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Thermally-induced phase transformations in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-KNbO}_3$ ceramics

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Abstract

The structures and functional properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-xKNbO}_3$ (NBT-KN) solid solutions, with x in the range from 0.01 to 0.09, were investigated using a combination of high-resolution synchrotron x-ray powder diffraction (SXPd) and ferroelectric property measurements. For low KN contents, an irreversible transformation from cubic to rhombohedral phases was observed after the application of a high electric field, indicating that the polar nanoregions (PNRs) in the unpoled state can be transformed into metastable long-range ordered ferroelectric domains in the poled state. In contrast, the near-cubic phase of the unpoled ceramics was found to be remarkably stable and was retained on cooling to a temperature of -175 °C. Upon heating, the field-induced metastable ferroelectric rhombohedral phase transformed back to the nanopolar cubic state at the structural transformation temperature, T_{ST} , which was determined as approximately 225 °C and 125 °C for KN contents of 3%

and 5% respectively. For the field-induced rhombohedral phase in the poled specimens, the pseudo-cubic lattice parameter, a_p , exhibited an anomalous reduction while the inter-axial angle increased towards a value of 90° on heating, resulting in an overall increase in volume. The observed structural changes were correlated with the results of temperature-dependent dielectric, ferroelectric and depolarisation measurements, enabling the construction of a phase diagram to define the stable regions of the different ferroelectric phases as a function of composition and temperature.

Key words: sodium bismuth titanate; phase transition; relaxor ferroelectric; synchrotron x-ray; piezoelectric ceramics

1. Introduction

Piezoelectric ceramics are widely used in many applications such as actuators, sensors and transducers.^{1, 2} PbZrO_3 - PbTiO_3 (PZT)-based materials are the most common piezoelectric ceramics due to their superior piezoelectric coefficients, which are obtained for compositions close to the morphotropic phase boundary (MPB) between ferroelectric rhombohedral and tetragonal phases.³ However, increasingly attention has been drawn to lead-free piezoelectrics due to environmental considerations.⁴

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT)-based solid solutions are one of the most promising candidates for lead-free piezoceramics due to a combination of high remanent polarisation and useful electromechanical properties.^{5, 6, 7, 8, 9, 10} Furthermore, the occurrence of frequency dispersion in the dielectric permittivity of NBT-based ceramics is attributed to the presence of polar nano-regions (PNRs)^{11, 12, 13}, similar to the behaviour of relaxor ferroelectrics (RF) such as PLZT and PMN¹⁴. NBT possesses a perovskite structure at room temperature with a sequence of phase transitions from rhombohedral to tetragonal to cubic at temperatures of approximately 300 °C and 540 °C.¹⁵ KNbO_3 (KN) is a classical ferroelectric compound and regarded as a useful component of lead-free piezoelectric ceramics due to its high Curie temperature, $T_c=435$ °C, and large spontaneous polarisation, $P_s=0.30$ C m⁻².¹⁶ In common with barium titanate, it undergoes a sequence of phase transitions from rhombohedral to orthorhombic to tetragonal and finally to a paraelectric cubic structure at temperatures of approximately -50 °C, 225 °C and 435 °C.^{16, 17}

In terms of phase transitions in NBT-based binary systems, it is not possible to define a conventional Curie temperature, T_c , due to the relaxor ferroelectric (RF) nature of the materials. The characteristic frequency-dependent maximum in permittivity associated with relaxor ferroelectrics manifests itself as a ‘shoulder’ on the ϵ_r - T plot for NBT-based ceramics. An additional high temperature frequency-independent maximum in the permittivity-temperature relationship, T_m , has been attributed to a progressive transformation between nanoscale regions having rhombohedral $R3c$ and tetragonal $P4bm$ symmetries.¹⁸ Furthermore, the loss of remanent polarisation and the associated degradation of the piezoelectric and ferroelectric properties provide an additional depolarisation temperature, T_d , which is usually found to be much lower than T_m . The latter transformation also creates an additional anomaly in the loss tangent-temperature curve of a poled specimen, which is sometimes referred to as the FE to RF transition temperature, T_{F-R} .¹⁹

Due to the presence of the PNRs in NBT-based materials, the term *ergodicity* is employed to denote whether or not the electric field-induced metastable long-range ordered FE order is stable after removing the electric field. For the ergodic-RF state, the electric field-induced RF to FE transformation is reversible, whereas for the nonergodic state it is irreversible.²⁰ Hence, only compositions having a nonergodic-RF state can be transformed to the metastable FE state under poling, with the subsequent observations of T_d and T_{F-R} . As shown in previous publications, a clear dielectric anomaly was also exhibited during heating in poled La-PZT²¹, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 ^{22,23} and NBT-BT solid solutions^{18,24,25,26,27}. Furthermore,

the frequency dispersion in both the ϵ_r - T and $\tan\delta$ - T curves below this temperature is found to be less significant due to the formation of long-range FE upon poling. Conversely, an abrupt increase in frequency dispersion at temperatures above T_{F-R} indicates the appearance of the nano-polar RF state.²⁸

For the $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $x\text{KNbO}_3$ binary system, the structure at room temperature has been reported by Pisitpipathsin²⁹, suggesting the existence of pure rhombohedral phase at low KN contents and the presence of mixed rhombohedral and orthorhombic phases for x values between 0.05 and 0.15. However, the occurrence of mixed pseudo-cubic and rhombohedral phases was reported by Fan for x in the range 0.04 to 0.06.³⁰ In a recent publication, it was observed using high-energy synchrotron XRD that NBT- x KN ceramics with $x=0.02$ - 0.08 displayed a pseudo-cubic structure in the unpoled state but also exhibited well-formed polarisation-field (P-E) hysteresis loops for low KN contents, indicating the presence of an electric field-induced FE phase.³¹ Subsequently, it was confirmed that a structural transformation from pseudo-cubic to rhombohedral had occurred under the influence of an alternating electric field.³²

The thermally-induced phase transformations in $(1-x)\text{NBT}$ - $x\text{KN}$ ($x=0$ - 0.12) ceramics were studied by Fan³⁰ by conducting temperature-dependent permittivity measurements on unpoled specimens. Both T_d and T_m were determined by identifying anomalies on the permittivity-temperature curves. By analogy with pure NBT, it was assumed that the structure for all compositions between T_m and T_d was tetragonal, although no evidence was presented to support this assertion. A similar approach was adopted by Jiang, although in the latter case the experiments were conducted on poled

specimens.^{19, 33} Two anomalies in the permittivity-temperature curves were defined as T_p and T_m , while one extra peak in the loss tangent-temperature curve, T_{ir} , was attributed to the irreversible transition from long-range ordered FE to a weak-polar phase. On the other hand, Hiruma referred to the lower-temperature anomaly as the structural transformation temperature from rhombohedral to tetragonal, T_{R-T} , but without direct evidence of the crystal structure at elevated temperatures.³⁴

The aim of the present study was to identify precisely the crystallographic parameters and to determine the structural transformation temperatures in (1-x) NBT-xKN ($x=0.01-0.09$) ceramics. For this purpose, both unpoled and poled ceramic specimens were characterised structurally using high resolution SXPD over a wide temperature range spanning the phase transformations. These results are complemented by temperature-dependent dielectric and ferroelectric measurements to determine the phase transition temperatures.

2. Experimental Procedures

(1-x) ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$)- $x\text{KNbO}_3$ ($x=0.01-0.09$) ceramic pellets were prepared by conventional solid state reaction. The mixed powders of Na_2CO_3 (99.8%, Fisher Scientific), K_2CO_3 (99%, Sigma Aldrich), Bi_2O_3 (99%, Sigma Aldrich), TiO_2 (99%, Fisher Scientific), Nb_2O_5 (99%, Fisher Scientific) were milled for 24 h in 2-propanol using zirconia balls and calcined for 10 h at 900 °C to realize the reaction. The calcined powders were milled again for 24 h and the final dry powders were then uniaxially pressed into 6.5 mm diameter pellets under a compaction pressure of 150 MPa. The pressed pellets were embedded in powders of the same composition to

avoid the evaporation of bismuth and potassium ions and sintered at 1180 °C for 3 h in air.

As-sintered ceramic specimens were ground lightly and coated with fast-drying silver suspension (Agar Scientific) to form electrodes. Ferroelectric polarisation-electric field (P-E) hysteresis measurements were carried out using the method described by Stewart et al³⁵ using a HP33120A Function Generator and a Chevin Research HVA1B HV amplifier. The applied voltage and current waveforms were recorded using a Measurement Computing USB-1608FS-Plus A/D card and analysed using LabVIEW-based software. The specimens for temperature-dependent dielectric and depolarisation measurements were poled in a silicone oil bath by applying 40 cycles of a sinusoidal AC electric field with an amplitude of 5 kV mm⁻¹ at a frequency of 2 Hz. The poled ceramic pellets were placed into a Carbolite CWF 1200 furnace and the temperature was recorded by means of a thermocouple placed adjacent to the alumina specimen holder. The capacitance was measured over a range of temperature, from 50 °C to 420 °C, at frequencies of 1, 10 and 100 kHz using a HP 4284A LCR meter, with a heating rate of 2 °C min⁻¹. Thermal depolarisation characteristics were investigated by measuring the electric charge released during heating of a poled specimen at a ramp rate of 2 °C min⁻¹ using a Keithley 6512 electrometer.

Powder samples were used for the synchrotron diffraction measurements on beamline I11 at the Diamond Light Source,³⁶ For the poled ceramic pellets, the silver paste was removed using acetone, followed by crushing and grinding by hand using a pestle and mortar. A similar method was used in the case of the unpoled ceramic pellets,

followed by annealing at 550 °C for 30 mins. It is assumed that this procedure does not affect phase identification and hence provides texture-free structural information for materials that have undergone an irreversible electric field-induced phase transformation, as reported by Garg and Rao.^{28,37} It was noted previously that poled NBT-KN specimens with low KN contents were observed to retain the rhombohedral distortion after crushing and grinding, indicating that these compositions exhibit nonergodic-RF behaviour, meaning that they are able to maintain the polarisation induced by the external electric field. The powder samples were loaded into glass capillaries of 0.3 mm diameter. The highest available photon energy of 25 keV was used to reduce the effect of sample absorption and the resulting diffraction patterns were recorded using a multi-analyser crystal (MAC) detector.³⁶ The time taken to record a high resolution diffraction pattern was typically 30 mins. The specimen temperature was controlled in the range from -175 °C to 225 °C using a Cryostream (80-500 K), allowing 60 s for equilibration at each temperature. The specimen was firstly cooled to -175 °C then heated to 225 °C, followed by cooling back to room temperature. The wavelength of $\lambda = 0.494731(10)$ Å of the incident x-ray beam was calibrated using a high quality silicon standard and full-pattern refinements were accomplished using *Topas* software, v3.0.³⁸

3. Results and discussion

3.1 Structural transformations in NBT-0.01KN

Full-pattern refinement of the diffraction patterns was carried out using *Topas* in order to identify the crystal structures of the phases present and to quantify the crystallographic parameters. Taking the NBT-0.01KN ceramic powders at room temperature as an example, a near-cubic structure with a slight rhombohedral distortion was observed for unpoled NBT-0.01KN, with slightly asymmetric $\{111\}_p$ and $\{211\}_p$ peaks being evident, as shown in Figure 1(a). In contrast, clear double $\{110\}_p$, $\{111\}_p$ and triple $\{211\}_p$ peak splitting was observed for the poled NBT-0.01KN, as illustrated in Figure 1(b), which indicates the presence of a more well-defined rhombohedral phase.

Several different single or mixed-phase structures were considered as potential candidates to fit the experimental patterns, including the *Cc* monoclinic phase described previously by Reaney³⁹ and Aksel.⁴⁰ However, the best fit was obtained using a single *R3c* rhombohedral phase. Similar observations were made for the other NBT-KN compositions investigated in the present study and therefore the patterns were fitted using the *R3c* space group in order to obtain the refined lattice parameters in the hexagonal setting of the rhombohedral structure. The resulting crystallographic parameters were transformed into the equivalent pseudo-cubic setting using the method described previously.³²

The experimental and calculated diffraction profiles for the full patterns and three

representative reflections, including $\{110\}_p$, $\{111\}_p$, and $\{211\}_p$, are compared in Figure 1. The best weighted profile R-factor value (R_{wp}) obtained for the unpoled and poled states were 9.65% and 7.71% respectively. The lattice parameters, a_p , for unpoled and poled NBT-0.01KN were determined as 3.8835(6)Å and 3.9028(8)Å respectively, indicating that the electric field-induced phase transformation caused an enlargement of the lattice parameter and volume. Furthermore, the inter-axial angles, α_p , for unpoled and poled NBT-0.01KN were calculated as 89.88° and 89.64°, indicating an enhanced rhombohedral distortion after poling.

Figure 1. Room-temperature SXPD patterns for (a) unpoled and (b) poled NBT-0.01KN ceramic powders. The inset figures are representative peak profiles for $\{110\}_p$, $\{111\}_p$ and $\{211\}_p$ (approximately at 2θ values of 11.2° , 12.6° and 17.6°). The black symbols represent experimental data, while the red line is the calculated pattern from Rietveld refinement using the rhombohedral $R3c$ space group and the green line is the difference between the experimental and calculated patterns.

Selected regions of the x-ray diffraction patterns obtained for unpoled and poled NBT-0.01KN ceramic powders in the temperature range from -175°C to 225°C are presented in Figure 2. For the unpoled state, an asymmetric $\{111\}_p$ and single $\{200\}_p$ peak were observed at -175°C , indicating that the pseudo-cubic structure with a slight rhombohedral distortion, as described above, was retained even after cooling to 200°C below room temperature. With increasing temperature, the $\{111\}_p$ peak became more symmetric, suggesting that the rhombohedral distortion in the unpoled powder reduced even further upon heating. Furthermore, all of the peaks shifted to lower angles due to thermal expansion.

In the case of the poled NBT-0.01KN, the rhombohedral phase observed at room temperature was also retained at -175°C , as indicated by the split $\{111\}_p$ and single $\{200\}_p$ peaks. Upon heating, the separation between the $(111)_p$ and $(\bar{1}\bar{1}1)_p$ peaks became smaller due to a reduction of the rhombohedral distortion. The crystal structure remained rhombohedral up to 225°C , indicating that the expected structural transformation from rhombohedral to cubic was incomplete at this temperature for NBT-0.01KN.

Figure 2. Selected SXPD peak profiles in the temperature range from -175 °C to 225 °C for (a) unpoled and (b) poled NBT-0.01KN.

The changes in the values of a_p , α_p and the unit cell volume, V_u , for unpoled and poled NBT-0.01KN powders within the temperature range from -175 °C to 225 °C are presented in Figure 3. For the unpoled powder, the lattice parameter, a_p , increased consistently with increasing temperature (Figure 3(a)). However, for the poled powder it was found that a_p increased slightly up to 25 °C and then decreased significantly upon further heating due to the gradual structural transformation from rhombohedral to cubic. This apparently anomalous reduction in a_p for the poled powder is associated with the most dramatic increase in inter-axial angle, which occurred between 25 °C and 225 °C, as illustrated in Figure 3(b). For both the unpoled and poled ceramic powders, the unit cell volume increased consistently with temperature, with V_u of the poled state being approximately 0.20% greater than that of the unpoled state for the majority of the temperatures studied. Although the rhombohedral to cubic transformation was still incomplete at 225 °C, the crystallographic parameters obtained for both unpoled and poled powders were very similar after heating to this

temperature and indicate a nearly cubic structure with an inter-axial angle of approximately 89.94° .

Figure 3. Changes in (a) lattice parameter, a_p , (b) inter-axial angle, α_p , and (c) unit cell volume, V_u , during heating from -175°C to 225°C for unpoled and poled NBT-0.01KN powders.

3.2. Influence of composition on structural transformations

Peak profiles of the $\{111\}_p$ and $\{200\}_p$ reflections for poled $(1-x)\text{NBT}-x\text{KN}$ ($x=0.01-0.09$) ceramic powders in the temperature range from 25°C to 225°C are presented in Figure 4. At 25°C , the structures for all compositions apart from NBT-0.09KN were observed to be rhombohedral, characterised by a double $\{111\}_p$ peak and single $\{200\}_p$ peak. With increasing temperature, the separation between the $\{111\}_p$ and $\bar{\{111\}}_p$ reflections reduces, indicating that a gradual structural

transformation from rhombohedral to cubic occurred. For NBT-0.01KN, the slight splitting of the $\{111\}_p$ reflection remained at the highest temperature of 225 °C, as noted above. However, it was found that increasing KN content resulted in a decrease of the structural transformation temperature, as reported previously.³³ Furthermore, all $\{200\}_p$ peaks are seen to shift to lower angles with increasing temperature due to thermal expansion.

For NBT-0.09KN, the application of the external poling electric field had no significant effect on the SXPD patterns, yielding single $\{111\}_p$ and $\{200\}_p$ peaks in the nominally poled sample.

Figure 4. Selected SXPD peak profiles for (1-x)NBT-xKN poled ceramic powders (a) x=0.01 (b) x=0.03 (c) x=0.05 and (d) x=0.09 in the temperature range from 25 °C to 225 °C.

The results obtained for the crystallographic parameters for all NBT-KN compositions during heating from 25 °C to 225 °C and subsequent cooling to 25 °C, are presented in Figure 5. For NBT-0.01KN, a_p decreases with increasing temperature up to 175 °C and then increases slightly up to 225 °C. Simultaneously, α_p increases consistently from 89.6° to 89.95° up to the maximum temperature of 225 °C. Both parameters reduce during cooling down to 25 °C. A rhombohedral phase, with $\alpha_p \approx 89.85^\circ$, was retained after cooling back to room temperature, indicating that an irreversible structural transformation occurred on heating. However, the maximum temperature of 225 °C was insufficient to complete the transformation to the cubic phase for the NBT-0.01KN composition. It is shown below that this transformation is associated with disruption of the FE order by thermal depoling.

Similar results were obtained for NBT-0.03KN and NBT-0.05KN, although in these cases a complete transformation to the cubic phase was observed, as indicated by the tendency for α_p towards 90°. The transformation temperatures, T_{ST} , were determined as approximately 225 °C and 125 °C for NBT-0.03KN and NBT-0.05KN respectively. After completion of the rhombohedral to cubic structural transformation, α_p remained approximately equal to 90° during subsequent heating and cooling while a_p varied in a manner consistent with thermal expansion.

In common with NBT-0.01KN, the a_p values for NBT-0.03KN and NBT-0.05KN initially reduced on heating followed by an increase up to the maximum temperature, as shown in Figure 5 (a) to (c). The temperature ranges over which this reduction in a_p was observed were 25 to 175 °C, 25 to 125 °C, and 25 to 75 °C for NBT-0.01KN,

NBT-0.03KN and NBT-0.05KN respectively. The reduction in a_p was generally associated with an increase in the inter-axial angle, α_{pc} , resulting in an overall increase in unit cell volume with increasing temperature, as illustrated in Figure 5 (e) to (h).

With reference to the unpoled state of ceramics (red open-circle), the electric field-induced structural transformation from pseudo-cubic to rhombohedral produced volume changes of +0.24%, +0.22% and +0.14% for NBT-0.01KN, NBT-0.03KN and NBT-0.05KN respectively. After heating to 225 °C and cooling back to 25 °C, the thermally-induced phase transformation from rhombohedral back to cubic resulted in a volume changes of -0.25% and -0.15% for NBT-0.03KN and NBT-0.05KN respectively. A relatively small volume change of -0.14% was obtained for NBT-0.01KN, indicating that the thermally-induced rhombohedral to cubic transformation was incomplete at 225 °C. In this case, an overall increase in volume of 0.10% was observed compared to the initial unpoled state. It is evident that the irreversible increase in volume caused by the electric field-induced phase transformation for both NBT-0.03KN and NBT-0.05KN can be recovered completely upon heating above 225 °C. It is shown below that the thermally-induced structural transformation also results in a thermal depolarisation process. In contrast, there is no significant volume change or structural transformation for NBT-0.09KN.

Figure 5. Lattice parameter, a_p , and inter-axial angle, α_p , for (a) NBT-0.01KN (b) NBT-0.03KN (c) NBT-0.05KN (d) NBT-0.09KN and unit cell volume for (e) NBT-0.01KN (f) NBT-0.03KN (g) NBT-0.05KN (h) NBT-0.09KN ceramic powders as a function of temperature. The unit cell volume of the initial unpoled state is indicated by the red open circle symbol in (e) to (g).

3.3. Thermal evolution of dielectric properties and depolarisation

The dielectric peak, T_m , and phase transition temperature, T_{F-R} , for poled (1-x)NBT-xKN ($x=0.01-0.09$) ceramic pellets were determined via

temperature-dependent dielectric measurements, as illustrated in Figure 6. All of the dielectric curves exhibit frequency dispersion, indicating a RF character. Two anomalies are evident in the permittivity-temperature (ϵ_r - T) curves for all compositions; the higher-temperature peak is defined as the maximum permittivity anomaly (T_m), but a prominent lower-temperature shoulder is also observed. The temperature for both anomalies decreases with increasing KN content.

The presence of two dielectric anomalies, which was observed for all compositions in the NBT-xKN system, is not usually found in typical RFs such as PLZT. A number of possibilities have been proposed to explain the lower-temperature shoulder, including a phase transition, structural transformation, ageing effect and the dielectric relaxation effect associated with PNRs. As shown below, the phase transition temperature from a field-induced metastable FE state to a RF state is indicated by the peak in the $\tan\delta$ - T curve rather than the low-temperature shoulder in the ϵ_r - T curve. Furthermore, it was found that the position of the shoulder does not correspond to the structural transformation temperature determined above. Therefore, the ageing effect and relaxation of PNRs remain as two possible origins of the low-temperature shoulder. However, no evidence has been found to support the ageing effect as a potential explanation; for example, the P-E hysteresis loops reported below do not exhibit any significant internal bias field. In a recent study on NBT-0.06BT by Jo et al. it was proposed that the low-temperature shoulder was associated with the loss of long-range ferroelectric order to form PNRs with rhombohedral $R3c$ and tetragonal $P4bm$ symmetry and was similar in form to the FE to RF transformation in conventional

RFs.¹⁸ It is likely that a similar mechanism is responsible in NBT-KN ceramics, although the symmetry of the PNRs in these materials appears to be single phase rhombohedral $R3c$, as reported above. Further investigations (using TEM, for example) would help to clarify the nature of the PNRs in these materials.

The origin of the high-temperature dielectric peak at T_m for NBT-KN ceramics is likely to be similar to that observed in other NBT-based systems and therefore could be attributed to a progressive change in the symmetry of the PNRs, from rhombohedral $R3c$ to tetragonal $P4bm$.¹⁸ Although the high temperature regime was not investigated during the present XRD studies, conventional diffraction techniques are unlikely to provide further insight into the mechanisms responsible for this transition. Instead, it will be necessary to employ other techniques that are more sensitive to changes in local symmetry, such as transmission electron microscopy (TEM) or pair distribution function (PDF) analysis.

In the $\tan\delta-T$ curves, an additional peak was observed for NBT-0.01KN and NBT-0.03KN, which was present for poled but not for unpoled specimens, in agreement with previous reports.³⁰ This peak is associated with the transition from a field-induced metastable FE phase to the RF phase at T_{F-R} , which is close to the depolarisation temperature, as discussed in the following section. Such a peak was not observed for NBT-0.05KN and NBT-0.09KN due to the instability of the remanent polarisation in these specimens. The T_{F-R} values for NBT-0.01KN and NBT-0.03KN were determined as 128 °C and 70 °C respectively.

Figure 6. Temperature-dependence of dielectric permittivity and loss tangent for poled ceramic pellets of (a) NBT-0.01KN (b) NBT-0.03KN (c) NBT-0.05KN (d) NBT-0.09KN at frequencies of 1 kHz, 10 kHz and 100 kHz.

The thermal depolarisation characteristics for poled (1-x)NBT-xKN ceramics with $x=0.01$ and 0.03 are illustrated in Figure 7. As discussed above, it is found that the cubic to rhombohedral structural transformation and the RF to metastable FE phase transition occur at the same time for these two compositions during poling. Furthermore, the metastable FE phase was retained after removing the external electric field, indicating that these two compositions are in a nonergodic-RF state at room temperature. In contrast, the high electric field has only a slight effect on the crystal structure for NBT-0.05KN and no effect for NBT-0.09KN, yielding a remanent polarisation, P_r , close to zero.

The P_r values for NBT-0.01KN and NBT-0.03KN start at approximately 0.15 C m^{-2}

and 0.24 C m^{-2} respectively. The P_r for NBT-0.03KN drops dramatically and immediately during heating, while the P_r for NBT-0.01KN remains at approximately 80% of its initial value until reaching 125°C . If we define the thermal depolarisation temperature, T_d , as the temperature at which the steepest change of polarisation occurs, the T_d values for NBT-0.01KN and NBT-0.03KN are approximately 120°C and 63°C , which are both slightly below the T_{F-R} values, of 128°C and 70°C respectively, obtained from the $\tan\delta-T$ curves, .⁴¹ This kind of behaviour has been reported previously by Sapper for the Mn-modified NBT-BaTiO₃ system⁴², suggesting that the T_d values generally tend to be slightly lower than the T_{F-R} values. Heating above T_d was found to cause randomisation of the FE domain orientations but the long-range ordered domains were still present.⁴² It was supposed that the macro-domains break up into randomly oriented nanodomains only at T_{F-R} . In the present study, it was an unexpected finding that the structural transformation temperatures, T_{ST} , for NBT-0.01KN and NBT-0.03KN are approximately 150°C greater than both T_d and T_{F-R} , indicating that the ferroelectric transitions at the latter temperatures do not destroy the large correlation length between dipoles within the PNRs, resulting in an observation of the rhombohedral $R3c$ structure by SXPd.

Figure 7. Thermal depolarisation curves for NBT-0.01KN and NBT-0.03KN poled ceramic pellets.

3.4. Thermal evolution of ferroelectric properties

To further investigate the phase transition temperature, T_{F-R} , for poled specimens, the polarisation-electric field (P-E) and current density-electric field loops (J-E) were obtained for (1-x)NBT-xKN ($x=0.01, 0.03, 0.05$) in the temperature range from 30 °C to 120 °C after poling under an AC electric field of 5 kV mm⁻¹, as presented in Figure 8. Typical ferroelectric behaviour was observed for NBT-0.01KN, with single sharp peaks being present in the J-E curves due to rapid polarisation switching at the coercive field.⁴³ Upon increasing the KN content to 3%, the coercive field reduced significantly, resulting in a high P_r value of 0.24 C m⁻² at room temperature. These results indicate the presence of a nonergodic-RF phase at room temperature, which is transformed irreversibly into a metastable FE phase under the influence of the electric field.

To be more specific, the transition from a nonergodic-RF phase to a metastable long-range ordered FE phase can be broken down into two steps. Firstly, the

correlated PNRs are embedded into an easily polarisable matrix and then long-range order is formed under the application of a high electric field, leading to the presence of micron-sized domains in the specimens.⁴⁴ In the second step, these micro-domains become aligned parallel to the external electric field, resulting in a metastable FE phase on a macroscopic scale and possessing a remanent polarisation even after removing the field. This type of electric field-induced transition from weak-polar to long-range ordered FE state for NBT-based solid solutions has been observed by Ma⁴⁵ and Guo⁴⁶ using in-situ TEM.

A well-saturated ferroelectric hysteresis loop with $P_r=0.24 \text{ C m}^{-2}$ was also observed for NBT-0.05KN. However, a slight constriction in the middle of the P-E loop and splitting of the polarisation switching peaks in the J-E loop are apparent, similar to those reported in other NBT-based solid solutions, including NBT-BT- $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$,⁴⁷ NBT-BT- CaTiO_3 ⁴³ and Mn-modified NBT-BT⁴⁸. This kind of reversible switching between PNRs and long-range ordered FE phase at room temperature provides evidence of ergodic-RF behaviour.

Increasing temperature gave rise to more complete, well-formed P-E loops for NBT-0.01KN with enhancement of P_r and decrease of E_c . At 120 °C, a slight splitting in the switching peak became evident in the J-E curve, indicating that the long-range ordered FE phase was partially destabilised due to the increase in temperature. This particular temperature is close to the T_{F-R} and T_d values reported above, which were 128 °C and 120 °C respectively. For NBT-0.03KN, a constricted P-E loop and splitting of the switching peaks in the J-E loop are apparent at 65 °C and above,

indicating that the polarisation vector in the metastable long-range ordered FE phase became unstable and the microdomains diminished into PNRs. The clearly split peaks in the J-E curve correspond to the electric field values that triggered the reversible transition between short-range PNRs and long-range ordered FE phase, denoted as T_F (forward transition) and T_B (backward transition) by Viola et al.⁴³ The presence of this reversible transition indicates a thermally-induced transformation to the ergodic RF state and the temperature at which P_r reduces to zero corresponds approximately to the values of T_{F-R} and T_d given above. Furthermore, the separation between T_F and T_B is enhanced with increasing temperature, as observed for NBT-0.03KN and NBT-0.05KN. For NBT-0.05KN, more PNRs undergo the reversible transformation with increasing temperature, leading to a pronounced constriction in the P-E loop with a significant drop of P_r from 0.14 C m^{-2} to approximately 0.02 C m^{-2} at 65°C and 120°C respectively.

Figure 8. The P-E and J-E loops for (1-x)NBT-xKN ceramics in the temperature range from 30 to 120 °C with a maximum electric field of 5 kV mm⁻¹ and frequency of 2 Hz for (a) x=0.01 (b) x=0.03 (c) x=0.05.

3.5. Phase diagram for the NBT-KN system

A phase diagram can be plotted by combining all of the data obtained for the poled (1-x)NBT-xKN (x=0.01-0.09) ceramics, as presented in Figure 9. In this figure, the T_{F-R} values were determined from the dielectric $\tan\delta$ - T measurements while the structural transformation temperatures, T_{ST} , were estimated as the temperatures at which the inter-axial angle, α_R , reached 90°. The T_m values determined from the ε_r - T curves (measured at a frequency of 100 kHz) are also plotted in Figure 9 to illustrate

their variation with composition.

For low KN contents, the materials exhibit a non-ergodic RF (NR) state for unpoled ceramics at room temperature, meaning that the structure can be transformed irreversibly into a rhombohedral FE state by the application of a high electric field. With increasing temperature, the field-induced FE state can be transformed back to the ergodic relaxor ferroelectric (ER) state at T_{F-R} , characterised by the development of a constricted P-E loop and frequency dispersion in the ϵ_r - T curve. The value of T_{F-R} decreases from 140 °C for pure NBT, as reported by Hiruma⁴⁹, to approximately 70 °C for NBT-0.03KN. The long-range structure of the material remains rhombohedral upon further heating to T_{ST} , when the transformation to cubic occurs. In common with T_{F-R} , the values of T_{ST} decrease with increasing KN content, from 260 °C for pure NBT⁴⁹ to 125 °C for NBT-0.05KN.

Above T_{ST} , the materials can be classified as having an ER state with an average cubic structure. This is due to the presence of PNRs embedded into a cubic matrix, which means that long-range structural characterisation techniques such as x-ray diffraction are unable to identify the local PNR structure.³⁹ Also, it should be noted that the region labelled as *cubic* will most likely comprise nanoscale regions having short-range rhombohedral and tetragonal ordering. The transformation between these symmetries is the most likely origin of the peak in dielectric permittivity at T_m , as discussed above.

The transformation to the paraelectric cubic phase, denoted as the Burns temperature⁴⁴, which occurs at temperatures much higher than T_m , has not been determined in the

present work. For high KN contents, the lack of remanent polarisation in the ferroelectric P-E loops and structural evidence showing the presence of the cubic phase in both unpoled and poled specimens indicates the existence of the ergodic-RF state at room temperature.

Figure 9. Phase diagram obtained from analysis of dielectric and structural studies on poled (1-x)NBT-xKN ceramics.

4. Conclusions

The structures of NBT-KN ceramics were investigated using high resolution SXPD. For low KN contents, it was demonstrated that the nanopolar near-cubic state could be transformed into a long-range ordered ferroelectric state by the application of a high electric field, indicating the presence of a non-ergodic RF state. In contrast, the NBT-KN ceramics with high KN content possessed an ergodic RF state and retained the cubic structure after the electric field was removed.

It was shown that the electric field-induced rhombohedral phase transformed back to cubic on heating to a certain structural phase transformation temperature, T_{ST} , which

was significantly higher than the thermal depolarisation temperature, T_d . It is evident that the oriented ferroelectric domain structure in a poled rhombohedral specimen is disrupted long before the crystallographic distortion is lost. The gradual transition between the rhombohedral and cubic states on heating was revealed by the evolution of crystallographic parameters, obtained from full-pattern fitting of the SXPD results. The thermal depolarisation temperature showed a good correlation with T_{F-R} , obtained from $\tan\delta$ - T plots, and the loss of remanent polarisation from temperature-dependent ferroelectric hysteresis measurements. The transition between irreversible and reversible polarisation switching behaviour as a function of composition and temperature was also clearly evident in the latter.

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