be pushed to higher temperatures by cation substitutions that reduce the unit cell volume. However, in this chapter, the inclusion of dopants only slightly decreases the overall unit cell volume (Figure 4.13d). Zhu *et al.* [107] suggest that a reduction in the average A site ionic radius (as is the case here) will shorten the O-B-O bond length, decrease dielectric polarizability and decrease long-range ferroelectric coupling. The doping of Zr^{4+} on the B sites may also facilitate the compression of c , due to a lower charge density weakening electrostatic interactions between octahedra and thus allowing increased RUM tilting in the TTB oxygen octahedral framework.

Indeed, Yang *et al.* [160] observed a reduction in the c lattice parameter when doping Zr^{4+} on the B sites in a similar gadolinium-doped strontium barium niobate (SBN) TTB. The observed Raman redshifts of ν_2 (Nb/Zr-O stretching) and ν_5 (O-Nb/Zr-O bend) vibrational modes (Figure 4.8a – b) also provide supporting evidence for the effect of doping smaller A site cations and a weakening of the BO_6 octahedral framework. However, it should be noted that the Zr^{4+} doping level is only of the order of 1 %, whilst the Y^{3+} , Ca^{2+} doping level is of the order of 5 %, and so cumulatively their effect is solely on a small fraction of octahedra. The effect on strain could be as significant, macrostrain can be tuned significantly by only a small chemical substitution [261-263], as is evident here from the observed changes in lattice parameters. It could also be that the lower dielectric polarizability of Zr^{4+} ($3.25 \text{ \AA}^3$) compared to Nb^{5+} ($3.97 \text{ \AA}^3$) [23], disrupts long range ferroelectric ordering.

On cooling through room temperature to T_1 , the a lattice parameter reaches a minimum and elongates beyond T_1 (Figure 4.13a inset). Conversely b continues to

contract (Figure 4.13a). These inflection temperatures $\left.\frac{da}{dT}\right|_{T_1}$ and $\left.\frac{dc}{dT}\right|_{T_1}$ diverge with doping with $\left.\frac{da}{dT}\right|_{T_1}$ showing a sharp decline (Figure 4.17b). T_1 shows a strong negative dependence on doping level and is also more closely related to the inflection point in the a lattice parameter (but not the c parameter), confirming that it is most likely related to the in-plane polar instability associated with the transition to the Aa structure. Notably, higher dopant levels ($z > 0.037$) do not exhibit the elongation of lattice parameter a below T_1 (Figure 4.17b), whilst the contraction of b is almost insensitive to doping (Figure 4.13b). Increased doping also leads to increasing frequency dispersion and relaxor-like behaviour for T_1 (Figure 4.9a – f).

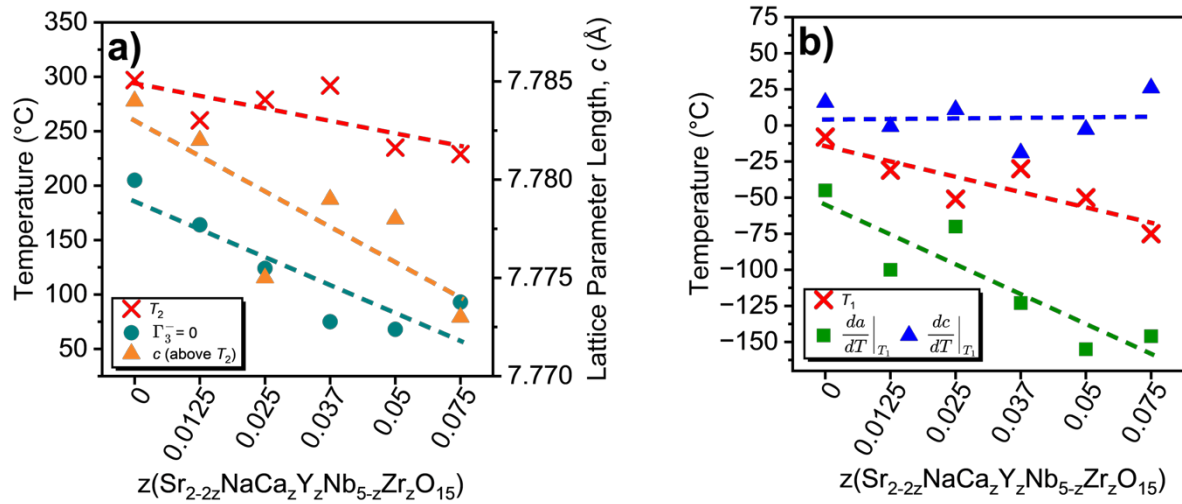


Figure 4.17a – b: Plots showing a) T_2 , $\Gamma_3^- = 0$ (Γ_3^- saturation temperature) and c lattice parameter length at T_2 and b) T_1 , inflection point temperatures $\left.\frac{da}{dT}\right|_{T_1}$ and $\left.\frac{dc}{dT}\right|_{T_1}$ as function of dopant level, z for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ ($z = 0$ [SNN1], 0.0125, 0.025, 0.037, 0.05, and 0.075) where T_1 and T_2 are extracted from 1 kHz ε_r – temperature plots (Figure 4.9a – f).

The analysis of the undoped material, SNN, suggests that the phase transition that causes a permittivity anomaly at T_1 is driven by elongation of lattice parameter a on cooling, accompanied by a contraction of c . Doping strongly inhibits this cooling-driven elongation of a (Figure 4.13a). Inhibition of the elongation of a , whilst b remains relatively unchanged, will reduce the in-plane orthorhombic strain resulting in a lowering of the temperature (T_1) at which the in-plane polar distortion (Γ_5^-) drives the

structural transition from $Ama2$ to Aa . A plot of the symmetry adapted orthorhombic strain, transforming as irrep Γ_4^+ , as a function of temperature is shown in Figure 4.14 and generally exhibits a reduction in strain at T_1 with increased doping levels. Simplistically, increased doping would be expected to lead to increased compositional disorder, suppressing any long-range phase transitions and disrupting the ferroelastic domain structure, resulting in the breakdown of the macroscopic polarisation [264], and this contributes to the relaxor-like frequency dispersion of the permittivity anomaly at T_1 .

4.3.6 Transmission Electron Microscopy (TEM)

As stated previously, transmission electron microscopy (TEM) sample preparation and analysis were undertaken by Dr. Robin Sjökvist and Professor Richard Beanland (University of Warwick), with figures and captions produced by Dr. Robin Sjökvist herein. Figure 4.18a – h shows TEM images and diffraction patterns demonstrating a reduced incommensurate period, and increased stacking fault density, across the dopant series (samples $z = 0, 0.037$ and 0.075). The incommensurate parameter can be determined using the procedure outlined by Van Tendeloo *et al.* [110, 265] for the TTB $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, *i.e.* by measuring the displacement of $\frac{1}{4}$ order superstructure reflections in $[-110]_{tet}$ selected area electron diffraction patterns (Figure 4.18d – f, indexing with the tetragonal aristotype $P4/mbm$ unit cell). In accordance with this observation, an increased density of stacking faults on $(110)_{tet}$ planes is observed with increased doping (Figure 4.18a – c and Table C2), with no obvious difference in orthorhombic twin domain size (Figure C5a – c).

The stacking faults accommodate the strain that the implicitly incommensurate tilt modulation S_3 produces in the rigid TTB framework of connected NbO_6 octahedra. Hence, if there is increased incommensurate octahedral tilting with doping, a higher density of stacking faults is required to resolve the associated strain. Tidey *et al.* [18] demonstrated the temperature invariance of the octahedral tilt system, S_3 , in terms of both amplitude and propagation vector. In this doped SNN series, however, the displacement amplitude of S_3 shows no obvious trend with dopant level (Figure 4.16), nor does it coincide with the elongation of c with cooling below T_2 (Figure 4.13c). This lack of correlation of S_3 displacement amplitude with increasing frequency of the incommensurate modulation at higher doping levels is most likely due to the inherent

strain the material can withstand before it is relieved *via* the formation of a stacking fault. The presence of an increased density of stacking faults in the SNN samples ($z = 0, 0.037$, and 0.075) with increasing doping is reflected in the more gradual increase in symmetry adapted orthorhombic strain as temperature approaches that of T_1 , shown in Figure 4.14.

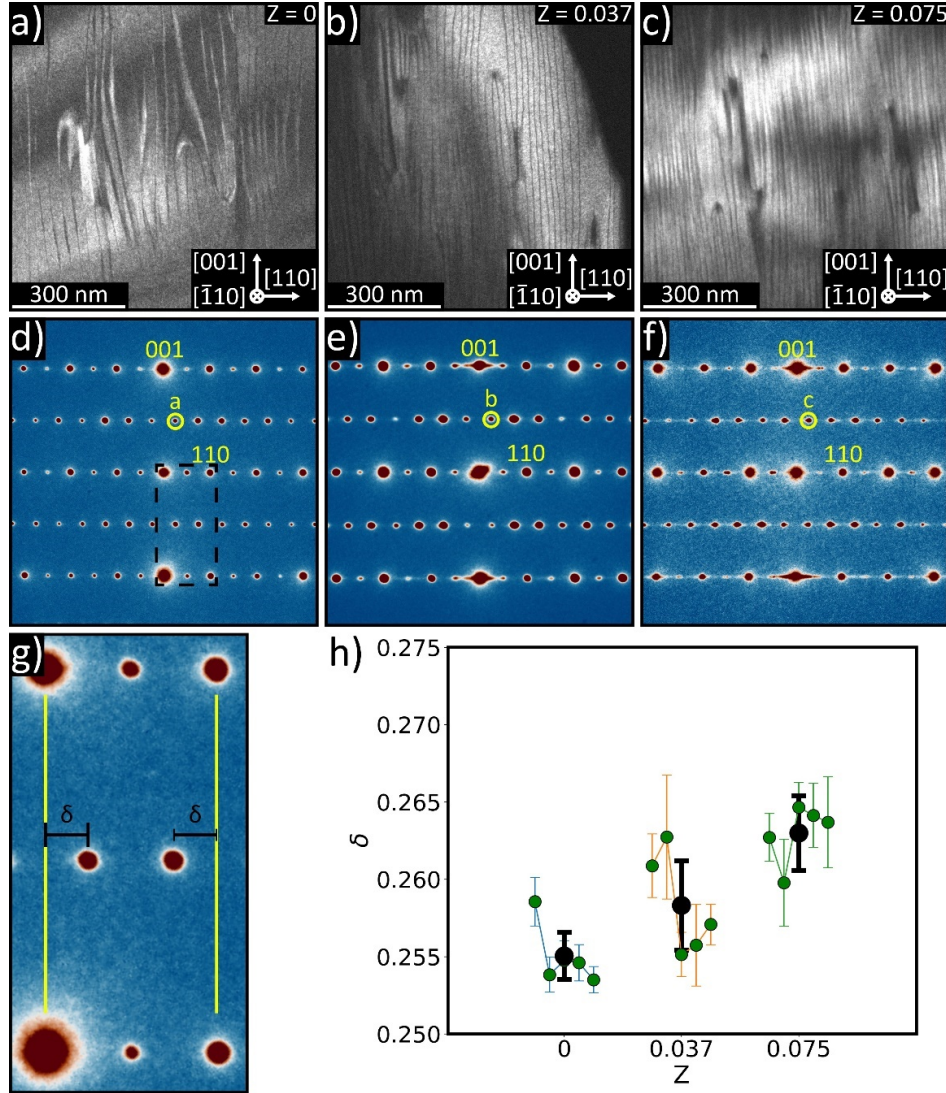


Figure 4.18a – h: Dark field TEM micrographs of a) SNN $z = 0$ (undoped), and doped samples b) $z = 0.037$, c) $z = 0.075$, with d), e), f) corresponding $[-110]_{tet}$ zone axis electron diffraction patterns respectively. Stacking faults appear as bright or dark lines in a), b) and c). The spots used for dark field imaging are circled in the diffraction patterns. All crystallographic indexing is with respect to the tetragonal prototype unit cell. g) shows an enlarged portion of d), indicating the position d of $\frac{1}{4}$ order spots used to estimate the incommensurate modulation. The measurements are summarized in h), ($\delta = 0.25$ indicates a commensurate structure). Five diffraction patterns from

different grains were measured (indicated by the green datapoints with coloured error bars) which were then used to construct a sample average and error (indicated by the black datapoints and their corresponding error bars).

According to the analysis of Levin *et al.* [108], increased incommensurate octahedral tilting would impart increased relaxor-like behaviour, as is observed here for increasing dopant levels in SNN1. Appendix C – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Figure C6 shows the crystal chemical framework for relaxor versus normal ferroelectric behaviour in TTBs proposed by Zhu *et al.* [107] the positions of the SNN1 dopant series studied here are included. The position of SNN1 in their work, however, differs as Sr/Na is disordered over the A1-site. Notably, Zhu *et al.* [107] (and references therein) report undoped SNN1 to be ferroelectric and commensurate with an orthorhombic $Im2a$ structure, whereas Tidey *et al.* [18] describe it as a near commensurate structure closely approximating to the orthorhombic, $Ama2$ phase. As may be seen, owing to the low dopant levels, all points lie in the relaxor regime, albeit with some suggestion that increased levels of doping leads to a small transition further into the relaxor regime (Figure C6). However, in general the crystal chemical framework of Zhu *et al.* [107], whilst applicable to a broad range of TTB systems, is not sufficiently sensitive for small levels of doping and that, in this case, both compositional disorder and microstructure are the more important factors governing dielectric behaviour.

4.4 Conclusion

An expanded series of conventional mixed oxide route ceramics $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ ($z = 0, 0.0125, 0.025, 0.037, 0.05$ and 0.075) have been successfully synthesized with the target phase confirmed by laboratory PXRD and SEM-EDX. Rietveld refinement of variable temperature synchrotron PXRD data provided a crystallographic understanding of the flattening of the dielectric permittivity–temperature profile of $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, namely the relative permittivities, ϵ_r , at the permittivity anomalies T_1 and T_2 . This analysis and its results provide valuable, more general insights into the crystallographic structure–property relationships that drive the flattening and stability of the temperature-dependent TTBs for use in wide operational temperature stable MLCCs.

It is demonstrated that a co-doping strategy of smaller A site cations (Ca^{2+} , Y^{3+}) and less polarisable B site cations (Zr^{4+}) in SNN decreases the *c*-lattice parameter, inhibiting the negative thermal expansion that is observed below the ferroelectric to paraelectric transition temperature, T_2 , in the undoped material. This reduction of *c* destabilises the out-of-plane polar mode, Γ_3^- , reflected in a lowering of the temperature at which the amplitude of this polar distortion mode rises above zero. This coincides with a decrease in T_2 , and a lowering of ϵ_r at T_2 with increased doping. Doping also suppresses the negative thermal expansion of the *a*-lattice parameter that is observed below the relaxor ferroelectric transition temperature, T_1 , in the undoped material. This delays the temperature onset of sufficient orthorhombic strain to drive the phase transition and coincides with a decrease in, T_1 , with little effect on ϵ_r at T_1 with doping, presumably due to the continued stability of the in-plane polar mode, Γ_5^- . Increased doping also leads to increasing frequency dispersion and relaxor-like behaviour at T_1 .

It is suggested that co-doping SNN with relatively minor amounts of smaller A-site cations and less polarizable B-site cations introduces compositional disorder which reduces long range ferroelectric coupling. Electron diffraction in the TEM shows a decrease in the period of the incommensurate modulation of octahedral tilting, which increases with doping. This is accompanied by the observation of stacking faults in TEM images that allow for the accommodation of strain in the rigid unit model (RUM) that the implicitly incommensurate tilt (S_3) modulation produces as it resolves against the commensurate TTB framework. Increased incommensurate octahedral tilting with increased doping results in a higher density of stacking faults to resolve the associated, increasing strain. Overall, this disrupts the ferroelastic domain structure and contributes to the relaxor-like frequency dispersion of the permittivity anomaly at T_1 . This, in turn, destabilises the ferroelectric polar mode and reduces the negative thermal expansion of the *c* lattice parameter with increasing temperature between T_1 and T_2 , leading to a flattening of permittivity at T_2 and a lowering of the ferroelectric to paraelectric transition temperature. The net result is a stable dielectric response over a large temperature range suitable for high temperature, temperature stable operational capacitors.

The Influence of Sodium (Na^+) Vacancy Content, $\Box_w$ on the Dielectric Properties and Crystallographic Structure of Pb and Bi free $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ Tetragonal Tungsten Bronze (TTB)

5.1 Introduction

This chapter reports the processing and characterisation of $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (abbreviated to SNN1 herein, where 1 denotes sodium [Na^+] stoichiometry) and Na^+ deficient (A-site Na^+ vacancy containing) counterparts of the nominal formula $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ ($\Box = \text{Na}^+$ vacancy). Composition formulae are abbreviated to SNNy herein, where y = degree of Na^+ non-stoichiometry. The compositions studied in this chapter are $w = 0$, $y = 1$ (SNN1), $w = 0.05$, $y = 0.9$ (SNN09), $w = 0.10$, $y = 0.8$ (SNN08), and $w = 0.15$, $y = 0.7$ (SNN07) where electrical neutrality is preserved across the A-sites.

The previous chapter (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) examined the effect of A- and B-site co-doping on the crystallographic structure-property relationships underlying the flattening and stability of the temperature dependent dielectric response of $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$. Dielectric anomalies studied in the former were transition temperatures T_1 (a relaxor ferroelectric peak) and T_2 (ferroelectric $\rightarrow$ paraelectric), and corresponding relative dielectric permittivities (ϵ_r) at T_1 and T_2 . Rietveld refinements of synchrotron (variable temperature) and laboratory (room temperature) powder X-ray diffraction (PXRD) patterns used a density functional theory (DFT) derived orthorhombic *Ama2* structural model [18]. The temperature evolution of Rietveld refined lattice parameters and symmetry-adapted modes were extracted from variable temperature synchrotron PXRD and analysed.

Subsequently, this chapter will build upon the methodology and analysis of Tidey *et al.* [18] and Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ to SNNy compositions studied herein. By appropriate adjustment of the pre-cursor powder ratios of the mixed oxide route, Na^+ vacancies were systematically (assumed to be) introduced into the A1 site of SNN1 to produce a series of ceramics of single pseudo – TTB phase ⁷.

Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ reported secondary perovskite Sr-modified NaNbO_3 phase (≤ 6 wt%), with an open question as to whether this secondary phase impacts the dielectric response of SNN1 and $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$. Discerning the true stoichiometry of $\text{Sr}^{2+}/\text{Na}^+$ in Sr-modified NaNbO_3 , in addition to determining the space group of this phase at such a low wt. %, poses a challenge. Moreover, the uncertainty in the stoichiometry of $\text{Sr}^{2+}/\text{Na}^+$ in Sr-modified NaNbO_3 , also places the true stoichiometry of the main pseudo–TTB phase into question. Energy dispersive X-ray spectroscopy (EDX) elemental mapping showed some evidence of Y^{3+} in the Sr-modified NaNbO_3 (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$).

Jang *et al.* [266] comments that the formation of secondary phases, like Sr-modified NaNbO_3 in SNN1, is a result of electrostatic instability which can be stabilised by A- and C-site vacancies. That is the Madelung energy, which is defined as the principle contributor to the binding energy of ionic crystal systems, is lowered in X systems when vacancies are introduced [267]. Hence, this chapter seeks to synthesise single phase SNN1 by introducing Na^+ vacancies and potentially reduce the Madelung energy that would lend to the formation of Sr-modified NaNbO_3 when synthesising SNN1 [49, 267]. The role of Na^+ vacancies on dielectric properties (T_1 , T_2 , ϵ_r at T_1 and T_2)⁸ and the flattening of the dielectric – temperature response will be evaluated here.

The SrNb_2O_6 – NaNbO_3 phase diagram was empirically constructed from a series of heat treatments followed by furnace cooling in the early [179] and late 1970s [180]

⁷ TTB compositions in this work, will be referred to as pseudo – TTB due to the orthorhombic nature of the *Ama2* structural assignment, akin to Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$.

⁸ For a more comprehensive literature review on A site doping and A site vacancies see Chapter 2 – Scientific Background and Literature Review, section 2.5.2. A-Site Doping and A-Site Vacancies.

(Chapter 2 – Background Science and Literature Review, section 2.7.5). Such phase diagrams [179, 180] demonstrate that single phase SNN1 is only attainable through A-site vacancies, in other words, unfilled SNN1 [152]. The impact of single phase SNN containing A-site vacancies on dielectric properties is an avenue of interest here and the vacancy formation may occur due to the inherent volatilisation of Na^+ during sintering [268] or the systematic introduction of Na^+ vacancies (as is the case in the reported compositions herein). For instance, $z = 0.05$ in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, appeared to have domain pinning from possible Na^+ vacancies (V'_{Na}) and/or oxygen vacancies ($V_{\text{O}}^{\bullet}$ or $V_{\text{O}}^{\bullet\bullet}$), potentially contributing to the unexpectedly low ϵ_r at T_2 relative to other z values. Current research has been devoted to understanding the role of A-site cation occupancies and cationic radii size effects, within the context of tolerance factors [107]. However, many of these tolerance factor calculations do not consider A-site vacancy effects in unfilled TTBs [107, 133, 177].

This chapter will, as in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, extend the use of the orthorhombic *Ama2* room temperature structure assignment of SNN1 [18]. Through sequential Rietveld refinement of variable temperature synchrotron PXRD, the methodology and analysis in the preceding chapter will be expanded here to $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ (SNNy, $y = \text{Na}^+$ stoichiometry) where $w = 0$, $y = 1$ (SNN1), $w = 0.05$, $y = 0.9$ (SNN09), $w = 0.10$, $y = 0.8$ (SNN08), and $w = 0.15$, $y = 0.7$ (SNN07). This chapter therefore aims to understand the interplay between sodium vacancy level (w), variable temperature Rietveld refined lattice parameters and symmetry – adapted modes on the dielectric properties of non-stoichiometric ceramics.

5.2 Experimental

5.2.1 Ceramic Processing

SrCO_3 (Sigma-Aldrich, > 99.9 %), Na_2CO_3 (Sigma-Aldrich, > 99 %), and Nb_2O_5 (Alfa Aesar, 99.9 %) chemical reagent powders were combined in the appropriate ratios, to form $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ polycrystalline ceramics. CAS codes, manufacturers, and purity of chemical reagent powders used above are tabulated in Table 3.1, Chapter 3 – Experimental Methods. SNNy ($y = \text{Na}^+$ content) where $w = 0$, $y = 1$ (SNN1), $w = 0.05$,

Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$

$y = 0.9$ (SNN09), $w = 0.10$, $y = 0.8$ (SNN08), and $w = 0.15$, $y = 0.7$ (SNN07), were processed using the conventional mixed oxide route (outlined in Chapter 3 – Experimental Methods), where y and w denote Na^+ and Na^+ vacancy content, respectively. Processed polycrystalline ceramic $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ nominal formulas, alongside composition codes used as abbreviations herein, are tabulated in Table 5.1.

Table 5.1: Processed ceramic nominal formulas for $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$ where $w = 0$, $y = 1$ (SNN1), $w = 0.05$, $y = 0.9$ (SNN09), $w = 0.10$, $y = 0.8$ (SNN08), and $w = 0.15$, $y = 0.7$ (SNN07), including corresponding sample codes used throughout this chapter (SNNy where y = sodium content) in addition to calcination and sintering temperatures with respective dwell times. Dual stage calcination and sintering steps are denoted by * and extended sintering dwell times by[†].

Nominal Formula $w,y(\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15})$	Composition Code (SNNy)	Calcination		Sintering	
		Temperature (°C)	Time (hours)	Temperature (°C)	Time (hours)
$\text{Sr}_2\text{NaNb}_5\text{O}_{15}$	SNN1	1200	12	1300	5
$\text{Sr}_{2.05}\text{Na}_{0.9}\Box_{0.05}\text{Nb}_5\text{O}_{15}$	SNN09	1200	6	1300	4
$\text{Sr}_{2.10}\text{Na}_{0.8}\Box_{0.10}\text{Nb}_5\text{O}_{15}$	SNN08	950, 1200*	4, 6	1240, 1320*	6, 25 [†]
$\text{Sr}_{2.15}\text{Na}_{0.7}\Box_{0.15}\text{Nb}_5\text{O}_{15}$	SNN07	1200	6	1350	10

SNNy ceramics were processed by Dr Thomas Brown and Dr Teresa Roncal-Herrero (University of Leeds). Subsequent preparation, characterisation and analysis was undertaken by Celine M. King (University of Leeds). Calcination was undertaken at 1200 °C for 6 hours with a heating and cooling rate of 300 °C/hour. SNN08 however, had an added precursor step at 950 °C for 4 hours. Binder burnout was performed at 550 °C with a heating and cooling rate of 60 °C/hour and held for 5 hours. Sintering temperatures ranged from 1300 – 1350 °C, for 4 – 5 hours with heating and cooling

rates of 300 °C/hour. SNN08 underwent extended dual stage sintering at 1240 °C for 6 hours, followed by 1320 °C for 25 hours with a heating rate of 300 °C/hour. The sintering processing route for SNN08 was adopted from a US patented synthesis route by the Nissan Motor Co. Ltd [269].

5.2.2 Structural and Electrical Characterisation

Experimental pellet densities were measured by obtaining pellet volumes and masses as described in Chapter 3 – Experimental Methods. Theoretical pellet densities were obtained from Rietveld refinements of room temperature (R.T.) Laboratory PXRD patterns using a DFT derived *Ama2* structural model for SNN1 [18] and a tetragonal *I4/mcm* structural model for Sr-modified NaNbO_3 [18, 238]. The use of the tetragonal *I4/mcm* model for Sr-modified NaNbO_3 was discussed in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, section 4.2.2. Structural and Electrical Characterisation. Electrical and structural characterisation, including relative permittivity (ϵ_r), dielectric loss ($\tan\delta$) – temperature response plots, polarisation (P) versus field (E) loops, Raman spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) were carried out as described in Chapter 3 – Experimental Methods.

High resolution, variable temperature crystal structure analysis was carried out through Rietveld refinement of synchrotron PXRD diffraction patterns collected at Beamline I11, Diamond Light Source (Didcot, United Kingdom). A beam energy of approximately 15 keV ($\lambda = 0.82409(7)$ Å) was used, measuring between a temperature range of -173 °C to 350 °C. Rietveld refinements were based on the previously mentioned DFT derived orthorhombic *Ama2* pseudo-TTB and *I4/mcm* Sr-modified NaNbO_3 [18, 238] structural models, where A-site vacancies are modelled to occupy both A1 and A2 sites. Peak profile contributions, including instrument, wavelength, and zero-point, were standardised against a NIST® 640 silicon standard. Variable temperature Rietveld refinements were executed by the least squares refinement program *TOPAS Academic* (Version 7.1.0) [212] in conjunction with *jEdit* (Version 5.7.0) text editor software. Irreducible representations (irreps) applying symmetry – adapted mode notation by Miller *et al.* [223] and lattice parameters were used as

refinement parameters and refined concomitantly. A brief background theory on irreps and their notation are described in Chapter 3 – Experimental Methods, section 3.3.1. Representation Analysis, Group Theory, and Notation.

5.3 Results and Discussion

5.3.1 Room Temperature (R.T.) Laboratory Powder X-Ray Diffraction (PXRD)

Phase purity, identification and pellet densities of $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$ (where $w = 0$, $y = 1$ [SNN1], $w = 0.05$, $y = 0.9$ [SNN09], $w = 0.10$, $y = 0.8$ [SNN08], and $w = 0.15$, $y = 0.7$ [SNN07]) were examined using room temperature (R.T.) laboratory PXRD. Rietveld refinements of laboratory PXRD patterns were performed against a DFT-derived orthorhombic *Ama2* structural model [18] as in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$. Rietveld fit plots for all compositions are shown in Figure 5.1a – d. Sample codes used throughout this chapter alongside weight percentages (wt. %), and weighted R-factors (R_{wp}) are tabulated in Table 5.1. Pellet densities were ≥ 93 %, where theoretical density did not account for any secondary phases. All R_{wp} values were < 10 % suggesting a good fit of the calculated diffraction patterns to the laboratory PXRD patterns.

The weight percentage of the SNN1 main pseudo – TTB *Ama2* phase, was ≥ 95 wt. % while secondary perovskite *I4/mcm* Sr-modified NaNbO_3 was < 5 wt.% as reported in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$. Na^+ deficient compositions (SNN09, SNN08, and SNN07) were seemingly single-phase pseudo – TTB (*Ama2*), based on laboratory PXRD. A visual inspection of calculated and experimental/observed patterns (Figure 5.1a – d) showed no obvious indication of SrNb_2O_6 peaks, such as those of Sr-modified NaNbO_3 in SNN1. Referring to the metastable NaNbO_3 – SrNb_2O_6 phase diagram by Morin *et al.* [179], SNNy is suggested to be single phase at room temperature between SNN09 and SNN06 (*i.e.* where $w = 0.2$, $y = 0.6$ in SNN06) [49].

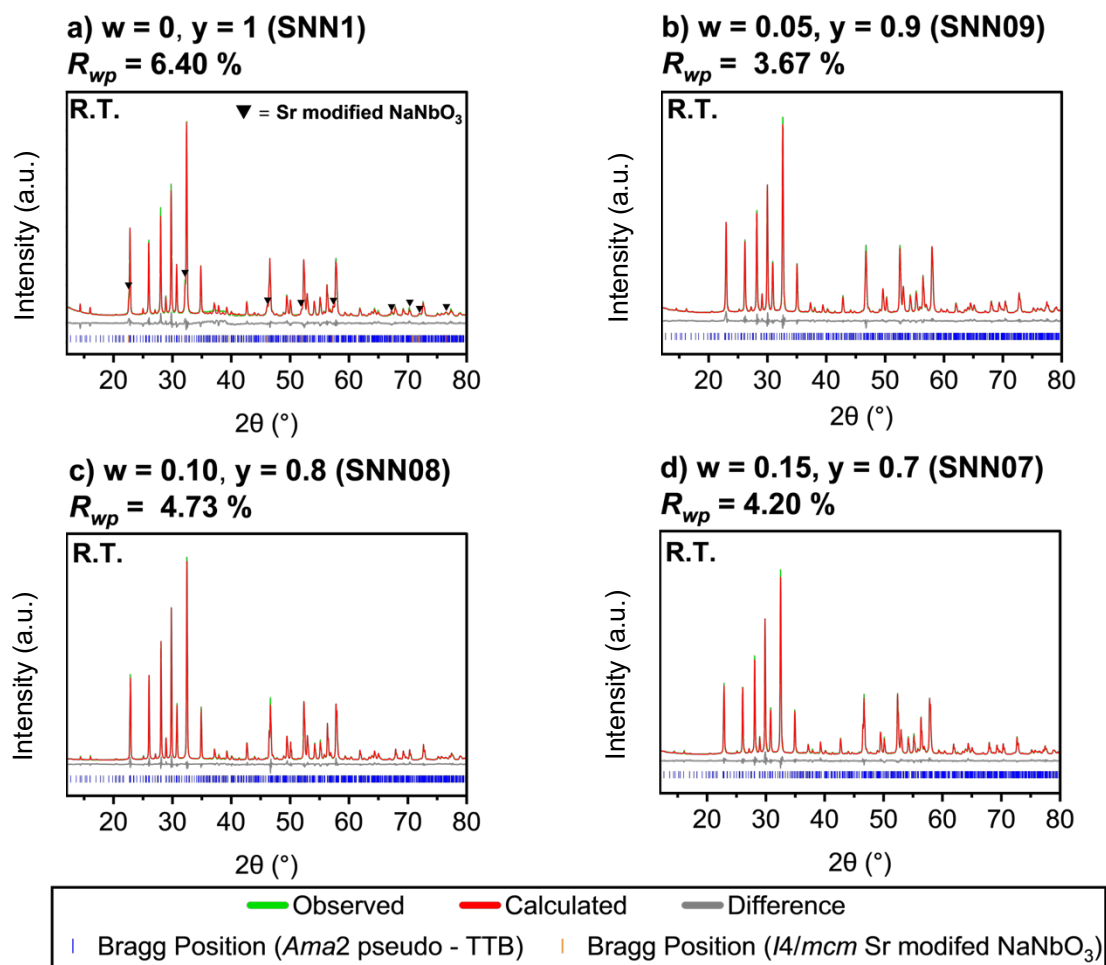


Figure 5.1a – d: Rietveld refinement fits of the orthorhombic *Ama2* structural model (pseudo – TTB) and tetragonal *I4/mcm* structural model (Sr modified NaNbO_3 , indicated by ▼) against diffraction patterns obtained through laboratory PXRD at room temperature (R.T.) of w,y (where a) $w = 0, y = 1$ (SNN1), b) $w = 0.05, y = 0.9$ (SNN09), c) $w = 0.10, y = 0.8$ (SNN08), and d) $w = 0.15, y = 0.7$ (SNN07).

Li *et al.* [250] recently reported a SrNb_2O_6 secondary phase in $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN1) synthesised by the conventional mixed oxide route. Here, the ICSD crystallographic database [270] was used to obtain a monoclinic $P2_1/c$ SrNb_2O_6 structural model (collection code ICSD-25054 [ICSD release 2025.1]). The inclusion of the SrNb_2O_6 structural model in refinements of SNN09, SNN08, and SNN07 offered no improvement to the overall fit and indicated 0 wt. % of monoclinic SrNb_2O_6 . Inclusion of a Sr-modified NaNbO_3 *I4/mcm* structural model (< 0.5 wt. %) was found to slightly improve R_{wp} by ≤ 0.09 %. Based on these observations, SNN09, SNN08, and SNN07

ceramics are assumed to be single pseudo TTB *Ama2* phase from laboratory PXRD, suggesting they have been successfully synthesised.

Table 5.2: Summary of room temperature laboratory PXRD crystallographic data showing pseudo – TTB and secondary phase (▼ = Sr-modified NaNbO_3) weight percentages (wt.%), weighted profile R-factors (R_{wp}), theoretical densities, geometric densities, and pellet density (%) for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15})$ (SNNy, y = sodium content) where w = 0, y = 1 (SNN1), w = 0.05, y = 0.9 (SNN09), w = 0.10, y = 0.8 (SNN08), and w = 0.15, y = 0.7 (SNN07).

Sample Code	Pseudo – TTB Phase (wt. %)	Secondary Phase (wt. %)	R_{wp} (%)	Theoretical Pellet Density (g cm^{-3})	Geometric Pellet Density (g cm^{-3})	Pellet Density (%)
SNN1	95.52	4.48 ▼	6.41	5.03	4.68	93
SNN09	100	0	3.67	5.07	4.84	95
SNN08	100	0	4.73	5.06	4.75	94
SNN07	100	0	4.20	5.07	4.78	94

5.3.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX)

Backscattered scanning electron micrographs (SEM) micrographs, corresponding grain size distribution plots, and energy dispersive X-ray spectroscopy (EDX) elemental mapping for all $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$ compositions are shown in Figure 5.2 – Figure 5.5. Quantified grain size data are summarised in Table 5.3.

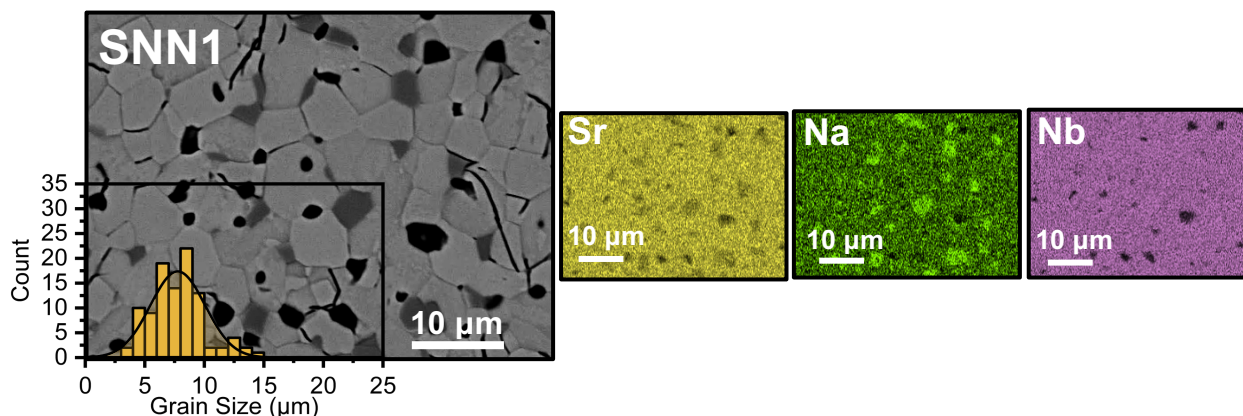


Figure 5.2: Backscattered SEM micrograph, corresponding grain size distribution plot (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac) cations for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15})$ where $w = 0$, $y = 0$ (SNN1).

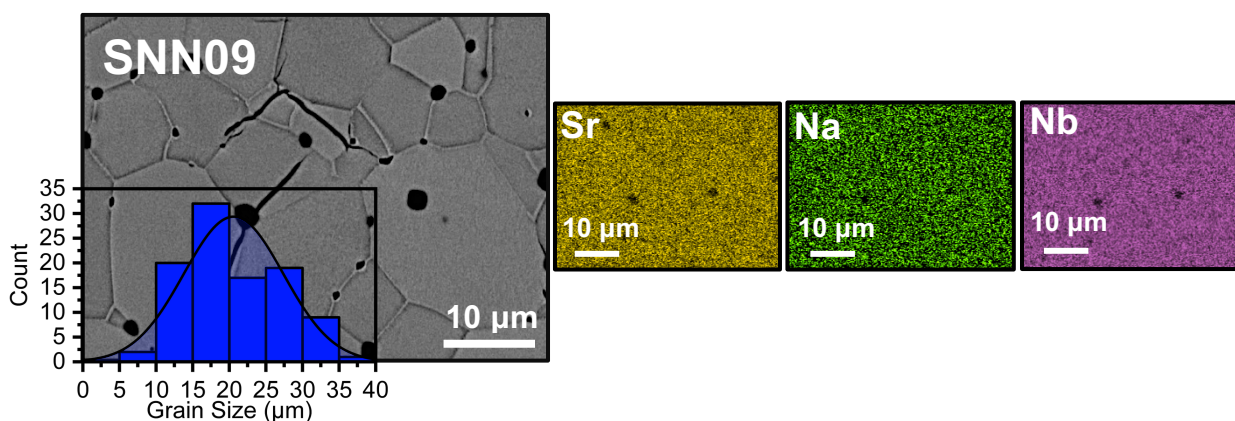
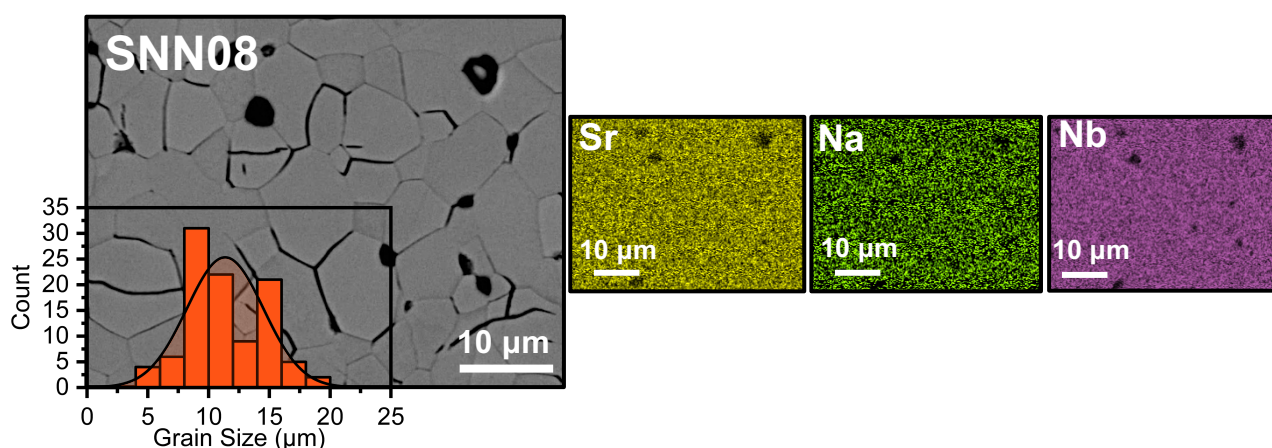


Figure 5.3: Backscattered SEM micrograph, corresponding grain size distribution plot (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac) cations for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15})$ where $w = 0.05$, $y = 0.9$ (SNN09). Figure 5.4:



Backscattered SEM micrograph, corresponding grain size distribution plot (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac) cations for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15})$ where $w = 0.1$, $y = 0.8$ (SNN08).

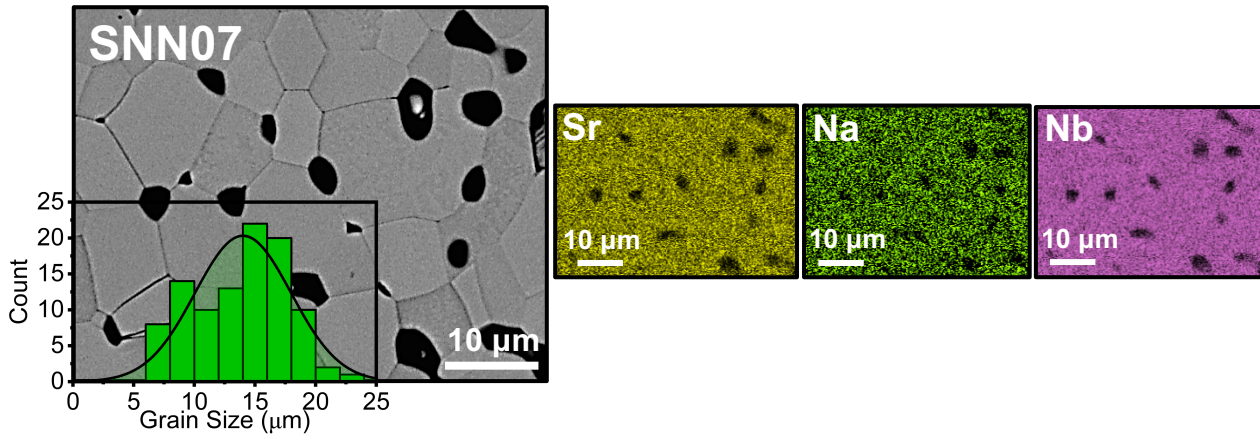


Figure 5.5: Backscattered SEM micrograph, corresponding grain size distribution plot (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Na^+ (green), Nb^{5+} (lilac) cations for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15})$ where $w = 0.15$, $y = 0.7$ (SNN07).

Table 5.3: Grain size data summary for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15})$ (SNNy, y = sodium content) where SNN1 ($w = 0$, $y = 1$), SNN09 ($w = 0.05$, $y = 0.9$), SNN08 ($w = 0.10$, $y = 0.8$) and, SNN07 ($w = 0.15$, $y = 0.7$). Grain size underestimation from cross-sectional micrographs were considered by applying a multiplication of a factor of 1.56 as proposed by Mendelson [244].

Sample Code	Average Grain Size (μm)	Standard Error (μm)	Minimum Grain Size (μm)	Maximum Grain Size (μm)
SNN1	7.8	0.2	3.8	14.8
SNN09	20.6	0.7	5.5	35.5
SNN08	11.4	0.3	5.3	18.4
SNN07	14.1	0.4	6.3	26.3

As reported in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, SEM-EDX micrographs of SNN1 had relatively smaller, evenly distributed, dark Na^+ -rich and Sr^{2+} -deficient grains attributed to Sr-modified NaNbO_3 secondary phase (Table 5.3 and Figure 5.2). SEM-EDX micrographs of SNN09 (Figure 5.3), SNN08 (Figure 5.4), and SNN07 (Figure 5.5) have a uniform microstructure alongside a homogenous distribution of Sr^{2+} , Na^+ and Nb^{5+} cations, supporting the single pseudo – TTB phase reported by laboratory PXRD (Figure 5.1a – d). Porosity and microcracks are present across all compositions,

irrespective of the high densities (93 – 95 %). The destructiveness of mechanical grinding and polishing during SEM sample preparation, reported in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ is restated here, which is possibly the cause of the unexpected microcracks and porosity.

Average grain size increased from $7.8 \pm 0.2 \mu\text{m}$ (SNN1) to $20.6 \pm 0.7 \mu\text{m}$, (SNN09), then reduces and remains effectively constant thereafter ($11.4 - 14.1 \mu\text{m}$). SNN09 ($20.6 \pm 0.7 \mu\text{m}$) showed the highest average grain size and standard error, compared to SNN08 ($11.4 \pm 0.3 \mu\text{m}$) and SNN07 ($14.1 \pm 0.4 \mu\text{m}$). Minimum grain size increased from $3.8 \mu\text{m}$ for SNN1 to $5.5 \mu\text{m}$ for SNN09, varying minimally with increasing vacancy content to $5.3 \mu\text{m}$ for SNN08 and $6.3 \mu\text{m}$ for SNN07. Maximum grain sizes increased from $14.8 \mu\text{m}$ (SNN1) to $35.5 \mu\text{m}$ (SNN09) but showed no clear trend with varying with Na^+ vacancy content at $35.5 \mu\text{m}$ for SNN09, $18.4 \mu\text{m}$ for SNN08, and $26.3 \mu\text{m}$ for SNN07. All compositions showed a uniform distribution of grain size, with no abnormal grain growth ($> 50 \mu\text{m}$).

5.3.3 Raman Spectroscopy

Local, structural distortions intrinsic to the NbO_6 pseudo – TTB octahedral framework in SNNy compositions were examined using Raman spectroscopy. Intrinsic vibrational modes that span the octahedral framework discussed in the TTB literature are positioned at the following wavenumbers: $\sim 250 \text{ cm}^{-1}$ (ν_5 , O–Nb–O bend), $\sim 630 \text{ cm}^{-1}$ (ν_2 , Nb–O bend), and $\sim 850 \text{ cm}^{-1}$ (ν_1 , Nb–O stretch) [19, 271]. The Raman spectra are presented in Figure 5.6a. Raman shifts and FWHMs of the ν_2 and ν_5 vibrational modes are shown in Figure 5.6b and Figure 5.6c respectively. The intensity of the peak and therefore the Raman shifts and full width at half maxima (FWHM) for ν_1 are insignificant relative to ν_2 and ν_5 and are not analyzed further here.

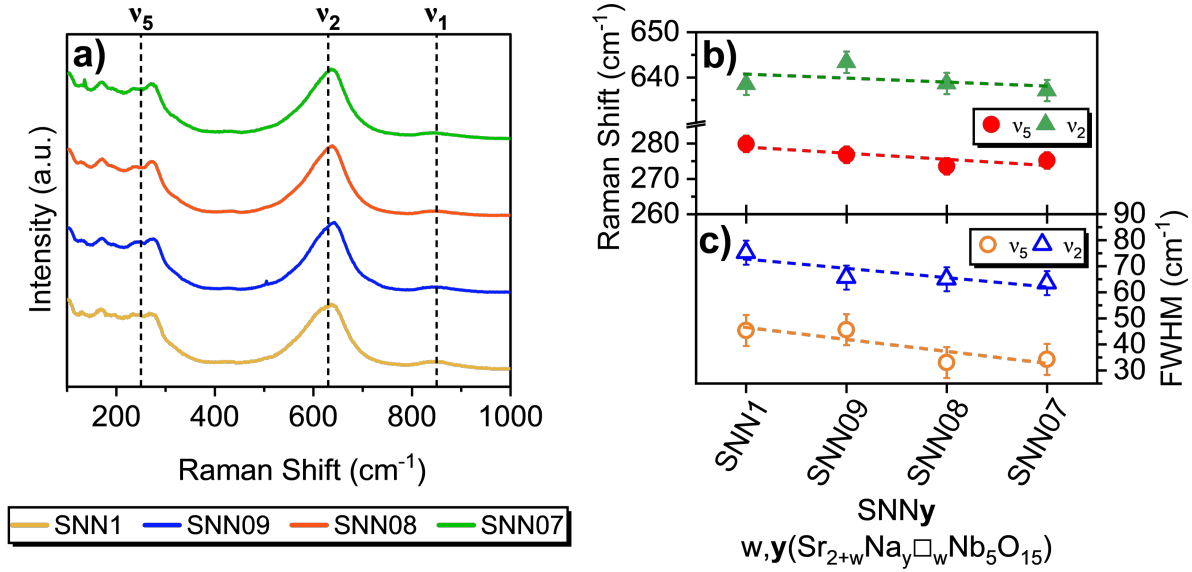


Figure 5.6: Plots showing a) room temperature normalised intensity plots as a function of Raman shift between a Raman shift range of 100 -1000 cm^{-1} , b) Raman shift (peak position), and c) FWHM of v_5 and v_2 vibrational modes and a function of Na^+ vacancy content for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15})$ (SNNy, y = sodium content) for where, $w = 0$, $y = 1$ (SNN1, yellow), $w = 0.05$, $y = 0.9$ (SNN09, blue), $w = 0.10$, $y = 0.8$ (SNN08, orange), and $w = 0.15$, $y = 0.7$ (SNN07, green).

Raman shifts trend downwards (*i.e.* red shifts) with Na^+ vacancies (Figure 5.6), indicating that Na^+ vacancies soften (and thus reduce the energy of) the v_5 and v_2 vibrational modes. This suggests a weakening of the Nb^{5+} and O^{2-} ion interaction [160, 182], effectively reducing the strain of the pseudo – TTB octahedral framework. The FWHM of v_5 and v_2 mode follow a downward trend with increasing Na^+ vacancies, however, differences remain within error of each individual measurement and may not be a significant trend.

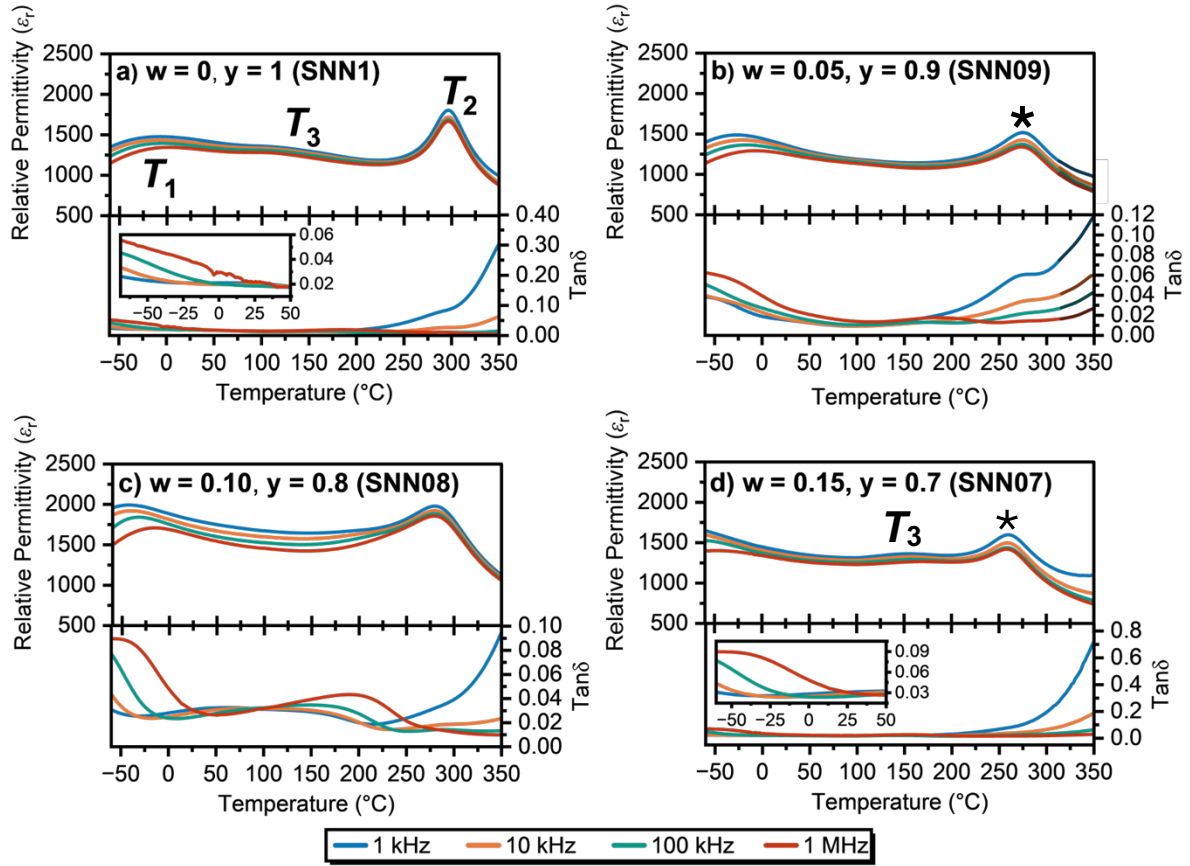
5.3.4 Dielectric and Ferroelectric Characterisation

Multi-frequency relative permittivity (ϵ_r) and dielectric loss tangent ($\tan\delta$) changes over the temperature range of $-50\text{ }^\circ\text{C}$ to $350\text{ }^\circ\text{C}$ are shown in Figure 5.7a – d. Multi-field polarisation (P) versus field (E) hysteresis loops measured at incremental fields from 5 kV/cm up to 40 kV/cm are presented in Figure 5.8a – d. Transition temperatures T_1 and T_2 are present across all compositions, with a minor frequency dispersion at T_2

(denoted by * in SNN09 and SNN07 in Figure 5.7b and Figure 5.7d respectively). All compositions show a characteristic ferroelectric hysteresis loop, with a clear saturation maximum of polarisation (P_{max}). Notably, SNN09 shows a more symmetrical shape, indicating a slightly lossy response [95] (Figure 5.8d).

SNN08 exhibits a relaxor-like frequency dependence spanning the entire measured temperature range (Figure 5.7c). A third, albeit more subtle dielectric anomaly, designated as T_3 , is found solely in SNN1 (Figure 5.7a) and SNN07 (Figure 5.7d). The presence of T_3 has been previously mentioned, although with two different rationales [152]. The first being space charge polarisation from excess sodium vacancies (V'_{Na}) and/or oxygen vacancies ($V_{\text{O}}^{\bullet}$ or $V_{\text{O}}^{\bullet\bullet}$) resulting from Na^+ and/or O^{2-} volatilisation during ceramic processing [166, 251]. The second rationale is potential consecutive phase transitions from an orthorhombic (*i.e.* $Cmm2$, $Im2a$, $Ama2$) phase to a tetragonal ($P4bm$) phase at approximately ~ 100 °C followed by transition to the non-centrosymmetric paraelectric phase ($P4/mbm$) at T_2 [158]. The presence of T_3 has been previously mentioned, although with two different rationales [152].

The volatilisation of Na_2O is difficult to regulate during sintering, however it is thought that atmospheric powder facilitates a vapour pressure equilibrium between SNN1 pellets and the SNN1 atmospheric powder itself [272-274]. Hence, Na_2O volatilisation and thus excessive Na^+ vacancies (beyond that intended in SNNy compositions here) [272-274], were effectively suppressed through the use atmospheric powder when sintering compositions in this chapter. Defect equations depicting possible volatilisation of V'_{Na} , $V_{\text{O}}^{\bullet}$ and $V_{\text{O}}^{\bullet\bullet}$ during processing are shown in Chapter 4 – $\text{Sr}_{2-2z}\text{Ca}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ (section 4.3.2 Dielectric and Ferroelectric Characterisation). The consistency of the dielectric response with Na^+ vacancy content at T_2 is illustrated by a comparative plot of pellets from the same synthesis batch in addition to differing batches, together with their heating and cooling using compositions $w = 0$, $y = 1$ (SNN1) and $w = 0.10$, $y = 0.8$ (SNN08) shown in Appendix D – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$, Figure D2.



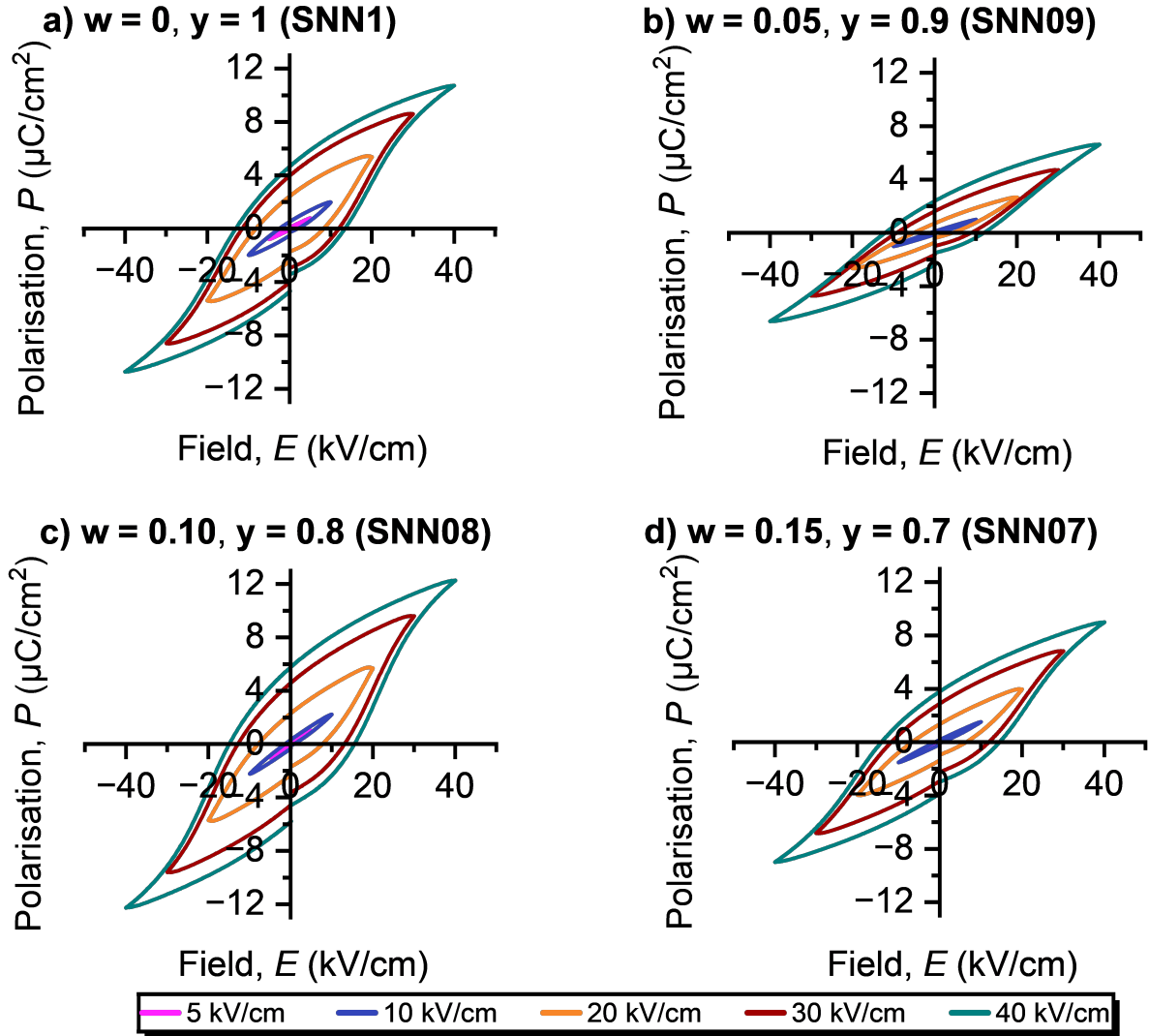


Figure 5.8a – d: Multi-field polarisation (P) versus field (E) ferroelectric hysteresis loops measured at incremental fields of 5 kV/cm, 10 kV/cm, 20 kV/cm, 30 kV/cm, 40 kV/cm for $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ where a) $w = 0$, $y = 1$ (SNN1), b) $w = 0.05$, $y = 0.9$ (SNN09), c) $w = 0.10$, $y = 0.8$ (SNN08), and d) $w = 0.15$, $y = 0.7$ (SNN07).

ϵ_r and $\tan\delta$ — temperature profiles of all compositions at 1 kHz are displayed in Figure 5.9a, alongside extracted T_1 , T_2 , ϵ_r at T_1 and T_2 values at 1 kHz plotted against Na^+ vacancy content in Figure 5.9b. Ferroelectric hysteresis loops at 40 kV/cm for all compositions are shown in Figure 5.9c with extracted values of $P_{\max}$, P_{rem} and E_c plotted as a function of Na^+ vacancies in Figure 5.9d. T_1 falls with Na^+ vacancy content while ϵ_r at T_1 increases from SNN1 ($T_1 = -8^\circ\text{C}$, $\epsilon_r = 1476$ at 1 kHz) to SNN07 ($T_1 = -71^\circ\text{C}$, $\epsilon_r = 1677$ at 1 kHz).

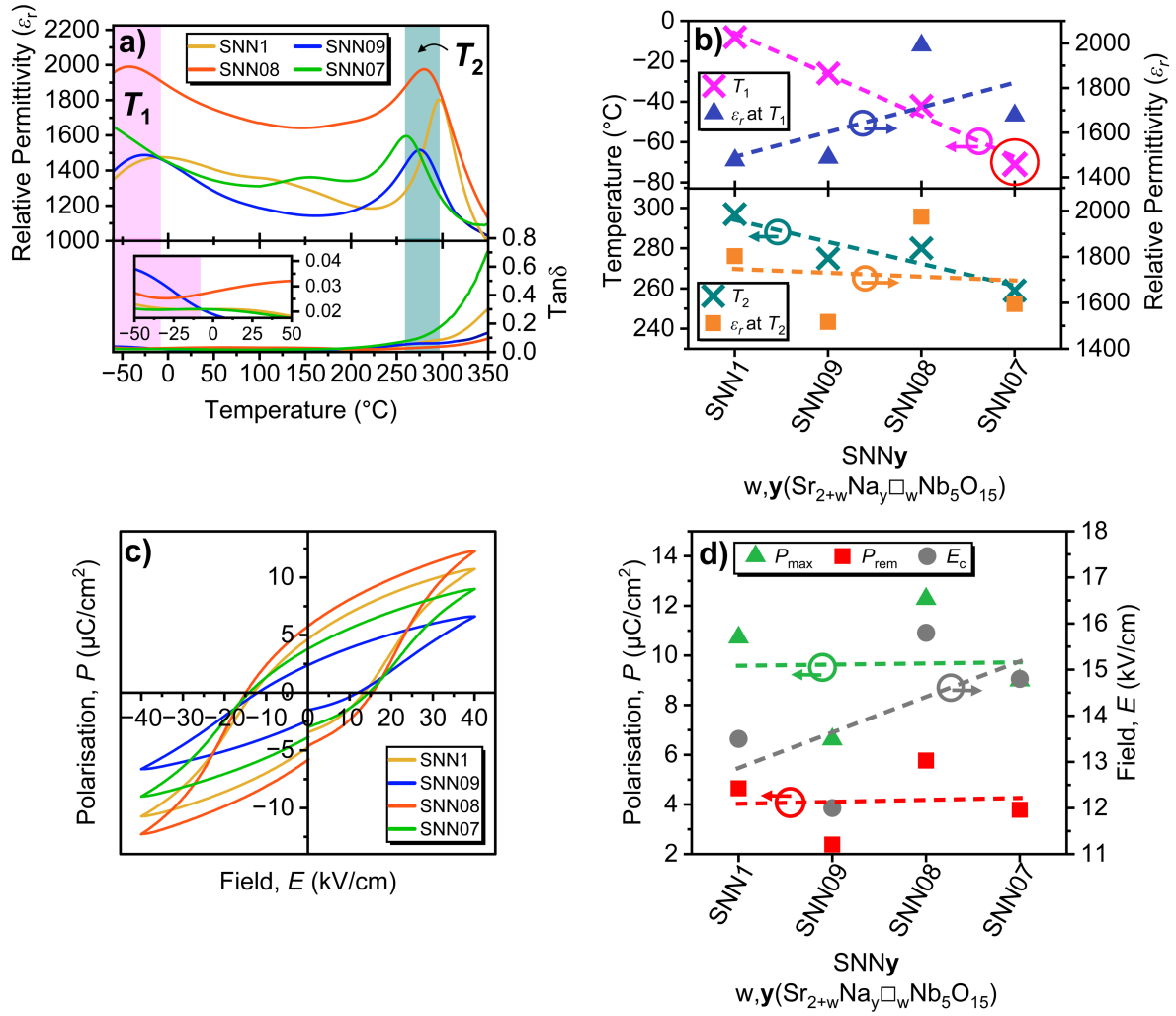


Figure 5.9a– d: Plots showing a) relative permittivity (ϵ_r) and dielectric loss tangent ($\tan\delta$) response as a function of temperature at 1 kHz with additional low temperature $\tan\delta$ response insets, b) T_1 , ϵ_r at T_1 (top) and T_2 , ϵ_r at T_2 (bottom) versus Na^+ vacancy content, y c) polarisation, P versus field, E ferroelectric hysteresis loops measured at 40 kV/cm and d) maximum polarisation ($P_{\max}$), remnant polarisation (P_{rem}) and coercive field (E_c) for $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ where $w = 0$, $y = 1$ (SNN1, yellow), $w = 0.05$, $y = 0.9$ (SNN09, blue), $w = 0.10$, $y = 0.8$ (SNN08, orange), and $w = 0.15$, $y = 0.7$ (SNN07, green). Note the T_1 value [red circle in b)] for SNN07 is beyond the measured temperature range (> -50 °C) and is plotted at -70 °C as an approximation.

Comparatively, T_2 only shows a minor shift from SNN1 ($T_2 = 297$ °C, $\epsilon_r = 1803$ at 1 kHz) to SNN07 ($T_2 = 259$ °C, $\epsilon_r = 1595$ at 1 kHz). ϵ_r at T_2 is highest for SNN1 ($T_2 = 297$ °C, $\epsilon_r = 1803$ at 1 kHz) and SNN08 ($T_2 = 280$ °C, $\epsilon_r = 1990$ at 1 kHz) relative to SNN09 ($T_2 = 275$ °C, $\epsilon_r = 1517$ at 1 kHz) and SNN07 ($T_2 = 259$ °C, $\epsilon_r = 1595$ at 1 kHz).

Trends in $P_{\max}$ and P_{rem} echo those observed for ε_r at T_2 , corresponding to $P = (\varepsilon_r - 1)E\varepsilon_0$ [252]. SNN1 ($P_{\max} = 10.7 \mu\text{C}/\text{cm}^2$, $P_{\text{rem}} = 4.6 \mu\text{C}/\text{cm}^2$ at 40 kV/cm) and SNN07 ($P_{\max} = 9.0 \mu\text{C}/\text{cm}^2$, $P_{\text{rem}} = 3.4 \mu\text{C}/\text{cm}^2$ at 40 kV/cm) are broadly similar, with SNN09 ($P_{\max} = 6.6 \mu\text{C}/\text{cm}^2$, $P_{\text{rem}} = 2.4 \mu\text{C}/\text{cm}^2$ at 40 kV/cm) and SNN08 ($P_{\max} = 12.2 \mu\text{C}/\text{cm}^2$, $P_{\text{rem}} = 3.8 \mu\text{C}/\text{cm}^2$ at 40 kV/cm) showing the lower and higher values of $P_{\max}$ and P_{rem} respectively. E_c minorly increases from SNN1 ($E_c = 13.5 \text{ kV}/\text{cm}$ at 40 kV/cm) to SNN07 ($E_c = 14.8 \text{ kV}/\text{cm}$ at 40 kV/cm), with SNN09 ($E_c = 12 \text{ kV}/\text{cm}$ at 40 kV/cm) showing a significantly lower value.

Na^+ vacancies effect T_1 and ε_r at T_1 to a far greater extent in comparison to T_2 and ε_r at T_2 , while ε_r at T_2 shows no clear trend with increasing Na^+ vacancies. Indeed, the ε_r - T response is notably becoming flatter from SNN1 to SNN07 because of the change around T_1 only, suggesting the exploitation of A-site vacancies in SNN1 may represent fertile ground for the application of unfilled SNN1 in temperature stable MLCCs.

5.3.5 Variable Temperature High Resolution Synchrotron Powder X-Ray Diffraction (PXRD)

Weight percentages of the pseudo – TTB phase and secondary phases (Sr-modified NaNbO_3 and/or SrNb_2O_6), in addition to R_{wp} at room temperature (R.T.), -173°C , 350°C , and average R_{wp} through the measured temperature range ($-173^\circ\text{C} - 350^\circ\text{C}$) are shown in Appendix C – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$, Figure C3 and Figure C4. As in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, DFT-derived *Ama2* (pseudo – TTB) and tetragonal *I4/mcm* (Sr modified NaNbO_3 perovskite) structural models [18, 238] were refined against synchrotron PXRD patterns. Rietveld refinement fitting plots of an orthorhombic *Ama2* pseudo – TTB structural model [18] against R.T. synchrotron PXRD patterns of SNNy compositions are shown in Figure 5.10a – d. Sr-modified NaNbO_3 is highlighted by ▼ for SNN1 (Figure 5.10a) and a possible minor, secondary impurity phase marked by ▽ in SNN09, SNN08, and SNN07 (Figure 5.10b – d).

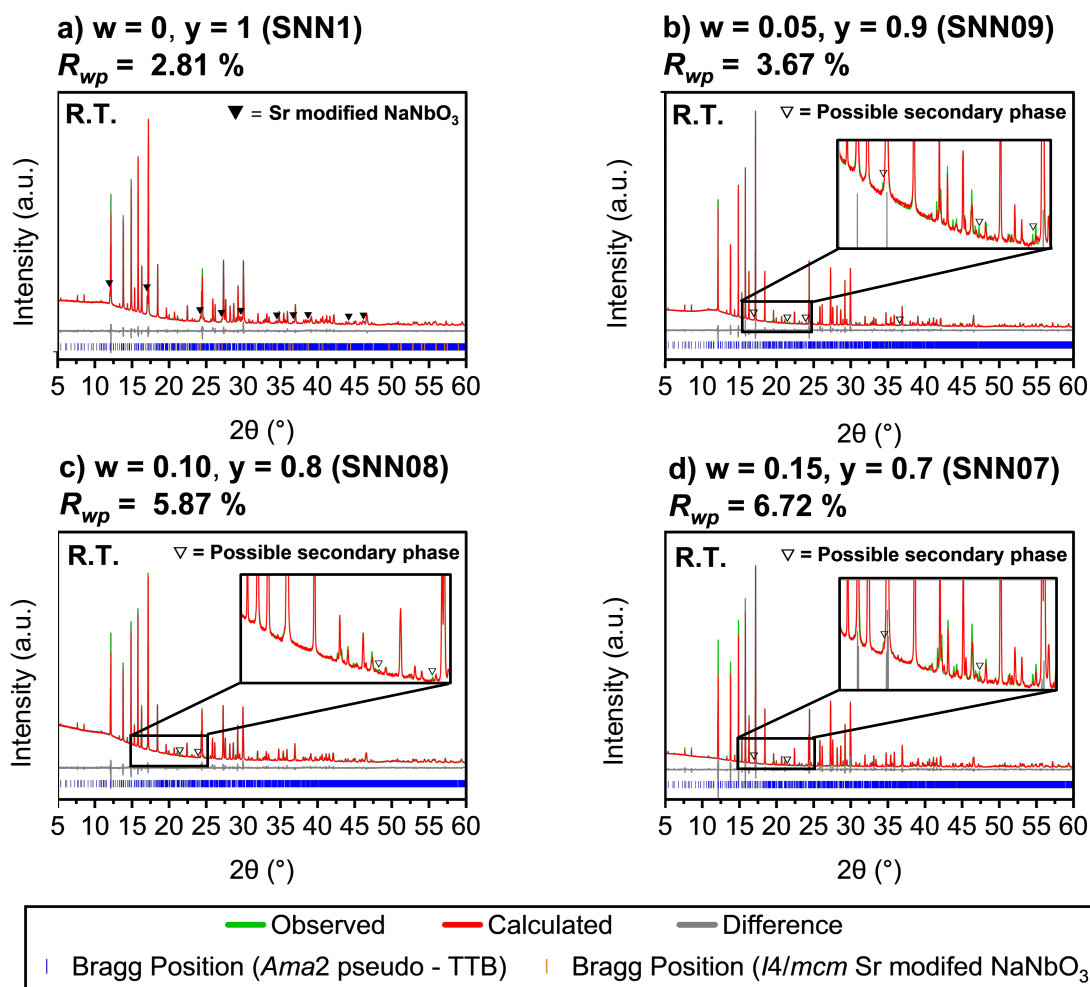


Figure 5.10a – d: Rietveld refinement fits of the orthorhombic *Ama2* (pseudo – TTB) structural model against diffraction patterns obtained through variable temperature synchrotron PXRD collected at beamline I11 Diamond Light Source at room temperature (R.T.) of $w,y(\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15})$ where a) $w = 0, y = 1$ (SNN1, yellow), b) $w = 0.05, y = 0.9$ (SNN09, blue), c) $w = 0.10, y = 0.8$ (SNN08, orange), and d) $w = 0.15, y = 0.7$ (SNN07, green). Secondary phase tetragonal *I4/mcm* (Sr modified NaNbO_3) is highlighted by ▼ in SNN1 and possible unknown secondary phase (< 1 wt%) is marked by ▽ for b) SNN09, c) SNN08, and d) SNN07 with corresponding insets.

Given the higher resolution of synchrotron PXRD data, *I4/mcm* and *P2₁/c* structural models for Sr-modified NaNbO_3 and/or SrNb_2O_6 respectively, were included in Rietveld refinements of SNN09, SNN08, and SNN07. Compositions showed no evidence of the SrNb_2O_6 phase but did show a quantifiable indication of the Sr modified NaNbO_3 phase (< 1 wt. %) that marginally improved R_{wp} ($\leq 0.07 \%$). However,

a visual inspection of the fit showed no distinct secondary phase peaks to suggest this phase was physically present in Na^+ deficient compositions (SNN09, SNN08, and SNN07), consistent with that reported from laboratory PXRD refinement fits (Figure 5.1b – d and Table 5.2). Indeed, refinement models of secondary phases (Sr modified NaNbO_3 and/or SrNb_2O_6) may well be attempting to fit to the low signal to noise ratio data at higher $2\theta^\circ$ angles. The lack of Sr modified NaNbO_3 and/or SrNb_2O_6 agrees with the uniform distribution of Sr^{2+} , Na^+ and Nb^{5+} from SEM-EDX micrographs and elementary mapping (Figure 5.2 – Figure 5.5).

If a second phase is present, it is unlikely that such a low wt.% would have significant impact on the refined lattice parameters and symmetry–adapted modes analysed here. Inclusion of the secondary phases did at times render refinements unstable, the repercussions of which would consequently hinder sequential Rietveld refinements spanning the measured temperature range. As such, the monoclinic $P2_1/c$ SrNb_2O_6 and Sr modified NaNbO_3 phases were omitted from variable temperature Rietveld refinements. SNN09, SNN08, and SNN07 were analysed as single phase *Ama2* pseudo – TTB.

The section to follow will concentrate on extracted variable temperature Rietveld refined lattice parameters and symmetry–adapted strain and distortion mode trends with increasing Na^+ vacancies in $w,y(\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15})$. The effect on T_1 , T_2 , ϵ_r at T_1 and T_2 will be examined. Variation in lattice parameters is governed by structural distortions of the lower symmetry structure (*Ama2*), transforming as irreducible representations (irreps) of the high symmetry parent structure (aristotype, $P4/mbm$). Lattice parameter lengths (a , b , c) and unit cell volume temperature evolution are plotted in Figure 5.11a – d, while orthorhombic strain (in %) is shown in Figure 5.12. As indicated in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, section 4.3.5. Variable Temperature High Resolution Synchrotron Powder X-Ray Diffraction (PXRD), the refined lattice parameter temperature evolution does not perfectly align with the symmetry-adapted distortion modes. Hence, more confidence is placed on the analysis of the refined lattice parameter temperature evolution.

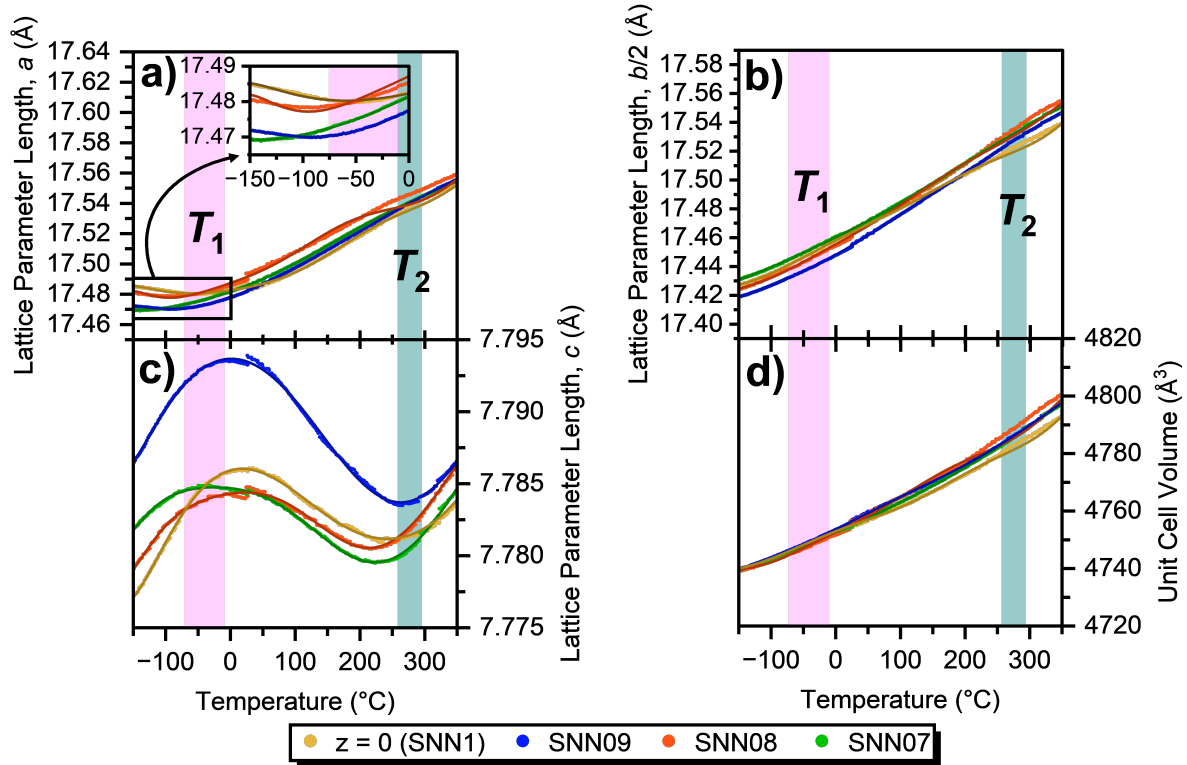


Figure 5.11a – d: Rietveld refined lattice parameters temperature evolution where a) lattice parameter a , b) lattice parameter b , c) lattice parameter c , and d) unit cell volume for $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ (SNNy, y = sodium content where $w = 0$, $y = 1$ (SNN1, yellow), $w = 0.05$, $y = 0.9$ (SNN09, blue), $w = 0.10$, $y = 0.8$ (SNN08, orange), and $w = 0.15$, $y = 0.7$ (SNN07, green) and high order polynomial fits (dark lines in respective colours of SNNy composition) as a function of temperature. T_1 (pink) and T_2 (teal) ranges are obtained from 1 kHz dielectric data (Figure 5.7a – d).

As in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, the irreps and their order parameter directions (OPDs [in brackets, *i.e.* $\Gamma_1^+(a)$]) refined in this chapter are $\Gamma_1^+(a)$, $\Gamma_2^-(a)$, $\Gamma_4^+(a)$, $\Gamma_3^-(a)$, and $S_3(0,a;0,0)$ [18]. Macroscopic strains transforming as irrep Γ_1^+ denote the volumetric symmetry strain, while Γ_4^+ corresponds to the orthorhombic strain in the ab plane [18]. Atomic displacements along c are represented by irreps transforming as Γ_2^- , describing the antiferroelectric antipolar mode, and Γ_3^- , describing the out-of-plane ferroelectric polar mode [18]. The temperature evolution of refined Γ irreps are illustrated in Figure 5.13a – d. Schematic visualisations of the irreps refined in this chapter and Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ are shown in Appendix A – Visualisation of Strain and Distortion Mode Irreducible Representations (Irreps).

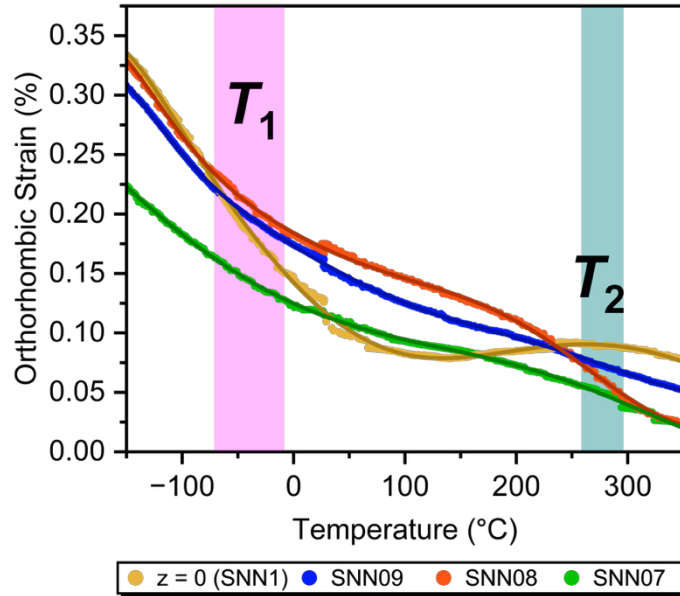


Figure 5.12: Orthorhombic strain as a function of temperature for $w,y(\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15})$ (SNNy, y = sodium content) where $w = 0$, $y = 1$ (SNN1, yellow), $w = 0.05$, $y = 0.9$ (SNN09, blue), $w = 0.10$, $y = 0.8$ (SNN08, orange), and $w = 0.15$, $y = 0.7$ (SNN07, green). T_1 (pink) and T_2 (teal) ranges are obtained from 1 kHz dielectric data (Figure 5.7a – d). Orthorhombic strain (%) is calculated by $\left(\frac{2(a - \frac{b}{2})}{(a + \frac{b}{2})}\right) \times 100$ where a and b are lattice parameters.

Modes transforming as irreps representing in plane octahedral tilts [$S_1(0,a;0,0)$], and shears [$M_5^+(a,a)$ and $M_5^-(a,a)$] were constrained to zero as reported by Tidey *et al.* [18]. Such modes would distort the pseudo – TTB octahedral framework beyond what is structurally and energetically realistic in TTBs [18]. Here, the irrep transforming as the S_3 mode is solely representative of the in-plane octahedral tilt system, specifically termed as a rigid unit mode distortion (RUM) [18, 256, 257], shown in Figure 5.14.

The temperature evolution of the lattice parameters and symmetry-adapted strain and distortion modes of (undoped) SNN1 were described in detail in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ section 4.3.3. Variable Temperature Synchrotron X-ray Powder Diffraction (PXRD) after Tidey *et al.* [18]. The phase transitions when cooling from above T_2 are summarised in Figure 5.15. As in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, refinements spanning the measured temperature range (-173 °C – 350 °C) were performed using only the *Ama2* ferroelectric structural model (emboldened in Figure

5.15). This allows for a direct analysis of the structural trends occurring around the dielectric anomalies T_1 and T_2 (and their corresponding ε_r at T_1 and T_2) with decreasing Na^+ vacancies from $w = 0, y = 1$ (SNN1) to $w = 0.15, y = 0.7$ (SNN07).

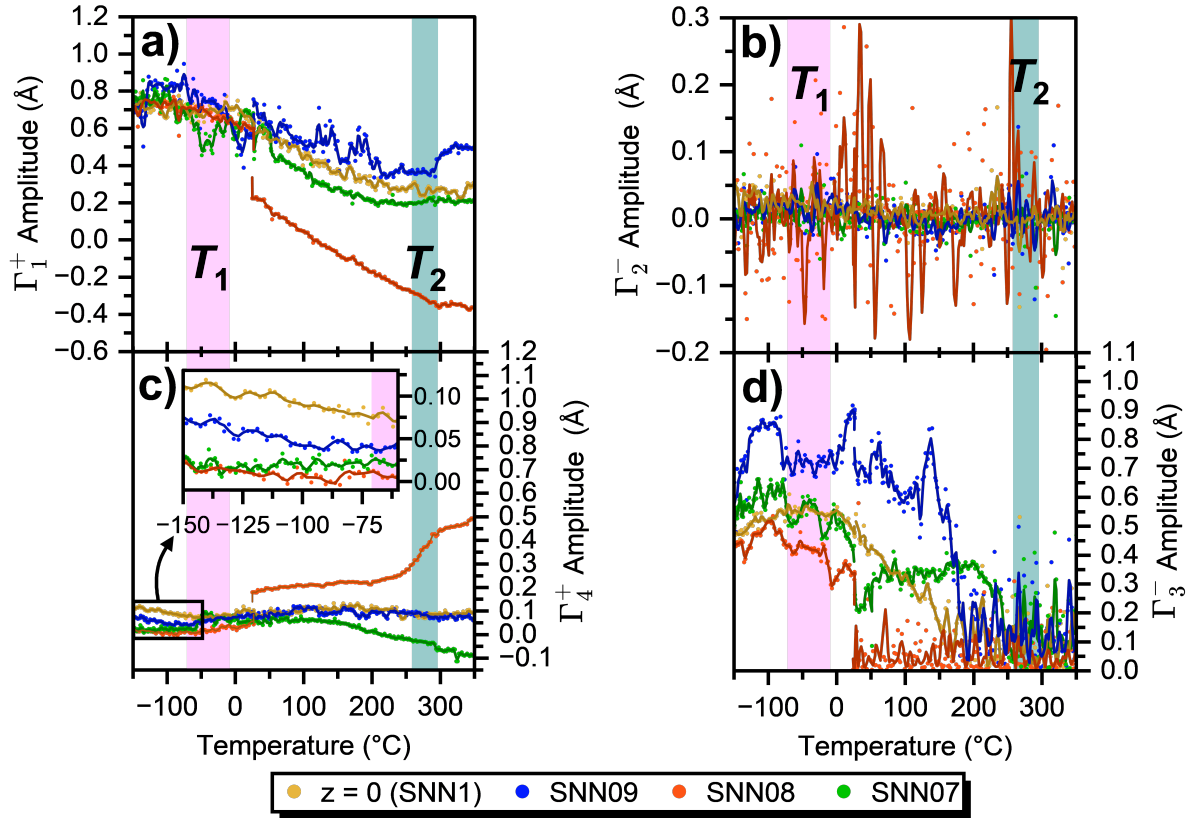


Figure 5.13a – d: Rietveld refined Γ modes ($k = 0, 0, 0$) evolution with temperature where a) the volumetric symmetry strain (Γ_1^+), b) orthorhombic strain (Γ_4^+), c) antiferroelectric (Γ_2^-) distortion amplitude and d) the ferroelectric distortion (Γ_3^-) amplitude moduli for $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ (SNNy, y = sodium content) where $w = 0, y = 1$ (SNN1, yellow), $w = 0.05, y = 0.9$ (SNN09, blue), $w = 0.10, y = 0.8$ (SNN08, orange), and $w = 0.15, y = 0.7$ (SNN07, green). T_1 (pink) and T_2 (teal) ranges are obtained from 1 kHz dielectric data (Figure 5.7a – d).

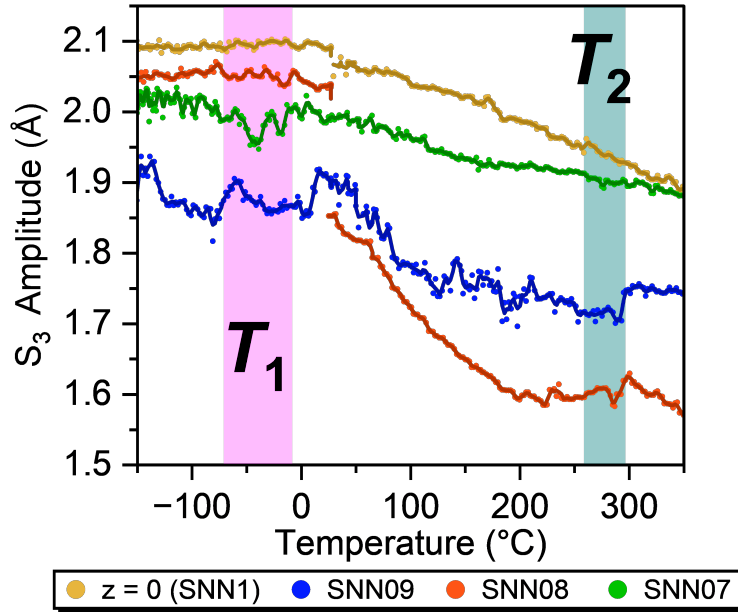


Figure 5.14a: Rietveld refined irrep S_3 symmetry-motivated displacement mode evolution with temperature, where a) shows the S_3 amplitude variation with temperature for $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ where $w = 0$, $y = 1$ (SNN1, yellow), $w = 0.05$, $y = 0.9$ (SNN09, blue), $w = 0.10$, $y = 0.8$ (SNN08, orange), and $w = 0.15$, $y = 0.7$ (SNN07, green). T_1 (pink) and T_2 (teal) ranges are obtained from 1 kHz dielectric data (Figure 5.7a – d).

The temperature variability of Rietveld refined lattice parameters, and symmetry-adapted strain and distortion modes of SNN1 are described in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, section 4.3.3. Variable Temperature Synchrotron X-ray Powder Diffraction (PXRD). To briefly recap, on cooling from above T_2 there is a constant contraction in the a , b lattice parameters, whilst c elongates upon further cooling (Figure 5.11a – c), coinciding with the ferroelectric polar mode transforming as irrep Γ_3^- , rising above zero up to T_1 (Figure 5.13d). Below T_1 , lattice parameter a begins elongating, deviating from b , which continues to contract with cooling (Figure 5.11a – b). At T_1 , the orthorhombic strain mode transforming as irrep Γ_4^+ begins to evolve with cooling (Figure 5.13c), showing an increase in tensile strain in the ab plane.

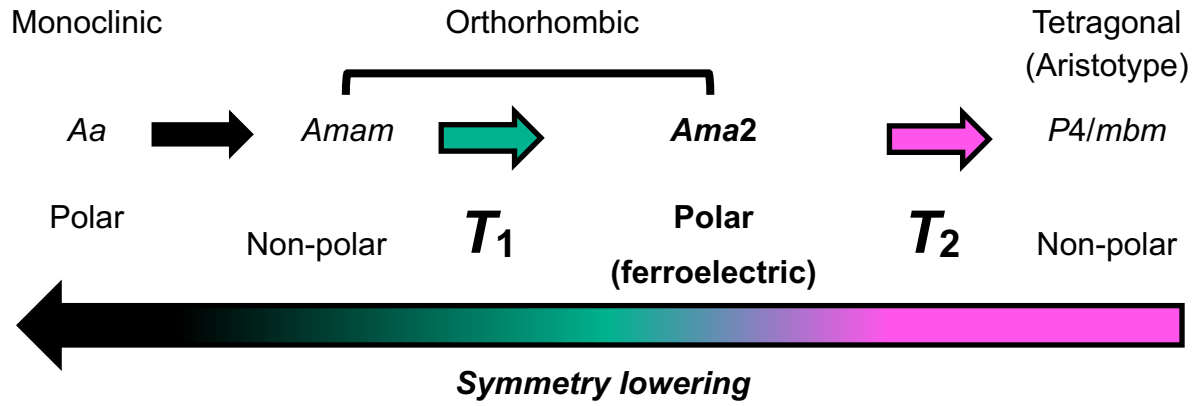


Figure 5.15: Schematic of the symmetry lowering phase transitions of SNN1 [18] upon cooling from above T_2 , described in further detail in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ (section 4.3.3. Variable Temperature Synchrotron X-ray Powder Diffraction (PXRD)) with phase crystal structure, polarity, and phase transition temperatures T_1 (pink) and T_2 (teal) highlighted.

The overall contraction of the c lattice parameter with doping was shown to destabilise the out-of-plane polar mode, Γ_3^- , lowering T_2 , notably affecting the elongation of c on cooling. The elongation of lattice parameter a was shown to be intimately linked to T_1 , indicating the onset of orthorhombic strain in the ab plane. The formation of an incommensurate modulation was attributed to compositional disorder (*i.e.* Sr and Na distributed across the A1/A2 sites and possibly B-site co-doping such as in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) perturbing the coherent tilting of the pseudo-TTB oxygen octahedral framework. The incommensurate modulation is suggested to disrupt long range phase transitions, disturbing ferroelastic domain structures, effectively breaking down macroscopic polarisation, thus facilitating the relaxor-like frequency dispersion behaviour at T_1 [264]. The incommensurate modulation is suggested to disrupt long range phase transitions, disturbing ferroelastic domain structures, effectively breaking down macroscopic polarisation, thus facilitating the relaxor-like frequency dispersion behaviour at T_1 [264].

Drawing on the examination of refined lattice parameters, and symmetry-adapted strain and distortion modes of vacancy free SNN1, attention will now turn to the impact of increasing Na^+ vacancies in SNN1. Na^+ vacancies were systematically introduced into the A-site to form SNNy (SNN09, SNN08, and SNN07). T_2 , $\Gamma_3^- = 0$ (Γ_3^- saturation

temperature), c lattice parameter length above T_2 , T_1 , and inflection point temperatures $\left.\frac{da}{dT}\right|_{T_1}$ and $\left.\frac{dc}{dT}\right|_{T_1}$ extracted from high order polynomial fits (darker lines Figure 5.11a – d) are plotted against the level of Na^+ vacancies and shown in Figure 5.16a – b.

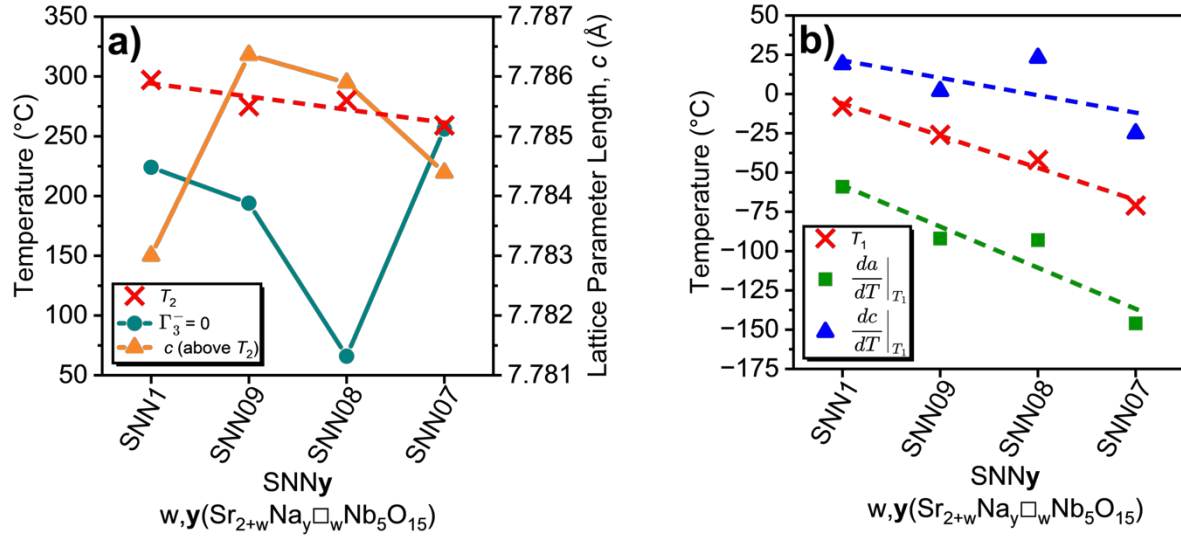


Figure 5.16a – b: Plots showing a) T_2 , Γ_3^- saturation temperature ($\Gamma_3^- = 0$) and c lattice parameter length above T_2 , and b) T_1 , inflection point temperatures, $\left.\frac{da}{dT}\right|_{T_1}$ and $\left.\frac{dc}{dT}\right|_{T_1}$ for $w = 0$, $y = 1$ (SNN1), $w = 0.05$, $y = 0.9$ (SNN09), $w = 0.10$, $y = 0.8$ (SNN08), and $w = 0.15$, $y = 0.7$ (SNN07). T_1 (pink) and T_2 (teal) ranges are obtained from 1 kHz dielectric data (Figure 5.7a – d).

The introduction of Na^+ vacancies in SNN1 leads to lattice parameters a , b , and c all increasing above T_2 , thus expanding the unit cell volume (Figure 5.11a – d). Dielectric spectroscopy shows that the anomaly temperature, T_2 , has a minor negative correlation with increasing Na^+ vacancy content (Figure 5.9a – b), that is significantly less than the reduction in T_2 with increased A and B-site doping in SNN1 (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Figure 4.17). However, reliable trends cannot be drawn from the refinement of Γ_3^- polar distortions and the c lattice parameter above T_2 as a function of Na^+ vacancy level (Figure 5.16a). Indeed, across the measured temperature range, the overall c lattice parameter shows no trend with increasing Na^+ vacancy level, nor is there any appreciable effect on the elongation of c on cooling from T_2 down to T_1 (*i.e.* negative thermal expansion (NTE)), with exception to SNN09

which shows a larger overall c lattice parameter spanning the measured temperature range (Figure 5.11c).

In the SNNy compositions studied here, A-site Na^+ vacancies are assumed to be the sole species introduced into SNN1, whereas the B-site cation identity (Nb^{5+}) and its stoichiometry is assumed to remain constant. The lack of B site doping in SNNy may be the major reason for the reduced negative correlation of T_2 with increasing Na^+ vacancy content and the greatly reduced suppression of the NTE of the c lattice parameter. B-site doping of lower charge density Zr^{4+} (relative to Nb^{5+}) was suggested to facilitate lattice parameter c compression by reducing the electrostatic interaction between octahedral units, ultimately contributing to the in-plane tilt of the octahedral RUM framework throughout the pseudo-TTB oxygen octahedral framework. Moreover, the decreased dielectric polarizability of Zr^{4+} ($3.25 \text{ \AA}^3$) compared to Nb^{5+} ($3.97 \text{ \AA}^3$) [23] was also suggested to inhibit long range ferroelectric ordering, also contributing to a lowering of T_2 with B site doping. Moreover, the decreased dielectric polarizability of Zr^{4+} ($3.25 \text{ \AA}^3$) compared to Nb^{5+} ($3.97 \text{ \AA}^3$) [23] was also suggested to inhibit long range ferroelectric ordering, also contributing to a lowering of T_2 with B site doping.

A-site, Na^+ vacancies can be thought as “empty” space in the A1 site itself. Intuitively, one would expect that the lack of cation in the A1-site may promote flexibility spanning the pseudo-TTB octahedral framework [107]. Yet, structural mechanistic reasoning for A-site vacancy induced effects remains a subject of debate in perovskite-based systems [275]. Studies on perovskite ferroelectrics have commented that A-site vacancies increase the average A – O bond length, owing to the electrostatic repulsion of the oxygen anions enclosing the A-site(s) [176, 276, 277] and as a result eliminates cation electrostatic shielding at the A-site [241]. More recently and relevant to the pseudo-TTB SNN1 system studied here, a DFT-guided model by Zeiger *et al.* [177] has shown that vacant A1-sites require 13 % more space relative to the same site occupied by a cation (*i.e.* Na^+). Therefore A-site vacancies may be considered to have an effective size [176] that may perturb the in-plane tilt of the octahedral RUM framework transforming as the irrep S_3 , in the ab plane in a similar fashion to A-site dopants (Figure 5.14 suggests a similar trend in S_3 with vacancies as in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ with dopants, Figure 4.16).

Tidey *et al.* [18] suggested that T_2 should shift to lower temperatures because of cation substitutions that increase the unit cell volume. The introduction of Na^+ vacancies here, expands the unit cell volume (Figure 5.11d) which indeed is accompanied by a small decrease in T_2 (Figure 5.9b). Furthermore, using the crystal-chemical framework reported by Zhu *et al.* [107], an increased average A-site size (where Na^+ vacancies are 13 % larger than that occupied by Na^+ [177]), would be expected to lengthen the O–B–O bond, promoting dielectric polarizability and facilitating long range ferroelectric ordering. However, the A1 tolerance factor (t_{A1}) correspondingly increases with Na^+ vacancies, driving the in-plane tilt of the octahedral RUM framework to an incommensurate modulation, facilitating relaxor ferroelectric behaviour. Both the increased average A-site radii size (favouring ferroelectric behaviour) and larger t_{A1} (favouring relaxor ferroelectric behaviour) with increasing Na^+ vacancies, creates competition between the two parameters. Ultimately, such competition results in relaxor ferroelectric behaviour dominating [107]. A possible intermediary relaxor ferroelectric domain structure, previously attributed to SNN1 [278], to better represent these competing factors has been proposed by Cao *et al.* [166] (Figure 5.17).

Hence, the reduction in T_2 with Na^+ vacancies is a result of the facilitated in-plane tilt of the octahedral RUM framework in the ab plane stabilising an incommensurate modulation. This does not affect the distortion amplitude of the irrep transforming as the ferroelectric out of plane polar mode, Γ_3^- , and the c lattice parameter *per se* (Figure 5.16a), but rather it disrupts the coherence of Γ_3^- along c . This disruption facilitates relaxor behaviour which broadens and ultimately flattens T_2 . Force-field simulations and dark-field TEM imaging by Sjökvist *et al.* [242] showed that in-plane octahedral tilts minimally affect the central metal cation shift of the polar Γ_3^- distortion mode, suggesting it is the correlation of the Γ_3^- mode along c that takes precedence and thereby affects T_2 .

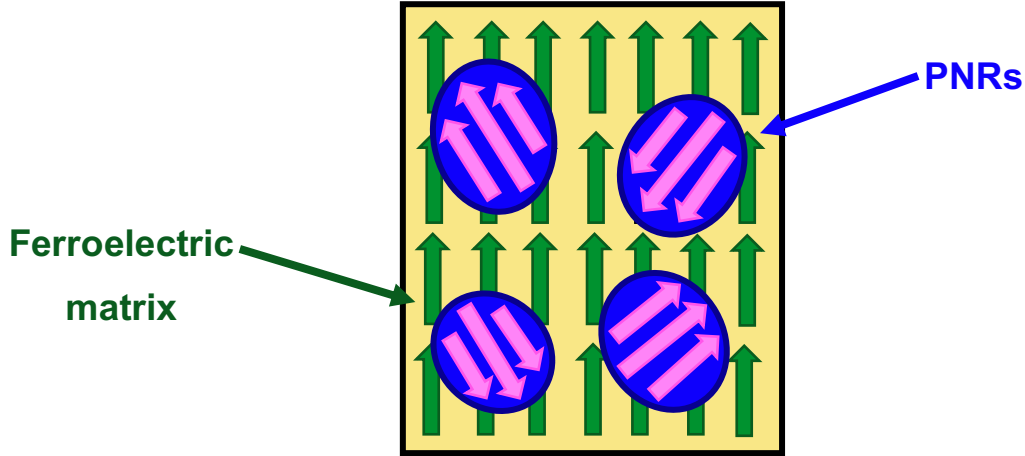


Figure 5.17: Domain diagram showing polar nanoregions (PNRs, blue circles and pink arrows) embedded in a long range ferroelectric matrix (green arrows), taken and adapted from Figure 6a, Cao *et al.* [166] arising from the irrep transforming as the ferroelectric polar mode along c , Γ_3^- (Figure 5.13d).

Attention will now be turned to T_1 . Cooling from T_1 , lattice parameter b continues to contract, whilst a reaches a minimum and begins to elongate (Figure 5.11a – b). The elongation of a becomes increasingly suppressed with Na^+ vacancies, although b continues to contract and remains relatively invariant between SNNy compositions. Inflection temperatures $\left.\frac{da}{dT}\right|_{T_1}$ and $\left.\frac{dc}{dT}\right|_{T_1}$ deviate with increased Na^+ vacancies, with $\left.\frac{da}{dT}\right|_{T_1}$ showing a steep decline (Figure 5.16b). T_1 and $\left.\frac{da}{dT}\right|_{T_1}$ negatively correlate to increasing Na^+ vacancies, whilst $\left.\frac{dc}{dT}\right|_{T_1}$ virtually exhibits no change (Figure 5.16b). Notably, the steep decline in $\left.\frac{da}{dT}\right|_{T_1}$, relative to $\left.\frac{dc}{dT}\right|_{T_1}$ with Na^+ vacancies is similar to that of increasingly doped SNN1 (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$).

As discussed above, Na^+ vacancies have an effective size and, simplistically, they could be viewed as a “virtual dopant”. In a similar fashion to the real dopants introduced in Chapter 4, their inclusion might also be expected to lead to increased compositional disorder and give rise to an incommensurate modulation of octahedral tilting, resulting in the breakdown of the macroscopic polarisation and potentially the formation of polar nano-regions (PNRs), which contribute to the relaxor-like frequency dispersion of the permittivity anomaly at T_1 .

Na^+ vacancies could therefore facilitate in-plane RUM octahedral tilts transforming as the irrep S_3 , in a similar fashion to dopants. The S_3 amplitude discussed in the above sections shows no trend with Na^+ vacancies across the measured temperature range (Figure 5.14). This is much like that observed with doped compositions in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$. The T_1 dielectric anomaly is driven by the elongation of lattice parameter *and* the concurrent contraction of *c* with cooling. The suppression of the elongation of *a* with Na^+ vacancies, diminishes the orthorhombic strain (Figure 5.12) in the *ab* plane at T_1 , reflected by the slight red shift of ν_2 and ν_5 modes with Na^+ vacancies from Raman spectroscopy. Ultimately, this facilitates an in-plane polar distortion (Γ_5^-) which drives the *Ama2* to *Aa* transition [18] at T_1 . The large effective size of the A1-site vacancy would perturb the in-plane tilt of octahedral tilt RUM framework, effectively enhancing this effect with more vacancies, giving rise to an incommensurate modulation, and thus a pronounced relaxor behaviour and frequency dispersion at T_1 . Hence PNRs arise, breaking down long range, macroscopic ferroelectric polarisation [264]. The role of the in-plane tilt of octahedra in the RUM likely influences the instability of the irrep transforming as Γ_5^- to facilitate the *Aa* structural transition at T_1 .

Planar defects, namely stacking faults in the *ab* plane are thought to reduce the symmetry of the *Ama2* structure to *Aa* (reported in the standard form *Cc* in the work of Sjökvist *et al.* [242]) facilitating the instability of the irrep transforming as Γ_5^- at T_1 [18, 242]. The S_3 OPD defines the incommensurate modulation to have a directionality along *b* of the *Ama2* unit cell [18], where stacking faults are thought to occur to adjust to orthorhombic strain introduced by the incommensurate tilt system resolving alongside the commensurate tilt system. Hence, assuming Na^+ vacancies have an effective size, increasing the amount of vacancies could possibly increase the degree of incommensurate distortion of the octahedral framework, effectively increasing stacking fault density, and consequently reducing orthorhombic strain to facilitate the in-plane polar instability, Γ_5^- , and ultimately lowering T_1 (Figure 5.12). The competition between the in-plane polarisation, Γ_5^- may compete with the out of plane polarisation, Γ_3^- , leading to an inconsistent trend in ϵ_r at T_1 . Indeed, the S_3 mode does not correlate to the elongation of lattice parameter *c*, nor is there any general trend spanning the

measured temperature range. This emphasises that Γ_3^- only activates at temperatures closer to T_1 , and increasing Na^+ vacancies decrease the coherence of Γ_3^- along c .

5.4 Conclusion

Na^+ vacancies were systematically introduced into the A1 site in SNN1 to successfully synthesize SNN_y , where $w = 0$, $y = 1$ (SNN1), $w = 0.05$, $y = 0.9$ (SNN09), $w = 0.10$, $y = 0.8$ (SNN08), and $w = 0.15$, $y = 0.7$ (SNN07), as confirmed by laboratory PXRD and SEM-EDX. Rietveld refinement of variable temperature synchrotron PXRD data reveals the crystallographic reasoning behind the flattening of the dielectric permittivity–temperature profile of $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$ and these effects have been discussed with respect to the permittivity anomalies at temperatures T_1 (a relaxor-ferroelectric peak) and T_2 (ferroelectric transition) and to the corresponding relative permittivities, ϵ_r (ϵ_r at T_1 and T_2). The analysis and results in this chapter build upon the broad crystallographic structure-property relationship insights derived from the A- and B-site co-doped SNN1 series in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, extending this analysis to Na^+ deficient (A-site Na^+ vacancy containing) SNN1.

The results of this chapter reveal that the systematic introduction of Na^+ vacancies into the A-site had no notable effect on the c lattice parameter across the measured temperature range and by extension, the cooling driven elongation of c below T_2 (the paraelectric to ferroelectric transition temperature), with exception to SNN09. The inconsistency of lattice parameter c with Na^+ vacancies was reflected by the out-of-plane polar mode, Γ_3^- , which also showed no reliable trend in temperature at which the Γ_3^- polar distortion amplitude rises to above zero. Despite this, a negative correlation of Na^+ vacancies with T_2 was observed, smaller in magnitude than that observed with A-site and B-site co-doping, suggesting a more indirect effect along c related to the coherence of the octahedral units that give rise to the out-of-plane polar mode, Γ_3^- , rather than due to a shift of the central metal cation, Nb^{5+} . The Na^+ vacancies in the A1 sites are thought to have an effective size larger than the equivalent site occupied by Na^+ , facilitating an in-plane tilt of the octahedral pseudo – TTB framework, transforming as irrep S_3 , in the ab plane. Increasing numbers of Na^+ vacancies disrupt the long-range coherence of the out-of-plane polar mode, Γ_3^- , facilitating an

incommensurate modulation and likely formation of PNRs, decreasing T_2 . Taken together, this suggests that both A-site doping or vacancy inclusion and B-site doping are important for controlling the behaviour of the paraelectric to ferroelectric transition at T_2 .

Na^+ vacancies also suppress the cooling driven elongation of lattice parameter a below T_1 (low temperature, relaxor-like transition [$Ama2$ to Aa])). The in-plane octahedral tilt system represented by irrep transforming as S_3 , effectively relieves the orthorhombic strain induced by Na^+ vacancies *via* a suggested increased density of stacking faults resulting from the incommensurate modulation resolving against the commensurate modulation. The incommensurate modulation again leads to increasing frequency dispersion and relaxor-like behaviour at T_1 . In turn, relief of the orthorhombic strain originally induced by increased numbers of Na^+ vacancies effectively reduces the onset temperature of the $Ama2$ to Aa phase transition, *i.e.* the decrease in T_1 . The minor impact on ϵ_r at T_1 is thought to be obscured by the emergence of the stabilised in-plane polar mode, Γ_5^- at this transition.

The results of this chapter indicate that systematically introducing small amounts of Na^+ vacancies at the A-sites, effectively tilts the pseudo TTB octahedral framework which disrupts the long-range ferroelectric coupling along c , facilitating an incommensurate modulation, breaking down the ferroelastic domain structure, contributing to increased frequency dispersion and relaxor like behaviour at T_1 . The breakdown of the ferroelastic domain structure reduces T_2 a small amount, to give a flattening of the permittivity temperature response with Na^+ vacancies. However, the temperature stability of Na^+ deficient SNN compositions may not deem them appropriate for application as temperature stable MLCC.

Structural and Dielectric Properties of Rare Earth and Tantalum Co-Doped Unfilled $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) Tetragonal Tungsten Bronze (TTB)

6.1 Introduction

The two previous results chapters in this thesis studied the role of dopants (Chapters 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) and vacancy levels (Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$) on the relaxor phase transition (at T_1) and the ferroelectric to paraelectric phase transition (T_2), on the corresponding temperatures of the transitions and the relative permittivity maxima (ϵ_r at T_1 and T_2). Rietveld refinement of variable temperature synchrotron powder X-ray diffraction patterns were undertaken based on a density functional theory (DFT) derived *Ama2* space group reported by Tidey *et al.* [18]. Results show that both a reduction in out-of-plane ferroelectric polarization and increased octahedral tilt are required to merge T_1 (low-temperature relaxor-like) and T_2 (T_c , ferroelastic to paraelectric transition) permittivity anomalies. Thereby flattening a material's temperature permittivity profile, achieved in SNN by co-doping A and B-sites or to some extent by introducing A-site vacancies to give an 'unfilled' SNN. The present chapter will investigate such insights for the structurally associated unfilled tetragonal tungsten bronze (TTB), $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN). Here, SBN will be co-doped with singular rare earths in place of Sr^{2+} on the A-site (La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , and Y^{3+}) and Ta^{5+} for Nb^{5+} on the B-site to form $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$ (SBRTN).

An emerging trajectory in TTB research has seen a shift toward optimising dielectric performance to maximise energy storage capabilities⁹. Desirable storage performance characteristics include a thin polarisation (P) versus field (E) hysteresis loop (large

⁹ For an in-depth literature review on SBN and related doped compositions see Chapter 2 – Background Science and Literature Review, section 2.6. Literature Review.

maximum polarisation [$P_{\max}$], small remanent polarisation [P_{rem}]), and a high breakdown strength (E_B) [126]. Current research has vastly improved the energy storage performance of SBN by the addition of A and B-site co-dopants [187]. Yang *et al.* [126] reported a gadolinium (Gd^{3+}) and tantalum (Ta^{5+}) co-doped SBN system ($\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{Gd}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.1, 0.2, 0.3$, and 0.5) to modulate relaxor ferroelectric (RFE) behaviour, outperforming BaTiO_3 and NaNbO_3 in recoverable energy density (W_{rec}) and energy recovery efficiency (η). Other similar A-site rare earth and B-site tantalum doped systems, such as $\text{Sr}_{0.475}\text{Ba}_{0.475}\text{La}_{0.1}\text{Hf}_{0.1}\text{Ti}_{0.1}\text{Sb}_{0.2}\text{Ta}_x\text{Nb}_{1.6-x}\text{O}_6$ ($x = 0, 0.1, 0.2$, and 0.3) [162], $\text{Sr}_{0.425}\text{La}_{0.1}\text{Ba}_{0.425}\text{Nb}_{1.4}\text{Ta}_{0.6}\text{O}_6$ [279], and $\text{Sr}_{0.515}\text{Ba}_{0.47}\text{Gd}_{0.01}\text{Nb}_{1.9-x}\text{Ta}_{0.1}\text{Sb}_x\text{O}_6$ ($x = 0.0, 0.02, 0.05$, and 0.08) [280] have also been reported. These works suggest rare earth/tantalum A- and B-site co-doping in SBN is also a potential candidate for high energy density MLCCs. Nonetheless, whilst the structure-property relationships of filled TTBs, such as SNN1, have been well reported (Chapter 2 – Background Science & Literature Review, section 2.7) and also explored here (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and progressively unfilled SNN1 in Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$), in comparison there have been few studies of unfilled TTBs, like SBN, or even “empty” TTBs¹⁰ [50, 89].

This chapter seeks to uncover the structure – dielectric property relationships of A-site doped rare earth and B-site tantalum doped SBN to disentangle the individual roles of R^{3+} and Ta^{5+} co-dopants on the RFE dielectric anomaly (T_m), drawing on concepts explored in Chapters 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$. The ferroelectric to paraelectric transition here, is the sole phase transition in SBN across the temperature range $-50\text{ }^{\circ}\text{C}$ to $350\text{ }^{\circ}\text{C}$, with early transmission electron microscopy studies showing some evidence of ferroelastic and ferroelectric domains being present in an orthorhombic crystal symmetry that is incommensurate *i.e.* having microstructural features that are common to SNN [281]. These compositions will be assessed as possible alternatives to SNN1 as materials for temperature stable dielectrics.

¹⁰ “Empty” TTBs have a much larger A site vacancy concentration relative to unfilled TTBs such as SBN, and the calcium analogue, $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (CBN).

6.1. Experimental Methods

6.1.1 Ceramic Processing

SrCO_3 (Sigma-Aldrich, > 99.9 %), BaCO_3 (Sigma-Aldrich, > 99.9 %), Nb_2O_5 (Alfa Aesar, 99.9 %), Ta_2O_5 and $\text{R} = \text{La}_2\text{O}_3$ (Sigma-Aldrich, 99.99 %), Nd_2O_3 (Sigma-Aldrich, 99.99 %), Sm_2O_3 (Sigma-Aldrich, 99.99 %), Gd_2O_3 (Sigma-Aldrich, 99.99 %), Dy_2O_3 (Sigma-Aldrich, 99.99 %), and Y_2O_3 (Sigma-Aldrich, 99.99 %) chemical powder reagents were combined to form polycrystalline $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0$ (SBN) and $x = 0.2$ (SBRTN). Here, $\text{R} = \text{La}^{3+}$ (SBLTN), Nd^{3+} (SBNTN), Sm^{3+} (SBSTN), Gd^{3+} (SBGTN), Dy^{3+} (SBDTN), and Y^{3+} (SBYTN). CAS codes of chemical reagent powders used here are shown in Table 3.1, Chapter 3 – Experimental Methods. Ceramics were prepared by the conventional mixed oxide route as described in Chapter 3 – Experimental Methods.

Table 6.2 summarises the nominal processed ceramic formulas with associated composition codes used as abbreviations through this chapter. Calcination was undertaken at 1100 – 1200 °C for 4 – 6 hours and sintering with a heating/cooling rate of 300 °C/hour. Sintering was undertaken for 4 hours at 1350 °C for SBN, SBGTN and SBLTN, while SBYTN required a lower sintering temperature of 1280 °C. SBNTN, SBSTN, and SBDTN compositions were sintered with a dual stage sintering regime of a precursor 4-hour sintering step at 1250 °C followed by another 4 hours at a slightly elevated temperature of 1300 – 1350 °C. The reasoning behind a dual stage sintering regime in SBNTN, SBSTN and SBDTN will be discussed in the section to follow (6.2. Results and Discussion).

Table 6.1: Nominal processed ceramic formula for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R} = \text{La}^{3+}$ (SBLTN), Nd^{3+} (SBNTN), Sm^{3+} (SBSTN), Gd^{3+} (SBGTN), Dy^{3+} (SBDTN), and Y^{3+} (SBYTN), with corresponding sample codes used throughout this work, in addition to cationic radii of rare earth A-site dopants (taken after Shannon [22] where CN = coordination number). Dual stage sintered composition temperatures and dwell times are denoted by an * (*i.e.* SBDTN is sintered at 1250 °C for 4 hours, followed by another sintering step at 1350 °C for 4 hours written as 1250, 1300 °C and 4, 4 hours in sintering temperature and time columns respectively).

Nominal Formula $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ $x = 0.2$	Composition Code (SBRTN)	Ionic Radii of A-site Dopant and Coordination Number (CN) after Shannon [22] (Å)	Calcination		Sintering	
			Temperature (°C)	Time (hours)	Temperature (°C)	Time (hours)
$\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$	SBN	N/A	1100	4	1350	4
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{La}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	SBLTN	1.216 (CN = IX)	1200	6	1350	4
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Nd}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	SBNTN	1.163 (CN = IX)	1100	6	1250, 1300*	4, 4*
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Sm}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	SBSTN	1.132 (CN = IX)	1200	6	1250, 1300*	4, 4*
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Gd}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	SBGTN	1.107 (CN = IX)	1200	6	1350	4
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Dy}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	SBDTN	1.083 (CN = IX)	1200	6	1250, 1350*	4, 4*
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Y}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	SBYTN	1.075 (CN = IX)	1100	6	1280	4

6.1.2 Structural and Electrical Characterisation

Experimental pellet densities were obtained from measured pellet masses and volumes as described in Chapter 3 – Experimental Methods. The least squares refinement program, *TOPAS Academic* (Version 7.1.0) [212] and *jEdit* (Version 5.7.0) text editor software were used to perform Rietveld refinements of room temperature (R.T.) laboratory powder X-ray diffraction (PXRD) patterns. Theoretical pellet densities were acquired from lattice parameters obtained through Rietveld refinement of R.T. laboratory PXRD patterns. Rietveld refinements of R.T. laboratory PXRD patterns were performed against a *P4bm* structural model as shown by high-resolution neutron [282] and X-ray [283] diffraction and despite prior identification of incommensurate structure composed of an intergrowth of orthorhombic structures by TEM [281]. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy were undertaken as described in Chapter 3 – Experimental Methods. Electrical characterisation techniques used in this chapter were relative permittivity (ϵ_r) – temperature measurements and ferroelectric polarisation (P) versus field (E) hysteresis loops. For further detail on sample preparation and methodology for electrical characterisation see Chapter 3 – Experimental Methods.

6.2 Results and Discussion

6.2.1 Room Temperature Laboratory X-ray Diffraction (PXRD)

Room temperature (R.T.) laboratory powder X-ray diffraction (PXRD) was used to examine phase purities, densities and lattice parameter lengths of $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} = \text{La}^{3+}$, Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , and Y^{3+} . Laboratory PXRD patterns were refined against a tetragonal *P4bm* structural model (collection code ICSD-90136 [ICSD release 2025.1]), aligning with reports in the literature [88, 128, 282-287]. Rietveld refinement fitting plots of all compositions are shown in Figure 6.1a – g. Extracted lattice parameter lengths, unit cell volume, residual R-factors (R_{wp}) and pellet densities are summarised in Table 6.2. Pellet densities were $\geq 91\%$ and weighted R-factors were (R_{wp}) were $< 6\%$ highlighting a good fit of the *P4bm* structural model to laboratory PXRD patterns. Lattice parameters a , c , tetragonality (c/a), and unit cell volume (Table 6.2) were extracted from Rietveld refined laboratory PXRD patterns (Figure 6.1a– g) and plotted with respect to composition in Figure 6.2a – b.

Table 6.2: Room temperature laboratory PXRD crystallographic data extracted from Rietveld refinement against a tetragonal $P4bm$ structural model (lattice parameters $a = b \neq c$) showing TTB phase weight percentages (wt. %), weighted R-factors (R_{wp}), theoretical pellet densities, experimental pellet densities, and pellet density (%) for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $R = \text{La}^{3+}$ (SBLTN), Nd^{3+} (SBNTN), Sm^{3+} (SBSTN), Gd^{3+} (SBGTN), Dy^{3+} (SBDTN), and Y^{3+} (SBYTN).

Composition Code	Lattice Parameter Information				R_{wp} (%)	Theoretical Pellet Density (g cm^{-3})	Geometric Pellet Density (g cm^{-3})	Pellet Density (%)
	a (Å)	c (Å)	Tetragonality, c/a	Volume (Å ³)				
$\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$	12.475	3.938	0.315654	611.631	3.76	5.22	5.00	94
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{La}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	12.482	3.930	0.314888	612.382	4.04	5.57	5.18	93
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Nd}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	12.480	3.930	0.314891	612.144	4.56	5.58	5.26	94
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Sm}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	12.477	3.929	0.314892	611.661	5.02	5.58	5.19	93
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Gd}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	12.475	3.929	0.314962	611.481	4.43	5.58	5.07	91
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Dy}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	12.476	3.929	0.314928	611.543	5.26	5.56	5.18	93
$\text{Sr}_{0.50}\text{Ba}_{0.47}\text{Y}_{0.02}\text{Nb}_{1.8}\text{Ta}_{0.2}\text{O}_6$	12.477	3.930	0.314957	611.691	5.87	5.32	5.19	93

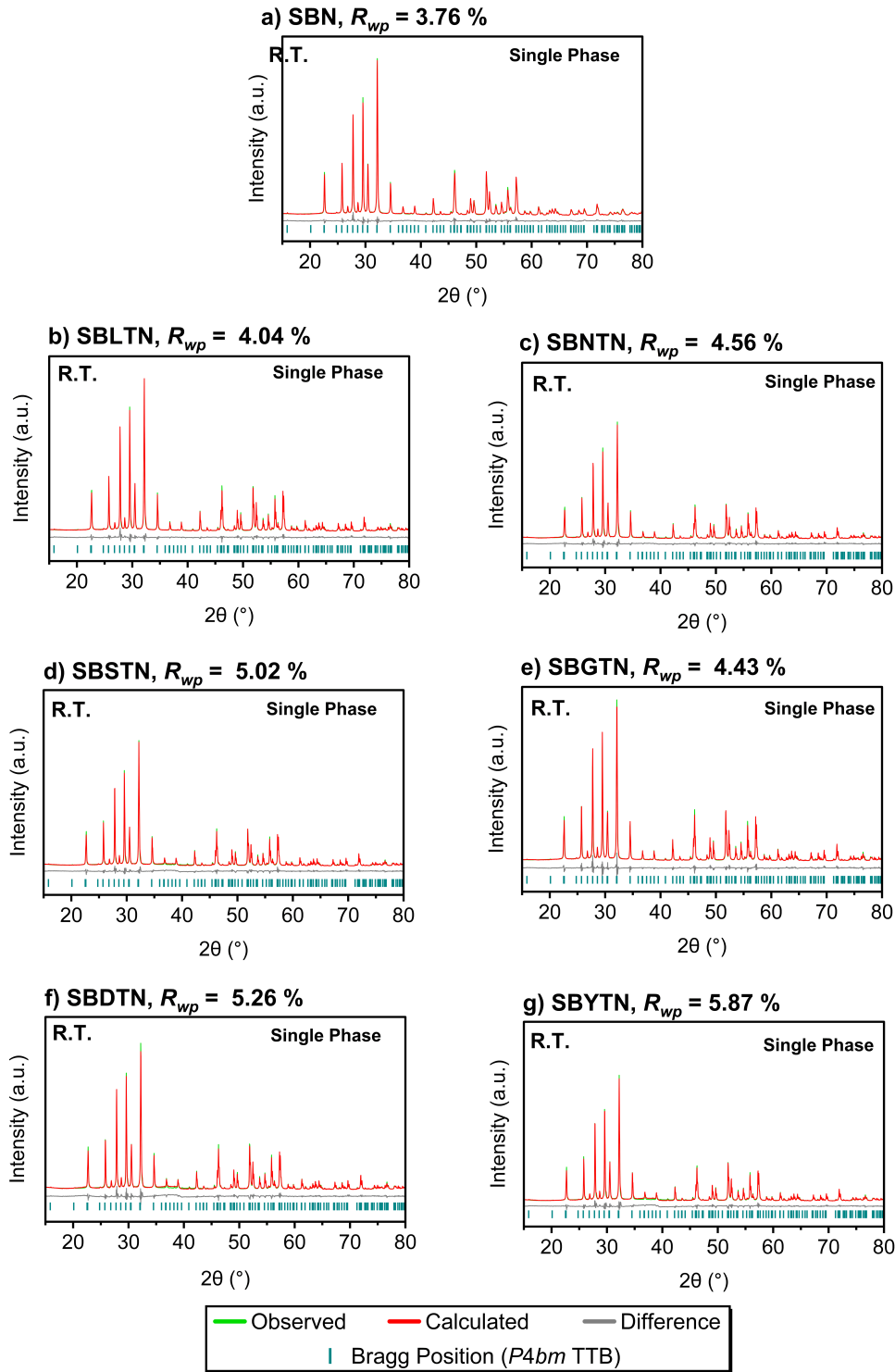


Figure 6.1a – g: Rietveld refinement fitting plots of the $P4bm$ structural model against laboratory PXRD patterns obtained at room temperature (R.T.). Tick marks indicate Bragg positions of the tetragonal $P4bm$ structural model (teal) for a) $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN), $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ where b) $\text{R} = \text{La}^{3+}$ (SBLTN), c) Nd^{3+} (SBNTN), d) Sm^{3+} (SBSTN), e) Gd^{3+} (SBGTN), f) Dy^{3+} (SBDTN), and g) Y^{3+} (SBYTN).

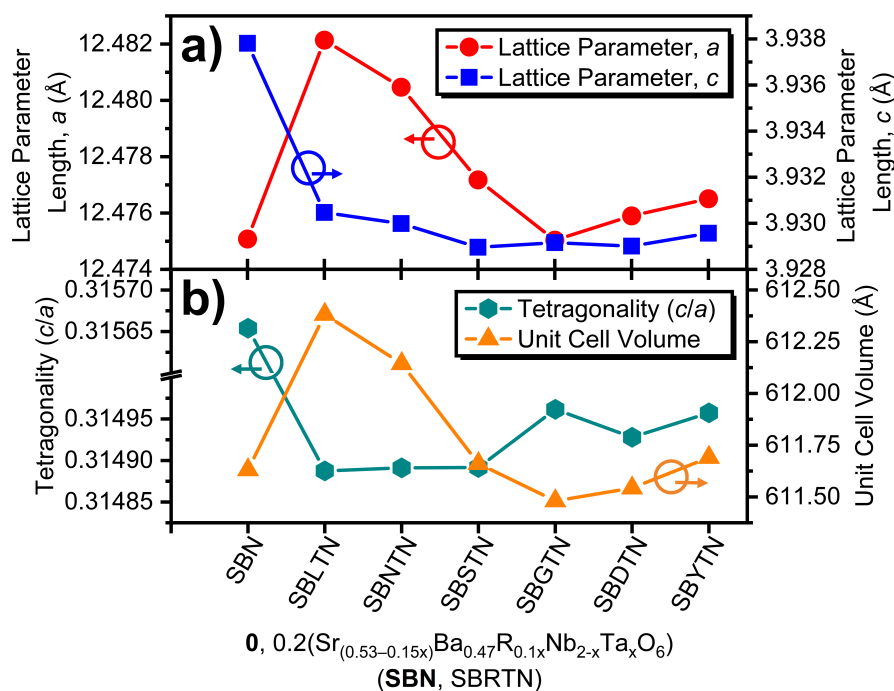


Figure 6.2a – b: Plots showing a) Rietveld refined lattice parameter a and c , b) tetragonality (c/a) and unit cell volume as a function of composition for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN), $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ where b) $\text{R} = \text{La}^{3+}$ (SBLTN), c) Nd^{3+} (SBNTN), d) Sm^{3+} (SBSTN), e) Gd^{3+} (SBGTN), f) Dy^{3+} (SBDTN), and g) Y^{3+} (SBYTN). Note the break in the y axis on b) suggesting tetragonality changes more on the addition of any of the dopants and this is more significant than any trend within the R^{3+} dopants.

Doping R^{3+} rare earth cations for Sr^{2+} on the A- site and Ta^{5+} for Nb^{5+} on the B-site into SBN to form SBRTN sees a contraction of the c lattice parameter (Figure 6.2a). Increasing the R^{3+} cation radii size from Y^{3+} (SBYTN) to La^{3+} (SBLTN) increases the a lattice parameter, while c remains largely invariant, indicating an expansion of the ab plane driving a small (ca. 0.16 %) increase in unit cell volume (Figure 6.2a). Likewise, ab plane expansion was reported for similarly doped and filled TTB compositions $\text{Ba}_2\text{RTi}_2\text{Nb}_3\text{O}_{15}$ (where $\text{R}^{3+} = \text{Bi}^{3+}, \text{La}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{and Gd}^{3+}$) [136], $\text{Ba}_4\text{RTiNb}_9\text{O}_{30}$ ($\text{R}^{3+} = \text{La}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) [288] and the empty TTB $\text{Ba}_4\text{R}_{0.67}\square_{1.33}\text{Nb}_{10}\text{O}_{30}$ ($\text{R}^{3+} = \text{La}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Dy}^{3+}$ and Y^{3+}) [89]. The expansion of the ab plane whilst c remains constant can be summarised by the change in tetragonality (c/a) [154], which is plotted versus composition in Figure 6.2b.

The tetragonality (c/a) of SBRTN composition here, increases with decreasing R^{3+} cation radii, whilst correspondingly the unit cell volume decreases, suggesting a possible reduction in orthorhombic distortion with decreasing R^{3+} (Figure 6.2b). Doping R^{3+} rare earths into SBN to form SBRTN decreases tetragonality (c/a), and correspondingly shows an increase in the magnitude of splitting between (001) and (310) reflections, shown in Appendix C – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$, Figure E1a – f. Peak splitting magnitudes of ($hk0$) and ($00l$) reflections (notably (001) and (310) reflections) has been shown by Gardner *et al.* [89] to decrease with increasing R^{3+} ionic radii in the closely related $\text{Ba}_4\text{R}_{0.67}\square_{1.33}\text{Nb}_{10}\text{O}_{30}$ ($\text{R}^{3+} = \text{La}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Dy}^{3+}$ and Y^{3+}) empty TTB.

Indeed, a close inspection of SBRTN laboratory PXRD diffraction patterns between $\sim 22\text{--}23^\circ 2\theta$ shows the presence of a subtle shoulder (310) peak on the (001) peak (Appendix C – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$, Figure E1a – f). However, there was no evidence of the magnitude of the splitting of the (001) and (310) reflections increasing from SBLTN ($\text{La}^{3+} = 1.360 \text{ \AA}$, CN = XII) to SBYTN ($\text{Y}^{3+} = 1.075 \text{ \AA}$, CN = IX) such as that reported by Gardner *et al.* [89]. An important point to note is that further quantitative and qualitative analysis of peak splitting magnitudes (*i.e.* (001) and (310) discussed here) between SBRTN compositions is limited by the resolution of the laboratory PXRD used in this chapter. Higher resolution PXRD instrumentation, such as variable temperature synchrotron PXRD used in the previous results chapters, could reveal the splitting of reflections which might indicate a possible lowering of symmetry from tetragonal $P4bm$ to, for example, orthorhombic $Ama2$ with increasing R^{3+} cationic radii.

6.2.2 Raman Spectroscopy

Raman spectroscopy was used to illustrate the structural distortions of the Nb/TaO_6 TTB octahedral framework of SBN and SBRTN compositions. Extrinsic lattice vibrations $< 200 \text{ cm}^{-1}$ from A1 and A2-site cation motion with respect to the Nb/TaO_6 [248] were notably broadened [126] with the introduction of Ta^{5+} and R^{3+} rare earth cation dopants into SBN to form SBRTN (Figure 6.3a). This suggests the introduction of R^{3+} rare earths into the A-site further facilitates A-site disorder in SBN, in addition to

B-site disorder by the introduction of Ta^{5+} into the B sites [126, 157, 289]. Rietveld refinements by Grendal *et al.* [283] suggest Sr^{2+} (1.44 Å, CN = XII[22]) is disordered on both the A1- and A2-sites, whilst larger Ba^{2+} (1.61 Å, CN = XII[22]) remains solely on A2-site. Hence, A1-site disorder is further facilitated by a disordered distribution of both Sr^{2+} and R^{3+} in SBRTN. Trends in extrinsic lattice vibrations $< 200 \text{ cm}^{-1}$ between different SBRTN compositions were essentially indistinguishable and not evaluated further here. Intrinsic lattice vibrations are highlighted in Figure 6.3a at 250 cm^{-1} (ν_5 , O-Nb/Zr-O bend), 630 cm^{-1} (ν_2 , Nb/Zr-O stretch), and 850 cm^{-1} (ν_1 , Nb/ZrO₆ deformation) [290]. Notably, ν_2 and ν_5 modes are coupled to the cationic motion parallel to the ferroelectric mode along the c axis [19, 249]. As in the previous two chapters, the ν_1 mode showed no significant full width and half maxima (FWHM) and peak position trends with composition. Modes ν_5 and ν_2 however, showed a slight red shift with the introduction of Ta^{5+} and an increase in R^{3+} cation radii from Y^{3+} to La^{3+} (Figure 6.3b), while the FWHM increased (Figure 6.3c), most notably for the ν_2 mode.

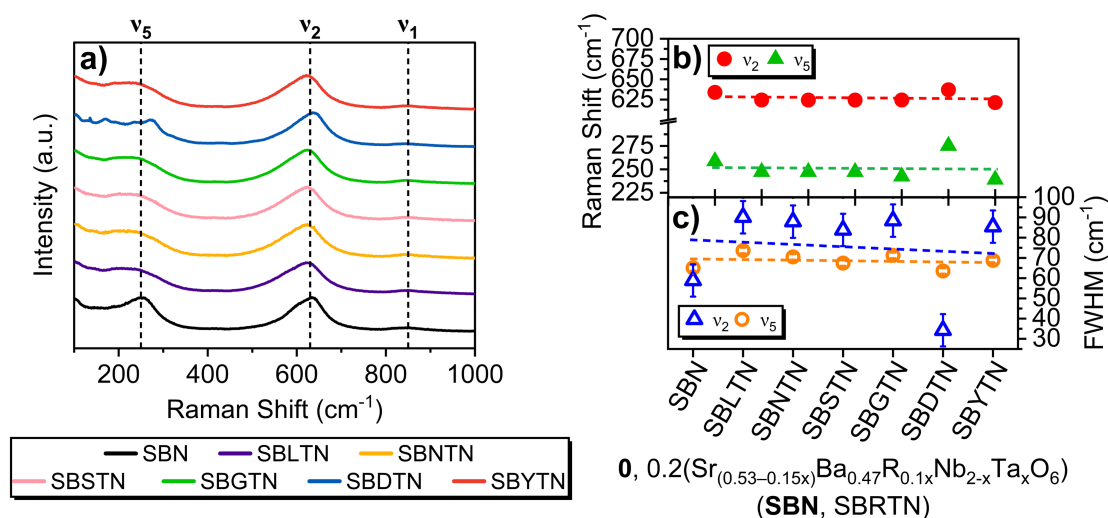


Figure 6.3a – c: Room temperature normalized intensity plots as a function of Raman shift for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) where $x = 0$ and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R} = \text{La}^{3+}$ (SBLTN), Nd^{3+} (SBNTN), Sm^{3+} (SBSTN), Gd^{3+} (SBGTN), Dy^{3+} (SBDTN), and Y^{3+} (SBYTN), between a) Raman shift within a spectral range of 100 -1000 cm^{-1} alongside plots of the b) Raman shift (peak position) and c) full width at half maximum (FWHM) of ν_5 and ν_2 vibrational modes versus composition.

A red shift in peak positions to lower frequency and thus lower energy, indicates a softening of the $\text{Nb}^{5+}/\text{Ta}^{5+}$ and O^{2-} interaction with increasing R^{3+} rare earth ionic radii, in spite of the increased strength of the Ta – O bonds in SBRTN, owing to the increased ionic character of Ta^{5+} relative to Nb^{5+} [291]. The introduction of smaller dopants into the A-site (*i.e.* Y^{3+} [1.08 Å, CN = XII] for Sr^{2+} [1.44 Å, CN = XII] [22]) weakens the ν_5 B – O bending ($\sim 250 \text{ cm}^{-1}$) and ν_2 B – O stretching vibrational modes ($\sim 640 \text{ cm}^{-1}$) and by extension a weakening of octahedral distortions, facilitating the tilting of the octahedral TTB framework [248]. Correspondingly, the increased FWHM mirrors the increased octahedral distortions along *c*, arising from the expansion of the *ab* plane (and unit cell volume) with increasing R^{3+} rare earth cationic radii, supporting laboratory PXRD lattice parameter trends. These data might suggest a lowering of T_m (in temperature and permittivity maxima), broadening of the dielectric permittivity anomaly and frequency dispersion, *i.e.* shift to a RFE.

6.2.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX)

Back scattered SEM micrographs, grain size distribution plots and corresponding SEM-EDX elemental mapping are shown in for Figure 6.4 – Figure 6.10. SBN and all SBRTN compositions. Grain size distribution plots are shown alongside back scattered SEM micrographs in Figure 6.4 – Figure 6.10 and are shown in Appendix C – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$, Figure E2a – g. SEM-EDX elemental mapping of all doped compositions showed a homogenous mixture of R^{3+} and Ta^{5+} with no evidence of chemically heterogeneous grains. This indicates dopants (R^{3+} and Ta^{5+}) have fully integrated into SBN to form $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN, where $x = 0.2$), supporting the single-phase nature of these TTBs that is suggested by laboratory PXRD analysis. Grains showed a pillar-like morphology which is thought to be a result of the lower surface energy of the (001) plane leading to anisotropic grain growth in

SBN [138]. Additionally, SBN and SBRTN compositions exhibit no microcracks and minimal porosity corresponding to high densities reported here ($\geq 91\%$ Table 6.2).

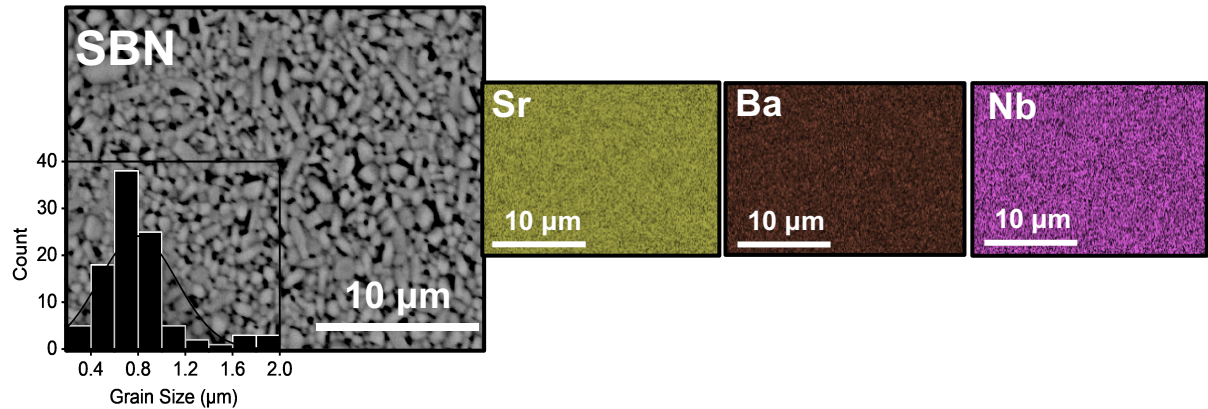


Figure 6.4: Back scattered SEM micrograph (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Ba^{2+} (orange), Nb^{5+} (lilac) cations for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN)

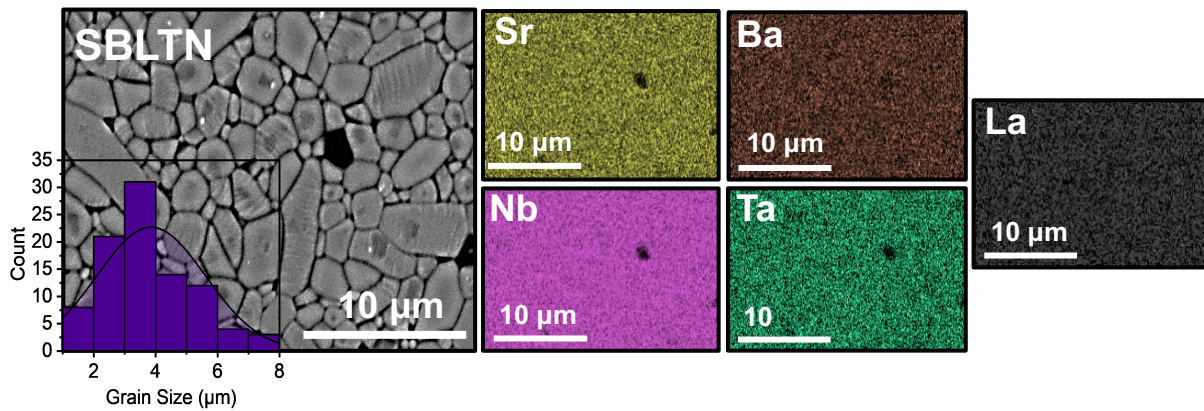


Figure 6.5: Back scattered SEM micrograph (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Ba^{2+} (orange), La^{3+} (grey), Nb^{5+} (lilac), and Ta^{5+} (teal) cations for $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$ and $\text{R} = \text{La}^{3+}$ (SBLTN).

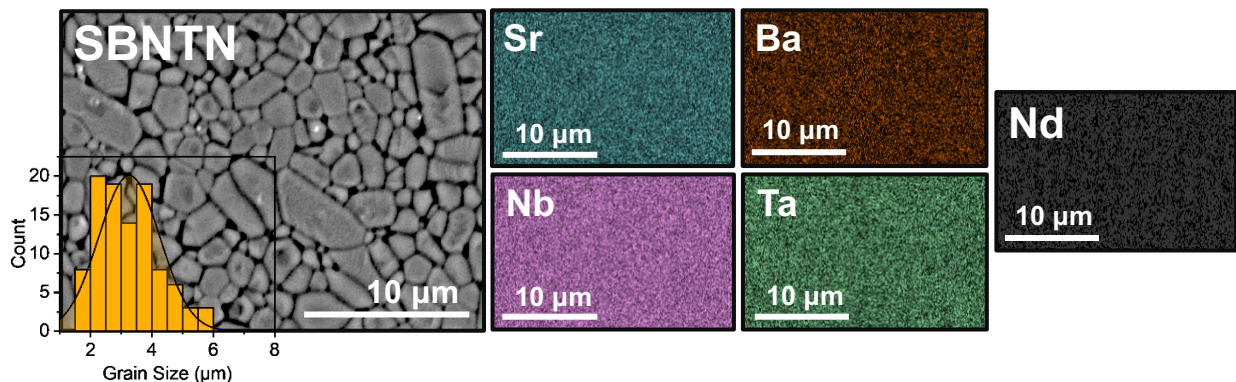


Figure 6.6: Back scattered SEM micrograph (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Ba^{2+} (orange), Nd^{3+} (grey), Nb^{5+} (lilac), and Ta^{5+} (teal) cations for $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$ and $\text{R} = \text{Nd}^{3+}$ (SBNTN).

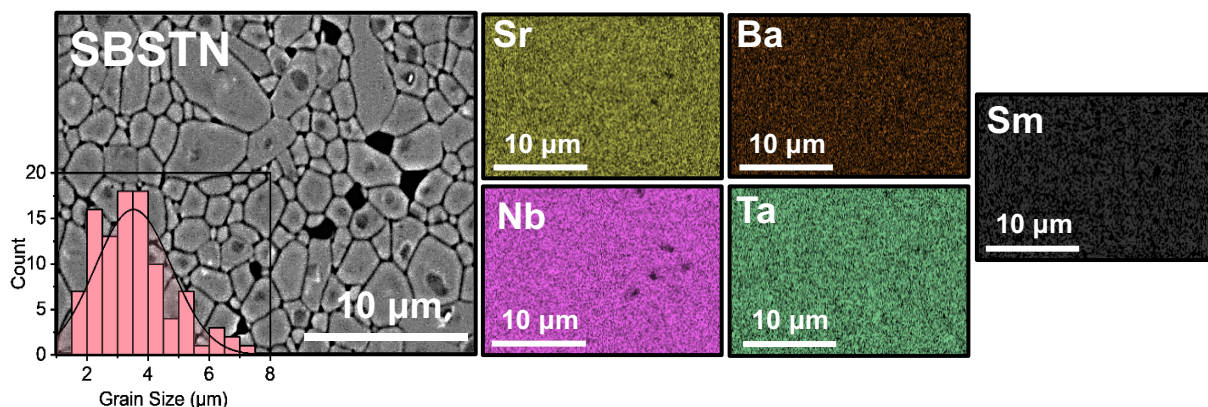


Figure 6.7: Back scattered SEM micrograph (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Ba^{2+} (orange), Sm^{3+} (grey), Nb^{5+} (lilac), and Ta^{5+} (teal) cations for $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$ and $\text{R} = \text{Sm}^{3+}$ (SBSTN).

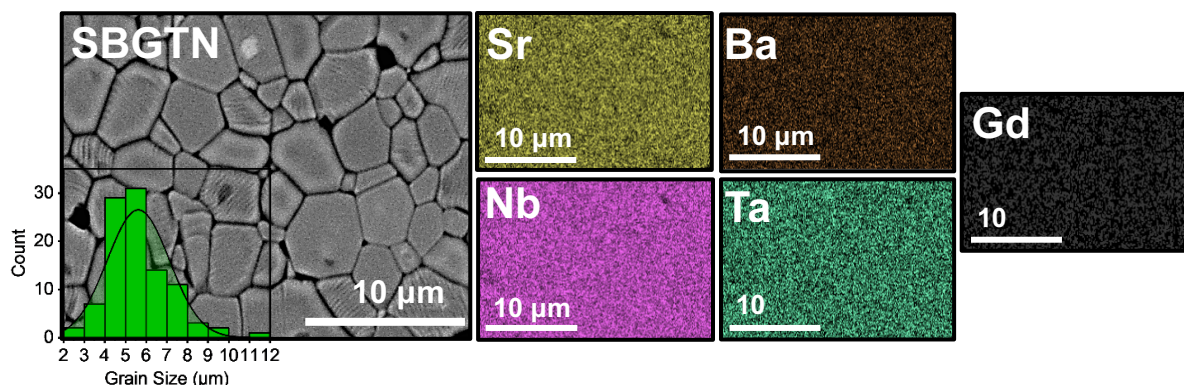


Figure 6.8: Back scattered SEM micrograph (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Ba^{2+} (orange), Gd^{3+} (grey), Nb^{5+} (lilac), and Ta^{5+} (teal) cations for $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$ and $\text{R} = \text{Gd}^{3+}$ (SBGTN).

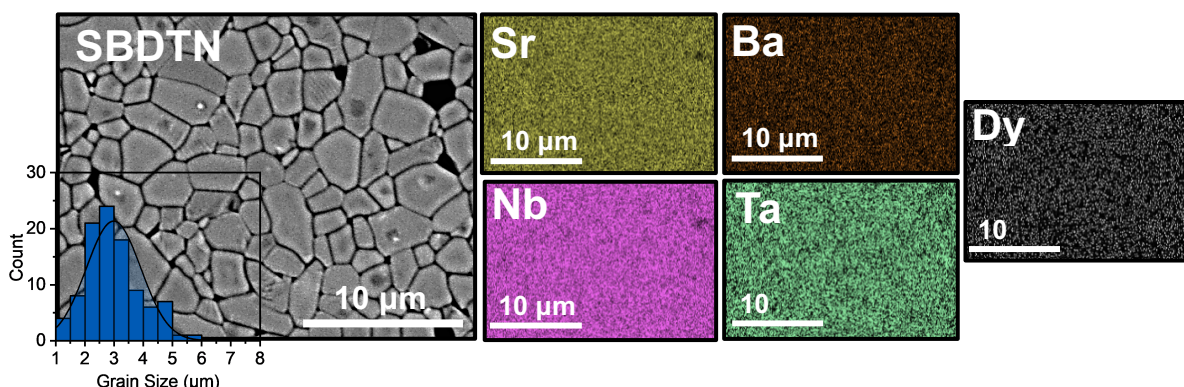


Figure 6.9: Back scattered SEM micrograph (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Ba^{2+} (orange), Dy^{3+} (grey), Nb^{5+} (lilac), and Ta^{5+} (teal) cations for $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$ and $\text{R} = \text{Dy}^{3+}$ (SBDTN).

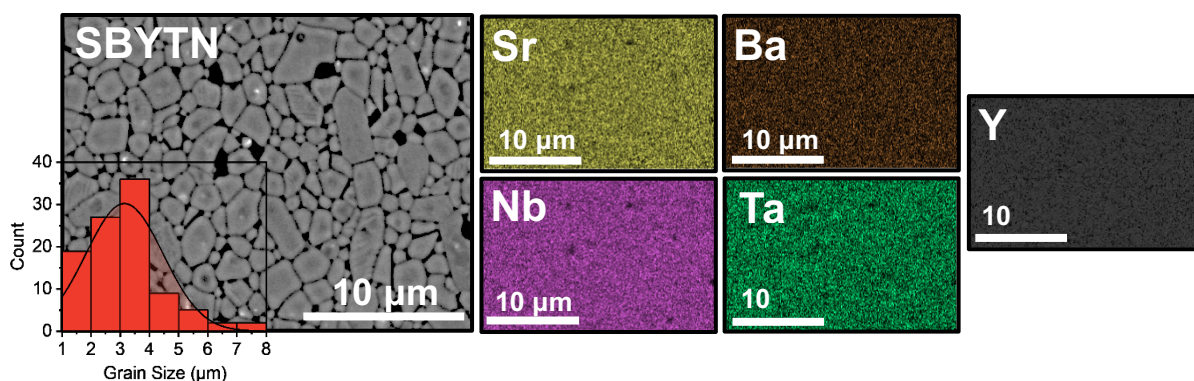


Figure 6.10: Back scattered SEM micrograph (left) and EDX elemental mapping (right) of Sr^{2+} (yellow), Ba^{2+} (orange), Y^{3+} (grey), Nb^{5+} (lilac), and Ta^{5+} (teal) cations for $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ where $x = 0.2$ and $\text{R} = \text{Y}^{3+}$ (SBYTN).

Grain size data are summarised in Table 6.3. Grain size slightly increased from $1.24 \pm 0.05 \mu\text{m}$ for SBN with the introduction of any R^{3+} and Ta^{5+} such that grain size then remains largely uniform ($4.65 - 8.77 \mu\text{m}$, Table 6.3). Minimum and maximum grain size was lowest at $0.5 \mu\text{m}$ and $3.05 \mu\text{m}$, respectively, for SBN. Earlier in this research, initial SBDTN, SBSTN, and SBSTN compositions exhibited abnormal grain growth ($> 50 \mu\text{m}$), presenting as a “duplex” microstructure, where the abnormally large grains were embedded within smaller, uniform grains [292, 293]. This “duplex” structure is shown in Appendix C – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$, Figure E3a – d. Formation of a liquid phase has been reported to be the root cause of abnormal grain growth *via* a localised divergence of stoichiometry in SBN [292-298]. Transmission electron microscopy by Lee *et al.* [292] revealed a Nb^{5+} rich, Ba^{2+} deficient low temperature phase, which was retained at sintered grain boundaries, possibly arising from incomplete calcination earlier in the ceramic synthesis process [296].

Dual stage sintering introduces a lower temperature pre-sintering step, causing any liquid phase to form a phase more closely resembling the intended stoichiometry prior to reaching the desired sintering temperature [292]. This methodology (dual stage sintering) introduces a lower temperature pre-sintering step, causing any liquid phase to form a phase more closely resembling the intended stoichiometry prior to reaching the desired sintering temperature [292].

Table 6.3: Grain size data summary for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R} = \text{La}^{3+}$ (SBLTN), Nd^{3+} (SBNTN), Sm^{3+} (SBSTN), Gd^{3+} (SBGTN), Dy^{3+} (SBDTN), and Y^{3+} (SBYTN). Underestimation of grain sizes attributed to cross-sectional imaging was considered *via* multiplication of a factor of 1.56 as proposed by Mendelson [244].

Sample Code	Average Grain Size (μm)	Standard Error (μm)	Minimum Grain Size (μm)	Maximum Grain Size (μm)
SBN	1.24	0.05	0.51	3.05
SBLTN	4.65	0.15	1.55	8.67
SBNTN	4.91	0.21	2.17	11.94
SBSTN	5.09	0.15	2.40	9.24
SBGTN	8.77	0.23	4.00	17.33
SBDTN	6.01	0.27	1.00	13.95
SBYTN	5.49	0.19	2.39	11.18

The above methodology (Table 6.1) was extended to SBDTN, SBSTN, and SBNTN compositions in this chapter (SBYTN solely required a lower calcination and sintering temperature), resulting in a successfully uniform distribution of small grain sizes, with no evidence of abnormal grain growth (Figure 6.4 – Figure 6.10). The small average grain sizes of SBRTN compositions reported in Table 6.3 ($< 10 \mu\text{m}$), are beneficial in increasing electrical breakdown field, E_B [299]. Indeed, the doping of wider band gap Ta_2O_5 [162] into SBN here, is thought to increase E_B [289, 291, 300]. An increased E_B allows for higher applied fields and temperatures [126], whilst limiting conduction losses [301], improving capacitive performance for use in temperature stable MLCCs.

6.2.4 Dielectric and Ferroelectric Properties

Multifrequency relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) temperature response plots and multifold polarisation (P) versus field (E) hysteresis loops are shown in Figure 6.11a – g and Figure 6.12a – g respectively. All compositions show a temperature of permittivity maxima that becomes more frequency dependent on doping (T_m), with a large maximum ϵ_r at T_m (ϵ_r at $T_m > 2000$). T_m undergoes a large shift to lower temperatures with the introduction of R^{3+} and Ta^{5+} into SBN to form SBRTN (Figure 6.11a – g). The introduction of R^{3+} and Ta^{5+} in SBN to form SBRTN, results in a diffuse, frequency dependent ϵ_r – temperature response at T_m , indicating the strong RFE behaviour of co-doped SBRTN compositions studied here. Using the framework of Zhu *et al.* [107] the average A-site cation radii ($A1+A2/2$) marginally decreases with the introduction of R^{3+} dopants. However, as the R^{3+} cation radius increases from Y^{3+} to La^{3+} , the size difference relative to Sr^{2+} becomes smaller. Much like Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$, the variation in both parameters is minor, as are the $\text{R}^{3+}/\text{Ta}^{5+}$ co-dopant levels ($x = 0.02$) yet the material is exhibiting strong RFE behaviour, which isn't fully described by the Zhu *et al.* [107] framework (Chapter 2 – Background Science and Literature Review, Figure 2.20 [orange box] and Appendix C – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Figure C6).

Decreasing R^{3+} radii from SBLTN to SBYTN increases T_m , coinciding with the decrease in unit cell volume [18] and increase in c/a [89] from laboratory PXRD. This indicates the contraction of lattice parameter a (and thus the ab plane in the $P4bm$ tetragonal setting) is primarily driven by $\text{Sr}^{2+}/\text{R}^{3+}$ disorder, destabilising long range ferroelectric polar ordering through octahedral tilt and contributing to RFE-like behaviour (as discussed in Chapters 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$).

Moreover, the narrow P - E hysteresis loops of SBRTN compositions suggest their possible RFE nature and suitability as capacitor materials for high energy density MLCCs. ϵ_r and $\tan\delta$ — temperature response plots measured at 1 kHz are shown in Figure 6.13a, while T_m , ϵ_r at T_m at 1 kHz are extracted and plotted *versus* composition in Figure 6.13b. Likewise, P - E hysteresis loops measured at 40 kV/cm are shown in

Figure 6.13c, with maximum polarisation (P_{max}), remanent polarisation (P_{rem}) and coercive field (E_c) extracted and plotted against composition (Figure 6.13d). However, it should be noted $T_{\text{R.T.}} < T_m$ for SBN whilst for SBRTN $T_{\text{R.T.}} > T_m$ and so P - E hysteresis measurements are likely undertaken on the paraelectric phases of SBRTN compositions (as evidenced by the near linear P - E loops). Here, interpretation of the P - E hysteresis loop data is used as an approximation for trends likely to be observed nearer to T_m based on insights from Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$. Ideally, such data would have been collected using low temperature P - E hysteresis instrumentation (ca. -46 °C, average SBRTN T_m), to better explore polarisation behaviour near the transition temperature, T_m of doped SBRTNs.

T_m shifts from 144 °C (SBN) to -62 °C (SBLTN), further increasing with decreasing cationic radii down to -37° (SBYTN) (Figure 6.13b) in agreement with Gardner *et al.* [89] for the $\text{Ba}_4\text{R}_{0.67}\text{Nb}_{10}\text{O}_{30}$ ($\text{R}^{3+} = \text{La}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Dy}^{3+}$ and Y^{3+}) system. No clear trend, however, is evident in ϵ_r at T_m from SBLTN ($\text{La}^{3+} = 1.216 \text{ \AA}$, CN = IX) to SBYTN ($\text{Y}^{3+} = 1.075 \text{ \AA}$, CN = IX) (Figure 6.13b). The P_{max} decreases with the introduction of R^{3+} and Ta^{5+} . Here the B-site cation dopant, Ta^{5+} has a different polarizability to Nb^{5+} (as Zr^{4+} was in SNN Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) thus contributing to B site disorder despite having an ionic radii (0.64 Å, CN = VI [22]) equivalent to Nb^{5+} . In addition, the R^{3+} disorder could be introducing octahedral tilt that may lower P_{max} . This disorder may also reduce the coercivity of the P - E loops.

The following paragraph discusses P - E hysteresis loops measured at 40 kV/cm from Figure 6.13c and corresponding values extracted at 40 kV/cm of P_{max} , P_{rem} and E_c in Figure 6.13d. Doping with R^{3+} and Ta^{5+} into SBN to form SBRTN compositions sees the P_{max} fall from $\sim 8 \mu\text{C}/\text{cm}^2$ (SBN) to $\sim 4\text{-}5 \mu\text{C}/\text{cm}^2$ (average SBRTN) while P_{rem} decreases from $\sim 2 \mu\text{C}/\text{cm}^2$ (SBN) to $\sim 0.04 \mu\text{C}/\text{cm}^2$ (average SBRTN). The latter is except for SBTGN and SBLTN which showed elevated P_{rem} values of $0.6 \mu\text{C}/\text{cm}^2$ and $0.4 \mu\text{C}/\text{cm}^2$ respectively. Turning to trends with decreasing R^{3+} cationic radii (SBLTN to SBYTN), P_{max} slightly increases from $4.4 \mu\text{C}/\text{cm}^2$ (SBLTN) to $5.2 \mu\text{C}/\text{cm}^2$ (SBYTN) but broadly remains consistent across the compositional series. E_c also remains constant from SBLTN to SBYTN, with lower E_c values (1 kV/cm) relative to SBN (7

kV/cm) reflect the narrower RFE-like nature of the SBRTN P - E hysteresis loops [125, 302].

Mechanistic origins of RFE- behaviour in TTBs and the structurally related perovskites, remains a point of contention [303]. Fluctuating and dynamic, strain and electrostatic fields have been attributed to chemical disorder in a nano- or micrometre sized polar clusters (namely polar nanoregions [PNRs]) or individually polarised unit cells [304]. The low E_c and P_{rem} and relatively larger P_{max} in SBRTN can be attributed to the high dynamism and thus improved switching ability of PNRs [305]. This suggests improved RFE character in SBRTN compositions, illustrating their potential capacitive (energy storage) capabilities.

The dramatic shift of T_m to lower temperature with the introduction of R^{3+} and Ta^{5+} , despite favourable RFE characteristics at R.T., puts into question the suitability of such compositions for high-temperature, temperature stable capacitor applications. However, it should be noted the $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{Gd}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (where $x = 0.2$) system investigated by Yang *et al.* [126] of which these SBRTN compositions are based, showed a stable W_{rec} between R.T. up to 140 °C ($W_{\text{rec}} \sim 5 \text{ J/cm}^3$ at 400 kV/cm and $\eta > \sim 80 \%$ at 350 kV/cm). The authors noted temperature stability and capacitive performance was equal, if not superior to $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, and/or BaTiO_3 perovskites [126], highlighting the potential of the extended rare earth SBRTN compositional series here. However, a full demonstration of the capacitive performance of SBRTN compositions to examine the effect of: i) temperature, ii) applied field, and iii) fatigue cycling, necessitates charge-discharge analysis (W_{rec} , W_{loss} , η).

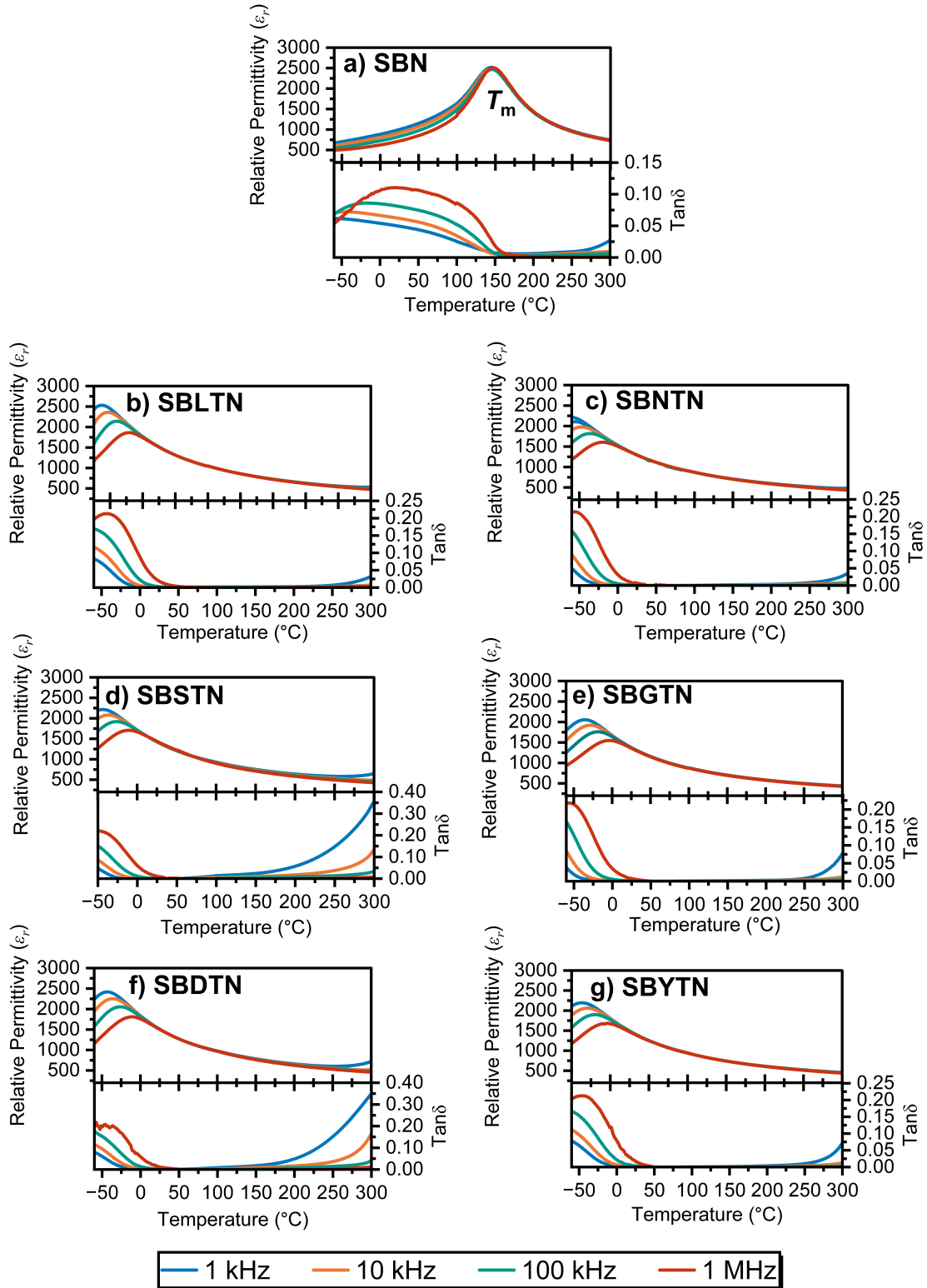
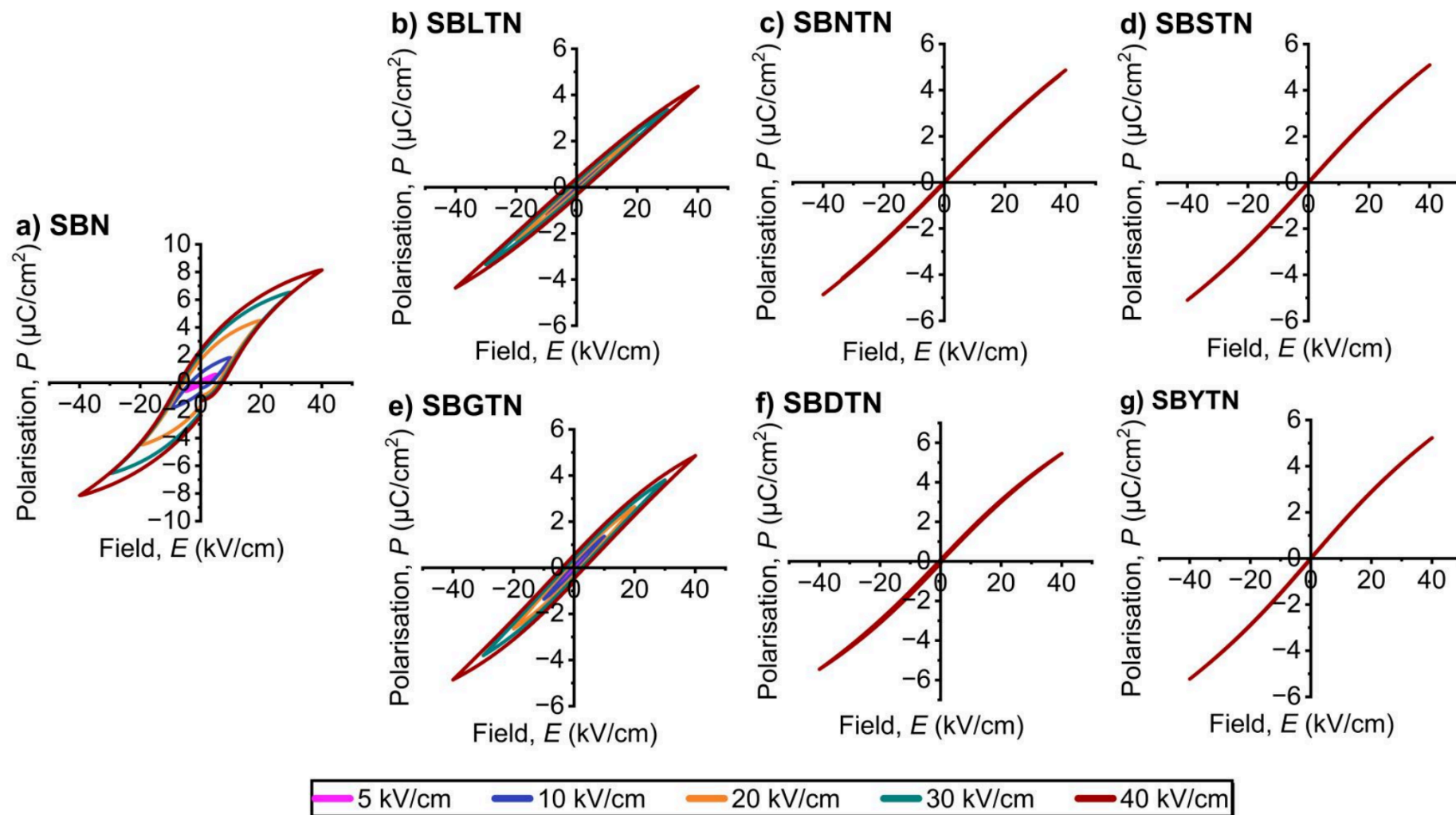


Figure 6.11a – g: Multi-frequency relative permittivity (ϵ_r) and dielectric loss tangent ($\tan\delta$) response plots as a function of temperature for a) $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and b) $\text{R} = \text{La}^{3+}$ (SBLTN), c) Nd^{3+} (SBNTN), d) Sm^{3+} (SBSTN), e) Gd^{3+} (SBGTN), f) Dy^{3+} (SBDTN), and g) Y^{3+} (SBYTN).



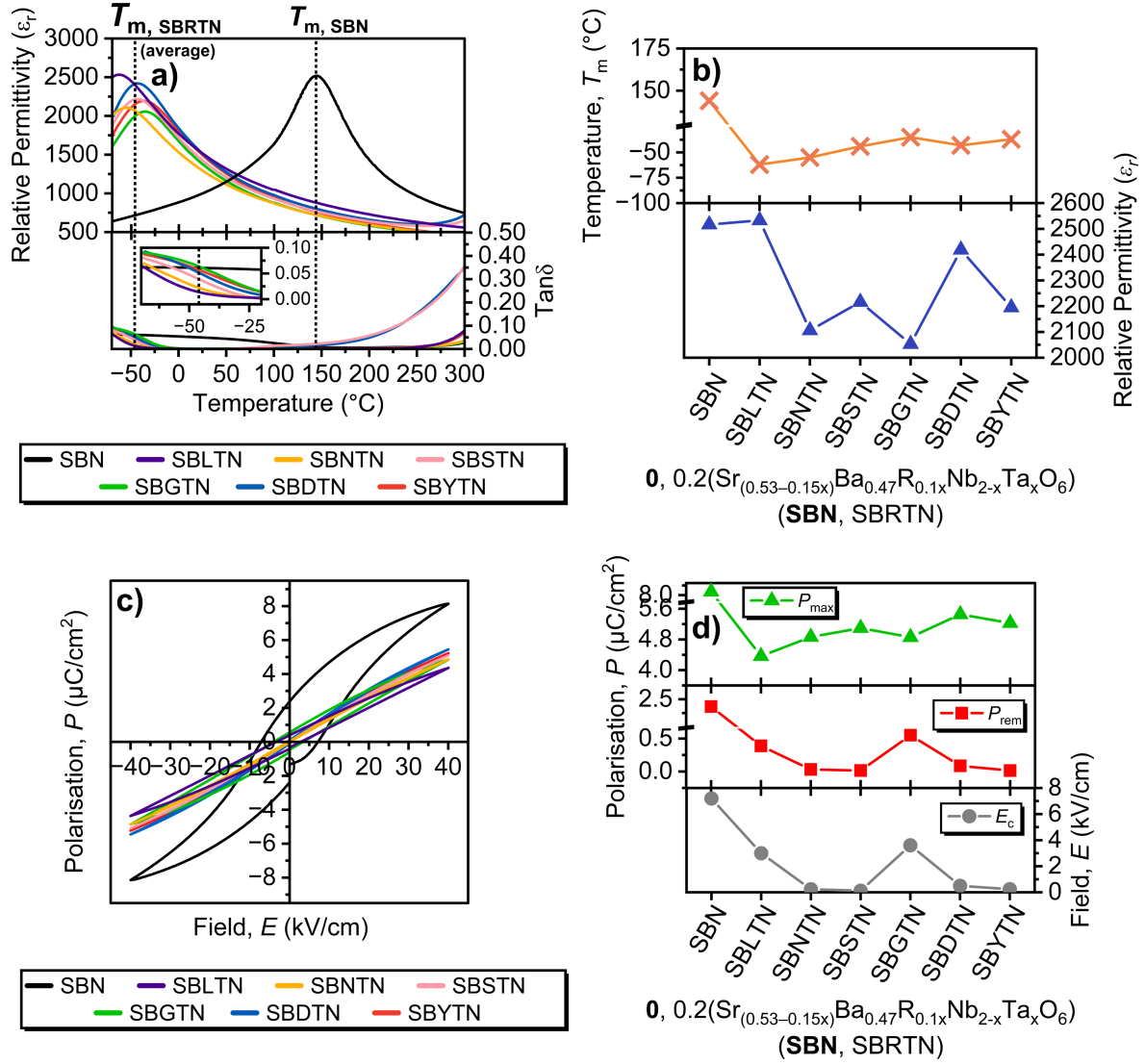


Figure 6.13a – d: Plots showing a) Relative permittivity (ϵ_r) and dielectric loss tangent ($\tan\delta$) response temperature evolution plots at 1 kHz for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ $\text{R} = \text{La}^{3+}$ (SBLTN), Nd^{3+} (SBNTN), Sm^{3+} (SBSTN), Gd^{3+} (SBGTN), Dy^{3+} (SBDTN), and Y^{3+} (SBYTN) where b) T_m , ϵ_r at T_m , c) polarisation, P versus field, E hysteresis loops for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ d) maximum, remnant polarisation (P_{max} and P_r) and coercive field (E_c) versus R (rare earth). For b) and d) note the scale break on the left-hand y axes, indicating the addition of any of the dopants is more significant than any trend within the R^{3+} dopants.

The modified Curie-Weiss (CW) law may be used to quantify the diffusivity of SBN and SBRTN RFE phase transitions through the CW coefficient, γ^{11} (Figure 6.14a – b).

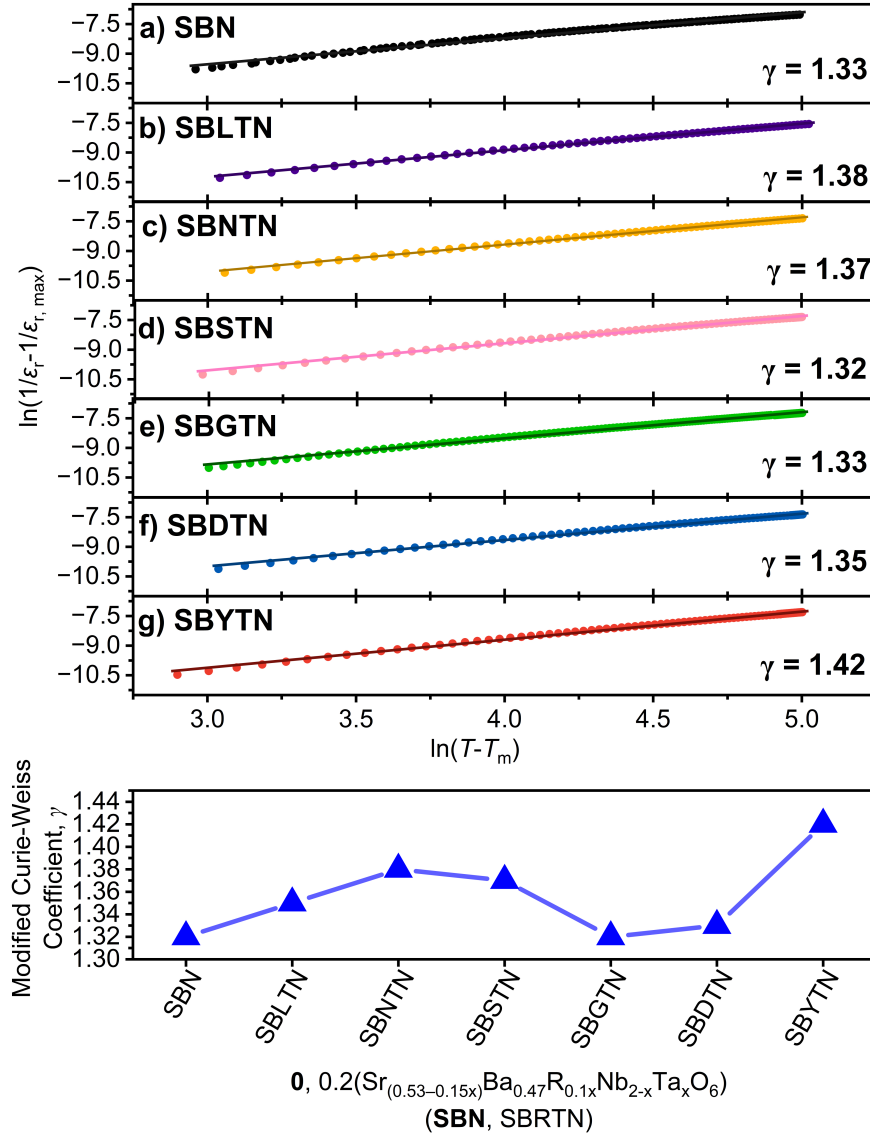


Figure 6.14a – b: Plots showing a) modified Curie-Weiss plots of $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R} = \text{La}^{3+}$ (SBLTN), Nd^{3+} (SBNTN), Sm^{3+} (SBSTN), Gd^{3+} (SBGTN), Dy^{3+} (SBDTN), and Y^{3+} (SBYTN) measured at 1 kHz and b) plot showing modified CW law coefficient, γ as a function of composition.

¹¹ Curie-Weiss (CW) law and corresponding equations are described in Chapter 2 – Background Science and Literature Review, section 2.3. Polar Dielectrics, subsection 2.3.2 Relaxor Ferroelectrics (RFEs).

The result shows the modified CW coefficient changes little across the dopant series (Figure 6.14b), which is unexpected given that A- and B-site co-doping in SBN is expected to enhance RFE behaviour when R^{3+} increases in cationic radii. However, the amount of R^{3+} dopant is small ($R^{3+} = 0.02$) and it may be that the degree of disorder is dominated by the addition of the dopant independent of the size difference of the R^{3+} cation relative to Sr^{2+} [306], *i.e.* the addition of any of the dopants is more significant than any trend within the R^{3+} dopants. Nonetheless, it should be noted reports on similar TTB systems using the modified CW law and consequently extracting γ as a metric for RFE behaviour have shown to be sensitive to dopant level [126, 159, 280, 307, 308]. Broadly, the large difference in T_m and T_B (or T_{CW} in reference [126]) from Figure E4a – g (Appendix E – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$) for SBRTN compositions relative to SBN reflects the increased relaxor behaviour of co-doped SBRTN doped compositions (SBN [$T_B - T_m = 17^\circ\text{C}$], average SBRTN [$T_B - T_m = 37^\circ\text{C}$]). Likewise, a more simplistic approach plotted in Figure 6.15, shows the difference between $T_{m(1\text{kHz})}$ and $T_{m(1\text{ MHz})}$ ($T_{m(1\text{kHz})} - T_{m(1\text{ MHz})}$) that highlights an increased frequency dispersion from 1 MHz to 1 kHz from SBYTN to SBLTN.

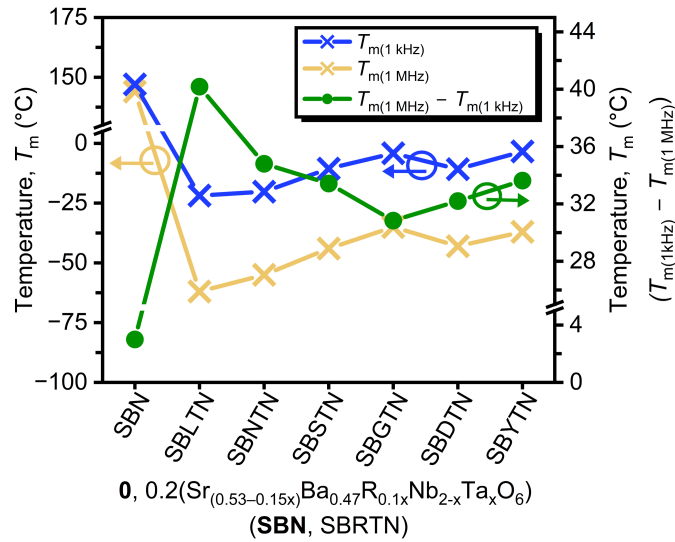


Figure 6.15: Transition temperatures T_m at 1 kHz ($T_{m(1\text{kHz})}$), 1 MHz ($T_{m(1\text{ MHz})}$) (left) and the difference ($T_{m(1\text{kHz})} - T_{m(1\text{ MHz})}$) (right) as a function of composition for $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $R^{3+} = \text{La}^{3+}$, Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , and Y^{3+} . Note scale break on left hand temperature axis, indicating the addition of any of the dopants is more significant than any trend within the R^{3+} dopants.

6.3 Conclusions

$\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) has been co-doped on the A- and B-site to form single phase $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} = \text{Y}^{3+}$, Dy^{3+} , Gd^{3+} , Sm^{3+} , Nd^{3+} , and La^{3+} , as shown by laboratory PXRD. Laboratory PXRD Rietveld refinement using a $P4bm$ tetragonal structural model at R.T., indicates an expansion of the ab -plane whilst c remains constant. There is a large decrease in tetragonality (c/a) with R^{3+} and Ta^{5+} doping, followed by a minor decrease in tetragonality with increasing R^{3+} cationic radii. Raman spectroscopy showed an increase in FWHM of ν_2 and ν_5 modes with increasing R^{3+} radii, suggesting an increase in disorder from SBYTN to SBLTN, supporting the expansion of the ab -plane indicated by laboratory PXRD. ν_2 and ν_5 vibrational mode Raman shifts showed a red shift highlighting a weakening of the B – O bonding ($\text{Nb}^{5+}/\text{Ta}^{5+}$ and O^{2-} interaction) with increasing R^{3+} cationic radii, attributed to larger A-site R^{3+} cations distorting the octahedral TTB framework. Taken together, these data suggest B-site doping disrupts ferroelectric ordering and A-site doping introduces ab -plane disorder which allows an increased range of octahedral tilts (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$).

Relative permittivity (ϵ_r) – temperature response plots demonstrated a significant shift of T_m to lower temperature from SBN to SBRTN, consistent with the structural effects of doping reported above. Increasing R^{3+} radii from SBYTN to SBLTN saw little change of T_m , coinciding with the minor increase in unit cell volume and decrease in c/a from laboratory PXRD. This disruption of the ferroelectric ordering, the expansion of the lattice parameter a , and the increased range of octahedral tilts all contribute to the RFE-like behaviour as is seen in co-doping of SNN1. However, the increased RFE behaviour was not reflected in the CW law coefficient, γ , from SBN to SBLTN.

SBRTN is discussed as a structurally related, volatile (*i.e.* Na^+) free alternative to SNN for use in temperature stable MLCCs. Thin hysteresis loops lending to a low E_c , P_{rem} and higher P_{max} in the SBRTN series are ascribed here to the dynamism of PNRs contributing the observed RFE character. However, the capacitive performance of SBRTN compositions for application in capacitors requires further analysis using charge-discharge analysis to better evaluate temperature stability, field and fatigue resistance. Doping smaller R^{3+} cations on the A-sites (for Sr^{2+}) enhances A-site

disorder, while Ta^{5+} (for Nb^{5+}) on the B-sites would introduce a higher E_B because of wider bandgap Ta^{5+} oxide. Collectively, the disorder introduced into the SBN TTB framework to form SBRTN, further facilitates RFE character to modulate capacitive performance.

Chapter 7 – Conclusions and Future Work

7.1. Final Overview

The energy transition from fossil fuels to renewable energy sources has drawn research interest in exploiting tetragonal tungsten bronzes (TTBs) for the temperature stable multilayer ceramic capacitor (MLCC) application space (Electrical Industry Standards-XR9, -55 °C to ≥ 300 °C). Environmental concerns with the usage of lead combined with the manufacturing incompatibility of bismuth *and* lead with nickel and copper base metal electrodes (BMEs) in MLCCs have seen research interests progress beyond perovskites to the compositionally versatile, yet relatively poorly understood, bismuth and lead-free TTBs. The application of TTBs, namely $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN) and $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN), for high temperature, temperature stable capacitors is an emerging area of research with exciting prospects. SNN and SBN studied in this thesis, show high promise owing to their dielectric performance and temperature stability which can effectively be modulated by leveraging their compositional flexibility *via* A-, B- site co-doping and/or the introduction of A-site vacancies.

SNN has shown potential as class II dielectric ceramic capacitor with X9R performance and beyond. There is plenty still to be understood from investigating the structure –property relationships that follow from cation doping this material. A property of particular interest is the cation-doping induced flattening of permittivity response to give a temperature stable performance between SNN's dielectric anomalies T_1 (relaxor ferroelectric peak), T_2 (ferroelectric to paraelectric transition) and their respective relative permittivities (ϵ_r at T_1 and T_2). A rigorous understanding of the phase transitions SNN undergoes on heating across the X9R temperature range has only recently been reported [18]. Moreover, the presence of volatile sodium (Na) in SNN and the Sr-modified NaNbO_3 secondary perovskite phase potentially make this system unstable below 1180 °C. This presents an opportunity to investigate TTB alternatives to SNN that are more thermally stable, such as SBN (or CBN). This thesis has developed an understanding of the structure-dielectric property relationships of SNN

and SBN when A- and B-site co-doping, and/or when A-site vacancies are introduced, with a view to developing these or related TTBs for temperature stable capacitors.

7.2. Conclusions

Individual system conclusions have already been detailed at the end of each of the results chapters (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Chapter 5 — $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ and Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$). These can be summarised to the following:

7.1.1 Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$

A flattening of the permittivity (ϵ_r) – temperature profile in nominally filled SNN is achieved by A- and B-site co-doping because the resulting compositional disorder reduces long range ferroelectric coupling of the out of plane polar mode and induces strain and octahedral tilts that stabilize the in-plane polar mode.

Doping smaller A site cations (Ca^{2+} , Y^{3+}) for Sr^{2+} and less polarisable B site cations (Zr^{4+}) for Nb^{5+} in SNN reduces the c lattice parameter, limiting negative thermal expansion (NTE) below the ferroelectric to paraelectric transition temperature, T_2 . The reduction of c destabilises the ferroelectric polar mode (Γ_3^-), lowering the temperature at which the amplitude of this polar distortion mode rises above zero, ultimately decreasing T_2 and ϵ_r at T_2 with doping.

Doping also reduces the negative thermal expansion of the a lattice parameter below the low temperature, relaxor-like peak (T_1), that is present in the undoped $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN1). The effect on ϵ_r at T_1 with doping however, is minor, as the in-plane polar mode, Γ_5^- , is continually stable across the series. The result is an impeded temperature onset to which there is sufficient orthorhombic strain to drive the phase transition occurring at T_1 ($\text{Ama}2$ to Aa), ultimately decreasing T_1 with doping. Transmission electron microscopy studies showed that increased doping, increased octahedral tilt, leading to a higher density of stacking faults to accommodate the associated strain increase. Thus, the ferroelastic domain structure is disrupted, contributing to relaxor ferroelectric (RFE)-like frequency dispersion at T_1 , which

destabilised the ferroelectric polar mode (Γ_3^-), and the associated reduction in the c lattice parameter with increasing temperature between T_1 and T_2 , flattening the permittivity (ϵ_r) – temperature profile.

7.1.2 Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$

A flattening of the permittivity (ϵ_r) – temperature profile of unfilled SNN is attained through the systematic introduction of increasing numbers of Na^+ vacancies into the A-sites. Increasing Na^+ vacancy numbers has no appreciable effect on c lattice parameter and the associated cooling driven c -axis elongation (NTE) below T_2 . By extension, the ferroelectric polar mode (Γ_3^-) amplitude shows no reliable trend in the temperature at which this distortion mode rises to above zero. A negative correlation of T_2 with Na^+ vacancy numbers, however, can be attributed to disruption to the coherence of the octahedral framework tilts that give rise to the out-of-plane polar mode, Γ_3^- , rather than to a change in the B-site cation (Nb^{5+}). Na^+ vacancies are considered to have an effective size on the A-site that is larger than the Sr or Na Shannon radii and so the vacancies play a similar role to A-site dopants. This change in A-site sizes facilitates tilting of the octahedral framework, through an incommensurate modulation. In turn, this breaks down the ferroelastic domain structure, disrupting long-range ferroelectric ordering (*i.e.* coherence of Γ_3^-), decreasing T_2 and by extension contributing to the relaxor-like nature of T_1 . Trends in ϵ_r at T_1 are conflated with the emergence of the stabilised in-plane polar mode, Γ_5^- at this transition. The suppression of the negative thermal expansion of the a lattice parameter with Na^+ vacancy numbers is associated with a decrease in T_1 . The decreased temperature onset of the $Ama2$ to Aa transition (T_1) with Na^+ vacancies, mirrors the results from A- and B-site co-doping (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{ZrO}_{15}$).

7.1.3 Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$

The introduction of A- and B-site co-dopants into $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) to form $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} = \text{La}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Dy}^{3+}, \text{and } \text{Y}^{3+}$ results in a reduction in the ferroelectric -RFE dielectric anomaly

of SBN and also produces increased frequency dispersion at T_m . A large decrease in tetragonality (c/a) with R^{3+} and Ta^{5+} doping, is followed by a minor decrease in tetragonality with increasing R^{3+} cationic radii, coinciding with little change of T_m and P_{max} from SBYTN to SBLTN. The introduction of Ta^{5+} which has a differing polarisability to Nb^{5+} (as has Zr^{4+} in Chapter 4 – $Sr_{2-2z}NaCa_zY_zNb_{5-z}Zr_zO_{15}$) suggests B-site disorder also disrupts ferroelectric ordering, reducing P_{max} . The expansion of the a/b -lattice parameters reflects that reported in A- and B-site co-doped filled SNN (Chapter 4 – $Sr_{2-2z}NaCa_zY_zNb_{5-z}Zr_zO_{15}$) and Na^+ A-site vacancy containing unfilled SNN (Chapter 5 — $Sr_{2+w}Na_y\Box_wNb_5O_{15}$) which relate to increased octahedral tilting, disrupting long-range ferroelectric polar ordering and ultimately reducing T_m here.

Overall, it is clear from the work reported on and presented in this thesis that significant variation of composition is possible in the complex TTB structure, and that whether large or small this can significantly impact on the dielectric properties. TTBs that exhibit normal ferroelectric behaviour, with a sharp maximum seen in temperature-dependent permittivity, can also exhibit diffuse or relaxor-like behaviour at one or more low temperature dielectric anomalies and these can merge with the normal ferroelectric anomaly upon compositional change, which is usually achieved by cation doping. In some systems major doping levels are required to induce RFE behaviour by transitioning from a commensurate to incommensurate TTB structure and these are described well by the Zhu *et al.* [107] framework. More subtle co-doping effects on TTBs already at the commensurate to incommensurate structural boundary are identified by Tidey *et al.* [18] and are explored more widely in this work. These co-doping effects relate to disruption of ferroelectric order and induction of an increased range of octahedral tilts. Here, minor co-dopants affect orthorhombic strain, microstructure and the dielectric response, moving the TTB from a normal ferroelectric response with a sharp permittivity maximum to a frequency dispersed RFE-response. This change is driven by a drop in out-of-plane polarisation and as stabilisation of the in-plane polarisation caused by A- and B-site disorder induced by the dopants.

7.3. Future Work

This thesis lays the groundwork towards future directions for SNN, SBN and other

related TTB systems. The temperature in-stability of filled SNN (and Na⁺ vacancy containing counterparts) may not deem the material appropriate for application in a temperature stable capacitor. This instability has already been reported in phase diagrams by Tang *et al.* [180] that show furnace cooled SNN to be thermodynamically unstable below 1180 °C. However, the investigation of phase breakdown of pre-formed SNN when heated at 800 °C and above has not been reported. The mechanism of SNN decomposition into Sr_{1-x}NaNbO₃ and/or SrNb₂O₆ is relatively underexplored and would provide a fundamental understanding of the true thermal stability of a range of SNN compositions with increasing Na⁺ vacancies. On the other hand, SBN is a volatile-free TTB and a potential temperature stable dielectric alternative to SNN, but its thermal stability must also be evaluated before considering it or co-doped variants for capacitor applications. Thus, *in-situ* powder X-ray diffraction (PXRD) of SNN composition variants and the SBN systems presented here could be undertaken to temperatures up to 1200 °C in future work.

The first two results chapters (Chapter 4 – Sr_{2-2z}NaCa_zY_zNb_{5-z}Zr_zO₁₅ and Chapter 5 — Sr_{2+w}Na_y□_wNb₅O₁₅) relied on the density functional theory (DFT) derived *Ama2* structural model for SNN [18] further guided by transmission electron microscopy (TEM) [242]. This suggests further enquiry into SBN through variable temperature synchrotron PXRD from -200 °C (given the large downward shift in *T_m* as seen in Chapter 6 – Sr_(0.53–0.15x)Ba_{0.47}R_{0.1x}Nb_{2-x}Ta_xO₆) to 350 °C could be undertaken in future work. Moreover, the collection of *P-E* hysteresis loop data in Chapter 6 – Sr_(0.53–0.15x)Ba_{0.47}R_{0.1x}Nb_{2-x}Ta_xO₆ was undertaken above *T_m* (at R.T.) and would have benefitted from probing the polarisation behaviour nearer to the transition temperature (*ca.* – 46 °C) for a direct comparison to SBN.

As stated previously, splitting of diffraction reflections which may suggest a possible lowering of symmetry from tetragonal *P4bm* to, for example, orthorhombic *Ama2* in SBN could be revealed using high-resolution variable temperature synchrotron PXRD. Assuming an *Ama2* setting or similar, parameters such as the out-of-plane polar mode (Γ_3^-), octahedral tilt (*S*₃) in addition to in-plane expansion (as shown in Chapter 6 – Sr_(0.53–0.15x)Ba_{0.47}R_{0.1x}Nb_{2-x}Ta_xO₆ in the *P4bm* setting) can be evaluated as a function

of temperature within the context of SBN, which is thought at this stage to exhibit the one dielectric anomaly, T_m .

However, it is important to appreciate the rigorous DFT and corresponding group theoretical analysis as well as the TEM that aided in assigning the *Ama2* refinement model [18, 242] that guided variable temperature synchrotron PXRD Rietveld refinements of the SNNs in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 — $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$. Although SBN is structurally related to SNN, applying a fundamental DFT and group theoretical analysis approach would require further collaboration with the Senn and Beanland groups at Warwick University (synchrotron beamtime access and PXRD analysis) and the Bristow group at Durham University (computational chemistry/DFT).

TEM was undertaken on A- and B-site co-doped compositions (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) where a high-density of stacking faults was revealed to occur because of compensation for octahedral tilt. Similarly, this would be expected in Na^+ vacancy containing SNN compositions (Chapter 5 — $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$) through a lattice parameter expansion below T_1 . Likewise, A- and B-site co-doped SBN (Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$) also showed evidence of *ab*-plane expansion with the introduction of R^{3+} and Ta^{5+} . The octahedra are formed by an oxygen anion framework, hence the degree of tilt will be related to the modulation in positions of oxygen anions [50, 107, 309]. Hence, TEM would be a technique worth investigating to further illustrate the degree of commensurate and incommensurate modulation with doping, again adding more detailed microstructural understanding.

The changes in ϵ_r at T_1 , ϵ_r at T_2 (Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 — $\text{Sr}_{2+w}\text{Na}_y\Box_w\text{Nb}_5\text{O}_{15}$) and ϵ_r at T_m (Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$) in addition to changes in the corresponding temperatures of T_1 , T_2 and T_m all contribute to a flat permittivity (ϵ_r) – temperature profile, which has been discussed at length in this thesis. To further assess and demonstrate the capacitive performance (recoverable energy density, $[W_{\text{rec}}]$, energy loss density $[W_{\text{loss}}]$, energy efficiency $[\eta]$) of these materials charge-discharge analysis is required. Undertaking this type of

analysis would serve to examine the effects of temperature, applied field, and voltage stability, in addition to fatigue cycling of the materials when in potential devices. Moreover, a large body of the TTB (and perovskite) literature uses W_{rec} and η as benchmarks for capacitive performance capability, allowing for a direct quantitative comparison to the literature.

Taken together the work in this thesis points to an overall strategy of A- and B-site co-doping of an unfilled TTB hosting non-volatile cations and with a normal ferroelectric T_c close to 300 °C. Doping here will lead to a lowering of T_c , broadening and flattening of the dielectric permittivity, potentially with induction to a RFE such that a flattened, high and wide temperature range of stable permittivity (ϵ_r) response is achieved. This has been empirically demonstrated with smaller A-site dopants and Ta^{5+} in alternative systems such as $\text{Ca}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ (CBN), however, further work is required to a) identify the optimum doping and b) device test [68].

Chapter 8 – References

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Appendix

Appendix A – Shannon Radii and Polarisabilities

Table A1: Table of cations in A- and B- site co doped compositions of $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN), $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ (SBN) studied in this thesis alongside their coordination, radii and polarisability taken after Shannon [22, 23].

Cation	Charge	Coordination	Shannon Radii (Å)	Shannon Polarisability (Å ³)
Sr	2+	XII	1.44	4.24
Na	1+	XII	1.39	1.80
Ba	2+	XII	1.61	6.40
Ca	2+	XII	1.34	3.16
Y	3+	IX	1.075	3.81
Dy	3+	IX	1.083	4.07
Gd	3+	IX	1.107	4.37
Sm	3+	XII	1.24	4.47
Nd	3+	XII	1.27	5.01
La	3+	XII	1.36	6.07
Nb	5+	VI	0.64	3.97
Zr	4+	VI	0.72	3.25
Ta	5+	VI	0.64	4.73
O	2-	II	1.35	2.01

Appendix B – Visualisation of Strain and Distortion Mode Irreducible Representations (Irreps)

Structural distortions of the orthorhombic *Ama2* structure are characterised as irreducible representations (irreps) of the higher symmetry parent structure aristotype, *P4/mbm* (Figure 2.15a – b) [18]. The present appendix section (Appendix A – Visualisation of Strain and Distortion Mode Irreducible Representations (Irreps)) will show schematic diagrams visualising the distortion of the aristotype (high-symmetry) *P4/mbm* structure into the *Ama2* structure *via* macroscopic strains (Γ_1^+ and Γ_4^+), atomic displacements (Γ_2^- and Γ_3^-), and a rigid unit tilting mode (S_3), abbreviated to RUM, discussed in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ shown in Figure B1a – b.

Macroscopic strains transforming as irrep Γ_1^+ represent the volumetric symmetry strain (Figure B2a), while Γ_4^+ denotes the orthorhombic strain in the *ab* plane (Figure B2b). Atomic displacements along *c*, transforming as irrep Γ_2^- , correspond to the antiferroelectric antipolar modes (Figure B2c), while irrep Γ_3^- represents the out-of-plane ferroelectric polar mode (Figure B2d). The RUM S_3 mode representing the dominant in-plane octahedral tilting framework is shown in Figure B3. Modes transforming as irreps representing a further in-plane octahedral tilt system (S_1), in addition to two types of octahedral shears (M_5^+ and M_5^-) were constrained to zero as reported by Tidey *et al.* [18] and as further discussed in the main texts of Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ and Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$.

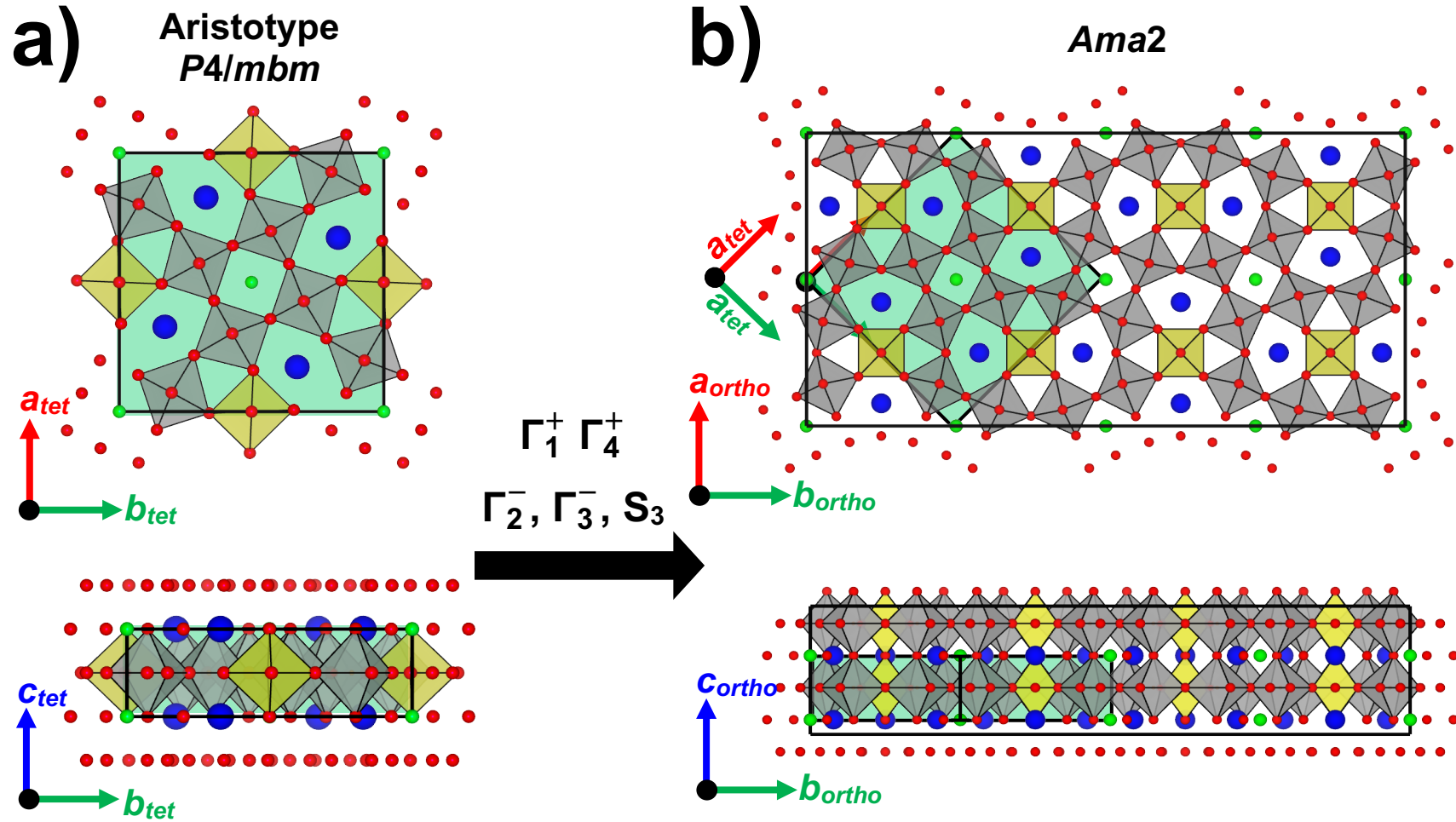


Figure B1a – b: Distortion of the a) high symmetry tetragonal aristotype $P4/mbm$ structure to the b) orthorhombic $Ama2$ structure through irreps transforming as macroscopic strain modes (Γ_1^+ , Γ_4^+), atomic displacements (Γ_2^- , Γ_3^-), and the S_3 RUM. The green shaded square in b) represents the superimposed aristotype $P4/mbm$ unit cell with respect to the $Ama2$ unit cell

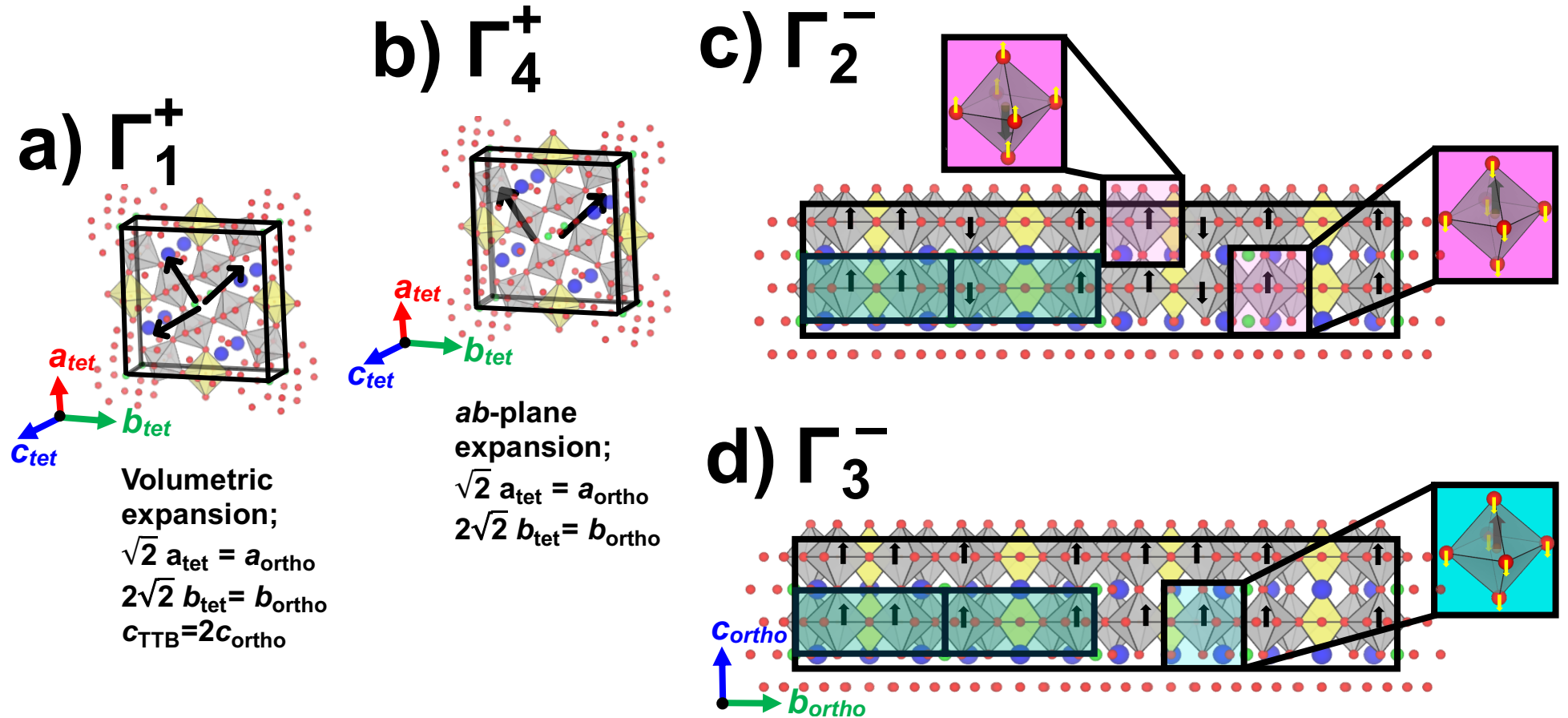


Figure B2a – d: Irrep transforming as a) the volumetric symmetric strain (Γ_1^+) showing expansion of the *a*, *b*, and *c* directions, b) orthorhombic strain, (Γ_4^+) showing expansion of the *a* and *b* directions (*ab*-plane), c) the out of plane antiferroelectric antipolar mode (Γ_2^-) and, d) out of plane ferroelectric polar mode (Γ_3^-) where in c) and d) black arrows denote the motion of the central metal cation (*i.e.* Nb⁵⁺, Zr⁴⁺, Ta⁵⁺), the green shaded box the *P4/mbm* aristotype unit cell, and the blue box inset shows the corresponding motion of the oxygen cations (yellow arrows) taken after Tidey [310].

S_3

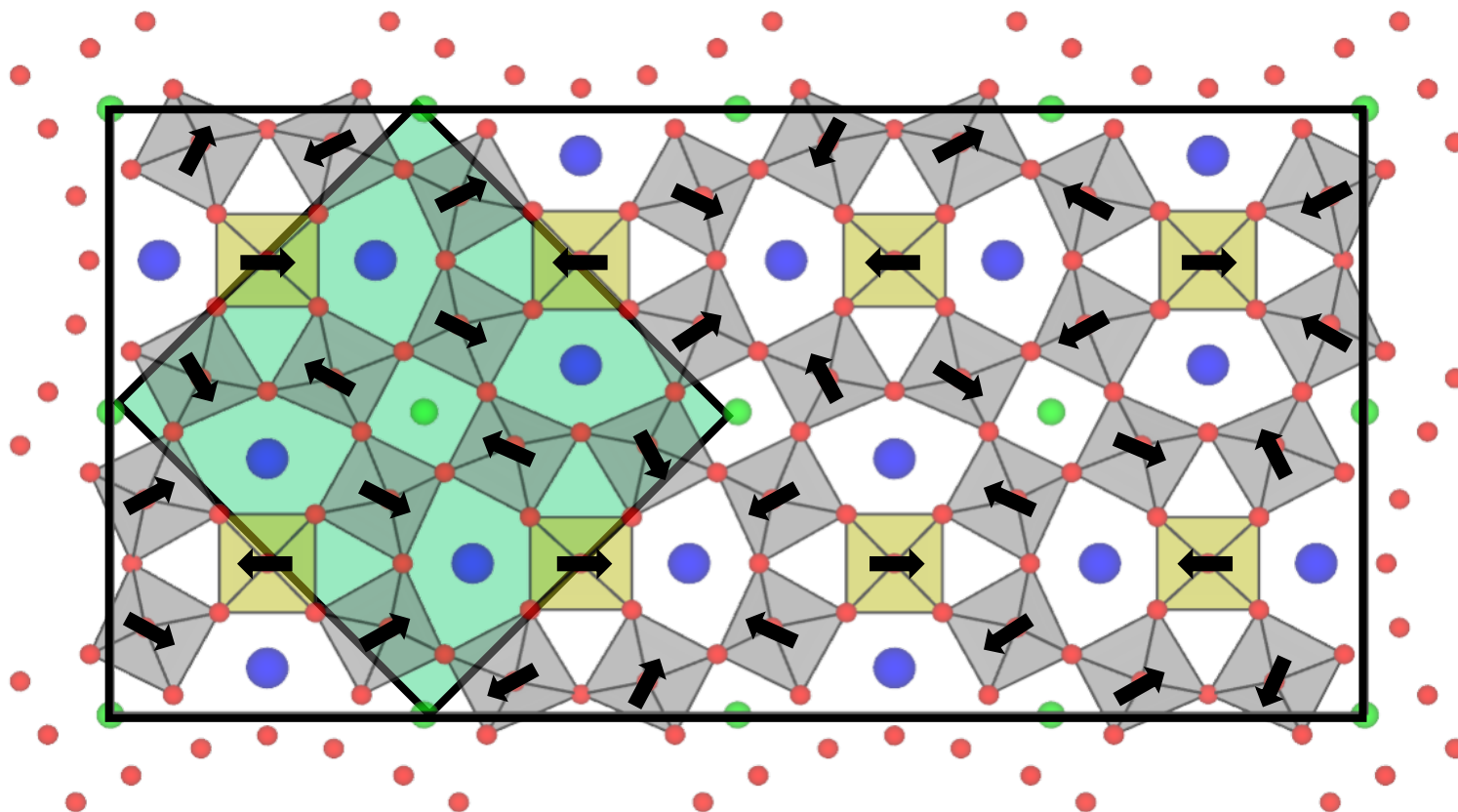


Figure B3: Irrep transforming as in-plane octahedral tilting (S_3) taken after Tidey *et al.* [18] where arrows denote the motion of the apical (top layer) oxygens where the BO_6 octahedra rotate about the c axis. The black lines indicate the $Ama2$ structure unit cell while the green shaded box denotes the superimposed $P4/mbm$ aristotype unit cell.

Appendix C – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$

This appendix (Appendix B – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$) includes supplemental data pertaining to Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$. Grain size distribution plots shown on backscattered scanning electron microscopy (SEM) micrographs in Figure 4.2 - Figure 4.7 in the main text are plotted in Figure C1 and dielectric reproducibility in Figure C2.

Weighted residual profiles (R_{wp}) at room temperature (R.T.), -173 °C, 350 °C and the average R_{wp} across the measured temperature range (-173 °C – 350 °C) are tabulated in Table C1. Large jumps in R_{wp} where are result of a transition in equipment from the Oxford Cryostream Plus (-173 °C → R.T.) and a Cyberstar hot air blower (R.T. → 350 °C) at beamline I11 Diamond Light Source (Didcot, United Kingdom). Rietveld refinement fitting plots at - 173 °C, and 350 °C are shown in Figure C3 a – f and Figure C4a – f, demonstrating the variation of fits at extreme ends of the measured temperature range for the $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ compositional series. Sr modified NaNbO_3 peaks are denoted by ▼ in Figure C3a – f and Figure C4 a – f.

Transmission electron microscopy in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ was undertaken by Dr. Robin Sjökvist and Professor Richard Beanland (University of Warwick) as described in section 4.2.2. Structural and Electrical Characterisation. Areal density of stacking faults in TEM dark field images (Figure 4.18a – c in the main text) are tabulated in Table C2, while lower magnification images of the dark field micrographs presented in Figure 4.18a – h are shown in Figure C5a – c. Average A-site size ($[A1+A2]/2$) versus A1-site tolerance factor (t_{A1}) of TTB compositions listed in Table 2 in Zhu *et al.* [107] and compositions studied in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ is shown in Figure C6.

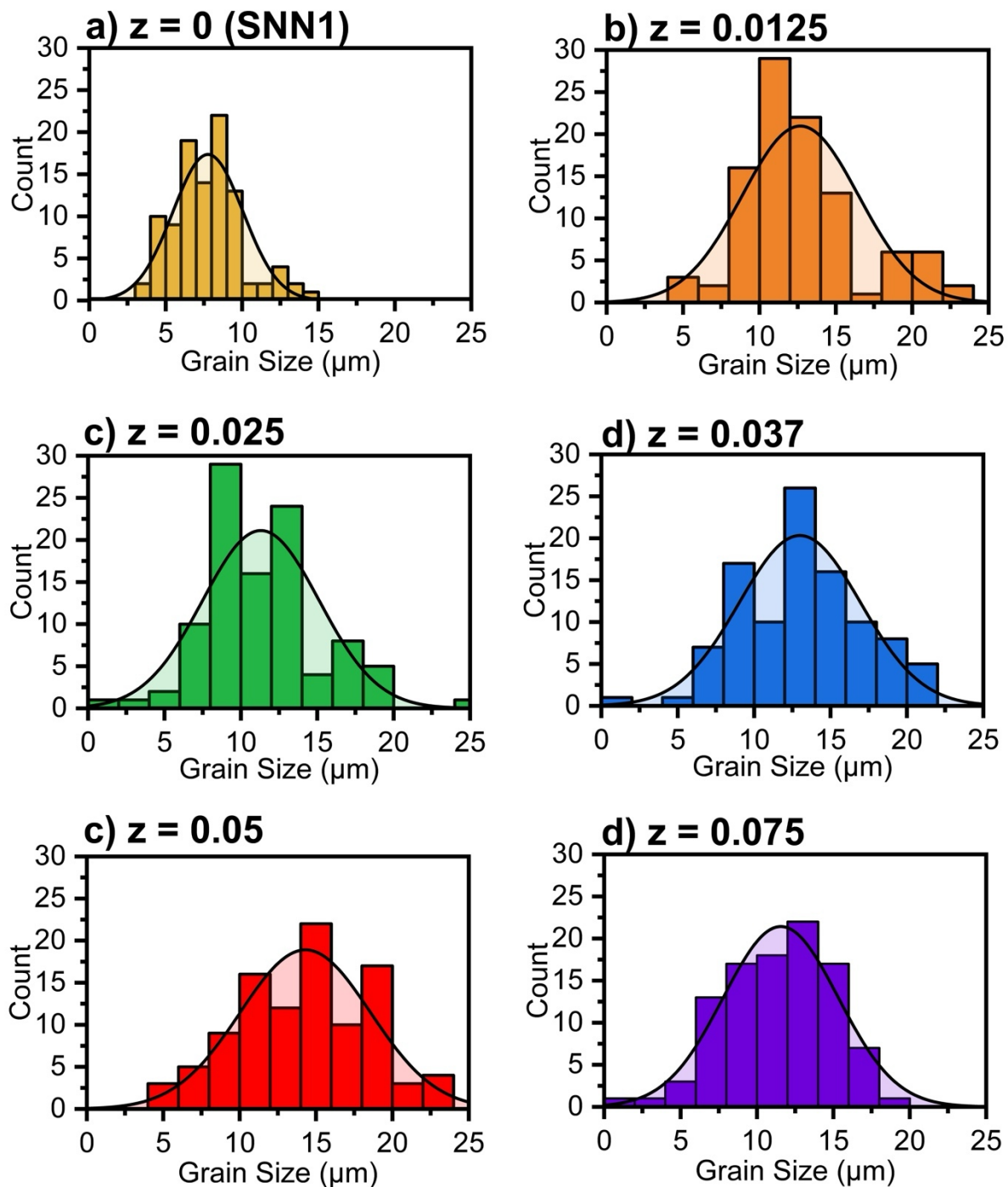


Figure C1: Grain size distribution plots shown in scanning electron microscopy (SEM) micrographs in Chapter 4 – $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$, Figure 4.2 – Figure 4.7 for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$.

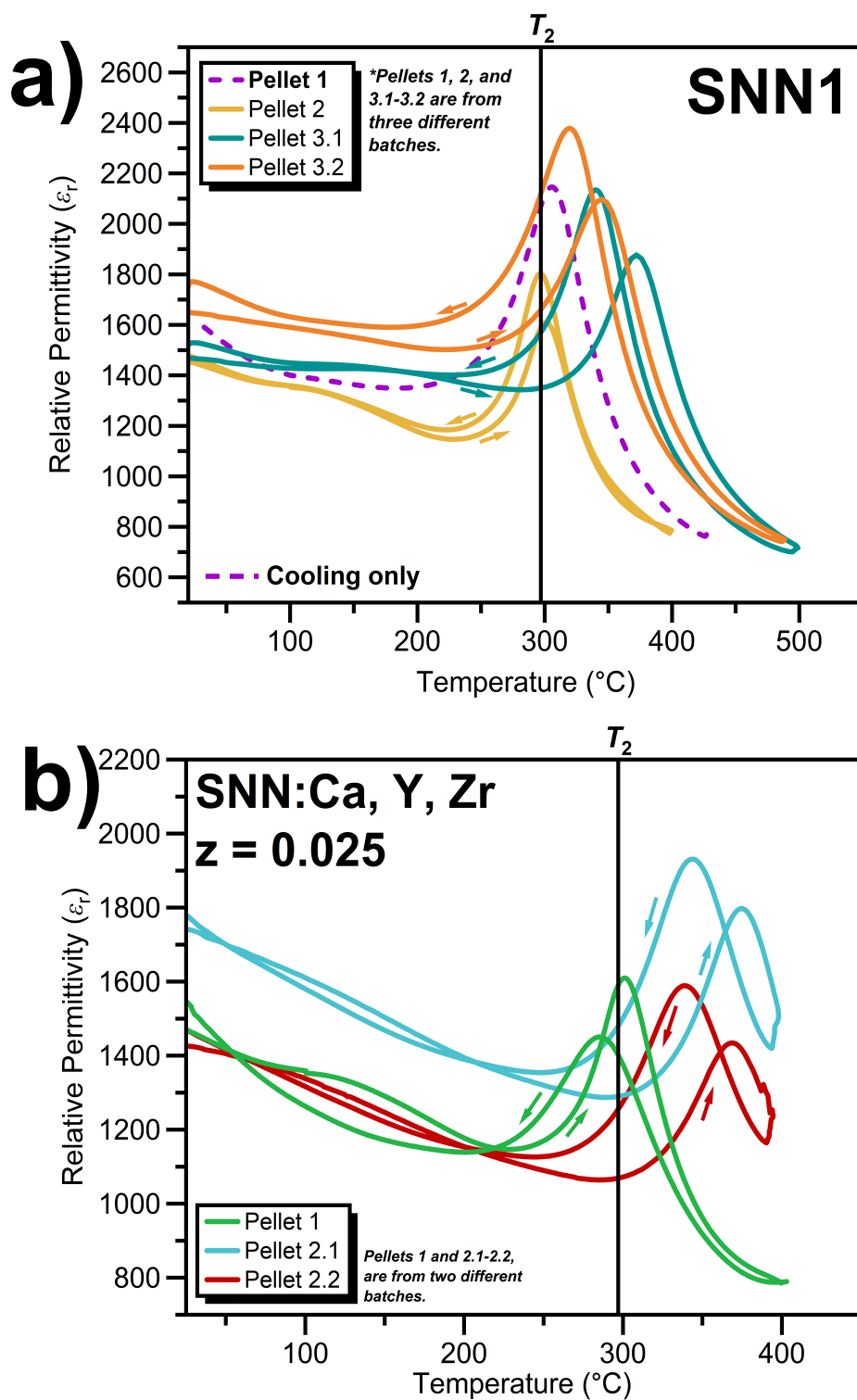


Figure C2: Comparative plots (at 1 kHz) of pellets of the same batch together with additional batches showing heating and cooling regimes for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1) and b) $z = 0.025$, with arrow directions denoting heating and cooling profiles.

Table C1: Crystallographic information obtained from synchrotron PXRD illustrating the pseudo – TTB and secondary Sr modified NaNbO_3 phase weight percentages (wt. %) ($\blacktriangledown$ = Sr modified NaNbO_3), weighted profile residuals (R_{wp}), theoretical densities, geometric densities, and pellet density (%) at room temperature (R.T.), -173 °C, 350 °C and the average R_{wp} across the measured temperature range (-173 °C – 350 °C) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0$ (SNN1), $z = 0.0125$, $z = 0.025$, $z = 0.037$, $z = 0.05$, and $z = 0.075$.

Composition Code	Pseudo – TTB Phase (wt. %) at R.T.	Secondary Phase (wt. %) at R.T.	R_{wp} (%)			
			R.T.	-173 °C	350 °C	Average (-173 °C – 350 °C)
$z = 0$	96.04	3.96	2.80	2.39	3.60	3.09
$z = 0.0125$	94.89	5.11	4.15	4.08	7.07	5.80
$z = 0.025$	93.71	6.29	5.20	5.10	6.26	5.90
$z = 0.037$	95.51	4.49	4.01	2.36	4.02	3.38
$z = 0.05$	95.07	4.93	6.26	5.44	6.92	6.52
$z = 0.075$	94.29	5.71	2.91	3.92	3.86	3.19

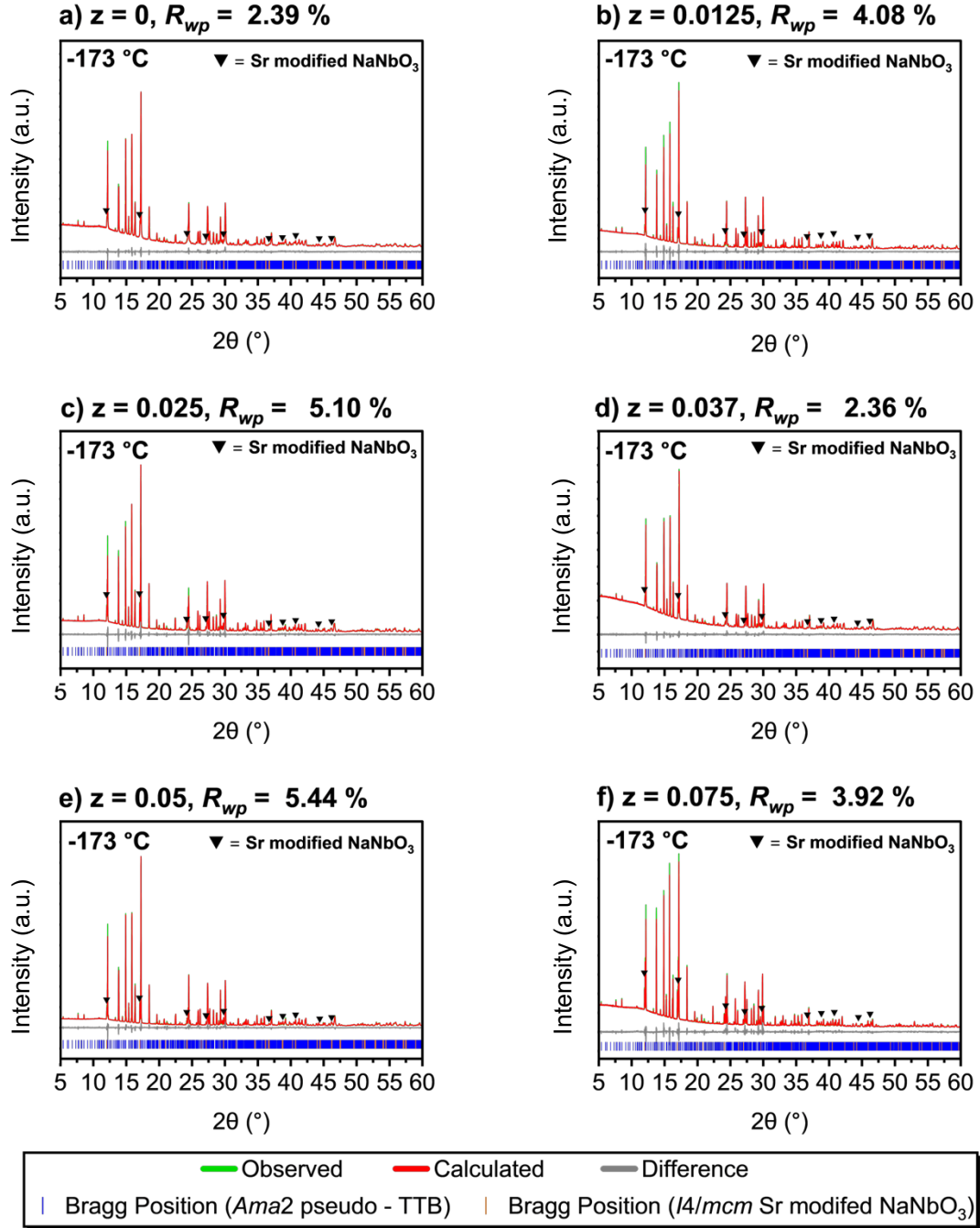


Figure C3: Rietveld refinement plots of the *Ama2* structural model against diffraction patterns obtained from synchrotron PXRD at the lowest measured temperature (-173 °C) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$. Tick marks indicate Bragg positions for the structural models of the main orthorhombic *Ama2* pseudo – TTB phase (blue) and tetragonal *I4/mcm* perovskite Sr-modified NaNbO_3 phase (orange), marked by ▼.

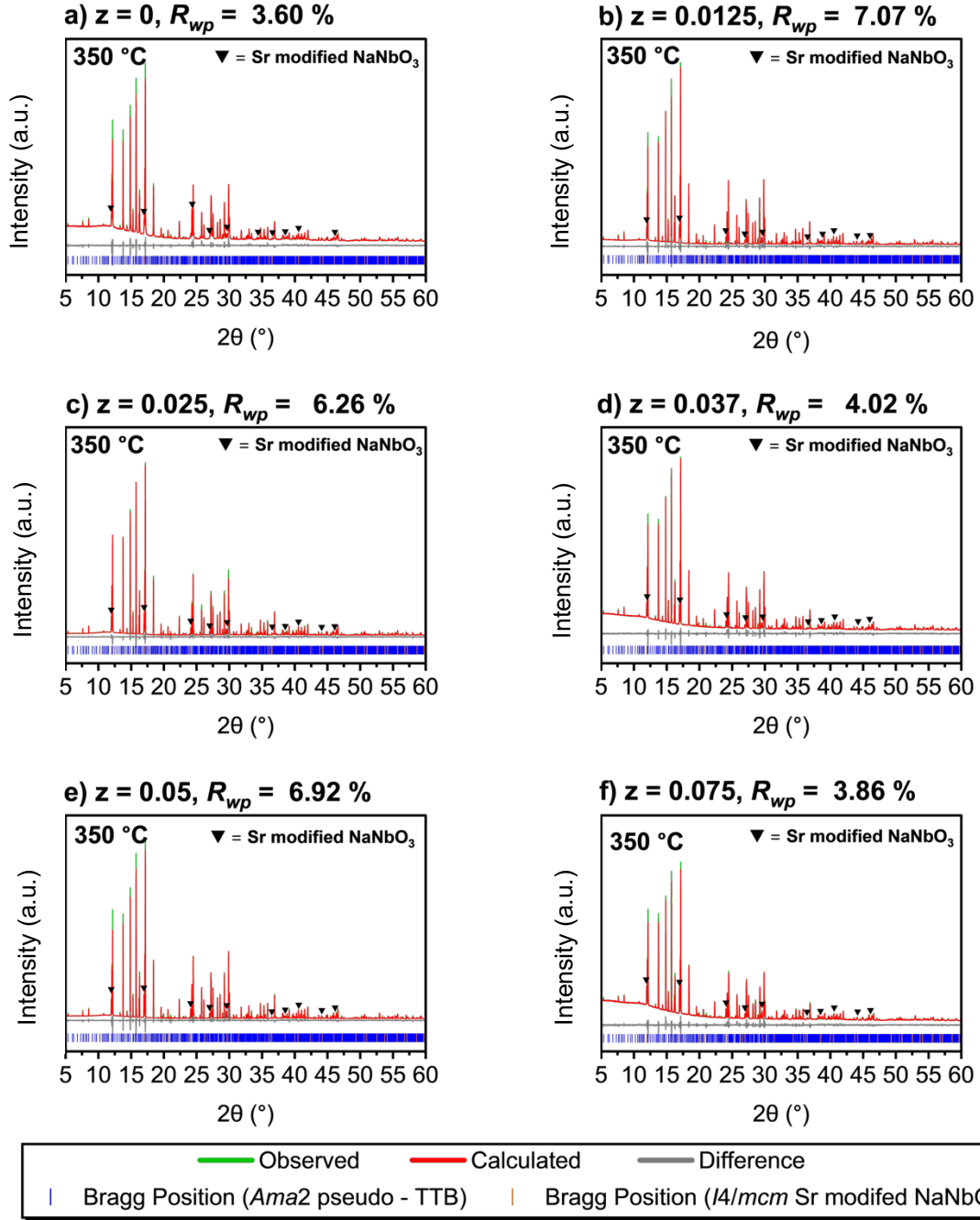


Figure C4: Rietveld refinement plots of the Ama2 structural model against diffraction patterns obtained from synchrotron PXRD at the highest measured temperature (350 °C) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where a) $z = 0$ (SNN1), b) $z = 0.0125$, c) $z = 0.025$, d) $z = 0.037$, e) $z = 0.05$, and f) $z = 0.075$. Tick marks indicate Bragg positions for the structural models of the main orthorhombic Ama2 pseudo – TTB phase (blue) and tetragonal $I4/mcm$ perovskite Sr-modified NaNbO_3 phase (orange), marked by ▼.

Table C2: Areal density of Stacking Faults in TEM dark field images (Figure 7a – c) for $\text{Sr}_{2-2z}\text{NaCa}_z\text{Y}_z\text{Nb}_{5-z}\text{Zr}_z\text{O}_{15}$ where $z = 0, 0.037$, and 0.075 , listing the distance between faults for ca. 5 grains of each doping level.

Sample Code	Number of Measurements	Mean Spacing (nm)	Standard Deviation (nm)	Median (nm)
$z = 0$	144	30.9	3.8	27.0
$z = 0.037$	215	19.9	5.2	17.9
$z = 0.075$	160	17.4	3.8	15.2

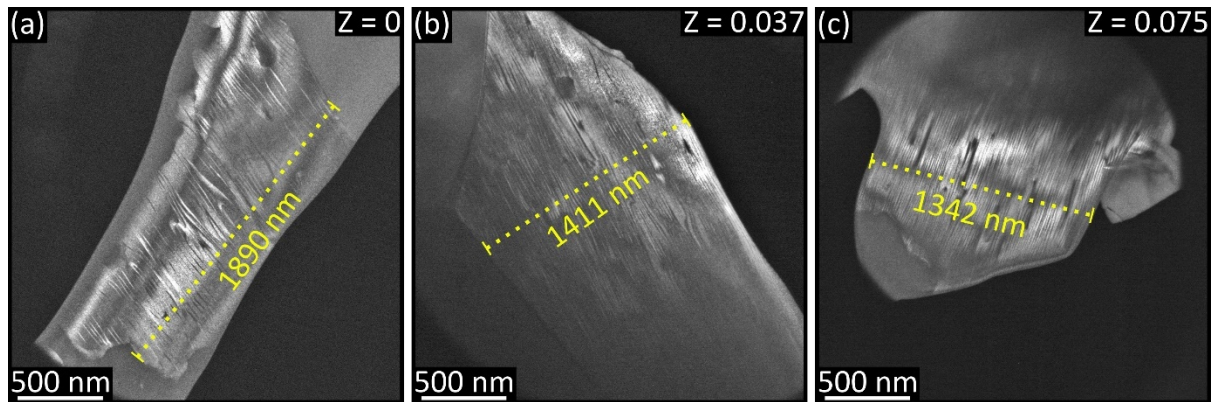


Figure C5a – c: Lower magnification view of the Dark Field micrographs presented in Figure 7 in the main text, showing similar domain sizes for a) SNN1 samples $z = 0$ (undoped), doped samples b) $z = 0.037$, and c) $z = 0.075$. All investigated samples contained domains well above $1 \mu\text{m}$ and no obvious differences in domain size distribution were observed.

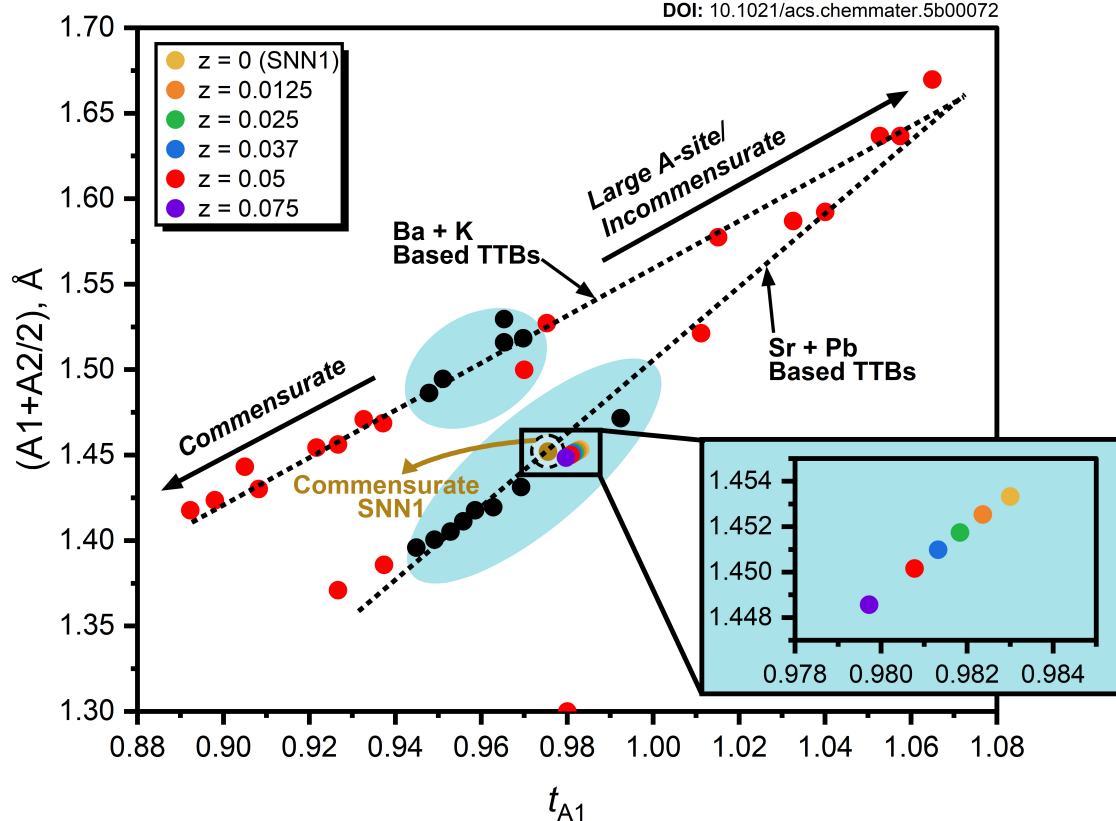


Figure C6: Average A-site size $([A1+A2]/2)$ versus A1-site tolerance factor (t_{A1}) of TTB compositions listed in Table 2 in Zhu *et al.* [107] including commensurate SNN and an inset showing stoichiometric $z = 0$ ([SNN], yellow), 0.0125 (orange), 0.025 (green), 0.037 (blue), 0.05 (red), and 0.075 (purple) from this work.

Appendix D – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$

This appendix (Appendix D – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$) includes supplemental data pertaining to Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$. Grain size distribution plots shown in backscattered scanning electron microscopy (SEM) micrographs in Figure 5.2 – Figure 5.5 in the main text are plotted in Figure D1. Dielectric reproducibility is shown in Figure D2. Weighted residual profiles (R_{wp}) at room temperature (R.T.), -173 °C, 350 °C, in addition to the average R_{wp} spanning the measured temperature range (-173 °C – 350 °C) are tabulated in Table D1. Rietveld refinement fitting plots at temperatures -173 °C and 350 °C are plotted in Figure D3a – d and Figure D4a – d respectively, highlighting the evolution of fits spanning the lowest (-173 °C) and highest (350 °C) measured temperature PXRD patterns. Sr modified NaNbO_3 peaks are denoted by ▼ in SNN1 and a possible unknown secondary phase is signified by ▽ in Figure D3a – d and Figure D4a – d.

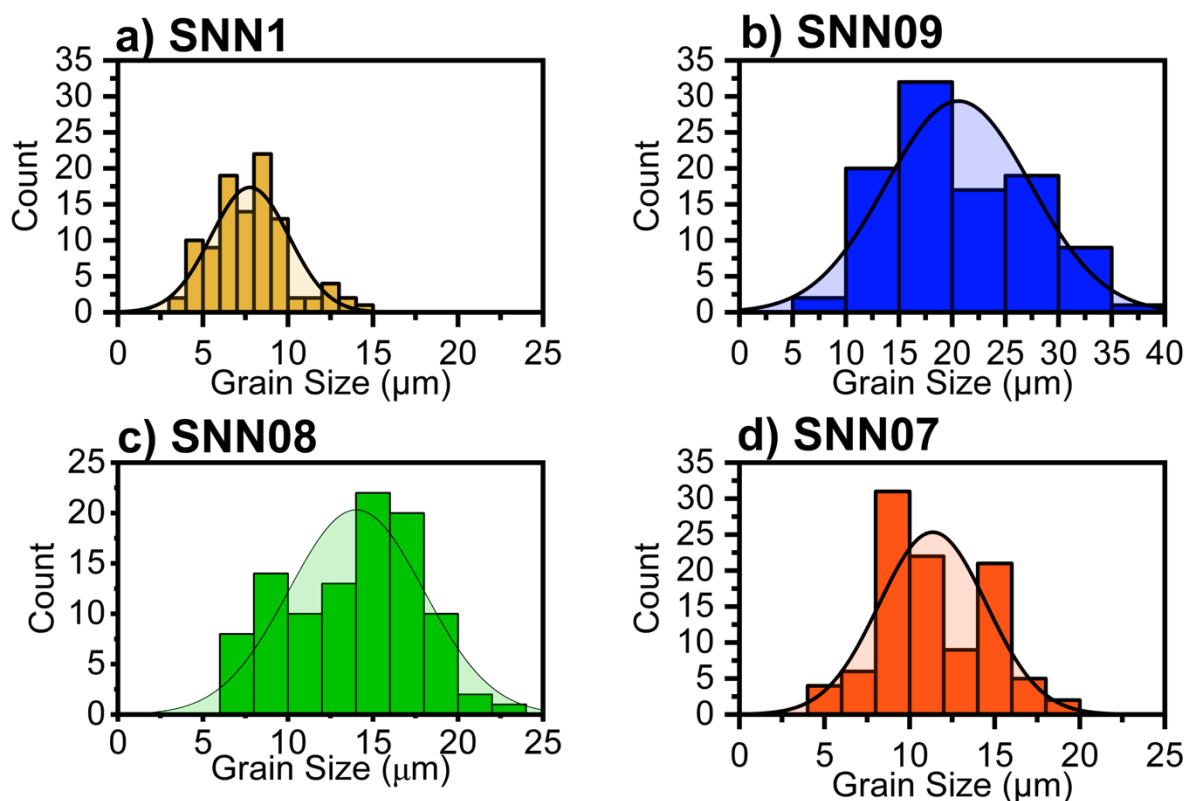


Figure D1: Grain size distribution plots superimposed onto backscattered scanning electron microscopy (SEM) micrographs in Chapter 5 – $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$, Figure 5.2 – Figure 5.5 for $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ where a) $w = 0$, $y = 1$ (SNN1), b) $w = 0.05$, $y = 0.9$ (SNN09), c) $w = 0.10$, $y = 0.8$ (SNN08), and d) $w = 0.15$, $y = 0.7$ (SNN07).

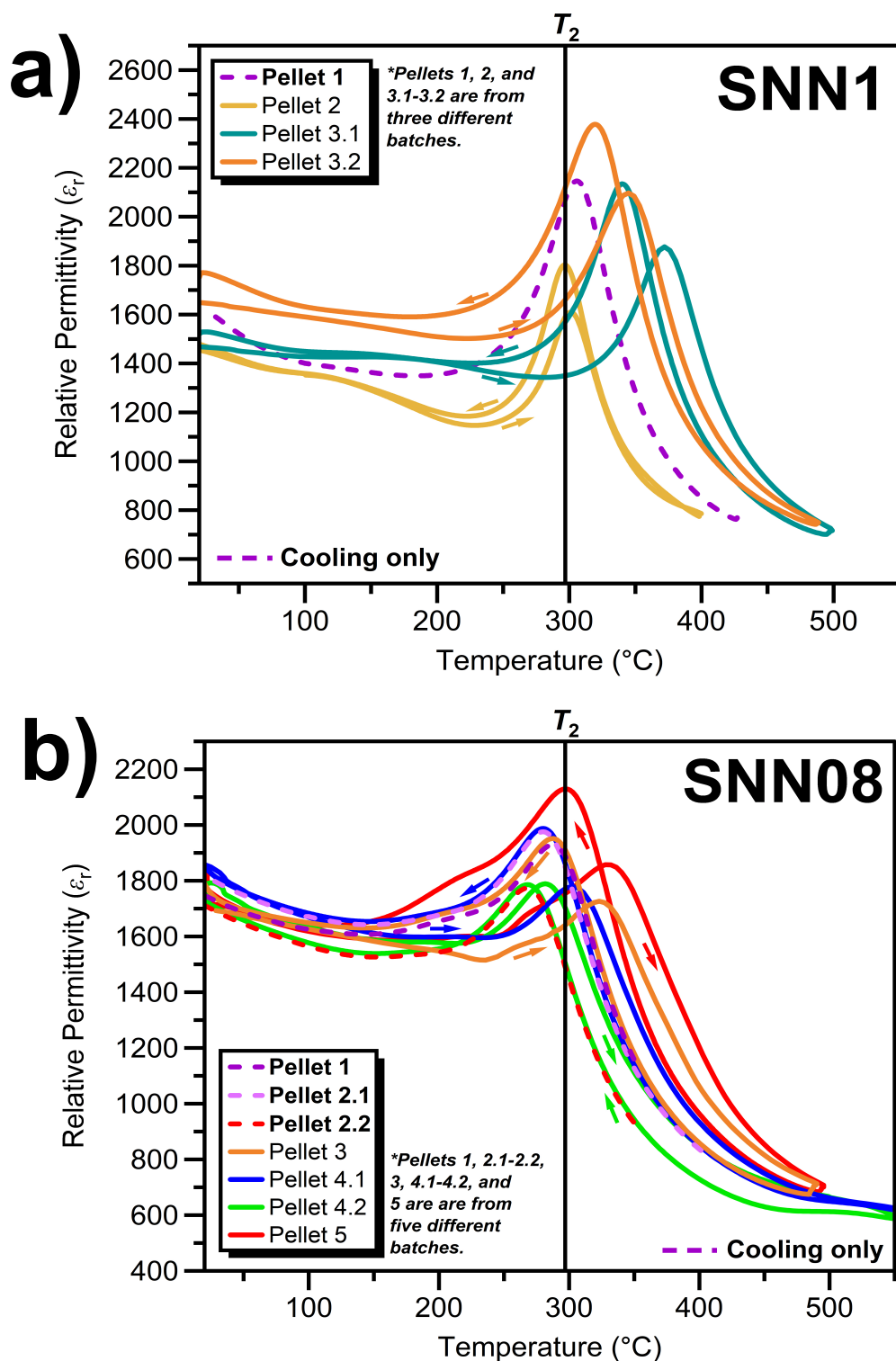


Figure D2: Comparative plots (at 1 kHz) of pellets of the same batch together with additional batches showing heating and cooling regimes for $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ where a) $w = 0$, $y = 1$ (SNN1) and b) $w = 0.10$, $y = 0.8$ (SNN08), with arrow directions denoting heating and cooling profiles.

Table D1: Crystallographic information obtained from synchrotron PXRD illustrating the pseudo – TTB and secondary Sr modified NaNbO_3 phase weight percentages (wt. %) ($\blacktriangledown$ = Sr modified NaNbO_3 ,), weighted profile residuals (R_{wp}), theoretical densities, geometric densities, and pellet density (%) at room temperature (R.T.), -173 °C, 350 °C and the average R_{wp} across the measured temperature range (-173 °C – 350 °C) for Sr modified NaNbO_3 peaks are denoted by $\blacktriangledown$ in SNN1 and a possible unknown secondary phase is signified by ∇ where $w = 0$, $y = 1$ (SNN1), $w = 0.05$, $y = 0.9$ (SNN09), $w = 0.10$, $y = 0.8$ (SNN08), and $w = 0.15$, $y = 0.7$ (SNN07).

Nominal Formula	Composition Code	Pseudo – TTB Phase (wt. %) at R.T.	Secondary Phase (wt. %) at R.T.	R_{wp} (%)			
				R.T.	-173 °C	350 °C	Average (-173 °C – 350 °C)
$\text{Sr}_2\text{NaNb}_5\text{O}_{15}$	SNN1	96.1	3.9 $\blacktriangledown$	2.81	3.72	3.69	3.02
$\text{Sr}_{2.05}\text{Na}_{0.9}\square_{0.05}\text{Nb}_5\text{O}_{15}$	SNN09	99	< 1.0 $\blacktriangledown$, 0 ∇	3.39	3.35	4.42	3.67
$\text{Sr}_{2.10}\text{Na}_{0.8}\square_{0.10}\text{Nb}_5\text{O}_{15}$	SNN08	99	< 1.0 $\blacktriangledown$, 0 ∇	2.72	2.92	9.19	5.87
$\text{Sr}_{2.15}\text{Na}_{0.7}\square_{0.15}\text{Nb}_5\text{O}_{15}$	SNN07	99	< 1.0 $\blacktriangledown$, 0 ∇	5.87	4.47	10.86	6.72

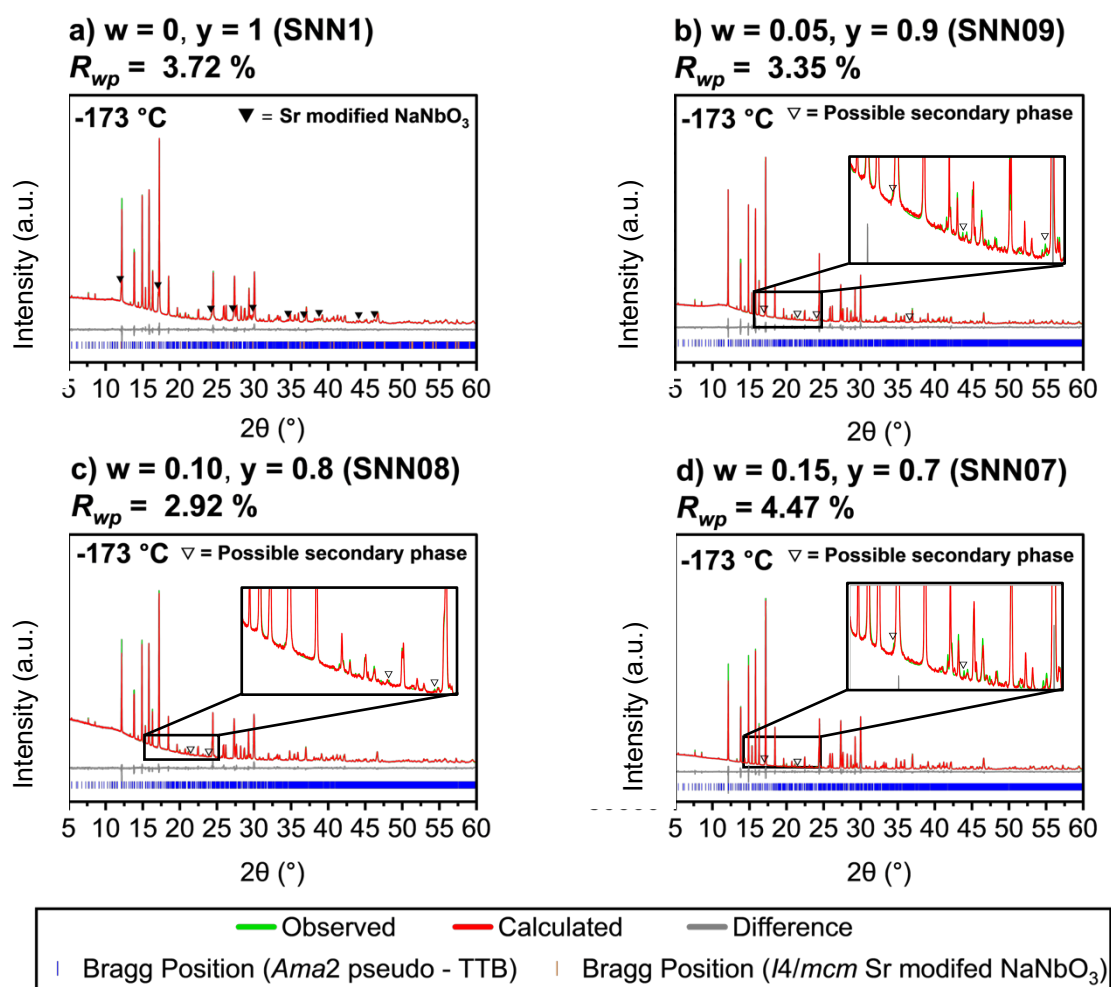


Figure D3: Rietveld refinement fits of the orthorhombic *Ama2* (pseudo - TTB) structural model against diffraction patterns obtained through variable temperature synchrotron PXRD collected at beamline I11 Diamond Light Source at the lowest measured temperature (-173 °C) of $\text{Sr}_{2+w}\text{Na}_y\text{Nb}_5\text{O}_{15}$ where a) $w = 0, y = 1$ (SNN1), b) $w = 0.05, y = 0.9$ (SNN09), c) $w = 0.10, y = 0.8$ (SNN08), and d) $w = 0.15, y = 0.7$ (SNN07). Secondary phase tetragonal *I4/mcm* (Sr modified NaNbO_3) is highlighted by ▼ in SNN1 and a possible unknown secondary phase (< 1 wt%) is marked by ▽ for b) SNN09, c) SNN08 and d) SNN07.

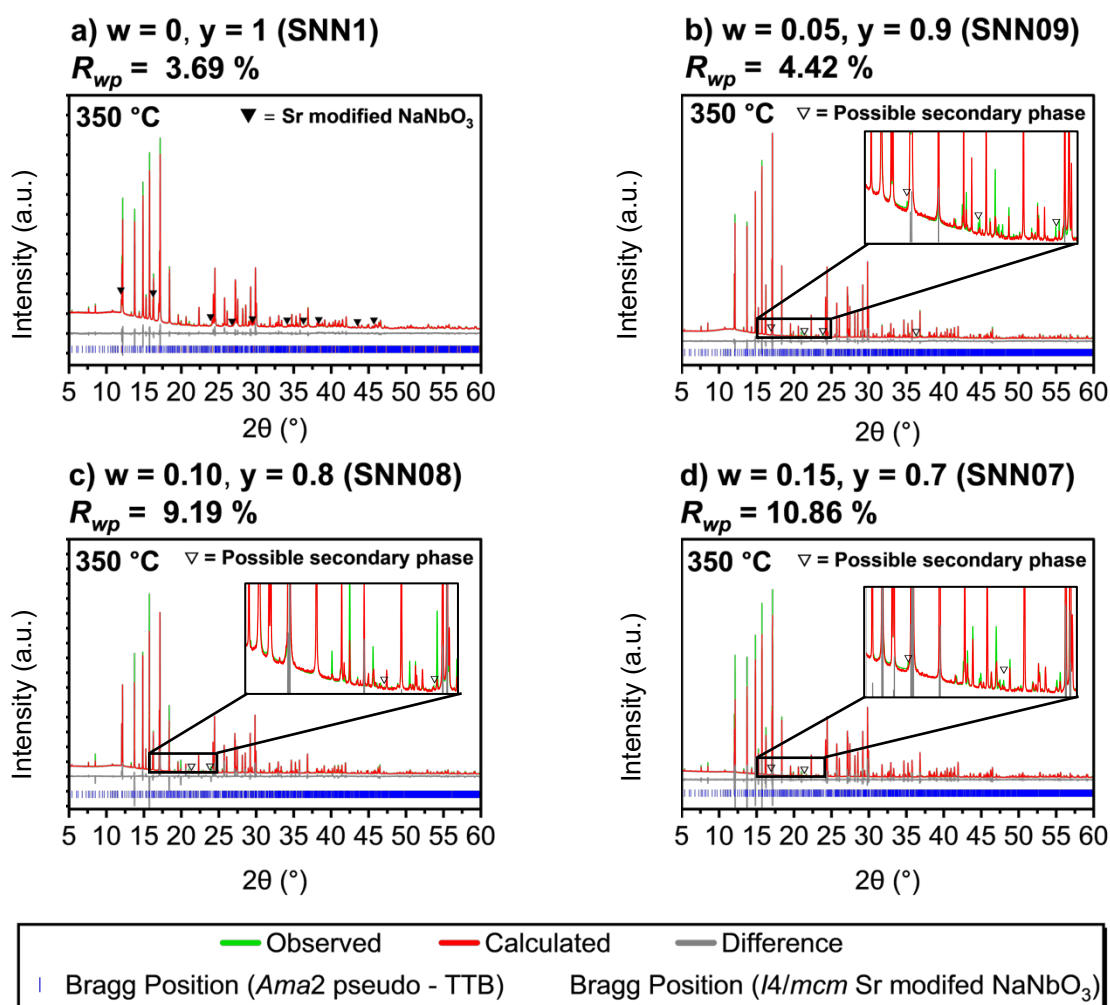


Figure D4: Rietveld refinement fits of the orthorhombic *Ama2* (pseudo – TTB) structural model against diffraction patterns obtained through variable temperature synchrotron PXRD collected at beamline I11 Diamond Light Source at the highest measured temperature (350 °C) of $\text{Sr}_{2+w}\text{Na}_y\text{□}_w\text{Nb}_5\text{O}_{15}$ where a) $w = 0, y = 1$ (SNN1), b) $w = 0.05, y = 0.9$ (SNN09), c) $w = 0.10, y = 0.8$ (SNN08), and d) $w = 0.15, y = 0.7$ (SNN07). Secondary phase tetragonal *I4/mcm* (Sr modified NaNbO_3) is highlighted by ▼ in SNN1 possible unknown secondary phase (< 1 wt%) is marked by ▽ for b) SNN09, c) SNN08 and d) SNN07.

Appendix E – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$

This appendix (Appendix E – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$) pertains to Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$. Supplementary data here includes extracted laboratory PXRD patterns focusing on (001) and (310) splitting magnitudes from (Figure E1a – g, from Figure 6.1a – g in the main text), grain size distribution plots shown in backscattered scanning electron microscopy (SEM) micrographs (Figure E2a – g, from Figure 6.4 – Figure 6.5 in the main text), additional optical light microscope micrographs showing a “duplex” microstructure are shown in Figure E3. Finally, Curie-Weiss (CW) law fitting plots from dielectric permittivity – temperature data (Figure E4a – g and Figure E5a – g from Figure 6.11a – g).

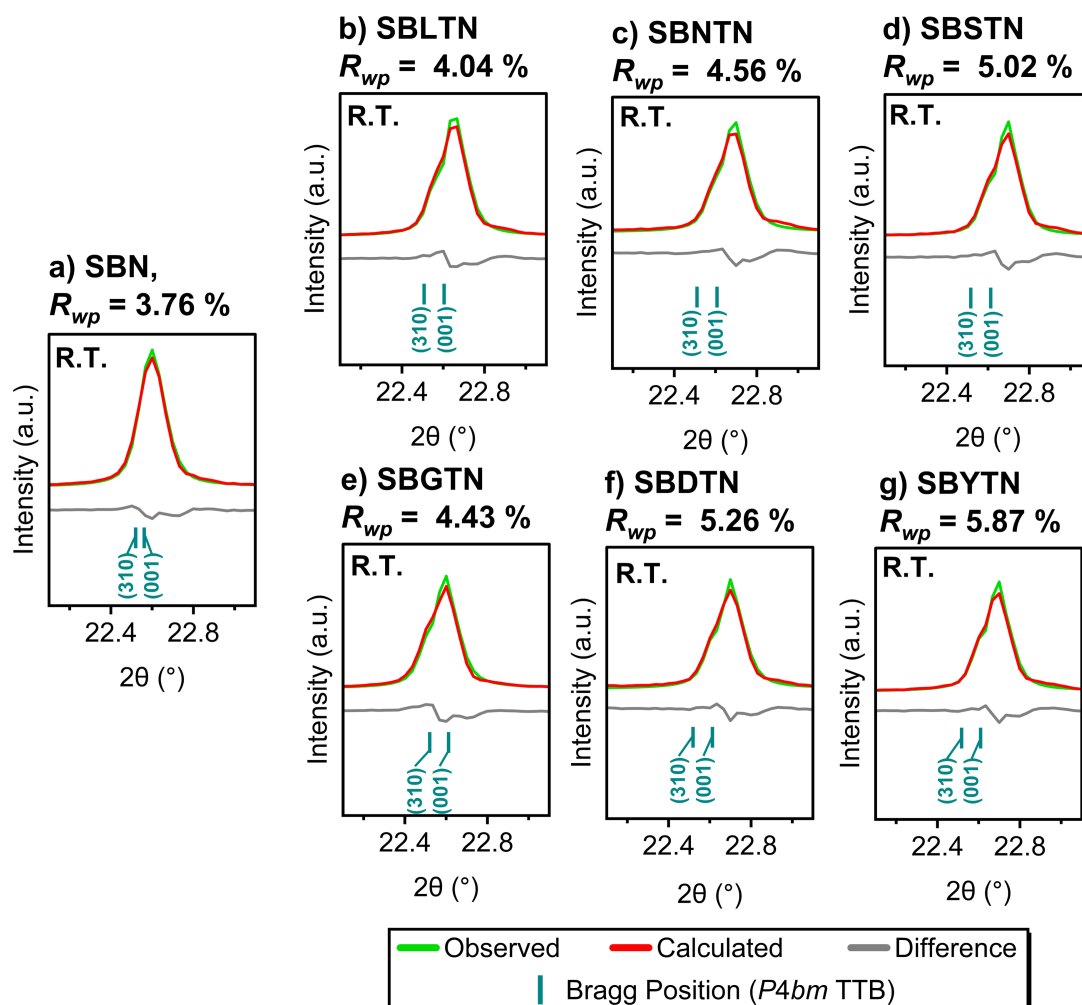


Figure E1a – g: Room temperature laboratory PXRD patterns refined against a $P4bm$ structural model highlighting the increased splitting magnitude of the (001) and (310) peaks for a) $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} =$ b) La^{3+} (SBLTN), c) Nd^{3+} (SBNTN), d) Sm^{3+} (SBSTN), e) Gd^{3+} (SBGTN), f) Dy^{3+} (SBDTN), and g) Y^{3+} (SBYTN). The splitting magnitude between (001) and (310) increases from SBN to SBRTN compositions alongside a presence of a small shoulder representing the (310) reflection in SBRTN compositions. Differences between splitting magnitudes of (001) and (310) reflections from SBYTN to SBLTN are indistinguishable and limited by the resolution of laboratory PXRD instrumentation used here.

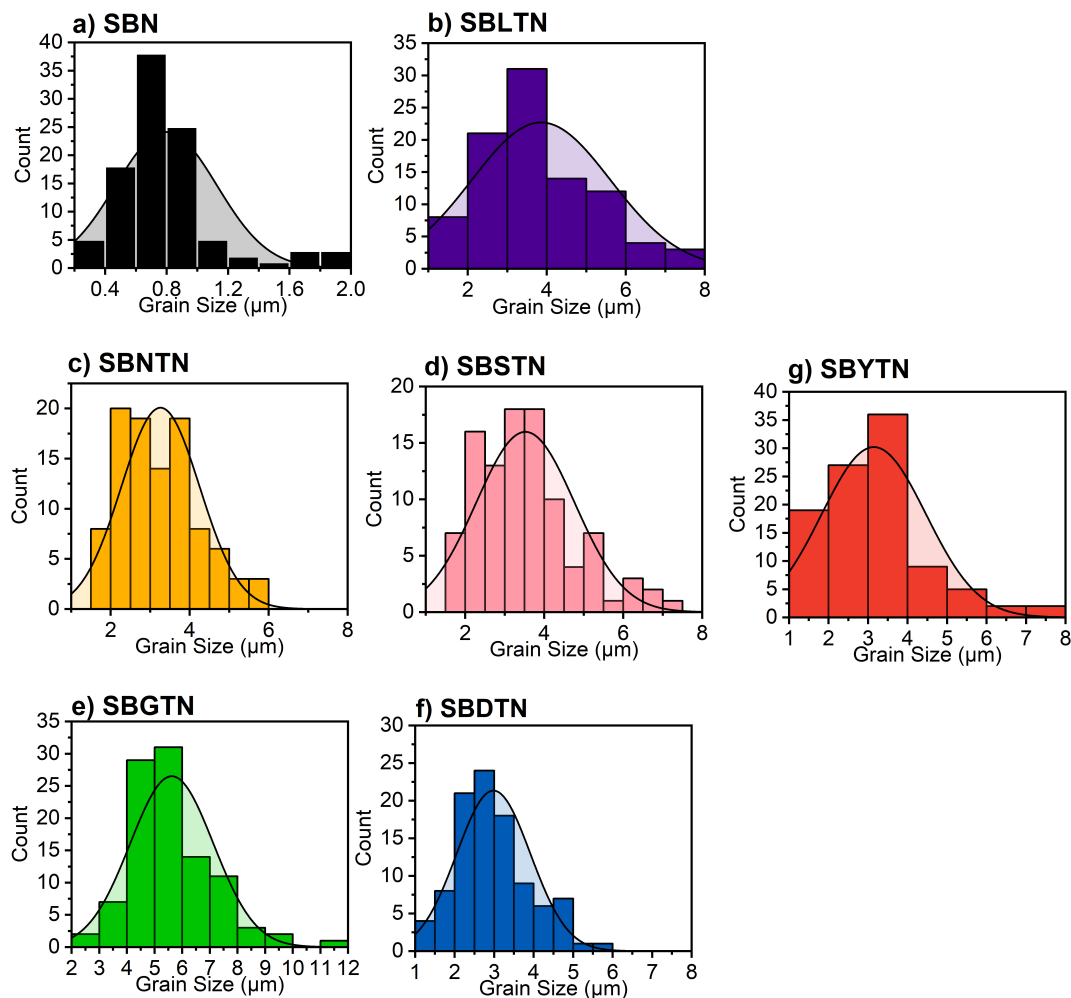


Figure E2a – d: Grain size distribution plots obtained from back scattered SEM micrographs for a) $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} =$ b) La^{3+} (SBLTN), c) Nd^{3+} (SBNTN), d) Sm^{3+} (SBSTN), e) Gd^{3+} (SBGTN), f) Dy^{3+} (SBDTN), and g) Y^{3+} (SBYTN). Grain size distribution plots are superimposed onto SEM micrographs in Figure 6.4 – Figure 6.5 in the main thesis text (Chapter 6 – $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$).

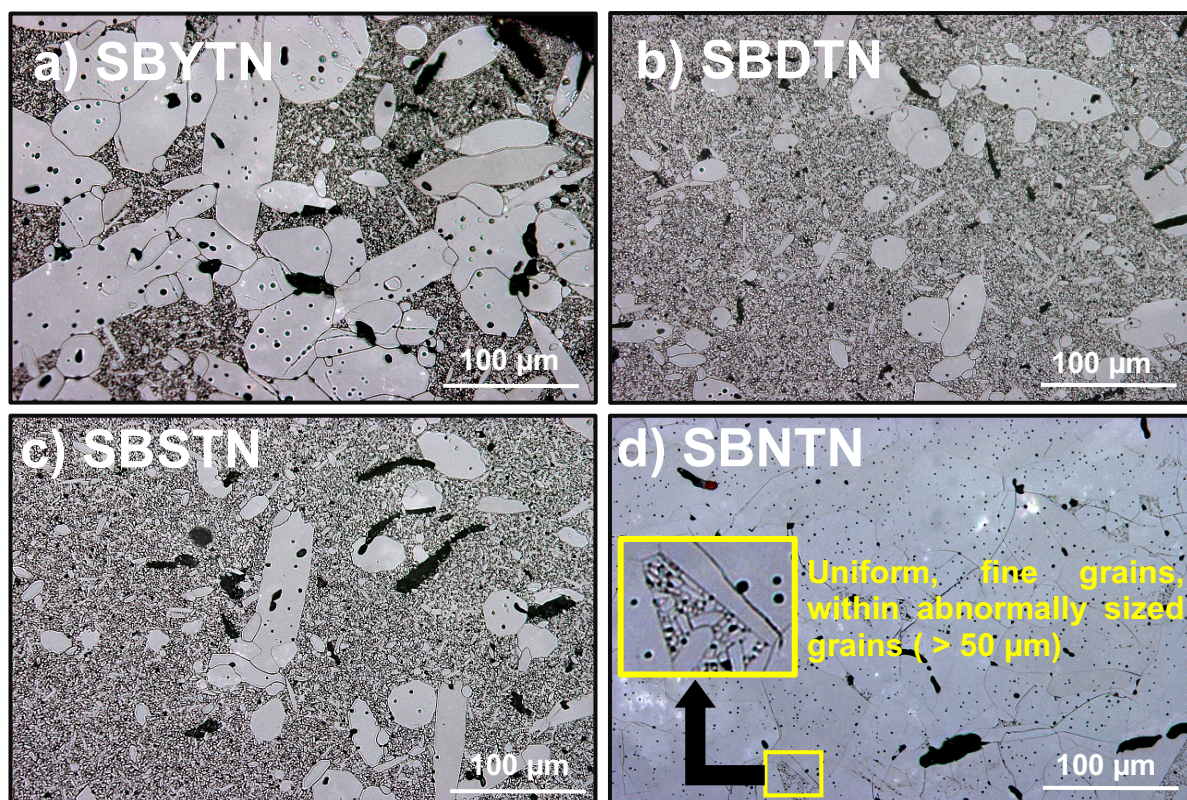


Figure E3a – d: Optical light microscope micrographs at 20x (objective lens) magnification of $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} =$ a) Y^{3+} (SBYTN), b) Dy^{3+} (SBDTN), c) Sm^{3+} (SBSTN), and d) Nd^{3+} (SBNTN) exhibiting a “duplex” structure where uniform, fine, grains within abnormally sized grains (outlined in the yellow box in d) Nd^{3+} (SBNTN).

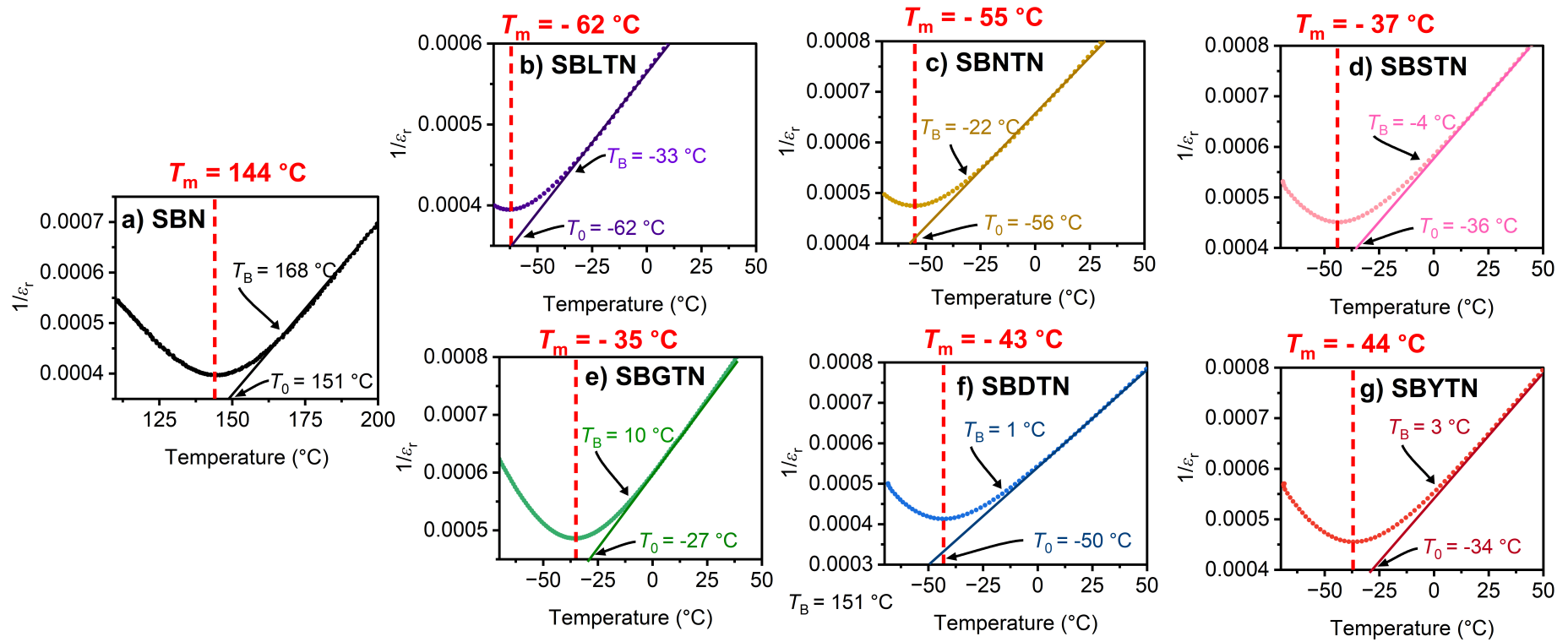


Figure E4a – g: Modified Curie-Weiss plots showing the deviation of $1/\epsilon_r$ from linear, deviating from Curie-Weiss law for plots for a) $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} =$ b) Y^{3+} (SBYTN), c) Dy^{3+} (SBDTN), d) Gd^{3+} (SBGTN), e) Sm^{3+} (SBSTN), f) Nd^{3+} (SBNTN), and g) La^{3+} (SBLTN).

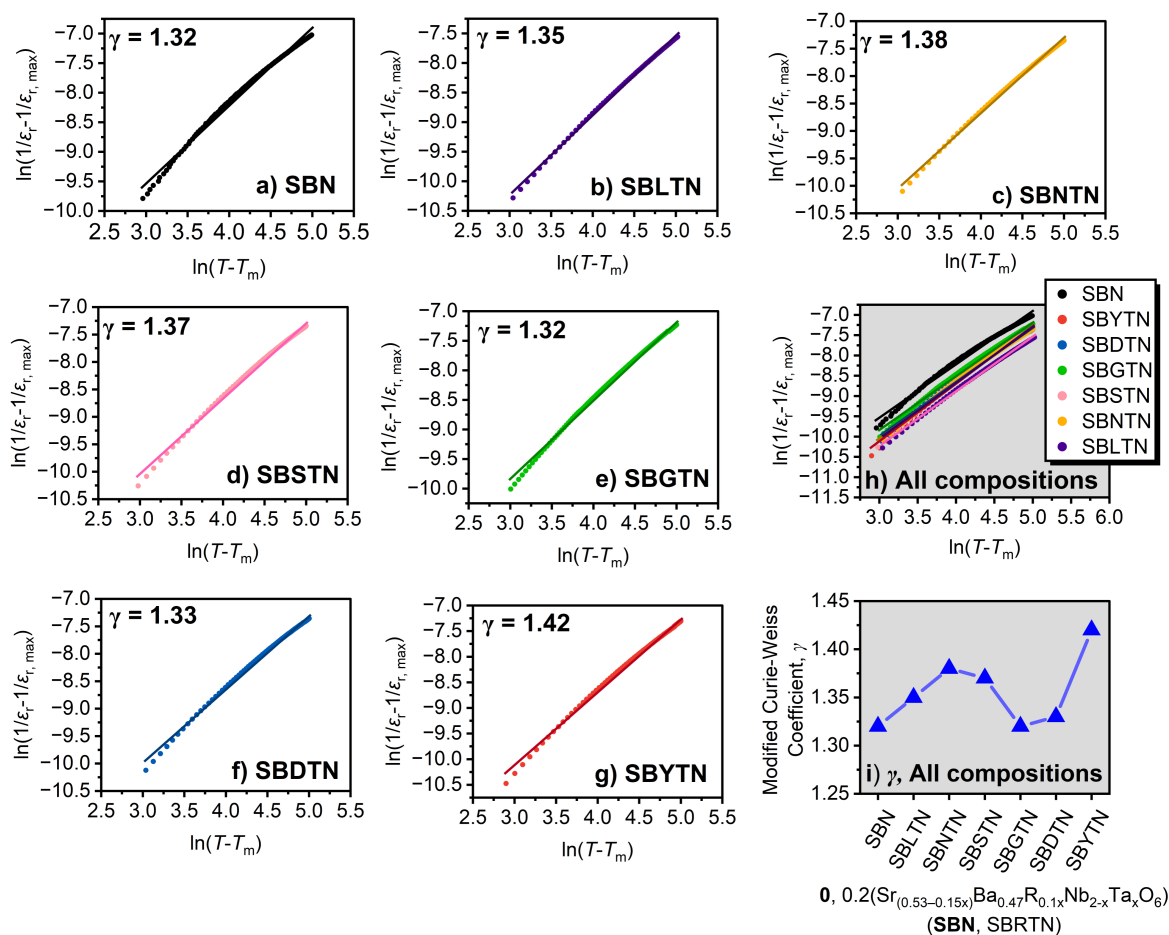


Figure E5a – g: Modified Curie Weiss linear fit plots for a) $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (SBN) and $\text{Sr}_{(0.53-0.15x)}\text{Ba}_{0.47}\text{R}_{0.1x}\text{Nb}_{2-x}\text{Ta}_x\text{O}_6$ (SBRTN) where $x = 0.2$ and $\text{R}^{3+} = \text{b}) \text{Y}^{3+}$ (SBYTN), c) Dy^{3+} (SBDTN), d) Gd^{3+} (SBGTN), e) Sm^{3+} (SBSTN), f) Nd^{3+} (SBNTN), and g) La^{3+} (SBLTN), h) SBN, and all SBRTN compositions, and i) modified Curie-Weiss coefficient, γ , as a function of compositions.