

Contrasting strain mechanisms in lead-free piezoelectric ceramics

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CONTRASTING STRAIN MECHANISMS IN LEAD-FREE PIEZOELECTRIC CERAMICS

A Thesis

By

Neamul Hayet Khansur

Submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy



School of Materials Science and Engineering Faculty of Science University of New South Wales

June 2015

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Abstract 350 words maximum:

Piezoelectric ceramics find a wide range of applications in advanced technological fields. Most of the currently used piezoelectric ceramics contain lead (Pb). Environmental concerns and limitations in high-temperature performances of market leading Pb(Zr,Ti)O₃ has spurred the field of lead-free electroceramics research. Compositions based on Bi_{1/2}Na_{1/2}TiO₃, Na_{1/2}K_{1/2}NbO₃, BiFeO₃ and BaTiO₃ have long been considered as candidates to replace lead containing piezoelectric ceramics. Although lead-free compositions based on these systems exhibit electromechanical properties for potential device application, further enhancement of properties and reliability is required. To achieve this, extensive knowledge of structure- property relationships at multiple length scales, especially during the actuation condition is essential. However, systematic studies of the multi- length-scale structural contributions (lattice deformation, domain wall motion, phase transformations) to the field-induced strain in lead-free electroceramics are lacking.

To understand the microscopic origin of strain in lead-free electroceramics several compositions have been studied using *in situ* high-energy x-ray diffraction. Their microscopic strain response has been elucidated under electric field. Strain contributions have been analysed for each system and have been correlated with their macroscopic properties.

The first material was a ceramic/ceramic composite of particulate phase $0.93(Bi_{1/2}Na_{1/2})TiO_3$ -0.07BaTiO_3 and matrix phase $0.92(Bi_{1/2}Na_{1/2})TiO_3$ -0.06BaTiO_3-0.02(Na_{1/2}K_{1/2}NbO_3). Under applied electric field, this material system showed that the local response of the particulate phase can be used to tailor bulk material properties. A microscopic strain mechanism in ceramic/ceramic composite system was proposed on the basis of these diffraction studies.

A microscopic strain mechanism in ceramic/ceramic composite system was proposed on the basis of these diffraction studies. Domain switching in a core-shell BaTiO₃-KNbO₃ piezoelectric ceramics has also been investigated. The core-shell BT-KN has been shown to exhibit remarkably large reversible domain switching during the application of electric fields.

Electromechancial coupling behavior in bulk BiFeO₃ has been quantified from diffraction data. The strain mechanism has been contrasted with thin-film BiFeO₃. Interestingly, despite the different mechanism, rhombohedral bulk BiFeO₃ ceramic can exhibit a similar strain/field ratio to thin-film BiFeO₃. This comparative study of strain responses will enable the research field to focus on identified important structural aspects that are essential to improve piezoelectric properties in future lead-free systems.

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Abstract

Piezoelectric ceramics are found in a wide range of applications in advanced technological fields. Most of the piezoelectric ceramics used today are based on the solid solution of lead zirconate and lead titanate (PZT). These materials have demonstrated exceptional properties over a range of operating conditions. However, environmental concerns of these market leading piezoelectric materials, have spurred research in lead-free piezoelectric ceramics.

Compositions based on $Bi_{1/2}Na_{1/2}TiO_3$, $Na_{1/2}K_{1/2}NbO_3$, $BaTiO_3$, $BiFeO_3$ have long been considered as candidates to replace lead-containing piezoelectric ceramics. Although lead-free compositions based on these systems exhibit electro-mechanical properties suitable for potential device applications, further enhancement of properties and reliability is required. To achieve this, extensive knowledge of structure-property relationships at multiple length scales, especially during the actuation condition is essential. However, systematic studies of the multi-length-scale structural contributions to the field-induced strain in lead-free electro-ceramics are lacking.

Diffraction is a useful technique to highlight structure-property relationships. To understand the microscopic origin of strain in lead-free electro-ceramics, three contrasting material types have been studied using *in situ* high-energy x-ray diffraction. Their microscopic strain response has been elucidated under electric field and the strain contributions for each system have been correlated with their macroscopic properties.

The first material was a ceramic/ceramic composite of particulate phase $0.93(Bi_{1/2}Na_{1/2})TiO_3-0.07BaTiO_3$ and matrix phase $0.92(Bi_{1/2}Na_{1/2})TiO_3-0.06BaTiO_3-0.02(Na_{1/2}K_{1/2}NbO_3)$. Under applied electric field, this material system showed that the local response of the particulate phase can be used to tailor bulk material properties. A

microscopic strain mechanism in ceramic/ceramic composite system was proposed on the basis of these diffraction studies.

The second system of interest was a core-shell structured BaTiO₃-KNbO₃ (BT-KN). A large reversible non-180° ferroelectric domain switching during the application of electric fields was observed. The nature of the reversible domain switching has been contrasted with conventional electro-ceramics such as BT and PZT for unipolar actuation. The core-shell BT-KN exhibited a higher magnitude of non-180° ferroelectric domain switching than BT and PZT. A model which incorporates a residual stress driving force and reduction in grain boundary domain pinning was hypothesised to explain the magnitude of reversible non-180° ferroelectric domain switching in coreshell microstructured BT-KN.

The final system was that of bulk BiFeO₃ (BFO). Here, the strain mechanism has been contrasted with thin-film BFO. Interestingly, despite confirming a different mechanism, bulk BFO ceramic can exhibit a similar strain/field ratio to thin-film BFO. Additionally, relaxations of switched non-180° ferroelectric domains were observed in the bulk BFO. The relaxation behaviour was hypothesised to be related to the elastic anisotropy of the material, residual stress and conductive nature of the domain walls.

This comparative study of strain responses will enable the research field to focus on identified important structural aspects that are essential to improve piezoelectric properties in future lead-free systems.

List of publications and presentations

Selected journal publications:

- N.H. Khansur, H. Kawashima, S. Wada, J.M. Hudspeth, J.E. Daniels, "Enhanced Extrinsic Domain Switching Strain in Core-shell Structured BaTiO₃-KNbO₃ Lead-free Piezoelectric Ceramics" *Acta Materialia*, 98 (2015)
- N.H. Khansur, T. Rojac, D. Damjanovic, C. Reinhard, K.G. Webber, J.A. Kimpton, J.E. Daniels, "Electric-field-induced Domain Switching and Domain Texture Relaxations in Bulk Bismuth Ferrite" *Journal of the American Ceramic Society*, (2015)
- N.H. Khansur, C. Groh, W. Jo, C. Reinhard, J.A. Kimpton, K.G. Webber, J.E. Daniels, "Tailoring of unipolar strain in lead-free piezoelectric using the ceramic/ceramic composite approach", *Journal of Applied Physics*, 115 (2014)
- M.C. Ehmke, N.H. Khansur, J.E. Daniels, J.E. Blendell, K.J. Bowman, "Resolving structural contributions to the electric-field-induced strain in leadfree (1-x)Ba(Zr_{0.2}Ti_{0.8})O₃-x(Ba_{0.7}Ca_{0.3})TiO₃ piezoceramics", *Acta Materialia*, 66 (2014)

Conference presentations:

- i. N.H. Khansur, J.A. Kimpton, J.E. Daniels, *In situ* high-energy XRD study on bulk BiFeO₃, AS User Meeting 2014, Melbourne, Australia
- ii. N.H. Khansur, M. Acosta, C. Groh, W. Jo, J. Rödel, J.E. Daniels, *In situ* diffraction studies of electric-field-induced strain in polycrystalline composite materials, ICAE, 2013, Jeju, Korea
- iii. N.H. Khansur, J.E. Daniels, High-energy X-ray diffraction in the characterisation of Electro-active materials, AXAA 2013, Sydney, Australia
- N.H. Khansur, J.E. Daniels, Combined X-ray And Neutron Structural Refinements Of (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ Lead-free Piezoelectrics, AIP Conference 2012, Sydney, Australia
- v. N.H. Khansur, J.E. Daniels, Combined Structural Refinements of Bismuth Sodium Titanate Based Lead-free Electroceramics, AANSS 2012, Lucas Heights, Australia

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1. Introduction

Piezoelectric materials are an important class of functional materials, and are an integral part in the development of innovative and high-performance devices for a range of technologies. Direct coupling^[1] of mechanical energy and electrical energy in piezoelectric materials has made them attractive for industrial applications. The applications for piezoelectric ceramics are wide-spread, covering areas of our workplace, homes and automobiles in the form of sensors, generators and actuators. In addition, smart systems or intelligent structures^[2] (i.e. integration of actuators, sensors and control with a material or structural component) based on electro-mechanical coupling properties have received significant attention because of their potential applications in automation, micromanipulation, ultra-precise positioning, and medical technology.^[3, 4] The relative ease and cost-effectiveness^[1, 5, 6] with which these materials can be adapted to useful and reliable devices is, to a great extent, the reason that piezoelectrics have been so successful over the years in finding an increasing number of applications.^[7] For example, a recent application of piezoelectric materials is in fuel injector devices.^[8] A fuel injector based on a piezoelectric actuator can improve overall efficiency of an automotive by precise fuel metering for improved combustion, that leads to better fuel economy and reduced emissions.

Applications of piezoelectric materials are dominated by lead-based Pb(Zr,Ti)O₃ (PZT) because of the excellent electro-mechanical coupling properties that have been recorded. Interestingly, even though the first reports^[9, 10] of PZT date back to 1950, its functional properties are still gradually evolving with processing technology, compositional engineering, and microstructure engineering.

The commercial manufacture and application of PZT materials has become a serious concern from the view point of environmental protection and health. For example, in a typical composition of PZT, Pb(Zr_{0.53}Ti_{0.47})O₃, lead constitutes more than 60 wt.% of the material. Generally high temperature reaction during ceramic processing (evaporation of lead oxide) and improper disposal of discarded lead-containing materials are two major ways that lead enters the environment. Another concern is that PZT ceramics may not be stable in an aqueous environment.^[11] Demand of lead-based high-end products (e.g., sensors, actuators, generators) ultimately increases the need for lead-mining. A recent telecast^[12] from the Australian Broadcasting Corporation (ABC) titled "Lead Astray" has highlighted the severe effect of lead-mining on the surrounding environment and human health. The toxicity of lead presents serious threats to human health such as in the functioning of brain neurotransmitters and the central nervous system. Lead accumulates in a range of biological organisms within the human food chain and is difficult to remove.^[13]

With the above concerns, regulations and policies against the use of lead-based materials have been increasingly enacted throughout the world. According to "the restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS) of the European Union, from 1 July, 2006, the new electrical and electronic equipment put on the market cannot contain lead.^[14] Asian countries such as China^[15] and Japan^[16] have also enacted similar policies and legislation to control the usage of lead-containing materials. However, lead-based piezoelectrics are exempt^[17] from the list of banned materials due to the fact that the piezoelectric properties of current lead-free candidates are still inferior to the lead-based materials. The health

concerns and resulting legislation has triggered extensive research efforts to seek replacements for PZT with new high-performance lead-free piezoelectric materials.

Despite promising research findings in recent years, it seems that no single lead-free material system can replace lead-based compositions across the whole diverse range of applications and environmental conditions.^[7] For example, lead-free compositions with high electric-field-induced strain and a wide operational temperature range are two major requirements for replacing PZT in actuator applications. Several compositions based on Bi_{1/2}Na_{1/2}TiO₃ (BNT), Na_{1/2}K_{1/2}NbO₃ (NKN), Bi_{1/2}K_{1/2}TiO₃ (BKT), BaTiO₃ (BT), BiFeO₃ (BFO) were reported to exhibit large electro-mechanical properties. In addition to compositional engineering, microstructural variations to create composite ceramic structures at the grain-scale have also been implemented. These material systems are attractive not merely from an application point of view but also from a scientific perspective with respect to the fundamental nature of electro-mechanical coupling.

Although lead-free compositions based on the above mentioned systems exhibit electromechanical properties for potential device application, further enhancement of properties and reliability is required. A detail understanding of structure-property relationships at multiple length scales, especially during the actuation condition is critical to improve electro-mechanical properties in existing compositions as well as to design new lead-free piezoelectrics. However, systematic studies of the multi-lengthscale structural contributions (e.g., contributions from lattice deformation, domain wall motion, and phase transformations) to the field-induced strain in lead-free electroceramics are lacking. This thesis therefore highlights microscopic origins of electricfield-induced strain response in three different lead-free compositions using *in situ* highenergy x-ray diffraction.

The aim of this thesis is to reconcile the types of structural contributions present at the microscopic length scales in different lead-free piezoelectric ceramics to their macroscopic properties. To establish structure-property relationships in lead-free piezoelectrics, three different types of composition have been studied using *in situ* high-energy x-ray diffraction. The lead-free compositions have been chosen to cover a range of compositional and/or microstructure modification that are promising for future actuator applications. Some of the significant issues specific to material type are highlighted below:

Ceramic/ceramic composite (CCM):

- i. How the particulate ferroelectric (FE) phase behaves in the relaxor (RE) phase matrix at the microscopic level in a ceramic/ceramic composite (CCM) material?
- ii. Can the local response of the FE phase be tuned to affect macroscopic properties of CCM?

Core-shell BaTiO₃-KNbO₃ (BT-KN):

i. What is the mechanism by which electric-field-induced strain in core-shell structured ceramics outperforms that of the same composition with a uniform microstructure?

Bulk BiFeO₃ (BFO):

i. What is the major structural contributor to the observed macroscopic strain in bulk BFO?

ii. What are the contributing factors for domain wall stability in bulk BFO?

Investigation of microscopic structural responses with applied electric field using the xray diffraction method, and their correlation with the macroscopic response, can contribute understanding the microscopic origin of strain response in promising leadfree piezoelectric materials.

This thesis therefore aims to investigate the electric-field-induced changes to the crystalline structure of a) ceramic/ceramic composite of $0.92(Bi_{1/2}Na_{1/2})TiO_3$ - $0.06BaTiO_3$ - $0.02(Na_{1/2}K_{1/2}NbO_3)$ and $0.93(Bi_{1/2}Na_{1/2})TiO_3$ - $0.07BaTiO_3$, b) core-shell structure BT-KN, and c) bulk BFO using *in situ* high-energy x-ray diffraction method. It is expected that this study will highlight structural characteristics associated with high electric-field-induced strain such that new, improved lead-free piezoelectric materials can be developed.

2. Literature review

This chapter summarises the fundamental concepts required for the description and understanding of the lead-free piezoelectrics discussed in this thesis. The first part highlights the basics of electro-mechanical coupling phenomena in dielectrics and existing lead-free materials systems known for electro-mechanical coupling. The latter part discusses structure-property relationships and methods used to elucidate these relationships.

2.1. Electro-mechanical coupling

Coupling in dielectrics depends on the polarisability and crystal structure of the materials. In the following subsections, a description of dielectrics and coupling in dielectrics are outlined.

2.1.1. Dielectrics and polarisation

All electrical insulators are dielectrics with no long-range transport of charge. An applied electric field (\mathbf{E}) induces a dipole moment by rearranging the charge transport and the materials acquire a polarisation (\mathbf{P}). For a perfect dielectric the total dielectric displacement (\mathbf{D}) can be expressed as

$$\mathbf{D} = \kappa_0 \mathbf{E} + \mathbf{P} \tag{2-1}$$

where κ_0 , a zero rank tensor, is the permittivity of the vacuum. **E**, **P** and **D** are first rank tensors. The effect of an electric field on a dielectric is dependent on dipole moments. Thus, the macroscopic polarisation is the sum of all dipole moments related to a unit volume. The macroscopic polarisation and the applied electric field are directly related by a proportionality factor χ (a second rank tensor), dielectric susceptibility, as

$$\mathbf{P} = \kappa_0 \chi \mathbf{E} \tag{2-2}$$

Additionally, the dielectric susceptibility χ can be expressed by relative dielectric constant, *K*

$$\chi = K - 1 \tag{2-3}$$

where K is the ratio between permittivity κ and permittivity of vacuum κ_0 .

Polarisation in dielectrics involves primarily four types of "polarisation mechanisms", namely: electronic, ionic, orientation and space charge (Figure 2-1).



Figure 2-1 Representation of microscopic polarisation mechanisms (a) displacement of negatively charge electron shell against positively charge core, (b) displacement of the positive and negative sublattices in ionic crystals, (c) alignment of dipoles along field direction, and (d) spatial inhomogeneity of charge carrier densities (after Ref. [6, 18, 19]).

A group of dielectrics possesses a unique polar axis even with no external perturbation. This class of dielectrics can be classified as polar dielectrics. Subgroups of polar dielectrics are piezoelectrics, pyroelectrics, and ferroelectrics. In the following section the principle of coupling phenomenon in these subgroups is discussed briefly.

2.1.2. Piezoelectricity

Piezoelectrics are characterised by the linear coupling between electrical and mechanical energy. This type of electro-mechanical coupling can only be observed in non-centrosymmetric crystals.^[1]. When a crystal develops an electric polarisation as a function of applied mechanical stress, this is called the direct piezoelectric effect. The piezoelectric tensor, d_{ijk} , relates the second rank stress tensor, σ_{jk} , to the first rank polarisation tensor, P_i , in the form of

$$P_i = d_{ijk}\sigma_{jk} \tag{2-4}$$

On the other hand, when an electric field is applied to a non-centrosymmetric crystal, strains are developed. This phenomenon is known as the converse piezoelectric effect. The strain tensor, S_{jk} , is related to the applied electric field, E_i , by

$$S_{jk} = d_{ijk}E_i \tag{2-5}$$

It is worth noting that the values of d_{ijk} for the direct and converse piezoelectric effect are equal.

Pyroelectricity is a phenomenon that arises from the temperature dependence of the spontaneous polarisation of polar dielectrics. Pyroelectric materials are also piezoelectric, the strain arising from thermal expansion will lead to the development of a surface charge. However, this contribution is small (<10%) compare to true pyroelectricity.

2.1.3. Ferroelectricity

Ferroelectric crystals exhibit a spontaneous polarisation (P_s) that can be switched by applying a sufficiently strong electric field. This spontaneous polarisation is a result of the positioning of the cations and anions within the unit cell of the crystal.

Ferroelectric materials of ABO₃ perovskite structure the most practically relevant polar materials (i.e. exhibit P_s), such as barium titanate BaTiO₃ (BT). Using the example of BT, structural aspects of perovskite polar dielectrics are summarized below.

Upon heating, most ferroelectrics pass through a transition point (the Curie temperature, T_c), above which they revert to a non-polar state. On the unit cell level this transition implies a change of space group; i.e. phase transformation. The high-temperature (above 130 °C) polymorph of BT is cubic (paraelectric, PE) and the structure can be visualized as the large cation Ba²⁺ on the A-site, the smaller cation Ti⁴⁺ on the B-site, and anions O²⁻ in the face centres. Below T_c (<130 °C) the crystal structure is tetragonal (Figure 2-2) phase with a unique polar axis along the *c* direction; thus the materials (BT) develop spontaneous polarisation along *c*-axis.



Figure 2-2 Crystal structure of tetragonal phase BaTiO₃.

As a consequence of this phase transformation from cubic to tetragonal, a homogeneous area in the crystal with uniform orientation of the polarisation axis is formed, known as domain. Additionally the development of spontaneous polarisation in the ferroelectric phase is accompanied by an apparent surface charge density and an associated depolarizing field E_D . The spontaneous polarisation direction and depolarising field are orientated in opposite directions. The electrostatic energy associated with E_D in the ferroelectric crystal is minimized by a process called twinning. In this twinning process the crystal is fragmented into many oppositely polarised regions which are known as 180° domains. Additionally, non-180° domains also develop if the crystal experiences mechanical stress during phase transformation. This process is schematically represented as in Figure 2-3



Figure 2-3 Representation of the formation of 180° and 90° ferroelectric domains in a tetragonal perovskite ferroelectric material. Distortion in the tetragonal phase has been exaggerated for better visualisation. Electrostatic energy due to the depolarisation field (*E*_D) is minimised by the formation of domain walls. (Ref. [20]). Micrograph of a BT ceramic showing domain structure.^[21]

Thus, the process of forming domains/domain walls depends on the combined effect of electrical and elastic boundary conditions during the ferroelectric phase transformation. As a consequence of these boundary conditions at each grain, the ferroelectric grains in polycrystals exhibit a multidomain state, i.e. this process leads to a complex domain structure with 180° and non-180° domains in polycrystalline ceramics.

In the multidomain state, spontaneously polarised dipoles are randomly orientated and no macroscopic polarisation is observed. These randomly orientated dipoles can be oriented by external applied field of a certain threshold value (E_{pol}), known as "poling" of ferroelectric materials. During the poling process domains can rearrange themselves (to those directions allowed by the specific crystallographic symmetry) within each grain along the direction of applied electric field. The signature of poling on ferroelectric materials can be visualised by electric-field-induced polarisation and/or strain loops. A schematic of the polarisation and strain loop for a typical ferroelectric material is shown in Figure 2-4.



Figure 2-4 Illustration of the effect of reorientation of domains under applied electric field on the polarisation and strain of a typical ferroelectric ceramic (after Ref. [19]). Movement of domains and polarisation orientation is shown for different states of applied field by A (initial random domain state), B (initiation of domain wall movement), C (orientated along field direction), D (remnant state), E (no net polarisation), and F (orientated along field direction, reverse field).

The characteristics of polarisation and/or strain loops can be summarised as:

State **A**: Initial state of ferroelectric material, randomly oriented domains without a net polarisation or field induced strain.

State **B**: Upon application of small electric fields the domain walls tend to vibrate. Above a certain threshold field, translation of domain walls sets in and polarisation increases linearly. In this region, domain wall movement is considered as reversible. With further increases in electric field, a large fraction of unfavourably orientated domains start to realign to the electric field direction. This stage gives rapid increase in polarisation.

State **C**: At this stage maximum possible alignment for domains is achieved. This region is known as the saturation region.

State **D**: With decreasing electric field the polarisation (or strain) value decreases to some degree and reaches remnant state P_{rem} at zero field.

State **E**: With further decrease in the applied field ($-E_c$) a reversal of polarisation occurs. At a certain negative field the polarisation becomes zero. At this state there is no net polarisation observed.

State \mathbf{F} : A further decrease of the applied field (negative bias) again a saturation region achieved like state \mathbf{C} but in opposite orientation of domains.

Generally, these macroscopic polarisation and strain loops are used to measure the fundamental parameters of piezoelectric and ferroelectric performances, i.e. figure of merit for a ferroelectric/piezoelectric ceramic can be estimated from these loops. Recalling Figure 2-4 the following parameters can be identified:

 E_{pol} : The poling field, a threshold value in polarisation hysteresis loops.

 P_{max} : Polarisation value achieved at maximum electric field in a *P*-*E* hysteresis loop.

 P_{rem} : Polarisation value measured after field removal; a larger the P_{rem} value generally related to a higher small-signal (zero-field) piezoelectric coefficient (d_{33}).

 S_{max} : Strain value achieved at the maximum applied electric field.

 S_{rem} : Strain value after removal of applied electric field.

 S_{usable} : Usable strain measured by subtracting remnant strain form maximum strain, i.e. $S_{\text{usable}} = S_{\text{max}} - S_{\text{rem}}$ important parameter for actuator application

 d_{33}^* : Large-signal piezoelectric coefficient is characterised by $S_{\text{max}}/E_{\text{max}}$; where *E* generally unipolar.

2.1.4. Relaxor ferroelectricity

Relaxor (RE) ferroelectricity is a closely related phenomenon to ferroelectricity. Generally, relaxor ferroelectricity arises from compositionally induced disorder.^[22] Relaxor ferroelectrics also exhibit large electro-mechanical coupling like ferroelectrics, but both groups of ferroelectrics are inherently different in several aspects that are summarized in Figure 2-5



Figure 2-5 Contrasting behaviour of ferroelectrics (FE) and relaxor ferroelectrics (RE) (a) relative permittivity as a function of temperature, (b) polarisation response, and (c) strain response as a function of applied electric field.

The first difference can be identified by the dielectric permittivity behaviour with temperature. Normal (or classical) ferroelectrics exhibit a sharp maximum of the relative permittivity at a temperature (T_c). On the contrary, relaxor ferroelectrics prominently exhibit a broad maximum and a significant frequency dispersion of the relative permittivity. Generally, the temperature of the maximum dielectric constant

 $(T_{\rm m})$ increases and its magnitude decreases with increasing frequency. This is one of the most significant differences or criteria to distinguish relaxor ferroelectrics from normal ferroelectrics. Polarisation and strain hysteresis loops of these two systems show distinct behaviour. Normal ferroelectrics exhibit a rectangular type *P-E* loop with significant $P_{\rm rem}$ and large $E_{\rm c}$ whereas, relaxor shows a slim *P-E* loop with negligible $P_{\rm rem}$ and small $E_{\rm c}$. In the case of strain response, a FE loop can be distinguished as butterfly loop whereas RE loops are like sprout shaped. One thing that may be noticed from the strain loop of RE materials is that the reversibility of strain behaviour with no remnant strain.

An unambiguous explanation of the mechanism behind relaxor ferroelectricity has not been established yet.^[23-27] Nevertheless it is believed that in relaxor materials the longrange dipolar interactions are disturbed by the translational lattice inhomogeneities, defects or segregation of chemical order-disorder. Consequently micropolar regions (clusters) with typical diameters of approximately 10 nm to 100 nm^[18] are formed in the materials. Because of these micropolar regions, external perturbation (mechanical stress or electric field) can induce a ferroelectric state in relaxor materials. Interestingly, this metastable phase (micropolar regions) exists for large temperature range; thus relaxor ferroelectrics can be used in wide operational temperature range.

2.2. Lead-free electro-ceramic systems

2.2.1. Lead-free systems

This section includes a brief overview of common lead-free piezoelectric materials which can be used as compositions in more complex materials systems. In particular, the compositions described here, are of most interest to the current thesis. Many other compositional variations exist with potentially promising properties. A good review of all these systems can be found elsewhere.^[28] The particular systems of interest here are,

- i. Bismuth Sodium Titanate (BNT) and Bismuth Potassium Titanate (BKT)
- ii. Sodium Potassium Niobate (NKN)
- iii. Bismuth Ferrite (BFO)

These basic composition materials which are often doped to enhance their properties are firstly introduced and discussed. More complex pseudo-binary and pseudo-ternary systems are then discussed. And finally discussion on the recently emerging ceramic/ceramic composite materials (CCM) and core-shell type structure for electric-field-induced strain enhancement included.

2.2.1.1. Bismuth sodium titanate $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) and bismuth potassium titanate $Bi_{1/2}K_{1/2}TiO_3$ (BKT)

In the 1960s Smolenskii *et al.*^[29] first reported the Bi_{1/2}Na_{1/2}TiO₃ (BNT) material. This material is considered to be a promising lead-free material because of the large remnant polarisation, $P_{\rm rem} = 38 \ \mu \text{C} \text{ cm}^{-2}$ and high Curie temperature ($T_{\rm c} = 320 \ ^{\circ}\text{C}$).^[30] The dielectric properties also display an interesting anomaly wherein a low temperature phase transition at 200 $^{\circ}\text{C}$ marks the transition from ferroelectric to antiferroelectric.^[31] However, because of the high coercive field, $E_{\rm c} = 7.3 \ \text{kV} \ \text{mm}^{-1}$, and relatively large conductivity, pure BNT is difficult to be poled and might not be a commercially useful piezoelectric material in its pure state. The issue of high conductivity which was attributed to volatilisation of Bi ions during sintering can be solved by the addition of excess bismuth.^[32] Research has been conducted to eliminate some of the drawbacks of pure BNT materials by the doping method. For example, Yi *et al.*^[33] was able to improve the piezoelectric constant and coupling coefficient of BNT by doping with La. Li *et al.*^[34] has used co-doping of K⁺ and Li⁺ on the Na⁺ site to increase the piezoelectric coefficient (d_{33}) and coupling factor (k_p) of BNT to 146 pC N⁻¹ and 36%, respectively, and reduce the coercive field to 3.7 kV mm⁻¹ while maintaining a high depolarisation temperature (T_d) . These authors have also fabricated a lead-free middle frequency filter with performance comparable to a Pb-based filter.^[34]

At room temperature, the structure of BNT can be identified as rhombohedral R3c space group and exhibit three different phases at different temperatures.^[35] In other words, BNT undergoes a sequence of phase transitions form a high temperature cubic ($Pm\overline{3}m$) phase to a tetragonal P4bm phase at 540 °C, and diffuse phase transition (DPT) from P4bm to a rhombohedral R3c phase between 200 °C and 320 °C. Although the high temperature phases are confirmed to be tetragonal and cubic but the room temperature phase is not conclusive yet. Recent high resolution x-ray diffraction studies on BNT by Aksel *et al.*^[36] showed that the room temperature structure of BNT is monoclinic *C*c rather than rhombohedral *R3c*. An electron diffraction study by Dorcet *et al.*^[37] and a neutron diffraction study by Lui *et al.*^[38] also showed that at room temperature BNT is not purely rhombohedral. These discrepancies in the structure of pure BNT are likely due to the complex nature of the structure over different length scales; which is highlighted by chemical ordering of the Bi/Na cations, displacements of cations and difference in local and average structure.^[39, 40]

 $Bi_{1/2}K_{1/2}TiO_3$ (BKT) was also first reported by Smolenskii *et al.*^[29] in the 1960s. At room temperature BKT is tetragonal with a depolarisation temperature of 270 °C.^[32]

Practical application of this material is limited due to the poor sintered densities achieved. Various sintering aids have been tried to improve the sintered density of BKT. It was reported^[41] that the electro-mechanical properties of BKT ceramics can be improved with the addition of excess bismuth oxide.

2.2.1.2. Sodium Potassium Niobate $K_{1/2}Na_{1/2}NbO_3$ (NKN)

 $K_{1/2}Na_{1/2}NbO_3$ (NKN) is solid solution composed of equivalent ratios of NaNbO₃ and KNbO₃; it is widely considered as one of the most promising alternatives to the conventional lead-based piezoelectric materials. NKN compositions exhibit a morphotropic phase boundary (MPB) between two orthorhombic phases where KNbO₃ is ferroelectric and NaNbO₃ is antiferroelectric.^[11] The piezoelectric coefficient for NKN is in the range of 80-160 pC/N and exhibits the maximum around 53 mol% NaNbO₃ composition.^[42] Fabrication of NKN ceramics is problematic due to the stability issue of NKN phase at high temperature. Above 1140 °C NKN phase is unstable and volatility of alkali components makes it difficult to control the stoichiometry of the composition. This limitation in sintering temperature makes it difficult to obtain high sintered density.^[11] However, the report of Saito *et al.*^[43] in 2004 has triggered the research in NKN with much interest. They reported a large-signal d_{33}^* of 750 pm V⁻¹ in NKN and is comparable to actuator-grade PZT. The high d_{33}^* was a combined effect of dopants and crystallographic texture.

2.2.1.3. Bismuth Ferrite BiFeO₃ (BFO)

Bismuth ferrite, BiFeO₃ (BFO), an interesting material with simultaneous ferromagnetic and ferroelectric properties, is a promising candidate to replace lead-based piezoelectrics in high temperature applications. The room temperature crystal structure of BFO is rhombohedral R3c. The spontaneous polarisation of rhombohedral structure
at room temperature is mostly attributed to the bismuth on the perovskite A-site, while magnetisation is attributed to the iron on the B-site.^[44] The remnant polarisation of BFO is 100 μ C cm⁻² along the polar [111] direction which is the largest among all known perovskite ferroelectrics. But the application in ferroelectric memory devices is limited due to the relatively high conductivity and fatigue tendency. On the other hand their piezoelectric properties are limited by the difficulty in poling (*E*_c approximately 7 kV mm⁻¹).^[45]

Thin films of BFO are attractive for micro- and nanoelectronic applications. Research on thin film form of BFO was triggered by several reports.^[46-48] These reports showed that epitaxially grown thin films of BFO can exhibit P_s almost an order of magnitude higher than bulk BFO. It was also established that the enhanced properties of thin film BFO is related to the change in crystallographic symmetry of BFO due to the lattice mismatch with the substrate. In other words, depending on the substrate lattice constant, the crystallographic symmetry of rhombohedral BFO can be tuned. This provides an interesting degree of freedom to tune the coupling response in BFO. While thin films are important for different applications, a significant fraction of existing piezoelectric devices rely on piezoelectric materials in the form of bulk ceramics. Significant effort has been made to improve the properties of bulk BFO by chemical modifications.^[49-57] However, the electro-mechanical properties are still inferior to thin film BFO. Therefore, an understanding of structural contributions to the field-induced strain in bulk BFO ceramics at microscopic level is essential for future development. Electricfield-induced strain response in pure bulk BFO ceramic has not been reported extensively. Rojac *et al.*^[58] have reported a large bipolar strain of 0.36% (peak-to-peak value) in bulk BFO ceramic at electric field amplitudes of 14 kV mm⁻¹ applied at 0.1

Hz. This large strain value is comparable to PZT-based piezoelectric ceramics. Recently Rojac *et al.*^[59] has reported conductive domain walls and their effects on piezoelectric properties of bulk BFO ceramics. It was highlighted that charged domain walls can interfere with the dynamics of domain walls within the grains and consequently affect the observed macroscopic response. The structural aspects of bulk BFO ceramics with applied electric field is examined in this thesis (Chapter 6) using *in situ* high-energy x-ray diffraction.

2.2.1.4. Pseudo-binary and pseudo-ternary Systems

A useful approach for achieving high-performance lead-free piezoelectric materials is compositional engineering. In this approach, the optimised composition of the material is achieved in the range of structural instability such as polymorphic phase transition (PPT) or morphotropic phase boundary (MPB). Based on compositional engineering, several lead-free pseudo-binary and -ternary solid solution materials are introduced in this section.

a. BNT-based systems

The first report of pseudo-binary BNT-based system modified with barium titanate BaTiO₃ (BT), (1-x)BNT-*x*BT was published by Takenaka *et al.*^[60] They reported an MPB between 6 to 7 mol% of BT by measuring dielectric and piezoelectric properties. According to x-ray diffraction, at the MPB a rhombohedral and a tetragonal phase coexist in this composition. They also proposed a phase diagram for the BNT-*x*BT system involving ferroelectric, antiferroelectric and paraelectric phases. However a report by Ranjan *et al.*^[61] suggested that the crystallographic structure is nearly cubic. Later Daniels *et al.*^[62] using *in situ* x-ray and Simons *et al.*^[63] by *in-situ* neutron diffraction showed that the MPB composition of BNT-*x*BT is pseudo-cubic that undergoes an electric-field-induce phase transformation to tetragonal or mixed phase tetragonalrhombohedral symmetry.

The improved electro-mechanical properties and unusual phase transformation behaviour of BNT-xBT composition has interested researchers a great deal to gain further insight into this material.

In solid solution of BNT-*x*BKT, an MPB is formed between rhombohedral (BNT-rich) and tetragonal (BKT-rich) structures. In the region of 16-22% BKT^[1] the coupling factor and piezoelectric coefficient were found to be improved. This composition has relatively higher depolarisation temperature (174 °C) than the BNT-*x*BT system. This system exhibits frequency dispersion similar to the parent BNT system.

b. BKT-based systems

BKT-based binary compositions, including compositions such as BKT-BT are tetragonal phase ferroelectric material. They exhibit enhanced piezoelectric properties and higher Curie temperature (T_c) than pure BT. The solid solution remains single phase in the entire compositional range.^[42] The maximum d_{33} value for this BKT based bulk ceramic is 100 pC N⁻¹ though their thermal stability is good in comparison to other lead-free systems.

c. BNT-based pseudo-ternary Systems

Reports of BNT-based ternary systems by Zhang *et al.*^[64-66] has sparked interest in this type of compositional modification. In this system, by adding a small fraction of NKN in the MPB composition of BNT-*x*BT, Zhang *et al.* showed large strain under high electric field. This composition showed large-signal piezoelectric constant (d_{33}^*) of approximately 550 pm V⁻¹ at 8 kV mm⁻¹ field, greater than achieved in PZT. This field-

induced strain response remains stable with temperature^[67] and cyclic fatigue^[68]. Several other BNT-based compositions with large strain have been reported by different authors.^[69-71] Interestingly, among all these compositions the strain is generated via an electric-field-induced reversible transition between pseudo-cubic relaxor and non-cubic ferroelectric phases at relatively high fields ($\geq 4 \text{ kV mm}^{-1}$).^[62, 72-74] The origin of electric-field-induced strain in this material is reviewed and discussed in details in Chapter 7.

2.2.1.5. Ceramic/ceramic composite (CCM) materials

Although the ceramic/ceramic composite approach to induce desired properties dates back to1980,^[75] this is a comparatively new approach for the modification of fieldinduced strain^[76] in lead-free piezoelectric ceramics. Shrout *et al.*^[75] demonstrated the ceramic/ceramic composite approach by designing a material that consist alternating layers of ferroelectric (FE) and antiferroelectric (AFE) to exhibit extended polarisation effect. Dausch et al.^[77, 78] with studies on PLZT (La-doped PZT) based multilayer composite thin films pointed out that the presence of a FE phase in an AFE matrix effectively reduced the electric field required for AFE-to-FE transition. They also proposed that the change in electric field amplitude can be estimated as a function of volume fraction of FE phase by a two-serially-connected capacitor model. Later, the ceramic/ceramic composite approach has been extensively utilised to tune targeted properties such as temperature stability of dielectric permittivity,^[79, 80] dielectric adjustability.^[81] A recent report by Lee et al.^[76] on the ceramic/ceramic composite approach in lead-free piezoelectric materials has sparked interest in the research community to modify strain property in lead-free piezoelectrics. They reported a ceramic/ceramic composite material (CCM) in which a ferroelectrically (FE) active Bi_{1/2}Na_{1/2}TiO₃ was incorporated in a relaxor (RE) phased Bi_{1/2}(Na_{3/4}K_{1/4})_{1/2}TiO₃-BiAlO₃. By forming a compositionally non-homogeneous phase structure (relaxor and

ferroelectric) at the grain length scale, they showed that the actuating field can be significantly reduced with the addition of 20 vol% of ferroelectric grains in a matrix of relaxor grains. Later, Groh *et al.*^[82, 83] also demonstrated the ceramic/ceramic composite effect in other BNT-based lead-free piezoelectrics by modelling and electrical properties measurements. However, an understanding of the origin of the strain at grain length scales for CCM materials is lacking. Detailed understanding of strain responses in CCM at grain length scales will be beneficial for the future development of lead-free piezoelectrics for actuator applications based on the ceramic/ceramic composite approach. In this thesis, (Chapter 4) it has been shown by *in situ* high-energy x-ray diffraction that the macroscopic strain response of matrix phase (in a CCM) can be tuned by the use of particulate materials.

2.2.1.6. Core-shell type microstructure

Core-shell type microstructure has been found to exhibit enhanced properties for dielectric ceramics^[84] and also piezoelectric ceramics.^[85] These type of core-shell structures were formed by addition of more complex compositions (rather than doping with atoms) such as $CdBi_2Nb_2O_9^{[84]}$ and $CaZrO_3^{[85]}$ in $BaTiO_3$ and NKN, respectively. Depending on the reaction kinetics of the sintering process, the microstructure exhibits a grain core-shell structure. The strain magnitude (large-signal d_{33}^*) of $CaZrO_3$ modified core-shell structured NKN was found to be approximately double than the commercially used PZT. This improved strain response in $CaZrO_3$ modified NKN has been attributed to the structural difference in the core and shell regions.

Wada *et al.*^[86, 87] has introduced another method of preparing core-shell structure. In this approach BT particle compacts were used as a substrate to grow epitaxial KN by liquid phase reaction in the regions between the particles (Figure 2-6).



Figure 2-6 Bright field (BF) image and chemical composition distribution of core-shell BT-KN ceramic (after Ref. [88]). The core region consists of Ba and Ti whereas the shell region consists of K and Nb.

Later, a comparative study^[89, 90] of field induced strain response in core-shell structured BT-KN and solid solution BT-KN (prepared by conventional mixed oxide method) by the same authors demonstrated promising property enhancements using this approach. Despite the relatively low sintered density of the core-shell BT-KN (relative density ~70%) compared to conventionally prepared solid solution BT-KN (relative density ~95%); the former showed an approximately three times larger strain response.^[89, 90] The increased response has been proposed^[89] to be associated with the interfacial boundary between core BT and shell KN, and enhanced polarisation rotation, although no direct experimental evidence exists. An attempt has been made in this thesis (Chapter 5) to highlight the strain response in this core-shell BT-KN material. This study showed that materials with the core-shell structure can exhibit unique domain switching behaviour which cannot occur in conventional polycrystalline ceramics. A new class of high strain materials can be developed by utilising enhanced reversible non-180° ferroelectric domain switching as observed in core-shell BT-KN in this thesis.

2.2.2. Diffraction methods for studying structure property relationships in electro-ceramics

X-ray and neutron diffraction studies of piezoelectric materials are a powerful experimental technique to gain information about intrinsic (lattice strain) and extrinsic (domain switching and phase transformations) contributions to the electric-fieldinduced strain. With these diffraction techniques, crystallographic structure, phase evolution, crystallographic texture and lattice strain can be studied.^[91]. Diffraction studies are invaluable in a sense that these are non-destructive methods and studies can be performed on bulk polycrystals, thin films, and single crystals. Wide varieties of diffraction instruments and characterisation approaches are now available but selection of the most appropriate source and instrument are very important. The ability of x-ray diffraction to probe matter on multiple length scales can be helpful for better understanding the way functional materials behave. In this thesis, *in situ* high-energy x-ray diffraction has been used to analyse field-induced structural variations in lead-free piezoelectrics.

Figure 2-7 represents the effect of applied electric field on diffraction patterns of a piezoelectric material. Lattice distortion due to the external field can be examined from the change in peak position (2θ) whereas domain texture can be analysed from relative changes in peak intensities. For instance, the change in intensities in (001)/(100) and (hhh)/(hh-h) can highlight field-induced domain texture variations in tetragonal and rhombohedral system, respectively. Electric-field-induced phase transformation can also be analysed by observing the change/evolution in diffraction patterns.



Figure 2-7 Electric-field-induced structural change in a piezoelectric material. Intrinsic lattice strain (Δd) can be estimated from the shift in peak position ($\Delta 2\theta$). Relative changes in intensities (e.g. 00*l*/*l*00 in a tetragonal system) highlight the change in domain volume fractions (domain texture). Development and/or loss of additional peaks can highlight an electric-field-induced phase transformation (e.g., splitting of 200 peak into 002 and 200 corresponds to cubic-tetragonal transformation).

These field-induced changes can be observed by recording diffraction patterns on an asprepared sample and after applying an external field, i.e. *ex situ* measurements. However, *ex situ* measurements cannot highlight intermediate steps which can provide information such as the critical field for structural change or dynamics of domain wall motion. Additionally, transient states which only exist under field would not be observed. In other words, *in situ* measurements of piezoelectric materials under field on conditions can provide useful insight for structural change in real environments. Several authors^[92-99] have demonstrated previously that *in situ* XRD and/or neutron diffraction methods can provide a powerful and direct means of quantifying the intrinsic and extrinsic contributions to the macroscopic properties of piezoelectric materials.

Although *in situ* measurements can be done using laboratory-based x-ray diffraction instruments,^[100,101] information is limited due to the experimental geometry. This geometrical constraint arises as a conventional x-ray source does not possess sufficient x-ray energy to penetrate most of the bulk materials of interest here, and is hence limited to reflection geometry. For instance, the penetration depth of a conventional x-ray source (Cu *Ka*) into PZT is in the range of 2 μ m. While diffraction measurements in reflection geometry can provide useful insight into the magnitude of the lattice strain for certain crystallographic orientations (those ferroelectric domains in which the (*111*), (*001*), or (*110*) planes lie parallel to the specimen surface), they do not provide full access to all scattering vector orientations relative to an applied field vector. This represents a substantial drawback, given that the macroscopic piezoelectric domain orientations present in the material. Thus a high-energy x-ray source with large penetration depth (typically several millimetres in PZT) into the sample is necessary to quantify the microscopic origin of strain response in piezoelectric ceramics.

The x-ray attenuation length is one of the most important parameters to be considered during the investigation of bulk samples. The attenuation length τ_0 can be estimated from the mass absorption coefficient μ which is listed in Ref. [102] by

40

$$\tau_0 = \frac{1}{\mu.\rho} \tag{2-6}$$

where ρ is the density of the material.



Figure 2-8 Transmission in different materials of 1 mm thickness as a function of x-ray energy. X-ray energies greater than 60 keV can allow large fractions of bulk materials to be probed.

Figure 2-8 shows calculated (using Equation 2-6) transmission of x-ray energies in different materials (i.e. materials have been studied in this thesis) of 1 mm thickness. Generally x-ray energies > $30 \text{ keV}^{[103]}$ can be regarded as high-energy x-rays. As can be seen in Figure 2-8, below these energies the transmission through a 1 mm section of the materials of interest is very low. However, as the energies exceed 60 keV, sufficient beam transmission is achieved to perform x-ray diffraction experiments in transmission (i.e. Debye-Scherrer) geometry.

Initially, high-energy x-rays were obtained from radioactive sources like ¹⁹⁷Au, ¹³⁷Cs or ¹⁹²Ir with nuclear γ radiation at 412, 660 and 317 keV, respectively.^[103] However, these nuclear sources are difficult to handle (maintain). Synchrotron sources are the most suitable source of high energy x-rays. Originally, synchrotrons were used in the field of particle physics to study collisions between subatomic particles with high energies. However, when charged particles are accelerated radially, they emit an electromagnetic radiation, called synchrotron radiation (light). Synchrotron radiation was named after its discovery in a General Electric Synchrotron accelerator built in 1946. Exceptional properties of synchrotron radiation can be summarised as:

- i. Broad energy spectrum
- ii. High flux (high photon intensity)
- iii. High brilliance

High brilliance with x-ray energies above 100 keV is obtained at synchrotron radiation sources with the first developments at the DORIS and later the PETRA storage rings at HASYLAB, Germany. Later, the European Synchrotron Radiation Facility (ESRF) introduced a dedicated high-energy x-ray beamline, ID15. Another three major synchrotron radiation sources with high-energy beamlines are the Advanced Photon Source (USA), Spring-8 (Japan), and Diamond Light Source (United Kingdom). With the advent of 3rd generation synchrotron sources, and associated insertion devices, it was possible to produce high-intensity beams of x-ray energies above 60 keV.

A synchrotron radiation beamline with a large area 2D detector^[104] is ideal for studying field-induced structural changes in bulk ceramic materials. At this high energy, a large area detector placed behind a sample in transmission mode enables simple experimental setups with fast data collection. The combination of high energy x-rays and a large area

detector also facilitates recording a large number of entire Debye-Scherrer rings in a comparatively small 2θ range. The scattering angle 2θ is related through Bragg's law to lattice spacing of the diffracting planes

$$n\lambda = 2d\sin\theta \tag{2-7}$$

where λ is the x-ray wavelength, *d* is the lattice spacing, and θ is the Bragg angle. This implies that the Bragg condition with the same *d*-spacing and 2θ angle can be satisfied by various x-ray wavelengths (i.e. x-ray energies). Shorter wavelength (i.e. higher x-ray energies) facilitates the probing of finer *d*-spacing within a relatively small 2θ region. For example, 0.8 Å *d*-spacing can be probed within 10° diffraction angle (2θ) for x-ray wavelength of 0.14618 Å. Thus, diffraction information from the sample can be obtained in a smaller 2θ region. In other words, a large number of entire Debye-Scherrer rings can be collected using one flat panel large area detector.

To summarise the advantages of using high energy x-rays and a large area detector:

- i. Penetration depth into the matter that allows probing bulk material.
- ii. Simple diffraction setup for *in situ* experiment.
- iii. Diffraction in forward direction for easy record with a large area detector.
- iv. Full scattering information can be recorded in small 2θ range.

3. Experimental methods

In this chapter, a brief overview of the diffraction setup and data processing steps are discussed. Additionally, the experimental setup for macroscopic electrical property measurement is also outlined.

3.1. Diffraction experiments

In situ high-energy x-ray diffraction experiments were carried out at beamline I12 JEEP, Diamond light source, United Kingdom and ID15B of the European Synchrotron Radiation Facility (ESRF). The basic experimental setup was similar for both beamlines. The data collection strategy was also similar. The major difference was the x-ray energy of the monochromatic beam that was calibrated as 84.82 keV ($\lambda = 0.146$ Å) and 87.12 keV ($\lambda = 0.142$ Å) for I12 and ID15B, respectively. A consistent beam of dimensions 150 μ m \times 150 μ m was used on the samples for all diffraction measurements. For the diffraction patterns to be measured *in situ*, samples were placed in a specifically designed electric field chamber where the applied electric field is perpendicular to the x-ray beam direction. The maximum electrical load of the sample cell is limited by the electric feedthroughs (currently capable of \pm 10 kV bias each). Therefore, depending on the sample thickness a maximum field beyond ± 20 kV mm⁻¹ can readily be applied to the sample.^[105] The sample chamber was filled with electrically inert liquid, i.e. silicon oil to apply high fields without the risk of sample breakdown. In the following sections, the experimental setup and data processing steps are outlined.

3.1.1. Experimental setup

The combination of high x-ray energies and a large area 2D (e.g., Pixium RF 4343 Flat panel) detector has a unique advantage in conducting *in situ* measurements in

transmission geometry. Full orientation dependent data with respect to scattering vector (**q**) angle to applied electric field vector (**E**) can be collected in a single diffraction image. A schematic of the experimental setup is shown in Figure 3-1. To calibrate detector parameters, including sample to detector distance, beam centre and tilts diffraction patterns were collected of standard cerium dioxide (NIST standard-CeO₂) powder using the identical experimental setup.



Figure 3-1 Schematic of the experimental geometry and diffraction pattern recorded with large area 2D detector. Inset shows a typical diffraction pattern from the area detector after radial integration.

3.1.2. Data processing

Using the Fit2D^[106] software, detector parameters were calibrated using the diffraction pattern of standard ceria powder. The information from calibrated data was used for integrating the diffraction images from samples. The diffraction images were sliced into 36 azimuthal sections, each covering an angular range of 10°. In the next step radial integration with Fit2D software produced 36 one-dimensional intensity versus 2θ plots.

The effect of applied field can be qualitatively analysed by plotting 2θ -intensity graphs, an example of which is shown in Figure 3-2. Figure 3-2a represents a change in relative intensities as a function of angle (ψ) of the electric field vector (**E**) to the scattering vector (**q**). It should be mentioned here that the ψ angle 0° and 90° represents diffraction information for **E** parallel and perpendicular to **q**, respectively. Figure 3-2b shows the effect of applied electric field on (200) type reflections along the field direction ($\psi = 0^\circ$). This data processing procedure enabled the quantification of full orientation dependence of lattice strain and domain switching strain.



Figure 3-2 (200) diffraction peak as function of (a) angle to the applied field vector (ψ), and (b) electric field (E).

To quantify electric-field-induced lattice strain and domain texture from the diffraction data, peak fitting procedures have been utilised extensively in this thesis. For example, in tetragonal or rhombohedrally distorted materials, the domain texture can be quantified using (200) or (111) type reflections. Figure 3-3 shows fitting of the (00l)-type diffraction peak in a tetragonal phase material.



Figure 3-3 The fit for the (002)-type diffraction peaks for a tetragonal phase material.

The peak positions (in 2θ), unit area peak intensity, and full width at half maxima (FWHM) have been extracted from the fitting scheme for further analysis (Chapter 6 and Chapter 7).

Rietveld refinement of diffraction patterns from as-processed samples (Chapter 6 and Chapter 7) has been conducted using the TOPAS^[107] structural refinement package.

3.2. Macroscopic property measurement

Macroscopic electrical properties (polarisation and strain hysteresis loops) (Chapter 4) were measured using a Sawyer-Tower setup at the Technische Universität Darmstadt, Germany. The setup consists of a high voltage amplifier, function generator, oscilloscope, strain sensor, capacitor, Measurement Bridge and impedance (Figure 3-4). Details of the setup can be found elsewhere.^[108]



Figure 3-4 Schematic block diagram of Sawyer-Tower setup for polarisation and strain measurements.(After Ref. [108])

4. Electric-field-induced strain in ceramic/ceramic composite

The results presented in this chapter have been published in the *Journal of Applied Physics* (2014, **115**, 124108). A copy of this paper is included in Appendix A. A major component of the ceramic processing procedure was conducted at the laboratory of Prof. Jürgen Rödel, Technische Universität Darmstadt. Dr. Claudia Groh and Dr. Wook Jo assisted with the ceramic processing.

<u>Abstract</u>

The electric-field-induced strain response mechanism in a polycrystalline ceramic/ceramic composite of relaxor (RE) and ferroelectric (FE) materials has been studied using *in situ* high-energy x-ray diffraction. The addition of ferroelectric phase material in the relaxor matrix has produced a system where a small volume fraction behaves independently of the bulk under an applied electric field. Inter- and intra-grain models of the strain mechanism in the composite material consistent with the diffraction data have been proposed. The results show that such ceramic/ceramic composite microstructure has the potential for tailoring properties of future piezoelectric materials over a wider range than is possible in uniform compositions.

4.1. Introduction

Considering the environmental concerns over the use of PZT and limitations in high temperature performance, research into lead-free electro-ceramics has increased dramatically in the last decade.^[7] New synthesis routes and information gained from detailed structural studies of existing high-performance lead-free compositions are leading to the development of new compositions of interest. From extensive knowledge of the PZT system, a common approach for the development of lead-free compositions is to search for systems with a morphotropic phase boundary (MPB). Promising lead-

free piezoelectrics include compositions based on sodium potassium niobate Na₍₁₋ $_{x}K_{x}NbO_{3}$ (NKN) and bismuth sodium titanate Bi_{1/2}Na_{1/2}TiO₃ (BNT).^[31, 60, 109-112] In 2007 Zhang et al.^[66] reported a new pseudo-ternary composition, replacing a small fraction of BNT with NKN from the Bi_{1/2}Na_{1/2}TiO₃-BaTiO₃ (BNT-BT) system, which showed large electric-field-induced strain values (0.45% at 8 kV mm⁻¹). This fieldinduced strain response remains stable against temperature^[67] and cyclic fatigue.^[68] While the strain response of this material is attractive for actuator applications, it is limited in device implementation due to the high actuating field ($\geq 6 \text{ kV mm}^{-1}$) and significant hysteresis. Several other BNT-based compositions with large strain have been reported by different authors.^[69-71] Interestingly, among all these compositions the strain is generated via an electric-field-induced reversible transition between pseudocubic relaxor and non-cubic ferroelectric phases at relatively high fields ($\geq 4 \text{ kV mm}^-$ ¹).^[62, 72-74] Further improvement of actuator properties with such compositions will require the lowering of the actuating field. One possible approach for achieving this is to modify the microstructure of these materials using a ceramic/ceramic composite method

As discussed in Section 2.2.1.5., producing ceramic/ceramic composites with a controlled microstructure in order to tailor the electrical properties (such as dielectric, piezoelectric and pyroelectric) in electro-ceramics is a well-known approach.^[79, 113, 114] However, it has not been applied to modify the properties of large strain BNT-based lead-free materials until recently. Several studies^[76, 82, 83, 86, 87, 89] have introduced ceramic/ceramic composite systems as a method to tune the electrical and electro-mechanical properties in lead-free ferroelectrics. For instance, Lee *et al.*^[76] have focused on the minimisation of the actuating field of large strain BNT materials by forming a

compositionally non-homogeneous phase structure (relaxor and ferroelectric) at the grain length scale. The improved properties of the ceramic/ceramic composite material have been explained by a series capacitor model where polarisation coupling throughout the material reduces the required actuating fields.^[76, 82] These studies show that the ceramic/ceramic composite structure is a promising path for the development of future lead-free electro-mechanical materials.

The development of new lead-free ceramic/ceramic composites for industrial applications will benefit from a detailed understanding of the underlying strain generation mechanisms. An attempt has been made in this chapter to highlight the strain generation mechanism in 0.92BNT-0.06BT-0.02NKN (BNT-BT-2NKN) and 0.93BNT-0.07BT (BNT-7BT) ceramic/ceramic composite materials^[82, 83] using *in situ* high-energy x-ray diffraction. The large strain BNT-BT-2KNN composition shows a reversible transition between a relaxor and ferroelectric phase with applied external electric field while BNT-7BT shows an irreversible phase transition to the ferroelectric state.^[115] In these ceramic/ceramic composite systems, the effect of volume fraction of ferroelectric (FE) phase BNT-7BT on the reversible transition of the relaxor phase BNT-BT-2NKN has been studied *in situ* using high-energy x-ray diffraction.^[62, 72] The macroscopically measured strain response has been correlated with the structural response. A microscopic strain mechanism has been proposed on the basis of diffraction studies.

4.2. Synthesis of ceramic/ceramic composite materials (CCM)

The ceramic/ceramic composite materials were prepared using ferroelectric (FE) $0.93(Bi_{1/2}Na_{1/2})TiO_3-0.07BaTiO_3$ (BNT-7BT) as a particulate component and relaxor (RE) $0.92(Bi_{1/2}Na_{1/2})TiO_3-0.06BaTiO_3-0.02(Na_{1/2}K_{1/2}NbO_3)$ (BNT-BT-2NKN) as the

matrix component. Six different compositions have been prepared by varying the volume fraction of FE (namely, 0FE, 10FE, 20FE, 30FE, 50FE and 100FE where 0FE represent pure matrix RE phase and 100FE represent pure FE phase). The ceramic/ceramic composite (CCM) processing was divided into two steps. In the first step, ceramic powders of RE and FE phase were synthesised separately and their macroscopic properties were characterised. In the second step, the CCM were synthesised by mixing RE and FE phase with different volume fractions of FE phase.

4.2.1. Powder and ceramic processing

4.2.1.1. RE and FE phase ceramic powders

Ceramic powders were fabricated by weighing stoichiometric amounts of the carbonates or oxides of the constituent elements. Table 4-I shows the batched powder used for ceramic fabrication. Impurity correction was done during the stoichiometry calculation by assuming the purity as 100 %. An analytical balance (Model 1702 MP8, Sartorius, Germany) was used to weigh the powders according to their stoichiometry calculation. Batch weighed powders were milled in a Nylon 6-6 milling container with a planetary ball mill (Pulverisette 5, Tritsch GmbH, Germany) for 24 h at 250 rpm. Mixed size yttria-stabilized zirconia milling balls (10 mm: 5 mm: 3 mm=1:2:2 weight ratio) were used as the grinding media and absolute ethanol was used as the milling medium.

The mixed slurry was dried in an oven at 90 °C. The dried powders were ground with an agate mortar (Carl Roth GmbH, Germany) to homogenise them. Ground powders were placed in an alumina crucible (alumina purity 99.8%) and calcined at 800 °C for 3 h in a furnace. To homogenise the particle size a second milling step was carried out for the calcined powder. The milling condition for the second milling step was the same as the first step. The dried ceramic powders were formed in disk shaped samples of 10 mm diameter with a pressing die. In the disk forming step, a Cold Isostatic Press (CIP) was used for high compaction. The compacted disk was sintered in a closed lid alumina crucible in a furnace at 1130 °C for 3 h. The sintered samples were polished to 0.8 mm thickness and electroded with Ag paint to measure electrical properties in a Sawyer-Tower setup. Figure 4-1 shows a schematic of the processing of the RE and FE phase materials.

Chemicals	Constituent element	*CAS#	Purity %	Company
Bi ₂ O ₃	Bi	1304-76-3	99.975	Alfa Aesar
TiO ₂	Ti	1317-70-0	99.600	Alfa Aesar
Na ₂ CO ₃	Na	497-19-8	99.500	Alfa Aesar
BaCO ₃	Ba	513-77-9	99.800	Alfa Aesar
K_2CO_3	K	584-08-7	99.000	Alfa Aesar
Nb ₂ O ₅	Nb	1313-96-8	99.900	Alfa Aesar

Table 4-I Chemicals used for ceramic processing

*Chemical Abstracts Service, a division of the American Chemical Society. Provides unique numerical identifier for chemical elements



Figure 4-1 Schematic of the RE and FE powder processing steps for CCM. As-prepared RE and FE phase powder was characterised by electrical property measurement of sintered disks.

4.2.1.2. Ceramic/ceramic composite materials (CCM)

RE phase and FE phases were mixed in different volume ratios. Initially the FE phase proportion was mixed as 10, 20, 30 and 50 vol %. Different milling conditions have been tested at this step to produce a homogenous mixture of two phase powders without altering their particle size distributions. Finally, batch powders were ball milled in a small glass container with no milling medium for 30 minutes. Mixed powders were pressed into green pellets with CIP at 300 MPa.



Figure 4-2 Schematic of the ceramic/ceramic composite (CCM) processing steps.

Disks were sintered at 1120 °C for 3 h in a closed lid alumina crucible. Sintered disks were ground and polished to 0.8 mm thickness. Finally disks were electroded with Ag paint and their macroscopic properties were measured with a modified Sawyer-Tower setup. Details of the synthesis route have been reported previously.^[83]

Bar-shaped ceramic samples of 0.8 mm \times 1 mm \times 6 mm suitable for *in situ* high-energy diffraction experiments were cut from sintered disks. Silver electrodes were applied to two opposing 1 mm \times 6 mm faces of the bar. The diffraction experiment setup and data collection strategy was the same as described in Chapter 3.1.

4.3. Results and discussion

The microstructure of the samples used in the current study has been investigated by SEM, TEM and EDX.^[82, 83] It was found that the average grain size of the samples is approximately 2 μ m and is consistent over the compositional range reported here. Compositionally sensitive measurements were performed on the 10 vol% FE (10FE) and 50 vol% FE (50FE) compositions and these showed that the materials have sub-

grain regions that are niobium rich. Additionally, grains containing these Nb rich areas were also sodium (Na) and potassium (K) rich. These previous results confirm that compositional inhomogeneity exists in such materials.

Macroscopically measured unipolar strain at 6 kV mm⁻¹ for different ceramic/ceramic composite is shown in Figure 4-3a. Characteristic parameters were derived from these strain loops as presented in Figure 4-3b, and these showed interesting trends in electrical properties as a function of particulate FE phase. The poling strain value at maximum field (6 kV mm⁻¹) varies between 0.39 to 0.45 % and is maximum for pure FE (100FE) materials. E_{pol} represents the field strength at which the sample is poled from the as-processed state; E_{pol} tends to decrease with increasing amount of FE phase. The effect of volume fraction of FE phase is more pronounced in the remnant strain which increases from zero for the pure relaxor (RE) phase material, to 0.26% for the pure FE phase material.



Figure 4-3 (a) Unipolar strain hysteresis, and (b) derived characteristic parameters of macroscopic strain (schematic illustration of derived characteristic parameters is shown in the inset) for ceramic/ceramic composite at 6 kV mm⁻¹. With increasing FE content the remnant strain increases while the poling strain at maximum field is approximately constant. The usable strain reduces with increasing FE content.

With 0% FE, no remnant strain is observed in the material due to a reversible structural transformation^[66,72] with applied electric field, which is characteristic of this composition. With increasing amount of FE phase the ceramic/ceramic composite

materials shows an increasing remnant strain that is maximum for pure FE materials (100FE). The remnant strain for 100FE is consistent with previous measurements reported for BNT-7BT that show a remnant strain of $0.24\%^{[116]}$ resulting from an irreversible phase transformation.^[62] In this case, with a maximum applied field of 6 kV mm⁻¹, the usable strain, S_{usable} (i.e. maximum strain - remnant strain) decreases continuously with increasing fraction of FE phase.

In situ high-energy x-ray diffraction experiments were carried out for all the compositions. Four selected compositions (0FE, 10FE, 20FE and 100FE) are presented here to elucidate the strain mechanism in relaxor/ferroelectric composites. All of the compositions in the as-processed state show single phase perovskite type diffraction patterns that can be indexed with a cubic $Pm\bar{3}m$ structure (Figure 4-4). The samples show electrical properties not consistent with pure cubic phase materials. Additionally, it is known that small distortions at the local scale exist in related compounds,^[117, 118] therefore the structure of the as-processed material is referred to as pseudo-cubic. No significant difference in the lattice parameter is observed for the four compositions within the resolution of the diffraction instrument used. However, the macroscopic strain response behaviour is significantly different for each composition; thus, it can be assumed that these crystallographically similar compositions respond differently under applied electric fields.



Figure 4-4 Experimental diffraction profiles for four different compositions in the asprocessed state. Single and symmetric diffraction peaks are seen throughout the patterns indicating a pseudo-cubic structure.

The electric-field-induced transformation behaviour in such perovskite materials can be qualitatively characterised by observing the (*111*) and (*200*) type pseudo-cubic reflections. *In situ* diffraction patterns for (*111*) and (*200*) type pseudo-cubic peaks of all four compositions with the electric field vector aligned with the diffraction scattering vector are presented in Figure 4-5. The 0FE composition (Figure 4-5a) shows a maximum lattice strain of 0.06% and 0.15% at 6 kV mm⁻¹ in the (*111*) and (*200*) peaks, respectively. No shoulder peak is observed in the (*200*) peak as shown in the bottom of Figure 4-5a. This observed lattice strain is completely reversible, and the peaks return to

their original positions and intensities upon removal of the electric field. This reversible electric-field-induced lattice strain behaviour is characteristic of relaxor type high-strain materials.^[72]



Figure 4-5 (111) (top) and (200) (middle) diffraction peaks for (a) 0% FE (b) 100% FE (c) 10% FE, and (d) 20% FE materials as a function of applied electric field. The variation in (200) shoulder peak intensity in as-prepared (E_0), at 6 kV mm⁻¹ (E_{max}) field and after removal of electric field (E_{rem}) for all compositions (bottom). These data represent scattering information with the applied electric field vector parallel to the diffraction scattering vector.

Data presented in Figure 4-5b for the 100FE composition show that the application of electric field of 6 kV mm⁻¹ (E_{max}) induces significant distortions in the (111) and (200) peaks. These distortions remain after the electric field is removed (E_{rem}). Thus, it can be

said that this composition shows an irreversible electric-field-induced phase transformation. The nature of phase transformation in this system has been previously reported as either pseudo-cubic to tetragonal or pseudo-cubic to mixed phase tetragonal and rhombohedral.^[62, 63] The observed (*111*) peak distortion and (*002*)/(*200*) peak splitting reveals that the field-induced transformation for the composition in this study is likely a mixed phase type transformation.

Figure 4-5c shows the 10FE composition (111) and (200) diffraction patterns under the applied electric field. A lattice strain of 0.07% and 0.18% is observed at 6 kV mm⁻¹ in the (111) and (200) peaks, respectively. The (200) peak in this composition develops a small low 2θ shoulder under the applied field. It also exhibits remnance in lattice strain after the removal of electric field (correlating with the macroscopic strain, Figure 4-3).

Figure 4-5d represents (111) and (200) diffraction patterns for the 20FE composition under the applied electric field. A lattice strain of 0.08% and 0.18% is observed at 6 kV mm⁻¹ in the (111) and (200) peaks, respectively. The (200) peak in this composition, however, reveals more information about the generated strain. In set of Figure 4-5d shows the low 2θ shoulder of the (200) diffraction peak develop during the application of the electric field in the 20FE ceramic/ceramic composite. The shoulder of the (200) peak is more pronounced in the 20FE (bottom of Figure 4-5d) composition than 10 FE (bottom of Figure 4-5c). Thus it can be assumed that development of the low 2θ shoulder depends on increasing volume fraction of FE phase in the ceramic/ceramic composite. The development of the shoulder during the application of the electric field is consistent with a small volume fraction of the bulk material undergoing a pseudocubic to tetragonal phase transformation. In the ceramic/ceramic composite studied here, this would imply that the small volume fraction of particulate phase has undergone the irreversible transition to the ferroelectric state, while the bulk of the sample has reversible electric-field-induced strain consistent with a conventional relaxor material. In other words, compositions such as 10FE and 20FE exhibit a combined effect of 0FE and 100FE in their field-induced response; as evident from the diffraction data.

Based on the *in situ* diffraction results, microscopic strain response mechanisms for the ceramic/ceramic composite have been proposed (Figure 4-6). At the initial zero field state the ceramic/ceramic composite can be represented as a polycrystalline ceramic composed of relaxor (RE) grains (Figure 4-6a). With the application of electric field differences in field-induced transformation in ceramic/ceramic composites can be visualised either in Figure 4-6b (Type I) or Figure 4-6d (Type II), where the former shows inter-grain and latter shows intra-grain composite effects. In the Type I mechanism proposed, ferroelectrically/ferroelastically strained FE grain induces a ferroelectric state on the neighbouring RE grains. A similar kind of induced effect can occur in smaller regions as shown in Type II. With further increase in electric field (Figure 4-6 c and e) the switched ferroelectric domains propagate strain on the surrounding RE matrix. A major fraction of the strained region can relax back with the removal of electric field, but not completely.



Figure 4-6 Representation of proposed mechanisms of electric-field-induced strain generation. (a) ceramic/ceramic composite in as-processed state with no ferroelectric (FE) domains; for simplicity all the grains have been labelled as relaxor (RE). Depending on the spatial distribution of compositional inhomogeneity when the field is applied it can follow either of the Type I (b and c) or Type II (d and e) mechanism. Type I shows the inter-grain composite effect where one of the grains irreversibly transforms from RE to FE, (b) with further increase in electric field the FE domains propagate to the surrounding RE grains (c). Type II shows the intra-grain composite effect where a region of RE grain irreversibly transforms into FE phase (d). Reversible transformation of RE phase has not been shown here for clarity.

The results of the *in situ* diffraction study suggests that the addition of FE phase materials at later stages of processing has produced a polycrystalline material where regions at the grain scale behave independently of the bulk. This has significant implications for the response mechanism of such materials. In particular, the length scale and magnitude of the compositional inhomogeneity may be tuned to increase local responses that may propagate throughout the material. Bintachitt *et al.*^[119] has reported that in PZT thin films, nonlinear response of piezoelectricity is not homogeneous throughout a compositionally uniform sample, i.e. the piezoelectric nonlinear response shows local deviation from the average due to differences in domain wall pinning. A local deviation in electric field distribution, polarisation and strain response has been shown by Jayabal et al.^[120, 121] for bulk materials by micromechanical modelling. This local deviation has been attributed to domain switching processes at the individual grain length scale. Here, it is shown that the electric-field induced strain response of BNT-7BT grains in a polycrystalline ceramic/ceramic composite dictates (or is coupled with) the strain response behaviour of the relaxor matrix. Thus, the local response of the particulate phase can be used to tune or nucleate specific behaviour to the bulk materials properties. The potential for tailoring the properties of functional ceramics using ceramic/ceramic composite structures at the granular scale therefore exists.

4.4. Conclusions

The electric-field-induced strain response in a ceramic/ceramic composite of relaxor and ferroelectric materials has been investigated by means of *in situ* high-energy x-ray diffraction. Evaluated microscopic strain response behaviour from diffraction information has been correlated with the macroscopic strain response for two ceramic/ceramic compositions (10FE and 20FE) and the two constituents (0FE and 100FE). It has been found that in the as-processed state 10FE and 20FE exhibit a

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pseudo-cubic structure similar to 0FE and 100FE. With applied electric field cycles, 0FE showed reversible lattice strain whereas 100FE showed an irreversible phase transformation. In the 10FE and 20FE composition data are consistent with a model where regions of FE grains transformed independent of the bulk. Based on the diffraction study, models for microscopic strain generation in ceramic/ceramic composites have been proposed.

5. Enhanced extrinsic domain switching strain in core-shell structured BaTiO₃-KNbO₃ lead-free piezoelectric ceramics

A manuscript based on the results reported in this chapter is currently in submission. Core-shell BT-KN samples for the experiments were provided courtesy of Mr. Hideto Kawashima and Prof. Satoshi Wada, Interdisciplinary Graduate School of Medical and Engineering, University of Yamanashi, Kofu, Yamanashi, Japan.

<u>Abstract</u>

Electric-field-induced non-180° ferroelectric domain switching in the morphotropic phase boundary (MPB) engineered material BaTiO₃-KNbO₃ (BT-KN) has been investigated using *in situ* high-energy x-ray diffraction. The core-shell BT-KN showed a large extent (approximately 95%) of reversibility in switched fractions of non-180° ferroelectric domains. The non-180° ferroelectric domain switching behaviour of core-shell BT-KN has been contrasted with that of polycrystalline BaTiO₃ (BT) and commercial lead zirconate titanate Pb(Zr,Ti)O₃ (PZT). The large and reversible non-180° ferroelectric domain switching of core-shell BT-KN offers a distinctive strain response. The results indicate a unique family of large strain lead-free materials based on enhanced reversible non-180° ferroelectric domain switching can be developed for future actuator applications.

5.1. Introduction

Research in the field of lead-free electro-ceramics has dramatically increased in the last decade in order to meet potential legislative requirements limiting the use of lead in certain product types.^[7, 122] Lead-based Pb(Zr,Ti)O₃ (PZT) is the market leader for industrial applications with exceptional electro-mechanical coupling properties over wide ranging environmental conditions. While the exact mechanism of the strain

enhancement in PZT is still debated,^[92, 96, 123-126] it is generally accepted that the exceptional properties are related to the structural and microstructural response in compositions close to the morphotropic phase boundary (MPB) region.^[21] The creation of MPB's within solid solutions of lead-free electro-mechanical materials has therefore been a common direction of research. Among others, compositions containing solid solutions of bismuth sodium titanate Bi_{1/2}Na_{1/2}TiO₃ (BNT) and barium titanate BaTiO₃ (BT), potassium niobate KNbO₃ (KN) and sodium niobate NaNbO₃ (NN) are just a few examples of the demonstrated capacity of MPB regions to enhance electro-mechanical coupling properties in lead-free systems.^[1, 60, 112, 127-132]

The creation of artificial MPB's (i.e. MPB engineered materials) is a useful technique for preparing new lead-free piezoelectrics with improved properties. Wada *et al.*^[86-88] have introduced artificial MPB's in BT-KN ceramics. In this approach, BT particle compacts were used as a substrate to grow epitaxial KN by liquid phase reaction in the regions between the particles. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive x-ray (EDX) spectroscopy studies showed that the BT particles in the compact are surrounded by KN layers, i.e. formation of core-shell structured BT-KN where BT is in the core region and the shell is KN.^[88] The heteroepitaxial interface between the core BT and the shell KN has also been confirmed by high resolution TEM.^[87] A comparative study of field induced strain response in core-shell structured BT-KN and solid solution BT-KN (prepared by conventional mixed oxide method) shows promising property enhancements using this approach. Despite the relatively low sintered density of the core-shell BT-KN (relative density ~65%) compared to conventionally prepared solid solution BT-KN (relative density ~95%); the former showed an approximately three times larger strain
response.^[89, 90] The increased response has been proposed to be associated with the interfacial boundary between core BT and shell KN, and enhanced polarisation rotation, although no direct experimental evidence exists.^[89]

In this study, BT-KN core-shell materials have been shown to exhibit remarkably large reversible domain switching during the application of electric fields. *In situ* high-energy x-ray diffraction was used to monitor the domain switching magnitude and associated lattice strain up to electric fields of 3 kV mm⁻¹. The resultant domain switching behaviour has been contrasted with BT and commercial PZT (PIC151, PI Ceramic, Germany) ceramics. The results indicate that a new family of large strain materials based on the enhanced reversible non-180° ferroelectric domain switching process may be developed for actuator applications.

5.2. Core-shell BT-KN samples

The BT-KN (KN/BT ratio 0.5) core-shell structured ceramics were prepared using a solvothermal method. Ethanol was used as the solvent, while KOH, K_2CO_3 , Nb_2O_5 (99.9%, Kanto Chemical, Japan), and BT single-crystal particles (BT, particle size of approximately 300 nm, Sakai Chemical Industry, Japan) were used as the starting materials. The BT and Nb_2O_5 powders were mixed at Nb_2O_5/BT molar ratio of 0.5 with polyvinyl butyral (2 wt%) as a binder in ethanol, dried at 130 °C, sieved, and then pressed into green compacts using a uniaxial press. The binder was burned out at 600 °C for 10 h, and the BT and Nb_2O_5 (BT-Nb₂O₅) mixture compacts were used as the substrate and a raw material of KN. The BT-Nb₂O₅ compacts were placed in a Teflon-coated autoclave container with ethanol, KOH, and K_2CO_3 , where the Nb concentration was 0.10 mol L⁻¹, the K/Nb atomic ratio was 10, and the KOH/K₂CO₃ molar ratio was 0.22. They were heated to 230 °C, and soaked for 20 h without stirring. After the

reaction, the BT-KN core-shell ceramics with a relative density of around 65 % were washed with ethanol and dried at 200 °C. The complete synthesis route has been previously reported in detail.^[86, 89]

Bar-shaped ceramic samples of 0.4 mm \times 1 mm \times 2 mm were cut using a diamond saw for *in situ* high-energy x-ray diffraction experiments. Gold electrodes were applied by sputtering onto two opposing 1 mm \times 2 mm polished faces. In addition to the core-shell BT-KN, pure BT ceramic and a commercial PZT (PIC151, PI Ceramic, Germany) ceramic sample suitable for *in situ* diffraction measurements were prepared. The experimental geometry and data collection strategy is described in Chapter 3.1.

5.3. Results and discussion

5.3.1. Structural analysis of as-processed BT-KN

A diffraction pattern from the as-processed material was collected prior to the application of electric fields (Figure 5-1). Qualitative analysis of the pattern shows the sample appears to be a single phase perovskite type structure with tetragonal symmetry. No orthorhombic (*Amm*2) KN phase is observed; although the microstructural study by TEM^[87] showed existence of BT and KN regions. This absence of the orthorhombic phase might be due to the resolution limit of the diffraction instrument used or due to the distorted orthorhombic unit cell. It is worth mentioning that the lattice mismatch is very small (0.5%) between the orthorhombic unit cell of KN and the tetragonal unit cell of BT. Epitaxial growth of the KN on the BT particles has likely resulted in a sufficient strain to the KN phase to allow this phase to exist in the tetragonal state.



Figure 5-1 Experimental diffraction profiles for core-shell BT-KN in the as-processed state. A single symmetric (*111*) reflection and doublet in (*200*) indicates tetragonal symmetry.

To determine the phase structure, full diffraction pattern refinements of the as-processed sample with various combinations of space groups (e.g., tetragonal P4mm, orthorhombic Amm^2 and cubic $Pm\bar{3}m$) were carried out. Figure 5-2 and Table 5-I show the results of full pattern structural refinements with different structural symmetries. Initial structural refinement with two phases ($P4mm + Amm^2$) revealed that the system is not well modelled using these two phases. Moreover, this two phase model (Figure 5-2a) does not improve the fit in the (200) peak compared to the single phase tetragonal model (Figure 5-2b). However, structural refinements (Figure 5-2c) with P4mm (a = 3.98472 Å, c = 4.01662 Å) and cubic $Pm\bar{3}m$ (a = 3.99570 Å) show better refinement results

(Table 5-I). The superior fit with the addition of the cubic phase with the tetragonal phase (P4mm) does not necessarily provide conclusive evidence of a cubic phase existing in the sample. Due to the ferroelastic nature of BT, significant domain wall scattering is observed in the positions expected for the cubic phase peaks.^[133] Thus, within the scope of this paper, the core-shell BT-KN has been considered as tetragonal although the possibility exists that the shell KN structure approaches a cubic (i.e. non-polar) state.

Space group	a /Å	b /Å	c /Å	Criteria of fit/ %
P4mm (81%)	3.98666	3.98666	4.01403	$R_p 6.185$
Amm2 (19%	4.02153	5.63414	5.66190	R_{wp} 8.296
				<i>GoF</i> 1.668
P4mm	3.98815	3.98815	4.01500	R_p 6.463
				R_{wp} 8.576
				GoF 1.724
P4mm (69%)	3.98472	3.98472	4.01662	R_p 6.08
Pm3m (31%)	3.99570	3.99570	3.99570	R_{wp} 7.842
· · · ·				GoF 1.580

Table 5-I Refined lattice parameters and fitting values for core-shell BT-KN ceramic.



Figure 5-2 X-ray diffraction patterns of as-processed core-shell BT-KN ceramic sample and results of crystallographic refinement using the space groups (a) *P4mm* and *Amm*2,

(b) P4mm, and (c) P4mm and Pm3m. Peaks are labelled with the pseudo-cubic perovskite unit cell indices.

5.3.2. Domain switching in core-shell BT-KN by in situ x-ray diffraction

The field-induced domain textures in tetragonal structures can be analysed by observing the variation in (002)/(200) reflections.^[134] Figure 5-3 shows the (002) and (200) reflections with the scattering vector parallel to the applied electric field vector during the application of $(E_{\text{max}} = 3 \text{ kV mm}^{-1})$ poling field.

The change in relative intensities of (002) and (200) peaks with applied field can be explained qualitatively as the change in volume fraction of 90° ferroelectric/ferroelastic domains in the tetragonal system. With the application of electric field, the (002) intensity increases at the expense of (200) intensity, and reaches a maximum value at 3 kV mm⁻¹ (E_{max}), i.e. the domain population with its *c*-axis (long axis) parallel to the electric field direction increases. Interestingly, with decreasing electric field, the intensity distribution of the (002) and (200) reflections return to values approximately equal to the initial state, i.e. $E_{\rm rem} \approx E_0$. Such a high magnitude of reversibility in switched non-180° ferroelectric domains is unreported in the literature and offers a distinctive strain mechanism for further development. In general, a contribution to the electro-mechanical response in conventional piezoelectric ceramics (e.g., PZT) is attributed to the movement of ferroelectric/ferroelastic domain walls.^[99] However, the major fraction of this electro-mechanical response is a one-time effect during electrical poling, in which non-180° domains are moved to metastable positions, giving rise to a significant remnant strain.^[135, 136] In order to achieve high field-induced strain during unipolar cycling; the material needs to possess reversible non-180° domain switching. Thus, the core-shell BT-KN has the potential to achieve high field-induced strain during unipolar cycles.



Figure 5-3 (a) (002)/(200) diffraction peak profiles as a function of applied electric field. (b) Selected states during the application of field; as-processed state (E_0), at 3 kV mm⁻¹ (E_{max}) and after the removal of electric field (E_{rem}).



Figure 5-4 (a) (002)/(200) intensity profiles at 3 kV mm⁻¹ as a function of scattering vector angle to the applied electric field vector. Open circle, solid line and dot line represent experimental data, total fit and fit peak components, respectively. (b) Calculated fraction of switched domains (η_{002}) as a function of orientation at selected field steps.

The quantification of the extent of domain texture can further highlight the domain switching behaviour of this core-shell BT-KN ceramic. The (002)/(200) peak profiles at selected scattering vector angles to the applied field vector are presented in Figure 5-4a. The variation in relative intensity with scattering vector as a function of angle to the applied field vector can be explained by non-180° ferroelectric (i.e. 90° domains in the tetragonal system) domain texture. To quantify the change in domain texture, the (002)/(200) reflections were modelled using double pseudo-Voigt functions. Extracted peak intensities have been used to calculate the fraction of switched domains (η_{002}) at each field step for all scattering vector orientations relative to the applied field vector using the method reported by Jones *et al.*^[137] This method considers the change in relative intensities of non-180° ferroelectric domains (e.g., 00h/h00 reflections for the tetragonal system) and multiplicities of that particular lattice plane to calculate the volume of non-180° ferroelectric domains (v_{002}) and consequently the fraction of switched domains (η_{002}) and can be expressed by Equation 5-1

$$\eta_{002} = v_{002} - \frac{1}{3} \tag{5-1}$$

where v_{002} is given by the intensity ratio of the poled (I_{002}) and unpoled (I_{002}) state using Equation 5-2

$$\nu_{002} = \frac{\frac{I_{002}}{I_{002}}}{\frac{I_{002}}{I_{002}} + 2\left(\frac{I_{200}}{I_{200}}\right)}$$
(5-2)

Figure 5-4b shows η_{002} as a function of angle to the applied electric field vector at three different field states during the poling cycle. At the initial state, E_0 , η_{002} is zero as no

domains have switched from the as-processed condition. At the maximum electric field, E_{max} , the maximum fraction of switched domains ($\eta_{002} = 0.2$) is observed along the field direction and the minimum ($\eta_{002} = -0.05$) at the perpendicular direction. Similar domain texture development is observed in tetragonal PZT with the application of electric field.^[135,138,139] Upon subsequent decrease of the applied electric field amplitude to zero (E_{rem}), η_{002} (along the electric field direction) decreases from 0.2 to 0.01, i.e. approximately 95% of the domains that initially switched experience reversible switching upon release of the electric field. In other words, the fraction of switched domains returns to populations very close to their initial state for all orientations. Thus, a large extent of non-180° ferroelectric domain switching in core-shell BT-KN may not be a one-time effect, a result that is contrary to conventional piezoelectrics such as PZT and BT.

5.3.3. Reversibility of switched non-180° ferroelectric domains and lattice strain in core-shell BT-KN, pure BT and PZT

The enhanced reversible domain switching behaviour in core-shell BT-KN ceramic has been compared with pure BT and tetragonal PZT (PIC151, PI Ceramic Germany) samples during a unipolar cycle, both in the poled state. Samples were poled using a single unipolar cycle (0.005 Hz). To calculate the fraction of switched non-180° ferroelectric domains in the poled samples, the average intensity method was used to estimate the expected diffraction peak intensities in samples with random domain orientations (i.e. unpoled sample).^[72] Changes in domain switching fraction ($\Delta \eta_{002} = \eta_{002(E_{\text{max}})} - \eta_{002(E_0)}$) and (*111*) lattice strain in poled specimens of core-shell BT-KN, pure BT and PZT ceramic are presented in Figure 5-5. The fraction of switched non-180° ferroelectric domains (Figure 5-5a and Figure 5-5b) in core-shell BT-KN is higher than BT and PZT, i.e. in the poled state, core-shell BT-KN exhibits an approximately two and three times greater value of $\Delta \eta_{002}$ than PZT and BT, respectively. Interestingly, while the $\Delta \eta_{002}$ value (Figure 5-5a) for core-shell BT-KN and BT decreases continuously with increasing angle to the applied electric field direction, an abrupt variation around 45° to the electric field direction is observed for PZT. This abrupt change is perhaps due to the previously observed phase transformation in polycrystalline PZT of this composition at intermediate angles to the applied field vector.^[140] The (111) lattice strain (Figure 5-5c) at maximum electric field observed in PZT (0.16%) (plotted using the right hand axis) is much larger than core-shell BT-KN $(\sim 0.04\%)$ and pure BT (< 0.01%). It is worth noting that the observed (111) lattice strain in tetragonal polycrystalline ceramics is not entirely intrinsic piezoelectric strain. It has been reported that in tetragonal polycrystals, grains with a [111] direction parallel to the applied field, are unable to accommodate strain via domain switching and thus elastically strain to compensate.^[138, 139] In addition, the lattice constant ratio in tetragonal systems, c/a, changes the local stress state at the grain scale due to strain from non-180° domain wall motion during the poling cycle, leading to variations in the magnitude of observed residual stress.^[141] It can be speculated that the lower c/a ratio facilitates a higher degree of non-180° domain switching in the poled specimen. Thus, the observed smaller domain switching fraction ($\Delta\eta_{002}$) and high (111) strain in PZT $(c/a \approx 1.0122)$ than the core-shell BT-KN $(c/a \approx 1.0062)$ is possibly due to the higher tetragonality and intergranular coupling.



Figure 5-5 Change in domain switching fraction as a function of (a) angle to the applied field vector at maximum field, and (b) applied electric field amplitude, and (c) (*111*) lattice strain as a function of applied field in poled core-shell BT-KN, BT and PZT.

Data in (b) and (c) represent the information for the scattering vector parallel to the applied electric-field vector.

During poling of conventional electro-ceramic materials such as BT and PZT, a significant fraction of non-180° ferroelectric domains re-orient and become fixed in metastable states resulting in a remnant domain texture within the polycrystal. The nature of the structural defects which leads to the pinning of domains walls in these metastable states can be attributed to several structural features including vacancy and interstitial defects, domain wall interactions, grain boundary defects, and interactions of domains across grain boundaries. In the core-shell BT-KN materials, it appears as though domains are restricted from being fixed in these metastable states upon poling, thus significantly more domain switching occurs during unipolar cycling. It should be mentioned here that the core-shell BT-KN sample showed an approximately equal extent of reversible domain switching for several repeated electric field cycles of 3 kV mm⁻¹, 4 kV mm⁻¹ and 5 kV mm⁻¹. The mechanism by which the metastable states are suppressed is likely related to the structure of the grain boundaries. In the core-shell microstructure, it is possible that the domains that exist in the core BT component do not completely propagate through the shell region to the grain boundary. Thus, the interaction of domains with grain boundaries and neighbouring grain domain structures is suppressed. Such a microstructure offers a remarkable variable to control the degree of domain switching in electro-ceramic materials and may lead to significant increases in usable strain of known compositions via microstructural engineering.

A restoring force which acts to reverse the switched domains may exist in the system. It is known in these materials that significant residual stress builds up in non-polar oriented grains.^[138, 139, 142] This stress acts to compress the sample from its poled state

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and thus return the domain texture to its original unpoled state. This residual stress has been shown to enhance the rate of polarisation reversal in tetragonal PZT materials upon application of field opposite to the poling direction.^[143] In the absence of domain wall pinning sites at the grain boundaries, this residual stress may in fact completely reverse the domain wall motion without any external bias.

A schematic diagram of this process is shown in Figure 5-6, presenting a comparative illustration of the energy landscapes of a domain wall for a conventional electroceramic and core-shell BT-KN. Assuming that the gradient of residual stress (red dashed line of the energy landscape) is the driving force to return the domain walls to the initial position and both system experiences similar gradient. Also, it is expected that due to the difference in microstructure, the nature and/or extent of defect-domain wall interaction energy landscape will be different. Although interaction of domain walls with defects at the grain boundaries may be considered the principle difference between a conventional electro-ceramic and core-shell BT-KN, it should be acknowledged that other defects might also exist. In conventional polycrystalline ceramics (Figure 5-6a), the domain wall is displaced by an applied electric field with its position changed from the initial position in the unpoled state (i.e. position A) to a position of higher potential energy under the maximum field (i.e. position B). In this process, the domain wall interacts with a large number of defects. Eventually, the domain wall settles at a local minimum, a metastable state (i.e. remnant state, C) caused by the interaction with defects at grain boundaries. These local minima in the energy landscape prevent the residual stress to act as an effective driving force to revert the domain wall to the initial position. Thus, remnance in domain wall motion is observed in these types of materials. In the case of core-shell BT-KN (Figure 5-6b), the domain wall is also displaced from

the original positon A to position B by an applied field, however, the domain wall interaction with grain boundary defects is suppressed by the shell (KN) region. As a consequence, the energy landscape is less varying (i.e. there is an absence of local energy minima) and the domain wall can revert to position C, close to the initial position A, with the release of electric field. In the absence of local energy minima, residual stress can act as an effective driving force to revert the domain wall to its initial position in systems like core-shell BT-KN.



Figure 5-6 Schematic diagram of the polycrystalline microstructure and an energy landscape, S(u), of a single domain wall in spatial dimension, u, for (a) conventional electro-ceramic (e.g., BT, PZT) and (b) core-shell BT-KN. The dashed line (red) of the energy landscapes indicates the energy offset due to residual stresses developing in the bulk material as non-180° domain switching occurs.

Considering the microstructure, perhaps in conventional polycrystalline ceramics the grain boundaries are a significant metastable state for domain walls, whereas in core-

shell BT-KN, the interfacial region, which is not necessarily a polar tetragonal phase, does not allow domain walls to be pinned at grain boundaries. Thus, in core-shell BT-KN, because there are no metastable states of the domains on poling, there is a huge range of domain switching available for actuation during unipolar cycling.

5.4. Conclusions

Enhanced reversible non-180° domain switching in MPB engineered core-shell BT-KN during poling and subsequent unipolar cycling has been observed by means of *in situ* high-energy x-ray diffraction. The core-shell BT-KN showed large and reversible non-180° domain switching during the application of external field. The nature of the reversible domain switching has been contrasted with conventional electroceramic such as BT and commercial PZT for unipolar actuation. The core-shell BT-KN exhibited a higher magnitude of non-180° domain switching fraction than BT and PZT. The reversibility of switched non-180° domains in core-shell BT-KN has been hypothesised to be due to much lower pinning energies (i.e. the absence of noticeable local energy minima) of metastable domain states after the application of external fields. Thus, the large extent of reversibility in switched non-180° domains of core-shell BT-KN offers a unique strain mechanism for further development for actuator applications.

6. Electric-field-induced domain switching and domain texture relaxations in bulk bismuth ferrite ceramic

A manuscript based on the results presented in this chapter currently is in submission. Bulk BiFeO₃ samples were provided courtesy of Dr. Tadej Rojac, Electronic Ceramics Department, Jozef Stefan Institute, Ljubljana, Slovenia.

<u>Abstract</u>

Bismuth ferrite, BiFeO₃ (BFO), is an important multiferroic material that has attracted significant attention for potential applications in functional devices. While thin films of BFO are attractive for applications in nanoelectronics, bulk polycrystalline BFO has great potential as a lead-free and/or high-temperature actuator material. However, the actuation mechanisms in bulk BFO are still to be resolved. Here, the microscopic origin of electric-field-induced strain in bulk BFO ceramic has been investigated using in situ high-energy x-ray diffraction. Quantification of intrinsic lattice strain and extrinsic domain switching strain from diffraction data showed that the strain response in bulk BFO is primarily due to non-180° ferroelectric domain switching, with no observable change in the phase symmetry. This strain mechanism is different to that previously reported in thin film BFO where epitaxial strain stabilises a tetragonal structure at zero field which is driven to a mixed tetragonal and rhombohedral-like structure at high field. Despite the different mechanism, rhombohedral bulk BFO ceramic can exhibit a similar strain/field ratio to thin film BFO. A strong post-poling relaxation of switched non-180° ferroelectric domains has been observed and suggested to be due to residual stresses with a possible contribution from the conductive nature of the domain walls in BFO ceramics.

6.1. Introduction

BFO is currently a highly investigated material due to its multiferroic properties (i.e. coexistence of magnetic and ferroelectric order).^[44, 46, 144, 145] In addition to its multiferroic ordering, BFO is strongly ferroelectric with high spontaneous polarisation $(P_s \sim 100 \ \mu\text{C cm}^{-2})^{[146]}$ and high Curie temperature $(T_c = 825 \ ^{\circ}\text{C})$.^[147] The unusually high T_c of BFO in comparison to other electro-ceramics such as BaTiO₃ $(T_c \sim 120 \ ^{\circ}\text{C})^{[1]}$ and Pb(Zr,Ti)O₃ (PZT) $(T_c \sim 360 \ ^{\circ}\text{C})^{[1]}$ has made it attractive for high temperature applications where the current market dominating piezoelectrics cannot be used. Moreover, the global restrictions on lead-based materials^[7] have further enhanced the potential of BFO ceramic as a lead-free alternative. While high T_c and P_s are attractive for piezoelectric devices, bulk BFO applications are currently limited by its high ferroelectric coercive field (~7 kV mm⁻¹),^[45] high electrical conductivity ($\sigma_{\text{DC}} 10^{-2}$ – 10^{-10} 10 S m⁻¹)^[45] and relatively low piezoelectric coefficients (~45 pC N⁻¹).^[148]

Significant effort has been invested to improve the properties of BFO by chemical modifications such as the formation of solid solutions with other ABO₃ type perovskite^[49-51] compositions and doping, e.g., with La³⁺,^[52] Co³⁺,^[53] Nd³⁺,^[54] Gd³⁺,^[55] Sm³⁺,^[56] as well as co-doped Co³⁺ and Nb⁵⁺.^[57] A great deal of work on BFO has also been done on the structure-property relationship in thin films^[46, 48, 149] and single crystals.^[146, 150-152] The field-induced strain response in epitaxial grown BFO thin films has been reported by Zeches et al.^[48] and Zhang et al.^[153] In these films, the large electric-field-induced strain (> 5%) was reported to be due to the coexistence and field induced transition between tetragonal-like and rhombohedral-like phases. Crystallographic structures of thin film BFO are often different from single crystal and bulk BFO depending on the lattice mismatch strain between the substrate and the film as well as film thickness. Although the crystallographic structure of bulk BFO ceramics at room temperature is well characterised,^[154, 155] the structure-property relationship under electric field is not well established.

Some reports have suggested that in bulk BFO ceramic, non-180° ferroelectric domain switching leads to preferential arrangements of long ferroelastic domains in the field direction. This is a major contributor for macroscopic electric-field-induced generated strain; however, the data was not a direct observation of this mechanism.^[58] Recently it has been shown by an *ex situ* x-ray diffraction study of poled bulk BFO ceramics that the poling process appears to only introduce non-180° ferroelectric domain texture changes;^[45] in this case, no observation of potential intermediate switching states or the dynamics of domain wall motion was made. This leaves an open question concerning the exact microscopic mechanism that is responsible for the measured macroscopic strain in polycrystalline BFO ceramics.^[58]

In this chapter, the electric-field-induced microscopic strain mechanisms of bulk BFO ceramics has been investigated. Measurements were made by means of *in situ* highenergy x-ray diffraction from bulk ceramics. It is shown that the primary strain generation mechanism in bulk BFO ceramics is due to non-180° ferroelectric domain switching. No phase transformation was observed, in contrast to measurements from epitaxially constrained thin film BFO under a compressive in-plane stress.^[48] However, the strain/applied field ratio (ε /E) at the maximum fields in the respective measurements is similar for both bulk BFO (~100 pm V⁻¹) and thin film BFO (~117 pm V⁻¹). Additionally, in bulk BFO, a relaxation process of the switched non-180° ferroelectric domains is observed that greatly affects the process of poling these materials. It is suggested that the relaxation may be due to large residual stresses in BFO with a possible contribution due to the conductive nature of domain walls. Understanding of these strain generation mechanisms and relaxation processes will be critical for the development of future BFO-based actuator materials and is also useful for the understanding of relaxation and switching processes in ferroelectrics in general.

6.2. Bulk BFO samples

BFO ceramics were prepared by reactive sintering of a mechanochemically activated stoichiometric mixture of Bi₂O₃ and Fe₂O₃. Details of ceramic sample preparation have been reported previously.^[45, 148] For *in situ* x-ray diffraction experiments, ceramic samples of dimensions $0.3 \times 0.5 \times 1 \text{ mm}^3$ were cut from sintered disks. Silver electrodes were applied to two opposing $0.5 \times 1 \text{ mm}^2$ faces of the bar. Details of the *in situ* high-energy x-ray diffraction experiments are outlined in Chapter 3.1.

6.3. Results and discussion

6.3.1. Structural analysis of as-processed BFO

Figure 6-1 shows the x-ray diffraction pattern of the as-processed BFO ceramic sample. The results show no sign of secondary phases within the detection limit of the instrument used. Structure analysis found the material to be rhombohedral *R*3*c* ($a_{hex} = 5.577$ Å, $c_{hex} = 13.869$ Å, $V_{hex} = 373.658$ Å³or $a_{rh} = 5.634$ Å, $\alpha_{rh} = 59.334^{\circ}$, $V_{rh} = 124.553$ Å³). Structural parameters are consistent with those previously reported.^[155]



Figure 6-1 X-ray diffraction pattern for as-processed bulk BFO ceramic. Full pattern structural refinement shows rhombohedral crystal structure with *R3c* space group. The insets show a magnified view of selected reflections. The peaks have been indexed with the pseudo-cubic parent cell as has been indicated by subscript, pc.

6.3.2. Microscopic strain response in bulk BFO ceramics by *in situ* x-ray diffraction

Electric-field-induced lattice strain, domain switching, and phase transformation behaviour in rhombohedral perovskite materials can be qualitatively characterised by observing the variation in $(111)_{pc}$ and $(200)_{pc}$ type reflections. In Figure 6-2, diffraction patterns are shown for $(111)_{pc}/(11\overline{1})_{pc}$ and $(200)_{pc}$ peaks during the application of unipolar electric field cycle ($E_{max}^{I} = 14 \text{ kV mm}^{-1}$). Here, the scattering vector is aligned such that the electric field vector, **E**, is normal to the scattering planes. The black dashed line on the figures indicates the peak position (in 2θ) for the as-processed state of BFO (before application of the electric field). From the diffraction patterns shown in Figure 6-2, changes in relative intensities of the $(111)_{pc}/(11\overline{1})_{pc}$ peaks (Figure 6-2a) and variation in the peak position and peak broadening of the $(200)_{pc}$ peak (Figure 6-2b) as a function of applied electric field are clearly visible. Some degree of peak broadening is also observed in the $(111)_{pc}$ reflection with applied field. It is clear that both the change in relative intensities (Figure 6-2a) and lattice strain (Figure 6-2b) exhibit some degree of reversibility upon removal of the field (E_{rem}^{I}).



Figure 6-2 Contour plots (top) of (a) $(111)_{pc}/(11\overline{1})_{pc}$ and (b) $(200)_{pc}$ reflections during the application of unipolar electric field cycle ($E_{\text{max}}^{I}=14 \text{ kV mm}^{-1}$). These data represent

scattering information with the applied electric field vector parallel to the diffraction scattering vector. The black dashed lines represent peak positions in the as-processed BFO, before application of the field. The peak profiles shown on the bottom of each contour plot represent observed peaks before applying the electric field (E_0), at maximum 14 kV mm⁻¹ (E_{max}^I) and after removing the electric field (E_{rem}^I).

The $(111)_{pc}/(11\overline{1})_{pc}$ and $(200)_{pc}$ peaks were modelled with a double and single pseudo-Voigt function, respectively. The $(111)_{pc}/(11\overline{1})_{pc}$ intensity ratio, $(200)_{pc}$ lattice strain and peak broadening (quantified by full width at half maximum-FWHM) are shown as a function of applied electric field in Figure 6-3. The data shown in Figure 6-3a indicate that with the application of electric field, the $(111)_{pc}$ domain population increases while the $(11\overline{1})_{pc}$ population decreases with a significant increase in rate at an approximate coercive field of ~10 kV mm⁻¹. In other words, the volume fraction of longer $(d_{111} > d_{11\overline{1}})$ domains increases parallel to the field direction upon application of the field. The $(200)_{pc}$ lattice strain tends to follow the trend of the domain switching with an increased rate of strain also occurring at ~10 kV mm⁻¹. Significant peak broadening (Figure 6-3b) of the $(111)_{pc}$ and $(200)_{pc}$ peaks at the maximum field indicates a microstrain developing within the polycrystal and/or a reduction in the domain size for grains of that orientation. This microstrain/domain size broadening shows hysteretic behaviour that follows the same trend as $(111)_{pc}/(11\overline{1})_{pc}$ intensity ratio. The $(200)_{pc}$ broadening in rhombohedral systems is expected to be larger than that of the $(111)_{pc}$ and $(11\overline{1})_{pc}$ peaks. This is likely due to two effects; 1) the fact that in rhombohedral symmetry, grains scattering the $(200)_{pc}$ peak parallel to the field direction can only

accommodate strain by lattice deformation, not non-180° ferroelectric domain switching, and 2) these grains will have four ferroelectric domain variants with approximately equal angle to the applied field, and thus may have a finer ferroelectric domain structures induced under field.^[156] These two effects contribute to microstrain broadening and crystallite size broadening, respectively.

Close observation of the full diffraction patterns at maximum field (E_{max}^{I} =14 kV mm⁻¹) revealed that the poling of the material does not induce any change in the crystallographic structure of the material, i.e. no new crystallographic phase is observed due to the applied electric field. Thus, no phase transformation strain is contributing to the generated macroscopic strain in this material. The origin of macroscopic strain in bulk BFO is due only to non-180° ferroelectric domain switching and associated lattice deformation.

Figure 6-4 shows the variation of $(111)_{pc}/(11\overline{1})_{pc}$ peak intensities (a) and change in $(200)_{pc}$ lattice spacing (b) as a function of the scattering vector angle to the applied electric field vector at 14 kV mm⁻¹. The variation in $(111)_{pc}/(11\overline{1})_{pc}$ intensity with scattering vector angle to the applied field vector can be explained as a strong domain texture in the rhombohedral system. The variation in lattice spacing (2 θ position) as a function of scattering vector angle shows that the lattice expands along the field direction and it contracts perpendicular to the field direction, relative to the unpoled state. This behaviour is consistent with that observed in rhombohedral PZT under field.^[157] The observed (200)_{pc} lattice strain in Figure 6-3a does not indicate only an intrinsic piezoelectric strain, but the combined contribution of intrinsic piezoelectric strain within the polycrystal caused by the large

ferroelastic deformation of grains that have a $(111)_{pc}$ direction aligned proximate with the field vector.^[138]



Figure 6-3 (a) $(111)_{pc}/(11\overline{1})_{pc}$ intensity ratio and $(200)_{pc}$ lattice strain as a function of applied electric field, and (b) Variation in full width half maxima (FWHM) of $(111)_{pc}$, $(11\overline{1})_{pc}$ and $(200)_{pc}$ peak as a function of applied field. Maximum peak broadening is observed for $(200)_{pc}$ peak. Data represented here have the applied field vector parallel to the diffraction scattering vector.



Figure 6-4 Contour plots of (a) $(111)_{pc}/(11\overline{1})_{pc}$ and (b) $(200)_{pc}$ at $(E_{max}^{T}=14 \text{ kV mm}^{-1})$ as a function of scattering vector angle to the electric field vector. The bottom graphs of each contour show the diffraction patterns with scattering vectors at 0° (parallel) and 90° (perpendicular) to electric field vector.

Electric-field-induced change in $(111)_{pc}/(11\overline{1})_{pc}$ relative peak intensities is related to the change in volume fraction of non-180° domains. Domains that are not aligned with the applied field vector switch by 180° and non-180° domain wall motion to increase the population of domains with their polarisation vector closer to the field direction. It should be noted that the 180° domain switching does not affect the change in relative

intensities in diffraction patterns and also only the non-180° domain switching contributes to the observed domain switching strain. In rhombohedral materials such as BFO, switching of 71° and 109° domains contributes to the ferroelastic strain, as has been also shown in rhombohedral PZT.^[158] The non-180° ferroelectric domain texture f_{111} for rhombohedral materials along specific directions relative to the applied electric field vector expressed as the multiple of random distribution (MRD) can be calculated according to Ref. [157] as:

$$f_{111} = 4 \times \left\{ \frac{\frac{I_{111}}{I_{111}'}}{\frac{I_{111}}{I_{111}'} + 3(\frac{I_{111}}{I_{111}'})} \right\}$$
(6-1)

where I_{111} and $I_{11\overline{1}}$ are the integrated intensities of the (111) and (111) reflections under applied electric field and I'_{111} and $I'_{11\overline{1}}$ are the integrated intensities of the same peaks for a sample before applying an electric field.

Figure 6-5 shows the calculated f_{111} for an applied unipolar cycle of 14 kV mm⁻¹. For rhombohedral systems, the maximum possible MRD value at a given scattering vector angle to the applied field is 4, indicating a saturated domain texture state. An MRD value of 1 represents randomly orientated domains and values below 1 represent a reduced population at that orientation. As shown from the f_{111} calculation for BFO at E_{max}^{I} (14 kV mm⁻¹) the MRD value increases to 1.92 along the field direction and decreases to 0.6 in the perpendicular direction. In this high-field state, the long $(111)_{pc}$ domain population increases at the expense of short $(11\overline{1})_{pc}$ domains along the field direction. Additionally, after reducing the field to 0 kV mm⁻¹, f_{111} reduces from 1.92 at E_{max}^I to 1.72 at E_{rem}^I .



Figure 6-5 Orientation dependence of domain texture f_{111} (MRD), calculated from the intensities of $(111)_{pc}$ and $(11\overline{1})_{pc}$ reflections. The black dashed line, triangles (red) and circles (blue) represent domain texture with no applied field (E₀), at 14 kV mm⁻¹ field during 1st unipolar cycle (E_{max}^{I}), and after the removal of 1st cycle field (E_{rem}^{I}), respectively.

6.3.3. Macroscopic strain calculation from x-ray diffraction data

The total electric-field-induced strain in BFO is the combined contributions of intrinsic lattice strain and extrinsic strain due to non-180° ferroelectric domain switching. At the grain scale, these strains are coupled together, with extrinsic strain from domain wall motion leading to an elastic deformation of surrounding grains in addition to their intrinsic strain response from the piezoelectric effect. From the *in situ* field-dependent x-ray data presented here, which includes the full orientation dependence of lattice strain and domain switching magnitudes, it is possible to calculate total strain using a weighted sum of all contributing components.

The total intrinsic lattice strain (S_{zz}^{int}) of all the grains along the field direction can be estimated using a volume weighted average of the *hkl* reflections according to Equation 6-2.^[159]

$$S_{zz}^{\text{int}} = \frac{\sum_{hkl} f_{hkl}(0)m_{hkl}s_{hkl}(0)}{\sum_{hkl} f_{hkl}(0)m_{hkl}}$$
(6-2)

where, $f_{hkl}(0)$ is the domain texture along the field direction (i.e. angle between applied field vector and scattering vector is 0°), m_{hkl} is the multiplicity factor of the *hkl* reflection and $s_{hkl}(0)$ is the lattice strain of *hkl* reflection.

Extrinsic contributions to the strain due to domain switching can be calculated by the method proposed by Jones *et al.*^[137] This method considers the lattice strain caused by non-180° ferroelectric domain switching and the distribution of non-180° ferroelectric domains at all orientations to the applied electric-field vector. For a rhombohedral

system with non-180° domain switching, extrinsic strain (S_{zz}^{ext}) can be calculated using the following equation:^[72, 157]

$$S_{zz}^{ext} = \frac{d_{kkk} - d_{kk\bar{k}}}{d_{kk\bar{k}}} \int_{\alpha=0^{\circ}}^{\alpha=90^{\circ}} \left[\left(\Delta f_{111}(\alpha) \cos^2 \alpha \right) \right] \sin \alpha d\alpha$$
(6-3)

where, d_{kkk} and $d_{kk\bar{k}}$ are the lattice spacing, $\Delta f_{111}(\alpha)$ is the change in the multiple of random distribution (i.e. $f_{111}(\alpha) - 1$) of non-180° ferroelectric 111 crystallographic pole, along the sample direction α with respect to the applied electric field. The geometrical factor of $\cos^2 \alpha$ term arises from the tensor transformation of the domain-switching strain along the applied field direction and $\sin \alpha$ is the transformation of a volume element in orientation space to a corresponding volume element in the sample.

The BFO ceramics studied here did not exhibit an electric-field-induced phase transformation, so the total macroscopic strain can be approximated by summing both intrinsic and extrinsic contributions.

$$S_{zz}^{Total} = S_{zz}^{int} + S_{zz}^{ext}$$
(6-4)

Figure 6-6 represents the calculated strain from the x-ray diffraction data. At the maximum field of 14 kV mm⁻¹, the calculated intrinsic strain is 0.05%, while the extrinsic strain due to non-180° ferroelectric domain switching is almost twice the intrinsic strain, i.e. 0.09%. The total strain at maximum field (sum of intrinsic and extrinsic strain) 0.14% is comparable to the reported macroscopic strain for the same material under a similar electric field strength.^[58] In epitaxially constrained thin film BFO, subjected to in-plane compressive stresses due to constrained in-plane lattice parameter, the observed strain has been shown to be due to a reversible phase

transformation from a tetragonal phase to a mixture of tetragonal and rhombohedral phases under applied electric field.^[48] In bulk BFO ceramic it is shown here that the major contributor to the strain response is non-180° ferroelectric domain switching in the rhombohedral phase without a phase transformation induced by the applied electric field. Although the strain response mechanism is clearly different between thin film and bulk BFO, the magnitude of the ratio of strain to applied field at the maximum field is similar in both cases. Zeches *et al.*^[48] has observed a strain of approximately 2% at a field of 170 kV mm⁻¹ in thin film BFO, giving a S_{max}/E_{max} of 117 pm V⁻¹ (apparent large-signal piezoelectric coefficient, d_{33}^*), which is similar to the value measured here for bulk BFO at 14 kV mm⁻¹ ($S_{max}/E_{max} \approx 100$ pm V⁻¹).



Figure 6-6 Intrinsic, extrinsic, and total (intrinsic + extrinsic) strain calculated from *in situ* x-ray diffraction data.

According to the above calculations, extrinsic domain switching strain in bulk polycrystalline BFO is the major (65%) contributor to the total strain at the maximum electric field. This behaviour is different from single phase rhombohedral PZT (pure and doped) where lattice strain is the major contributor.^[93, 97] In such measurements it is not possible to deconvolute the true intrinsic piezoelectric strain response from the elastic deformation resulting from microstructural constraints. The results however, show that the possible intrinsic piezoelectric coefficient for bulk BFO at large fields should be less than 35 pm V⁻¹.

6.3.4. Relaxation of switched domains in bulk BFO

Poling efficiency in bulk BFO has been shown to improve by applying subsequent poling cycles rather than using constant field for a long period.^[148] Therefore, a second unipolar cycle of the same magnitude (14 kV mm⁻¹) was applied to the sample.

Observation of the diffraction patterns within the 2nd cycle (E_{max}^{H}) reveal that again there is no crystallographic phase change. However, a higher degree of domain switching occurs in comparison to the first cycle. The strain observed for (200)_{pc} reflection and MRD values for the 1st and 2nd cycle are presented in Figure 6-7 as a function of applied field. Lattice strain for (200)_{pc} reflection (Figure 6-7a) increases for the second cycle; however, remnant strain value is similar for both cycles. From Figure 6-7b, it is clear that after the end of the first cycle and prior to the start of the second cycle, the electric-field-induced domain texture has relaxed from a value of $f_{111} = 1.72$ to 1.26 along the field direction (indicated by the black arrow in Figure 6-7b). An additional data collection between these two data sets allowed this phenomenon to be investigated as a function of time, as shown in Figure 6-7c. The relaxation of f_{111} as a function of time shows a decrease from 1.72 to 1.26 over 229 seconds.



Figure 6-7 (a) $(200)_{pc}$ lattice strain and (b) f_{111} as a function of applied electric field for 1st and 2nd cycle (here the electric field vector is parallel to the scattering vector). (c)

Relaxation of domain texture as a function of time between the end of the first cycle and the start of the second cycle.

The fitting of the available data with an exponential decay function gives a time constant (τ) of 39.5 seconds. The $(200)_{pc}$ peak broadening also follows a similar relaxation trend (not shown here). A relaxation of the domain texture, as observed here for bulk BFO, has not been readily observed in other well-known bulk ferroelectric materials such as PZT.^[135, 158] From data presented in Hall *et al.*,^[158] it can be inferred that poled rhombohedral PZT possess large remnant domain texture (approximately 2.8 MRD) even after seven days. According to the report of Hoffmann *et al.*,^[135] a rhombohedral PZT (60/40) composition shows maximum domain texturing ($I_{111}/I_{11\overline{1}}$ reaches from initial 0.24 to 0.99) at a poling field of 3.2 kV mm⁻¹ and remains almost constant after the removal of the field. From these reports it can be assumed that such large relaxations of the field induced domain texture are not present in rhombohedral PZT. Despite the differences in poling field and poling conditions among BFO and PZT's it can be stated that bulk BFO ceramics exhibit a large relaxation of switched domains after poling.

6.3.5. Discussion

Although the relaxation of switched non-180° ferroelectric domains in thin film BFO has been observed,^[160, 161] this is the first such direct observation in bulk BFO ceramics. Cruz *et al.*^[160] showed that in an epitaxial BFO (110) thin film, the stability (slower relaxation rate) of switched non-180° ferroelectric domains can be improved by minimising the substrate induced compressive stress. Baek *et al.*^[161] has also demonstrated the effect of stress on relaxation of switched non-180° ferroelectric

domains. However, the relaxation in the bulk BFO ceramics observed here is several orders of magnitude faster than that in thin films, which is of the order of hours.^[160, 161]

Some insight to the relaxation mechanism in bulk BFO may be gained by a comparison with rhombohedral bulk PZT, which does not show an obvious relaxation effect.^[135, 158] After poling, polycrystalline electro-ceramics experience an internal residual stress. This stress exists due to the residual elastic strain of grains, which do not deform during poling by non-180° ferroelectric domain switching. Such residual stresses have been observed,^[138, 139] and have also been suggested to affect the domain switching velocities under field.^[143] It is expected that the degree of elastic anisotropy of the material plays a significant role in the total residual stress of the strained polycrystal.

The bulk polycrystalline stiffness of BFO and rhombohedral PZT are similar. According to our measurement with dynamic mechanical analyser, the bulk elastic stiffness is of the order of 50 GPa and 55 GPa for BFO and PZT, respectively. However, no experimental single crystal elastic constant information exists for these materials. First principals calculations by Cohen *et al.*^[162] and Shang *et al.*^[163] suggest that the materials do differ in the degree of elastic anisotropy, hinting this may be a factor in their differing behaviour. Using these reported values, calculation of a shear anisotropic factor (A₁)^[164] for the {100} shear planes between the <011> and <010> gives 0.11 and 0.72 for PZT and BFO, respectively. A value of 1 would correspond to a highly isotropic material in terms of its elastic properties. These calculations indicate that PZT has a larger degree of elastic anisotropy than BFO. It may be thus expected that the residual stress, for a given volume fraction of non-180° domain switching, will be different in PZT and BFO as the stress magnitude is proportional to the elastic stiffness along non-polar directions and hence depends on the elastic anisotropy of the

material. A more isotropic elastic nature of BFO would also be expected to result in a reduction in the observed lattice strain along no-polar directions in BFO relative to PZT^[93, 165] which is supported by our results (see Figure 6-6).

The observed relaxation of non-180° ferroelectric domain texture (Figure 6-7(b)) is potentially the result of the large residual stress magnitude that is built up upon non-180° domain wall motion. During the 1st poling cycle domain walls move to metastable positions, however, these metastable positions are not fixed with sufficient energy to overcome the residual stress after the removal of the applied field, and thus relax to their unpoled positions.

In addition to the specific environment (e.g. stress distribution and/or mechanical constraint due to surrounding grains, i.e. elastic effects), the nature of the domain walls themselves might play a role. As has been observed in thin film BFO,^[166] bulk BFO ceramics also exhibit conductive domain walls.^[59] As any motion of non-180° ferroelectric domain walls involves change of both mechanical and electrical boundary conditions, the charge equilibrium may be accomplished faster if the domain walls are themselves conductive. Thus, domain wall conductivity might also contribute to the relaxation behaviour, i.e. the conductive domain walls in BFO might act to release domain walls from metastable positions accelerating their relaxation under the internal residual stress of the elastically deformed grains. In support of this conjecture, an increased low-frequency creep associated with motion of conducting domain walls has been observed in both converse^[59] and direct piezoelectric properties of BFO ceramics.^[167] It is worth mentioning that, in contrast to BFO, in bulk PZT (both undoped and doped) no conductive domain walls have been identified by atomic-force microscopy (AFM) analysis.^[59]
The intergranular stress states suggested above may also have implications for the general mechanical stability of these materials. One might predict that microcracking between grains in BFO ceramic samples can be initiated easily during the poling and subsequent electro-mechanical actuation process due to the large difference in strain magnitude of polar vs non-polar aligned grains. In fact, cracking has been observed in bulk BFO ceramics previously.^[148] Initiation of cracking would be expected to relieve the internal residual stress and be observed as a reduction in the elastic strain of the <001> oriented grains in the current experiment, as has been shown to occur in fatigued PZT materials.^[168] However, during the two cycles measured here, both non-180° ferroelectric domain texture and lattice strain increase in a correlated manner, thus no micro-cracking appears to occur in the initial two cycles of the samples examined. This is consistent with the absence of significant cracking in BFO poled with unipolar triangular field cycles.^[148]

6.4. Conclusions

The electric-field-induced strain response in bulk BFO ceramics has been investigated by means of *in situ* high-energy x-ray diffraction. It has been found that, in spite of the strain/applied field ratio similarities in bulk and thin film BFO, the origin of strain response in thin film and bulk BFO is different. The strain response observed in the bulk BFO ceramic is primarily due to the extrinsic non-180° ferroelectric domain switching. A large relaxation of switched non-180° ferroelectric domains in bulk BFO ceramics has also been observed with a time constant of the order of 40 seconds. This relaxation phenomenon has been proposed to be due to the stiffer nature of shear elastic constant (degree of elastic anisotropy), which generates a large internal residual stress in response to the domain switching. This may act in conjunction with the conductive nature of the domain walls to allow them to move more easily from their metastable poled state back towards their unpoled state.

7. Contrasting strain mechanisms in lead-free piezoelectric ceramics

This thesis has presented *in situ* high-energy x-ray diffraction studies of the microscopic origin of electric-field-induced strain in selected lead-free piezoelectric ceramics. Development of actuator properties in lead-free piezoelectric materials will benefit from a detailed understanding of the origin of strain at microscopic scale. It was found that the material systems studied represent three distinctive strain mechanisms mediated at the structural and microstructural length scale.

As discussed in Chapter 2, conventional piezoelectricity is the poling induced piezoelectricity where the poling process initiates a remnant strain/polarisation state in the material. Generally, the primary figure of merit for piezoelectric ceramics is given as the small-signal piezoelectric coefficient (d_{33}) . As the total achievable strain over a range of applied electric field is important for actuator applications, a mere emphasis on the d_{33} value may not be useful. Thus, the strain to electric field ratio (S/E), i.e. largesignal piezoelectric coefficient (d_{33}^*) , can be considered as a figure of merit for actuator applications. The maximum achievable strain (S_{usable}) is directly related to the S_{max} and S_{rem} (Please see Figure 2-4). In order to achieve maximum actuator performance in piezoelectrics, one needs to maximise S_{max} or minimise S_{rem} . In addition, the lower the E is, the higher the actuating performance is. The strain-electric field (S-E) loop measured during the poling cycle can highlight the inherent capacity of actuating performance in piezoelectric materials. From this point of view, in situ diffraction studies of promising lead-free compositions were also conducted during the poling cycles. Thus the origin of microscopic strain discussed in this study directly highlights the potential of actuator property of these materials.

To develop lead-free actuator materials with improved performance, two major ways can be identified, i) design of new materials with large S_{max} , and ii) modification (e.g., microstructure and/or chemical) of existing compositions to minimize S_{rem} and/or E_{pol} . Both of these pathways can benefit from the understanding of the strain mechanisms at microscopic length scales. In this chapter, the origins of microscopic strain in the lead-free piezoelectrics studied in this thesis are contrasted with each other and those reported in the literature.

7.1. Tailoring of unipolar strain for actuator applications

Although the promising macroscopic properties of BNT-xBT system were reported in 1991 by Takenaka et al.,^[60] the microscopic origin of electric-field-induced strain was not studied extensively until the last decade.^[62, 63, 116, 169, 170] The structure-property relationships at microscopic scales were partly hindered by the ambiguity ^[35-37] about the crystallographic structure of the parent BNT system. As a consequence, the phase identity is very complicated and at least six different phase diagrams^[60, 171-175] have been proposed for BNT-*x*BT system. Nevertheless, BNT-*x*BT ($0 \le x \ge 0.12$) systems have been considered as a "relaxor like" material because of their frequency dependence in temperature-dielectric permittivity measurements. The relaxor behaviour was confirmed in the recent reports by Jo et al.^[176, 177] It has also been reported that the origin of the field-induced change of electrical properties in BNT-based materials is perhaps related to the breaking of Bi-O hybridisation.^[178] From the current understanding it may be suggested that compositions close to MPB in the BNT-*x*BT system exist a long range cubic symmetry with short range rhombohedral and tetragonal symmetry at room temperature. Thus, these compositions are termed as pseudo-cubic in the as-processed state. This pseudo-cubic symmetry undergoes an electric-field-induced phase transformation to (long range ordering) lower symmetry.^[62] Later Simons et al.^[63]

reported that the electric-field-induced phase transformation occurs via simultaneous lattice distortion and change to the octahedral tilt system. Thus, lowering of symmetry and the resulting domain texture induced, i.e. combined extrinsic strains, are the major contributor to the macroscopic strain measured in BNT-xBT ceramics. In other words, electric-field-induced irreversible phase transformation and domain texture is the origin of electric-field-induced strain in the MPB compositions of the BNT-xBT series. However, due to the irreversible nature of the extrinsic contributions,^[63] the usable strain (S_{usable}) is low for actuator applications. For example, BNT-7BT, an MPB composition in the BNT-*x*BT system, exhibits a large S_{max} of 0.45% at 6 kV mm⁻¹ but only 0.19 % can be utilised due to the large remnant strain ($S_{\text{rem}} \sim 0.26\%$). Note that high S_{rem} and/or P_{rem} generally relates to high small-signal d_{33} , thus this material is promising to replace lead-based conventional piezoelectrics in applications that require a direct piezoelectric coupling. However, application of this material is limited due to the operational temperature range, i.e. the small-signal d_{33} value disappears around a temperature that is well below the Curie temperature, known as depolarisation temperature (T_d) .

At the current state, the applicability of BNT-*x*BT system as an actuator material (largesignal d_{33}^*) is hindered mainly by the high S_{rem} . Interestingly, the degree of irreversibility (i.e. S_{rem}) in extrinsic contributions has been found to decrease with increasing temperature.^[169] In other words, the phase transformation in these BNT-*x*BT compositions may become reversible at elevated temperatures. As the stability of electric-field-induced phase can be modified by temperature, then the possibility that the phase stability can be tuned by doping was explored,^[115] ultimately to minimise S_{rem} in BNT-*x*BT. In summary, the origin of electric-field-induced strain in BNT-*x*BT compositions is the irreversible relaxor to ferroelectric phase transformation. Due to the irreversible nature of this transition, the achievable S_{max} cannot be utilized. Therefore, destabilisation^[179] of the FE phase with field release is essential to minimise the S_{rem} and develop materials with large S_{usable} .

A recent trend in the research of lead-free actuator materials is to develop so called "giant-strain" materials. The research of this type of material system was spurred by the report of Zhang et al.^[66] on NKN modified BNT-xBT system (BNT-BT-NKN). In this system a large S_{usable} of 0.45% at 8 kV mm⁻¹ was measured. The most striking feature is that in addition to the giant S_{max} the remnant strain is almost negligible which enables the utilisation of the maximum possible inherent strain of the material for actuator applications. Initially, the giant strain in this system was attributed to the electric-fieldinduced phase transition of antiferroelectric (AFE) to ferroelectric (FE). Later it was reported that the phase transition is actually a reversible relaxor (RE) to ferroelectric (FE) type. A detailed report on the evolution of the structure-property relationships in BNT-BT-NKN has been published by Jo *et al.*^[115] With the help of several experimental observations such as temperature-dependent strain measurements,^[180] in situ TEM,^[181] and *in situ* x-ray and neutron diffraction,^[182] it was concluded that the BNT-BT-NKN system is a relaxor ferroelectric with pseudo-cubic symmetry (perhaps with short range tetragonal ordering) in the as-processed state. External perturbation by electric-field induces a rhombohedral symmetry. Moreover, the pseudo-cubic to rhombohedral transition is reversible. Therefore, the giant S_{usable} in BNT-BT-NKN system is related to the reversible nature of the electric-field-induced relaxor-ferroelectric transitions. Several other giant strain materials based on BNT-BKT have been reported.^[69, 70, 183-186] Although a comprehensive strain mechanism has not yet been reported, it is likely that the BNT-BKT based giant strain materials also follows the same electric-field-induced reversible relaxor-ferroelectric phase transition.^[69, 115] Despite the high S_{usable} , the applicability of giant strain materials is hindered by high actuating field ($E_{pol} \ge 4 \text{ kV} \text{ mm}^{-1}$) and significant hysteresis. Thus, novel mechanisms by structural and microstructural engineering to reduce the high actuating field are required.

Considering the above mentioned issues (e.g., high S_{rem} and high E_{pol}) in lead-free actuator materials, the ceramic/ceramic composite approach is encouraging. ^[76, 82, 83, 187] Groh *et al.*^[82] reported a ceramic/ceramic composite based on BNT-*x*BT and BNT-BT-NKN. It has been shown that this approach can reduce the critical electric field E_{pol} , and also strain hysteresis of giant strain materials.^[76] Therefore, the ceramic/ceramic composite approach can be useful to utilise the best properties from two different systems. Figure 7-1 shows strain loops for two different lead-free systems. Phase 1 (e.g. RE phase) ceramic exhibits very large S_{usable} but at high E_{pol} . On the other hand, Phase 2 (e.g. FE phase) ceramic shows large S_{max} at low E_{pol} but with relatively small S_{usable} . A combination of these two systems may improve the electric-field-induced strain property.



Figure 7-1 Representation of unipolar strain loops for (a) ceramic (Phase1) e.g., giant strain BNT-BT-NKN, and (b) ceramic (Phase2) e.g., BNT-7BT.

This thesis (Chapter 4) highlights the origin of the strain response in such piezoelectric ceramic/ceramic composites. It can be said that as the individual grains in polycrystalline ceramics do not behave uniformly under an applied field, tuning the microstructure by incorporating different phase grains can adjust the macroscopic properties. Thus, the ceramic/ceramic composite approach is promising for tailoring electrical properties for lead-free piezoelectrics.

Recently, Zhang *et al.*^[188] has reported ceramic/ceramic composite of semiconductor ZnO and BNT-*x*BT (x = 0.06) to suppress T_d while maintaining high small-signal d_{33} . Although, ceramic/ceramic composite systems have not been explored extensively for different lead-free systems so far, several promising candidates should be considered for future study such as ceramic/ceramic composite of BT or Ba(Zr_{1/5}Ti_{4/5})O₃ $x(Ba_{7/10}Ca_{3/10})TiO_3$ (BZT-*x*BCT)^[189] with giant strain materials.

7.2. Enhanced reversibility of non-180° ferroelectric domain switching by microstructure engineering

Non-180° ferroelectric domain switching is accompanied by a strain due to the exchange of non-equal crystallographic axes (a ferroelastic strain). Such strain may be one or two orders of magnitude larger than the intrinsic lattice strain. However, the majority of this domain switching strain is a one-time effect (i.e. only during the poling cycle) in conventional piezoelectric ceramics. In other words, as a large number of domains are already switched along the electric (poling) field direction after poling, these domains cannot contribute to the strain during unipolar cycling. The irreversibility of non-180° ferroelectric domain switching limits the actuator response in unipolar cycling. Interestingly, Ren^[190] has reported a large recoverable strain in an aged BaTiO₃ single crystal. It was shown that the symmetry-conforming property of point defects can act as a restoring force to revert switched fraction of non-180° ferroelectric domains. However, reversible non-180° ferroelectric domain switching in polycrystalline ceramics has not been reported. In this thesis (Chapter 5), it was found that an enhanced degree (95%) of reversibility in the switched fraction of non-180° ferroelectric domains can be achieved in core-shell microstructure of $BaTiO_3$ -KNbO3. It can be stated that in this type of microstructure, because there is no remnant state of the domains on poling, there is a large degree of domain switching associated strain available for actuation during unipolar cycling. This enhanced reversibility in switched domains presents a way to minimise S_{rem} , and hence, enables to utilise the maximum achievable inherent strain (S_{max}) of the lead-free piezoelectric ceramics for actuator applications. Thus, fabrication of core-shell microstructure provides a possible method to achieve large electric-fieldinduced strain in a wide range of lead-free piezoelectric systems.

A model of residual stress mediated reversible non-180° ferroelectric domain switching in core-shell microstructure ceramics has been proposed in this thesis. The extent of domain switching with respect to shell thickness should be considered for future study. Additionally, the effect of lattice mismatch between the different shell and core materials needs further attention.

7.3. Extrinsic domain switching and their stability in bulk $BiFeO_3$

Microscopic origin of electric-field-induced strain in pure bulk BFO has not been reported readily, likely because of the processing difficulties.^[45] This thesis highlights the origin of the electric-field-induced strain in bulk BFO. The origin of strain was found to be due to the non-180° ferroelectric domain switching with no measurable changes in crystallographic symmetry (Chapter 6). Interestingly, switched fractions of non-180° ferroelectric domain exhibited relaxation behaviour. In other words, switched domains are unstable after poling ($E_{\text{max}} = 14 \text{ kV mm}^{-1}$), i.e. the bulk BFO depoles with time.

This instability of switched domains (S_{rem} becomes progressively low) makes it difficult to use as sensor materials where direct piezoelectric coupling (small-signal d_{33}) is important. Moreover, applications of thin film BFO as multiferroics (e.g., control of magnetic properties with an electric field and vice versa) are also hindered by the instability of switched domains.^[160, 161, 191] However, relaxation (instability) of switched domains may be advantageous for actuator applications because more switchable domains are available for unipolar cycling. In other words, materials with small remnant state (in this case relaxation of domain texture and associated strain) after poling possess more domain switching strain during subsequent unipolar cycling. As mentioned earlier, in bulk form, BFO could be a critical material for lead-free piezoelectric applications at high operating temperatures. However, mechanisms need to be found to either a) ensure poling holds for sensor applications, or b) increase the rate of relaxation so that poling strain can be utilised in actuator applications. This thesis presents insight of the origin of strain and domain switching relaxation in bulk BFO. From the results presented here (Chapter 6), it can be stated that elastic anisotropy, residual stress and conductive nature of domain walls should be considered for the development of BFO based actuator at high operating temperature.

7.4. Summary

From the above considerations it can be said that minimisation of the remnant strain, $S_{\rm rem}$ is one of the primary requirements to achieve lead-free actuator materials with improved large-signal d_{33}^* . In this context, the possible pathways can be summarized by Figure 7-2. Current lead-free actuator materials (bulk ceramics) can be broadly categorised as a) phase change materials (e.g., relaxor to ferroelectric phase), and b) conventional electric-field-induced domain switching (DS) materials. Destabilisation of the electric-field-induced phase and reversible switching of non-180° ferroelectric domains can minimise the $S_{\rm rem}$ in phase change and conventional DS materials, respectively.



Figure 7-2 Possible pathways for achieving lead-free piezoelectric ceramics for actuator applications.

In this thesis, the focus was investigations of the electric-field-induced strain (i.e. microscopic origin) in lead-free piezoelectric ceramics that will benefit the development of materials for actuator applications. Therefore, actuator properties of the materials were highlighted by parameters such as large-signal d_{33}^* (= S_{max}/E_{max}). It should be acknowledged that, although S_{max}/E_{max} is one of the most important parameters to develop piezoelectric materials for actuator applications, there are several other parameters such as frequency dependence, temperature stability, fatigue properties, and blocking stress, that also need to considered for practical applicability of the

materials.^[17] Nevertheless, understanding of the electric-field-induced strain at microscopic length scales is critical to develop strategies to further improve the properties of a material through structural and/or chemical modification.

8. Conclusions

This thesis has investigated electric-field-induced structural contributions in three contrasting electro-mechanical materials systems. The conclusions drawn from these investigations yield outcomes of significance relating to a) the measurement of electric-field-induced structural changes in ceramic/ceramic composite materials, b) the unique domain switching mechanism in core-shell microstructures, and c) electric-field-induced domain switching and domain texture relaxations in single phase bulk BFO. All of these systems have potential implications for the development of lead-free piezoelectric ceramics for future applications.

Tuning of local response to tailor macroscopic properties, i.e. ceramic/ceramic composite approach is a useful method to develop materials for actuator applications. In this thesis it was found that a ferroelectric (FE) phase such as BNT-7BT can improve the actuating property of relaxor phase BNT-BT-NKN materials. *In situ* diffraction studies from the bulk of these materials showed that the particulate FE phase behaves independently of the matrix of relaxor (RE) phase. Thus, tailoring of macroscopic properties (e.g., strain response, critical applied field, and temperature stability) of the matrix phase with particulate phase should be considered for future development of lead-free piezoelectric materials using this microstructural engineering method.

Piezoelectric ceramics with a core-shell microstructure at the grain scale possess unique domain switching behaviour. It was found that BT-KN ceramics with such a microstructure exhibited enhanced reversibility of non-180° ferroelectric domains. It was hypothesised that the suppression of domain wall interaction with defects at grain boundaries led to the enhanced reversibility of non-180° ferroelectric domains. As a

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consequence, ceramics with this type of microstructure offers a unique strain mechanism for further development for actuator applications.

Rhombohedral phase bulk BFO ceramics exhibit large electric-field-induced non-180° ferroelectric domain switching strain. The intrinsic and extrinsic contributions to the macroscopic electric-field-induced strain ($d_{33}^* = 100 \text{ pm V}^{-1}$) in this material was quantified from *in situ* diffraction data. The major fraction (64%) of electric-field-induced strain in pure bulk BFO stems from extrinsic non-180° ferroelectric domain switching. No electric-field-induced phase transformation was observed. Additionally, in bulk BFO a relaxation process of the switched non-180° ferroelectric domains was observed that greatly affects the process of poling these materials. It was also hypothesised that the domain texture relaxations are related to the material elastic anisotropy and domain wall conductivity. Therefore, elastic anisotropy of crystals and related residual stress should be considered/modelled to identify promising compositions for actuator applications.

A comprehensive report on the microscopic origin of electric-field-induced strain response in potential lead-free piezoelectrics is lacking. Therefore, it is hoped, the contrasting strain responses outlined in this thesis will assist in guiding materials design for future sensor and actuator piezoelectric materials.

9. Future work

The proposed future works below may facilitate further understanding of strain mechanisms in these lead-free materials and piezoelectrics in general:

- i. Ceramic/ceramic composite of RE and FE phase such as RE phase BNT-BT-NKN, BNT-BKT and FE phase BT, BZT-BCT. As BT is has a low poling field ($E_{pol} \sim 0.42 \text{ kV mm}^{-1}$) it is expected that the composite approach with BT as a particulate phase could facilitate lower actuating fields for highstrain phase-change matrix systems. However, pitfalls associated with inhomogeneous distribution of particulate BT in the matrix as well as interfacial coherence and differences in sintering temperatures need to consider.
- ii. In order to confirm the hypothesis of domain wall interactions with grain boundaries a careful study of the effect of KN shell thickness on reversibility of switched domain in the core-shell microstructured BT-KN system would be required. One would expect a lower shell thickness to allow higher domain switching but perhaps at the expense of reversibility, while a larger shell thickness may greatly enhance reversibility but limit the magnitude of the non-180° ferroelectric switching.
- iii. Enhancement of sintered density of the core-shell microstructures. As reliability properties such as electrical break down and fatigue are often associated with low relative density, it would be expected increasing density may lead to greater reliability.

- iv. In order to understand potential of BFO for high-temperature piezoelectric applications, field-induced domain switching and domain relaxations at elevated temperature in bulk BFO would be useful.
- v. Frequency dependence measurements of electric-field-induced macroscopic strain in bulk BFO has been found to show unusual dispersion behavior.^[59]
 A detailed electric-field-induced diffraction study using time-resolved techniques with stroboscopic data collection may highlight the frequency-dependence of the electric-field-induced strain in bulk BFO.

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Appendix

Appendix A

Reprint of the manuscript published in *Journal of Applied Physics* titled "Tailoring of unipolar strain in lead-free piezoelectrics using the ceramic/ceramic composite approach" by N. H. Khansur, C. Groh, W. Jo, C. Reinhard, J. A. Kimpton, K. G. Webber, J. E. Daniels.





Tailoring of unipolar strain in lead-free piezoelectrics using the ceramic/ceramic composite approach

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Tailoring of unipolar strain in lead-free piezoelectrics using the ceramic/ceramic composite approach

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The electric-field-induced strain response mechanism in a polycrystalline ceramic/ceramic composite of relaxor and ferroelectric materials has been studied using *in situ* high-energy x-ray diffraction. The addition of ferroelectric phase material in the relaxor matrix has produced a system where a small volume fraction behaves independently of the bulk under an applied electric field. Inter- and intra-grain models of the strain mechanism in the composite material consistent with the diffraction data have been proposed. The results show that such ceramic/ceramic composite microstructure has the potential for tailoring properties of future piezoelectric materials over a wider range than is possible in uniform compositions. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4869786]

INTRODUCTION

Piezoelectric materials are used in a wide range of industrial and consumer applications with the market largely dominated by the lead-based composition Pb(Zr,Ti)O₃ (PZT).¹ Considering PZT's environmental concerns and limitations in high temperature performance, research into lead-free electroceramics has increased dramatically in the last decade.² New synthesis routes and information gained from detailed structural studies of existing high-performance leadfree compositions are leading to the development of new compositions of interest. From extensive knowledge of the PZT system, a common approach for the development of lead-free compositions is to search for systems with morphotropic phase boundary (MPB). Promising lead-free ferroelectrics (FEs) include compositions based on sodium potassium niobate $Na_{(1-x)}K_xNbO_3$ (KNN) and bismuth sodium titanate $Bi_{1/2}Na_{1/2}TiO_3$ (BNT).³⁻⁸ In 2007, Zhang *et al.*⁹ reported a new pseudo-ternary composition, replacing a small fraction of BNT with KNN from the Bi1/2Na1/2TiO3-BaTiO3 (BNT-BT) system, which showed large electric-field-induced strain values (0.45% at 8 kV/mm). This field-induced strain response remains stable against temperature¹⁰ and cyclic fatigue.¹¹ While the strain response of this material is attractive for actuator applications, it is limited in device implementation due to the high actuating field ($\geq 6 \text{ kV/mm}$) and significant hysteresis. Several other BNT-based compositions with large strain have been reported by different authors.¹²⁻¹⁴ Interestingly, among all these compositions the strain is generated via an electric-field-induced reversible transition between pseudocubic relaxor (RE) and non-cubic ferroelectric phases at relatively high fields $(\geq 4 \text{ kV/mm})$.^{15–18} Further improvement of actuator properties with such compositions will require the lowering of the actuating field. One possible

approach for achieving this is to modify the microstructure of these materials using a ceramic/ceramic composite method.

Producing ceramic/ceramic composites with a controlled microstructure in order to tailor the electrical properties (such as dielectric, piezoelectric, and pyroelectric) in electroceramics is a well-known approach.¹⁹⁻²¹ However, it has not been applied to modify the properties of large strain BNT-based lead-free materials until recently. Several studies²²⁻²⁷ have introduced ceramic/ceramic composite systems as a method to tune the electrical and electro-mechanical properties in lead-free ferroelectrics. Lee et al.²² have focused on the minimization of the actuating field of large strain BNT materials by forming a compositionally non-homogeneous phase structure (relaxor and ferroelectric) at the grain length scale. They showed that the actuating field can be significantly reduced with the addition of 20 vol. % of ferroelectric grains in the matrix of relaxor grains. The improved properties of the ceramic/ceramic composite material have been explained by a series capacitor model where polarisation coupling throughout the material reduces the required actuating fields.^{22,26} Wada et al.^{23,25} have reported another type of compositionally non-homogeneous barium titanate-potassium niobate BaTiO₃-KNbO₃ (BT-KN) ceramic. In this system, an artificial MPB has been created between single crystal particles of BT and an epitaxial shell of KN. Strain response in this very same composition was reported by Fujii et al.²⁴ and it has been found that the BT-KN composite exhibit approximately three times larger strain than the BT-KN solid solution ceramics.²⁸ This comparatively large strain response in BT-KN composite has been attributed to the polarization rotation at the strained epitaxial interface region.²⁴ These studies show the ceramic/ceramic composite structure is a promising path for the development of future lead-free electro-mechanical materials.

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FIG. 1. Schematic of experimental geometry and collected diffraction pattern with large area 2D detector. Inset shows a typical diffraction pattern from the area detector after radial integration.

The development of new lead-free ceramic/ceramic composites for industrial applications will benefit from a detailed understanding of the underlying strain generation mechanisms. An attempt has been made in this paper to highlight the strain generation mechanism in recently reported 0.92BNT-0.06BT-0.02KNN (BNT-BT-2KNN) and 0.93BNT-0.07BT (BNT-7BT) ceramic/ceramic composite materials^{26,27} using *in situ* high-energy x-ray diffraction. The large strain BNT-BT-2KNN composition shows a reversible transition between a relaxor and ferroelectric phase with applied external electric field, while BNT-7BT shows an irreversible phase transition to the ferroelectric state.²⁹ In these ceramic/ceramic composite systems, the effect of volume fraction of FE phase BNT-7BT on the reversible transition of the relaxor (RE) phase BNT-BT-2KNN has been studied in situ using high-energy x-ray diffraction.^{15,18} The macroscopically measured strain response has been correlated with the structural response. A microscopic strain mechanism has been proposed on the basis of diffraction studies.

EXPERIMENTAL

The ceramic/ceramic composite materials were prepared using FE 0.93(Bi_{1/2}Na_{1/2}TiO₃)-0.07(BaTiO₃) (BNT-7BT) as a particulate component and RE 0.92(Bi_{1/2}Na_{1/2}TiO₃)-0.06 (BaTiO₃)-0.02(K_{1/2}Na_{1/2}NbO₃) (BNT-BT-2KNN) as the matrix component. Six different compositions have been prepared by varying the volume fraction of FE (0FE, 10FE, 20FE, 30FE, 50FE, and 100FE). Details of the synthesis route have been previously reported.^{26,27} Macroscopic unipolar strains up to fields of 6 kV/mm were measured with disk-shaped samples by modified sawyer tower setup at a frequency of 50 mHz. Bar-shaped ceramic samples of 0.8 mm × 1 mm × 6 mm suitable for *in situ* high-energy diffraction experiments were cut from sintered disks. Silver electrodes were applied to two opposing 1 mm × 6 mm faces of the bar.

In situ high-energy x-ray diffraction measurements were carried out at beamline I12-JEEP of the Diamond Light Source, UK. A monochromatic x-ray beam of energy 84.82 keV (wavelength $\lambda = 0.146$ Å) and dimensions 150 μ m × 150 μ m was used. Diffraction patterns were collected in transmission geometry using a large area detector as shown schematically in Figure 1. The detector parameters, including distance, beam centre, and tilts, were calibrated

using a standard ceria powder pattern. For the diffraction patterns to be measured *in situ*, samples were placed in a specifically designed electric field chamber where the applied electric field is perpendicular to the x-ray beam direction.³⁰ In this geometry, diffraction information is simultaneously collected with the scattering vector at all possible angles to the applied field vector.

Diffraction images were collected during an applied unipolar electric field up to 6 kV/mm in steps of 0.6 kV/mm. These images were integrated into 36 azimuthal sections with 10° intervals using the software package FIT2D.³¹ Single or multiple pseudo-Voigt fitting functions have been fit to selected peaks within the diffraction patterns. The refined peak positions have been used in the following equation to calculate the lattice strain as a function of applied electric field

$$\varepsilon_{hkl} = -\Delta\theta \cot\theta_0$$

where ε_{hkl} is the lattice strain for specific *hkl* plane, θ_0 is the diffracted angle of the *hkl* reflection at initial state, and $\Delta \theta$ is the difference between the diffraction angle of the strained state and initial state.

RESULTS AND DISCUSSIONS

The microstructure of the samples used in the current study has been investigated by SEM, TEM, and and energy-dispersive x-ray (EDX).^{26,27} It is found that the average grain size of the samples is approximately 2 μ m and is consistent over the compositional range reported here. Compositionally sensitive measurements were performed on the 10FE and 50FE compositions and showed that the materials have sub-grain regions approximately 0.05 μ m in size that are niobium rich. Additionally, grains containing these Nb rich areas were also sodium (Na) and potassium (K) rich. These previous results confirm that compositional inhomogeneity exists in such materials.

Macroscopically measured unipolar strain at 6 kV/mm for different ceramic/ceramic composite is shown in Figure 2(a). Characteristic parameters were derived from these strain loops as presented in Figure 2(b) showed interesting trends in electrical properties as a function of particulate FE phase. The poling strain value at maximum field (6 kV/mm) varies from 0.39 to 0.45% and is maximum for pure FE (100FE) materials. E_{pol} represents the field strength at which the sample is poled from the as-processed state; E_{pol} tends to decrease with increasing amount of FE phase. The effect of volume fraction of FE phase is more pronounced in the remnant strain which increases from zero for the pure relaxor (RE) phase material to 0.26% for the pure FE phase material.

With 0%FE, no remnant strain is observed in the material due to a reversible structural transformation^{9,15} with applied field, which is characteristic of this composition. With increasing amount of FE phase the ceramic/ceramic composite materials shows an increasing remnant strain that is maximum for pure FE materials (100FE). The remnant strain for 100FE is consistent with previous measurements reported for BNT-7BT that show a remnant strain of 0.24% (Ref. 32) resulting from an irreversible phase



FIG. 2. (a) Unipolar strain hysteresis and (b) derived characteristic parameters of macroscopic strain (schematic illustration of derived characteristic parameters is shown in the inset) for ceramic/ceramic composite at 6 kV/mm. With increasing FE content the remnant strain increases, while the poling strain at maximum field is approximately constant. The usable strain reduces with increasing FE content.

transformation.¹⁸ In this case, with a maximum applied field of 6 kV/mm, the usable strain (i.e., maximum strain – remnant strain) decreases continuously with increasing fraction of FE phase.

In situ high-energy x-ray diffraction experiments have been carried out for all the compositions. Four selected compositions (0FE, 10FE, 20FE, and 100FE) have been presented here to elucidate the strain mechanism in relaxor/ferroelectric composites. All of the compositions in the as processed state show single phase perovskite type diffraction patterns that can be indexed with a cubic $Pm\bar{3}m$ structure (Figure 3). The samples show electrical properties not consistent with pure cubic phase materials. Additionally, it is known that small distortions at the local scale exist in related compounds;^{33,34} therefore, the structure of the as-processed material is referred to as pseudocubic. No significant difference in the lattice parameter is observed for the four compositions within the



FIG. 3. Experimental diffraction profiles for four different compositions in the as-processed state. Single and symmetric diffraction peaks are seen throughout the patterns indicating a pseudocubic structure.

resolution of the diffraction instrument used. However, the macroscopic strain response behaviour is significantly different for each composition; thus, it can be assumed that these crystallographically similar compositions are responding differently under applied electric fields.

The electric-field-induced transformation behaviour in such perovskite materials can be qualitatively characterized by observing the (111) and (200) type pseudocubic reflections. *In situ* diffraction patterns for (111) and (200) type pseudocubic peaks of all four compositions with the electric field vector aligned with the diffraction scattering vector are presented in Figure 4. The 0FE composition (Figure 4(a)) shows a maximum lattice strain of 0.06% and 0.15% at 6 kV/mm (E_{max}) in the (111) and (200) peaks, respectively. No shoulder peak is observed in the (200) peak as shown in the bottom of Figure 4(a). This observed lattice strain is completely reversible, and the peaks return to their original positions upon removal of the electric field. This reversible electric-field-induced lattice strain behaviour is characteristic of relaxor type high-strain materials.¹⁵

Data presented in Figure 4(b) for the 100FE composition show that the application of electric field of 6 kV/mm (E_{max}) induces significant distortions in the (111) and (200) peaks. These distortions remain after the electric field is removed (E_{rem}). Thus, it can be said that this composition shows an irreversible electric-field-induced phase transformation. The nature of phase transformation in this system has been previously reported as either pseudocubic to tetragonal or pseudocubic to mixed phase tetragonal and rhombohedral.^{18,35} The observed (111) peak distortion and (002)/(200) peak splitting reveals that the field-induced transformation for the composition in this study is likely a mixed phase type transformation.

Figure 4(c) shows the 10FE composition (111) and (200) diffraction patterns under the applied electric field. A lattice strain of 0.07% and 0.18% is observed at 6 kV/mm in the (111) and (200) peaks, respectively. The (200) peak in this composition develops a small low 2θ shoulder under the applied field. It also exhibits remnance in lattice strain after



FIG. 4. (111) (top) and (200) (middle) diffraction peaks for (a) 0%FE, (b) 100%FE, (c) 10%FE, and (d) 20%FE materials as function of applied electric field. The variation in (200) shoulder peak intensity in as-prepared (E₀), at 6 kV/mm (E_{max}) field and after removal of electric field (E_{rem}) for all compositions (bottom). These data represent scattering information with the applied electric field vector parallel to the diffraction scattering vector.

the removal of electric field (correlating with the macroscopic strain, Figure 2).

Figure 4(d) represents (111) and (200) diffraction patterns for the 20FE composition under the applied electric field. A lattice strain of 0.08% and 0.18% is observed at 6 kV/mm in the (111) and (200) peaks, respectively. The (200) peak in this composition, however, reveals more information about the generated strain. Inset of Figure 4(d) shows the low 2θ shoulder of the (200) diffraction peak develop during the application of the electric field in 20FE ceramic/ ceramic composite. The shoulder of (200) peak is more pronounce in 20FE (bottom of Figure 4(d)) composition than the 10 FE (bottom of Figure 4(c)). Thus, it can be assumed that development of the low 2θ shoulder depends on increasing volume fraction of FE phase in the ceramic/ceramic composite. The development of the shoulder during the application of the electric field is consistent with a small volume fraction of the bulk material undergoing a pseudocubic to tetragonal phase transformation. In the ceramic/ceramic composite studied here, this would imply that the small volume fraction of particulate phase has undergone the irreversible transition to the ferroelectric state, while the bulk of the sample has reversible electric-field-induced strain consistent with a conventional relaxor material. In other words, compositions, such as 10FE and 20FE, exhibit a combined effect of OFE and 100FE in their field-induced response; as evident from the diffraction data.

Based on the *in situ* diffraction results, microscopic strain response mechanisms for ceramic/ceramic composite have been proposed (Figure 5). At the initial zero field state, the ceramic/ceramic composite can be represented as a

polycrystalline ceramic composed of relaxor (RE) grains (Figure 5(a)). With the application of electric field differences in field-induced transformation in ceramic/ceramic composite can be visualized either by Figure 5(b) (type I) or Figure 5(d) (type II), where former shows inter-grain and latter shows intra-grain composite effects. In the proposed type I mechanism, ferroelectrically/ferroelastically strained FE grain induces a ferroelectric state on the neighbouring RE grains. This similar kind of induced effect can occur in smaller regions as shown in type II. With further increase in electric field (Figures 5(c) and 5(e)) the switched ferroelectric domains propagate strain on the surrounding RE matrix. A majority fraction of the strained region can be relaxed back with the removal of electric field but not completely.

The proposed model based on the in situ diffraction study suggests that the addition of FE phase materials at later stages of processing has produced a polycrystalline material where regions at the grain scale behave independently of the bulk. This has significant implications for the response mechanism of such materials. In particular, the length scale and magnitude of the compositional inhomogeneity may be tuned to increase local responses that may propagate throughout the material. Bintachitt *et al.*³⁶ has reported that in PZT thin films, nonlinear response of piezoelectricity is not homogeneous throughout a compositionally uniform sample, i.e., piezoelectric nonlinear response shows local deviation from the average due to difference in domain wall pinning. A local deviation in electric field distribution, polarisation, and strain response has been shown by Jayabal et al.^{37,38} for bulk materials by micromechanical modelling. This local deviation has been attributed to the domain



FIG. 5. Representation of proposed mechanisms of electric-field-induced strain generation. (a) Ceramic/ceramic composite in as-processed state without any FE domains; for simplicity, all the grains have been labelled as RE. Depending on the spatial distribution of compositional inhomogeneity when the field is applied it can follow either of the type I ((b) and (c)) or type II ((d) and (e)) mechanism. Type I showing the inter-grain composite effect where one of the grain irreversibly transforms from RE to FE (b) and with further increase in electric field the FE domains propagate to the surrounding RE grains (c). Type II shows the intra-grain composite effect where a region of RE grain irreversibly transforms into FE phase (d). Reversible transform mation of RE phase has not been shown here for clarity.

switching processes at the individual grain length scale. As the individual grains in polycrystalline ceramics do not behave uniformly under an applied field; tuning the microstructure by incorporating different phase grains can adjust the macroscopic properties. Here, we have shown that the electric-field induced strain response of BNT-7BT grains in a polycrystalline ceramic/ceramic composite is dictating (or coupled with) the strain response behaviour of the relaxor matrix. Thus, the local response of the particulate phase can be used to tune or nucleate specific behaviour to the bulk materials properties. The potential for tailoring the properties of functional ceramics using ceramic/ceramic composite structures at the granular scale therefore exists.

CONCLUSIONS

The electric-field-induced strain response in a ceramic/ ceramic composite of relaxor and ferroelectric materials has been investigated by means of in situ high-energy x-ray diffraction. Evaluated microscopic strain response behaviour from diffraction information has been correlated with the macroscopic strain response for two ceramic/ceramic compositions (10FE and 20FE) and the two constituents (0FE and 100FE). It has been found that in the as-processed state 10FE and 20FE exhibit a pseudocubic structure similar to OFE and 100FE. With applied electric field cycle OFE showed reversible lattice strain, whereas 100FE showed an irreversible phase transformation. In the 10FE and 20FE composition data are consistent with a model where regions of FE grains transformed independent of the bulk. Based on the diffraction study models for microscopic strain generation in ceramic/ceramic composites have been proposed.

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Appendix B

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Enhanced extrinsic domain switching strain in core-shell structured BaTiO₃-KNbO₃ ceramics

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ABSTRACT

Large electric-field-induced strain in piezoelectric ceramics is a primary requirement for their actuator applications. This macroscopic strain is generated from both intrinsic lattice strain and extrinsic domain switching and/or phase transformations. Among these contributions, non-180° ferroelectric domain switching can generate a large electric-field-induced strain due to the change in orientation of the coupled spontaneous strain. However, the large fraction of non-180° ferroelectric domain switching is a one-time effect during electrical poling. Here, we show that electric-field-induced non-180° ferroelectric domain switching in the microstructurally engineered material BaTiO₃-KNbO₃ (BT-KN) is largely reversible. In situ high energy X-ray diffraction showed approximately 95% reversibility in the switched fraction of non-180° ferroelectric domains during unipolar cycling. This reversibility is hypothesised to be due to the unique grain boundary structure of this material, where ferroelectric domain walls do not interact strongly with grain boundary defects. The domain switching behaviour of core-shell BT-KN has been contrasted with that of polycrystalline BaTiO₃ and commercial lead zirconate titanate Pb(Zr,Ti)O₃. The large and reversible non-180° ferroelectric domain switching of core-shell BT-KN offers a distinctive strain response. The results indicate a unique family of large strain lead-free materials based on enhanced reversible non-180° ferroelectric domain switching can be developed for future actuator applications.

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1. Introduction

Research in the field of lead-free electro-ceramics has dramatically increased in the last decade in order to meet potential legislative requirements limiting the use of lead in certain product types [1,2]. Lead-based Pb(Zr,Ti)O₃ (PZT) is the market leader for industrial applications with exceptional electro-mechanical coupling properties over wide ranging environmental conditions. While the exact mechanism of the strain enhancement in PZT is still debated [3–8], it is generally accepted that the unique properties are related to the structural and microstructural response in compositions close to the morphotropic phase boundary (MPB) region [9]. The creation of MPB's within solid solutions of lead-free electro-mechanical materials has therefore been a common direction of research. Among others, compositions containing solid solutions of bismuth sodium titanate $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) and barium titanate BaTiO₃ (BT), potassium niobate KNbO₃ (KN) and sodium

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niobate NaNbO₃ (NN) are just a few examples of the demonstrated capacity of MPB regions to enhance electro-mechanical coupling properties in lead-free systems [10-18].

In addition to compositional modifications, microstructural modification (i.e., tailored microstructure) such as a ceramicceramic composite approach can be utilised [19-23]. In the ceramic-ceramic composite approach, a ferroelectric phase (e.g., BNT, BNT-BT) has been used as a particulate component in a relaxor ferroelectric matrix to modify the actuating field and maximum electric-field-induced strain in compositions of $Bi_{1/2}(Na_{3/4}K_{1/4})_{1/2}TiO_3$ -BiAlO₃, and 0.92(Bi_{1/2}Na_{1/2}TiO₃)- $0.06(BaTiO_3)-0.02(K_{1/2}Na_{1/2}NbO_3)$ [19,21]. It has also been shown by an in situ high-energy X-ray diffraction study that the local response of the ferroelectric phase materials in such ceramic-ceramic composites can be critical to induce/nucleate specific behaviour in the matrix phase leading to the desired bulk material properties [22]. Thus, modification at the grain length scale can also be a useful method to enhance electro-mechanical properties.







The creation of artificial MPBs (i.e., MPB engineered materials) is a unique technique for preparing new lead-free piezoelectrics with improved properties. Wada et al. [24-26] have introduced artificial MPB in BT-KN ceramics. In this approach, BT particle compacts were used as a substrate to grow epitaxial KN by liquid phase reaction in the regions between the particles. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS) studies showed that the BT particles in the compact are surrounded by KN layers, i.e., formation of core-shell structured BT-KN where BT is in the core region and the shell is KN [26]. The heteroepitaxial interface between the core BT and the shell KN has also been confirmed by high resolution TEM [25]. A comparative study of field induced strain response in core-shell structured BT-KN and solid solution BT-KN (prepared by the conventional mixed oxide method) shows promising property enhancements using this approach. Despite the relatively low sintered density of the core-shell BT-KN (relative density \sim 70%) compared to conventionally prepared solid solution BT-KN (relative density ~95%); the former showed approximately three times larger strain response [27,28]. The increased response has been proposed to be associated with the interfacial boundary between core BT and shell KN, and enhanced polarisation rotation, although no direct experimental evidence exists [27].

In this study, BT–KN core–shell materials have been shown to exhibit remarkably large reversible domain switching during the application of electric fields. *In situ* high-energy X-ray diffraction was used to monitor the domain switching magnitude and associated lattice strain up to electric fields of 3 kV mm⁻¹. The resultant domain switching behaviour has been contrasted with BT and commercial PZT (PIC151, PI Ceramic Germany) ceramics. The results indicate that a new family of large strain materials based on the enhanced reversible non-180° ferroelectric domain switching process may be developed for actuator applications.

2. Experimental procedure

2.1. Material synthesis

The BT-KN (KN/BT ratio 0.5) core-shell structured ceramics were prepared using the solvothermal method. Ethanol was used as the solvent, while KOH, K₂CO₃, Nb₂O₅ (99.9%, Kanto Chemical, Japan), and BT single-crystal particles (BT03, particle size of approximately 300 nm, Sakai Chemical Industry, Japan) were used as the starting materials. The BT03 and Nb₂O₅ powders were mixed at Nb₂O₅/BT molar ratio of 0.5 with polyvinyl butyral (2 wt.%) as a binder in ethanol, dried at 130 °C, sieved, and then pressed into green compacts using a uniaxial press at 250 MPa. The binder was burned out at 600 °C for 10 h, and the BT03 and Nb₂O₅ (BT03-Nb₂O₅) mixture compacts were used as the substrate and a raw material of KN. The BT03-Nb₂O₅ compacts were placed in a Teflon-coated autoclave container with ethanol, KOH, and K₂CO₃, where Nb concentration was 0.10 mol L⁻¹, K/Nb atomic ratio was 10, and KOH/K₂CO₃ molar ratio was 0.22. They were heated to 230 °C, and soaked for 20 h without stirring. After the reaction, the BT-KN core-shell ceramics with a relative density of around 70 % were washed with ethanol and dried at 200 °C. The complete synthesis route has been previously reported in detail [24,27]. The microstructure of the core-shell BT-KN was analysed by the STEM (JEM-2100F, JEOL, Japan) and energy dispersive X-ray spectroscopy (EDS). Bar-shaped ceramic samples of 0.4 mm \times 1 mm \times 2 mm were cut using a diamond saw for in situ high-energy X-ray diffraction experiments. Gold electrodes were applied by sputtering onto two opposing $1 \text{ mm} \times 2 \text{ mm}$ polished faces. In addition to the coreshell BT–KN, pure BT [29] ceramic and a commercial PZT (PIC151, PI Ceramic, Germany) ceramic sample suitable for *in situ* diffraction measurements were prepared.

2.2. In situ high-energy X-ray diffraction

A monochromatic X-ray beam of energy 87.11 keV (wavelength λ = 0.142 Å) and dimensions 150 µm \times 150 µm was used for *in situ* diffraction measurements at beamline ID15B of the European Synchrotron Radiation Facility (ESRF). Diffraction patterns were collected in transmission geometry using a Pixium large area detector [30]. This geometry allows for the collection of diffraction data with scattering vector orientations at a range of angles to the applied electric field vector. Details of similar geometry experiments can be found elsewhere [31,32]. For the diffraction patterns to be measured in situ, samples were placed in a specifically designed electric field chamber where the applied electric field is perpendicular to the X-ray beam direction [33]. Diffraction images were collected during two cycles of applied unipolar electric field up to a maximum field ($E_{max} = 3 \text{ kV mm}^{-1}$) in 10 equal steps. The software package FIT2D [34] was used to integrate the diffraction images into 36 azimuthal sections with 10° intervals. Single or multiple pseudo-Voigt functions were used to model selected peaks of the diffraction patterns to extract the peak profile parameters. Fitting parameters were extracted to quantify intrinsic lattice strain and extrinsic domain switching magnitude. Errors on reported values were estimated from a combination of peak profile fitting error magnitude and the distribution of fitted values. Full pattern structural refinements of the as-processed BT-KN were carried out using Rietveld refinement software package TOPAS [35].

3. Results and discussion

3.1. Structural analysis of as-processed BT-KN

Fig. 1 illustrates a representative bright-field TEM image of an area in a single grain of core-shell BT-KN along with corresponding chemical compositional distribution obtained by EDS. The EDS maps in Fig. 1c-f clearly confirm the core-shell structure of BT-KN ceramic with most of the K and Nb ions are present in the shell while Ba and Ti ions are detected in the core region. Moreover, high resolution TEM observations of the BT-KN interface also reveal the heteroepitaxial growth of KN layers on the surface of the core BT [25,27].

A diffraction pattern from the as-processed material was collected prior to the application of electric fields (Fig. 2). Qualitative analysis of the pattern shows the sample appears to be a single phase perovskite type structure with tetragonal symmetry. No orthorhombic (*Amm*2) KN phase is observed; although the microstructural study by TEM (Fig. 1) showed existence of BT and KN regions. This absence of the orthorhombic phase might be due to the resolution limit of the diffraction instrument used or due to the distorted orthorhombic unit cell. It is worth mentioning that the lattice mismatch between the orthorhombic unit cell of KN and the tetragonal unit cell of BT is 0.5%. Epitaxial growth of the KN on the BT particles has likely resulted in a sufficient strain to the KN phase to allow this phase to exist in the tetragonal state.

To determine the phase structure, full diffraction pattern refinements of the as-processed sample with various combinations of space groups (e.g., tetragonal *P4mm*, orthorhombic *Amm2* and cubic $Pm\bar{3}m$) were carried out. Fig. 3 and Table 1 show the results of full pattern structural refinements with different structural symmetries. Initial structural refinement with two phases (*P4mm* + *Amm2*) revealed that the system is not well modelled



Fig. 1. Core-shell structure in BT-KN. TEM and EDS mapping images show that K and Nb exist in the shell region.



Fig. 2. Experimental diffraction profiles for core-shell BT–KN in the as-processed state. A single symmetric (*111*) reflection and doublet in (*200*) indicates tetragonal symmetry.

using these two phases. Moreover, this two phase model (Fig. 3a) does not improve the fit in the (200) peak compared to the single phase tetragonal model (Fig. 3b). However, structural refinements (Fig. 3c) with P4mm (a = 3.98472 Å, c = 4.01662 Å) and cubic $Pm\bar{3}m$ (a = 3.99570 Å) show better refinement results (Table 1). The superior fit with the addition of the cubic phase with the tetragonal phase (*P*4mm) does not necessarily provide conclusive evidence of a cubic phase existing in the sample. Due to the ferroelastic nature of BT, significant domain wall scattering is observed in the positions expected for the cubic phase peaks [36]. Thus, within the scope of this paper, the core–shell BT–KN has been considered

as tetragonal; although the possibility exists that the shell KN structure approaches a cubic (i.e., non-polar) state.

3.2. Domain switching in core-shell BT-KN by in situ X-ray diffraction

The field-induced domain textures in tetragonal structures can be analysed by observing the variation in (002)/(200) reflections [37]. Fig. 4 shows the (002) and (200) reflections with the scattering vector parallel to the applied electric field vector during the application of $(E_{\text{max}} = 3 \text{ kV mm}^{-1})$ poling field.

The change in relative intensities of (002) and (200) peaks with applied field can be explained qualitatively as the change in volume fraction of 90° ferroelectric/ferroelastic domains in the tetragonal system. With the application of electric field, the (002)intensity increases at the expense of (200) intensity, and reaches a maximum value at 3 kV mm⁻¹ (E_{max}), i.e., the domain population with its c-axis (long axis) parallel to the electric field direction increases. Interestingly, with decreasing electric field, the intensity distribution of the (002) and (200) reflections return to values approximately equal to the initial state, i.e., $E_{rem} \approx E_0$. Such a high magnitude of reversibility in switched domains appears to be distinctive to this material and offers a unique strain mechanism for further development. In general, a contribution to the electro-mechanical response in conventional piezoelectric ceramics (e.g., PZT) is attributed to the movement of ferroelectric/ferroelastic domain walls [38]. However, the major fraction of this electro-mechanical response is a one-time effect during electrical poling, in which non-180° domains are moved to metastable positions, giving rise to a significant remnant strain [39,40]. In order to achieve high field-induced strain during unipolar cycling; the material needs to possess reversible non-180° domain switching. Thus, the core-shell BT-KN has the potential to achieve high field-induced strain during unipolar cycles.

The quantification of the extent of domain texture can further highlight the domain switching behaviour of this core–shell BT–KN ceramic. The (002)/(200) peak profiles at selected scattering vector angles to the applied field vector are presented in Fig. 5a.



Fig. 3. X-ray diffraction patterns of as processed core–shell BT–KN ceramic sample and results of crystallographic refinement using the space groups (a) *P4mm* and *Amm2*, (b) *P4mm* and (c) *P4mm* and *Pm*3*m*. Peaks are labelled with the pseudocubic perovskite unit cell indices.

The variation in relative intensity with scattering vector as a function of angle to the applied field vector can be explained by non-180° ferroelectric (i.e., 90° domains in the tetragonal system) domain texture. To quantify the change in domain texture, the modelled (002)/(200)reflections were using double pseudo-Voigt functions. Extracted peak intensities have been used to calculate the fraction of switched domains (η_{002}) at each field step for all scattering vector orientations relative to the applied field vector using the method reported by Jones et al. [41]. This method considers the change in relative intensities of non-180° ferroelectric domains (e.g., 00h/h00 reflections for the tetragonal system) and multiplicities of that particular lattice plane to calculate the volume of non-180° ferroelectric domains (v_{002}) and consequently the fraction of switched domains (η_{002}) and can be expressed by Eq. (1):

$$\eta_{002} = v_{002} - \frac{1}{3} \tag{1}$$

where v_{002} is given by the intensity ratio of the poled (I_{002}) and unpoled (I'_{002}) state using Eq. (2):

$$v_{002} = \frac{\frac{I_{002}}{I_{002}}}{\frac{I_{002}}{I_{002}} + 2\left(\frac{I_{200}}{I_{200}}\right)}$$
(2)

Fig. 5b shows η_{002} as a function of angle to the applied electric field vector at three different field states during the poling cycle. In the initial state, E_0 , η_{002} is zero as no domains have switched from the as-processed condition. At the maximum electric field, E_{max} , the maximum fraction of switched domains ($\eta_{002} = 0.2$) is observed along the field direction and the minimum ($\eta_{002} = -0.05$) at the perpendicular direction. Similar domain texture development is observed in tetragonal PZT with the application of electric field [32,39,42]. Upon subsequent decrease of the applied electric field amplitude to zero ($E_{\rm rem}$), η_{002} (along the electric field direction) decreases from 0.2 to 0.01, i.e., approximately 95% of the domains that initially switched experience reversible switching upon release of the electric field. In other words, the fraction of switched domains returns to populations very close to their initial state for all orientations. Thus, a large extent of non-180° ferroelectric domain switching in core-shell BT-KN may not be a one-time effect, a result that is contrary to conventional piezoelectrics such as PZT and BT.

3.3. Reversibility of switched non-180° ferroelectric domains and lattice strain in core–shell BT–KN, pure BT and tetragonal PZT

The unique reversible domain switching behaviour in coreshell BT-KN ceramic has been compared with pure BT and tetragonal PZT (PIC151, PI Ceramic Germany) samples during a unipolar cycle, both in the poled state. Samples were poled using a single unipolar cycle (0.005 Hz). To calculate the fraction of switched

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Refined lattice parameters	and fitting values for	core-shell BT-KN ceramic.

Space group	a (Å)	b (Å)	c (Å)	Criteria of fit (%)
P4mm (81%) Amm2 (19%)	3.98666 4.02153	3.98666 5.63414	4.01403 5.66190	R _p 6.185 R _{wp} 8.296 GoF 1.668
P4mm	3.98815	3.98815	4.01500	R _p 6.463 R _{wp} 8.576 GoF 1.724
P4mm (69%) Pm3̄m (31%)	3.98472 3.99570	3.98472 3.99570	4.01662 3.99570	R _p 6.08 R _{wp} 7.842 GoF 1.580



Fig. 4. (a) (002)/(200) diffraction peak profiles as a function of applied electric field. (b) Selected states during the application of field; as processed state (E_0), at 3 kV mm⁻¹ (E_{max}) and after the removal of electric field (E_{rem}).

non-180° ferroelectric domains in the poled samples, the average intensity method was used to estimate the expected diffraction peak intensities in samples with random domain orientations (i.e., unpoled sample) [43]. Changes in domain switching fraction $(\Delta \eta_{002} = \eta_{002} \ (E_{\text{max}}) - \eta_{002} \ (E_{0}))$ and (111) lattice strain in poled specimens of core-shell BT-KN, pure BT and PZT ceramic are presented in Fig. 6. The fraction of switched non-180° ferroelectric domains (Fig. 6a and b) in core-shell BT-KN is higher than BT and PZT, i.e., in the poled state, core-shell BT-KN exhibits an approximately two and three times greater value of $\Delta \eta_{002}$ than PZT and BT, respectively. Interestingly, while the $\Delta \eta_{002}$ value (Fig. 6a) for core-shell BT-KN and BT decreases continuously with increasing angle to the applied electric field direction, an abrupt variation around 45° to the electric field direction is observed for PZT. This abrupt change is perhaps due to the previously observed phase transformation in polycrystalline PZT of this composition at intermediate angles to the applied field vector [44]. The (111) lattice strain (Fig. 6c) at maximum electric field observed in PZT (0.16%) (plotted using the right-hand axis) is much larger than core-shell BT-KN (\sim 0.04%) and pure BT (<0.01%). It is worth noting that the observed (111) lattice strain in tetragonal polycrystalline ceramics is not entirely intrinsic piezoelectric strain. It has been reported that in tetragonal polycrystals, grains with a [111] direction parallel to the applied field, are unable to accommodate strain via domain switching and thus elastically strain to compensate [32,42]. In addition, the lattice constant ratio in tetragonal systems, c/a, changes the local stress state at the grain scale due to strain from non-180° domain wall motion during the poling cycle, leading to variations in the magnitude of observed residual stress [45]. It can be speculated that the lower c/a ratio facilitates a higher degree of non-180° domain switching in the poled specimen. Thus, the observed smaller domain switching fraction ($\Delta \eta_{002}$) and high (111) strain in PZT ($c/a \approx 1.0122$) than the core-shell BT-KN ($c/a \approx 1.0062$) is possibly due to the higher tetragonality and intergranular coupling.

During poling of conventional electro-ceramic materials such as BT and PZT, a significant fraction of non-180° ferroelectric domains re-orient and become fixed in metastable states resulting in a remnant domain texture within the polycrystal. The nature of the structural defects which leads to the pinning of domains walls in these metastable states can be attributed to several structural features including vacancy and interstitial defects, domain wall interactions, grain boundary defects, and interactions of domains across



Fig. 5. (a) (002)/(200) intensity profiles at 3 kV mm⁻¹ as a function of scattering vector angle to the applied electric field vector. Open circle, solid line and dot line represent experimental data, total fit and fit peak components, respectively. (b) Calculated fraction of switched domains (η_{002}) as a function of orientation at selected field steps. Errors in (b) are approximately the size of the data point markers.



Fig. 6. Change in domain switching fraction as a function of (a) angle to the applied field vector at maximum field, and (b) applied electric field amplitude, and (c) (111) lattice strain as a function of applied field in poled core–shell BT–KN, BT and PZT. Data in (b) and (c) represent the information for the scattering vector parallel to the applied electric-field vector. Errors in (a), (b) and (c) are approximately the size of the data point markers.

grain boundaries. In the core-shell BT-KN materials, it appears as though domains are restricted from being fixed in these metastable states upon poling, thus significantly more domain switching occurs during unipolar cycling. It should be mentioned here that the core-shell BT-KN sample showed an approximately equal extent of reversible domain switching for several repeated electric field cycles of 3, 4 and 5 kV mm⁻¹. The mechanism by which the metastable states are suppressed is likely related to the structure of the grain boundaries. In the core-shell microstructure, it is possible that the domains that exist in the core BT component do not

completely propagate through the shell region to the grain boundary [46]. Thus, the interaction of domains with grain boundaries and neighbouring grain domain structures is suppressed. Such a microstructure offers a unique variable to control the degree of domain switching in electro-ceramic materials and may lead to significant increases in usable strain of known compositions via microstructural engineering.

A restoring force which acts to reverse the switched domains may exist in the system. It is known in these materials that significant residual stress builds up in non-polar oriented grains [32,42,47]. This stress is acting to compress the sample from its poled state and thus return the domain texture to its original unpoled state. This residual stress has been shown to enhance the rate of polarisation reversal in tetragonal PZT materials upon application of field opposite to the poling direction [48]. In the absence of domain wall pinning sites at the grain boundaries, this residual stress may in fact completely reverse the domain wall motion without an external bias.

A schematic diagram of this process is shown in Fig. 7, presenting a comparative illustration of the energy landscapes of a domain wall for the conventional electro-ceramic and core-shell BT-KN. It is assumed that the gradient of residual stress (red dash line of the energy landscape) is the driving force to return domain walls to the initial positions and both system experiences similar gradient. Also, it is expected that due to the difference in microstructure, the nature and/or extent of defect-domain wall interaction energy landscape will be different. Although interaction of domain walls with defects at the grain boundaries may be considered the principle difference between a conventional electro-ceramic and core-shell BT-KN, it should be acknowledged that other defects might also exist. In conventional polycrystalline ceramics (Fig. 7a), the domain wall is displaced by an applied electric field with its position changed from the initial position in the unpoled state (i.e., position A) to a position of higher potential energy under the maximum field (i.e., position B). In this process, the domain wall interacts with a large number of defects. Eventually, the domain wall settles at a local minimum, a metastable state (i.e., remnant state, C) caused by the interaction with defects at grain boundaries. These local minima in energy landscape prevent the residual stress to act as an effective driving force to revert the domain wall to the initial position. Thus, remnance in domain wall motion are observed in these types of materials. In the case of core-shell BT-KN (Fig. 7b), the domain wall is also displaced from the original position A to position B by an applied field, however the domain wall interaction with grain boundary defects is suppressed by the shell (KN) region. As a consequence, the energy landscape is less variable (i.e., there is an absence of local energy minima) and the domain wall can revert to position C, close to the initial position A, with the release of electric field. In the absence of local energy minima, residual stress can act as an effective driving force to revert the domain wall to its initial position in systems like core-shell BT-KN.

Considering the microstructure, perhaps in conventional polycrystalline ceramics the grain boundaries are a significant metastable state for domain walls, whereas in core-shell BT-KN, the interfacial region, which is not necessarily a polar tetragonal phase, does not allow domain walls to be pinned at grain boundaries. Thus, in the core-shell BT-KN, because there are no metastable states of the domains on poling, there is a huge range of domain switching available for actuation during the unipolar cycle.

4. Conclusions

Enhanced reversible non-180° domain switching in MPB engineered core-shell BT-KN during poling and subsequent unipolar cycling has been observed by means of *in situ* high-energy X-ray



Fig. 7. Schematic diagram of the polycrystalline microstructure and an energy landscape, *S*(*u*), of a single domain wall in spatial dimension, *u*, for (a) conventional electroceramic (e.g., BT, PZT) and (b) core–shell BT–KN. The dashed line (red) of the energy landscapes indicates the energy offset due to residual stresses developing in the bulk material as non-180° domain switching occurs. Interaction of domain walls with defects at the grain boundaries creates significant variations and local energy minima in conventional electroceramics, while these deviations are suppressed in the BT–KN microstructure. Without such local minima in the energy landscape, no metastable domain walls back to their initial state upon release of the external field. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diffraction. The core-shell BT-KN showed large and reversible non-180° domain switching during the application of an external field. The unique nature of the reversible domain switching has been contrasted with conventional electro-ceramic such as BT and commercial PZT (PIC151) for unipolar actuation. The coreshell BT-KN exhibited a higher magnitude of non-180° domain switching fraction than BT and PZT. The reversibility of switched non-180° domains in core-shell BT-KN has been hypothesised to be due to the much lower pinning energies (i.e., the absence of noticeable local energy minima) of metastable domain states after the application of external fields. Thus, the large extent of reversibility in switched non-180° domains of core-shell BT-KN offers a unique strain mechanism for further development for actuator application.

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