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DOI:

[10.1016/j.jeurceramsoc.2021.01.040](https://doi.org/10.1016/j.jeurceramsoc.2021.01.040)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Wang, G., Goetzee-Barral, A., Lu, Z., Keeble, D., & Hall, D. (2021). Thermally-induced local structural transformations in Na_{0.5}Bi_{0.5}TiO₃-KNbO₃ ceramics. *Journal of the American Ceramic Society*. <https://doi.org/10.1016/j.jeurceramsoc.2021.01.040>

Published in:

Journal of the American Ceramic Society

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

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Abstract

The local symmetry of $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}x\text{KNbO}_3$ (NBT- x KN, $x=0.01\text{-}0.07$) ceramics was thoroughly examined using high-energy synchrotron x-ray scattering and analysed using the Pair-Distribution Function (PDF) method. At room temperature, the structure of NBT- x KN ($x=0.01\text{-}0.07$) ceramics was best refined using monoclinic $C1c1$ structures within the local-range ($r < 22 \text{ \AA}$) and rhombohedral $R3c$ within medium-range ($22 \text{ \AA} < r < 52 \text{ \AA}$). Furthermore, the local monoclinic $C1c1$ structure exists from room temperature to $> 420 \text{ }^\circ\text{C}$ (above the temperature of the maximum dielectric peak, T_m), as confirmed by in-situ temperature-dependent PDF analysis.

Keyword: NBT; X-ray scattering; Pair distribution function; local structure

Introduction

Sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, NBT) has been thoroughly investigated, and is recognised as a potential lead-free replacement to lead-based piezoelectric ceramics such as lead zirconate titanate (PZT), for electro-mechanical actuators.¹⁻³ Similar materials are also reported to be excellent electrolyte materials for solid oxide fuel cells (SOFC) as well as superior energy density ceramic capacitors.⁴⁻⁸ The crystal structure of NBT has been the subject of debate for several decades, but it is commonly accepted as comprising an average long-range ordered rhombohedral $R3c$ phase.⁹⁻¹¹

However, the complexity of local disorder and octahedral tilting, observed under transmission electron microscopy (TEM) suggested a monoclinic $C1c1$ phase, reported by Levin and Reaney.¹² Furthermore, Rietveld refinement of high-resolution synchrotron x-ray diffraction (XRD) data also favoured monoclinic $C1c1$ phase over $R3c$.¹³⁻¹⁵ At elevated temperatures, structural transformations for many NBT-based materials were determined by anomalies in dielectric permittivity (ϵ_r -T.) curves.¹⁶⁻¹⁸ More detailed investigations examined under TEM have been reported by Dorcet and co-workers that the two anomalies in the ϵ_r -T data for NBT correspond to phase transformations from rhombohedral-orthorhombic, T_{R-O} , and orthorhombic-tetragonal, T_{O-T} .¹⁹⁻²⁰ Recently, the thermally-induced structural transformations for the solid solution $(1-x)\text{NBT}-x\text{KNbO}_3$ (NBT- x KN) were studied using high-resolution x-ray powder diffraction (SXPd).²¹ It was found that the structure retains pseudo-cubic symmetry (with slight rhombohedral distortion) for as-sintered samples in the temperature range from -175 to 225 °C. Crushed ceramic powders were used for measurements to obtain macroscopic structure using SXPd, while the local structural information for NBT- x KN ceramics is still unclear.

In the past few years, x-ray scattering (XRS) accompanied by pair-distribution function (PDF) analysis has been recognised as a unique combination and advanced characterisation tool to probe local structural information, particularly for relaxor ferroelectric materials. Compared to XRS, Neutron scattering (NS) is also an advantageous technique to evaluate NBT-based materials due to its sensitivity to oxygen-related features.²² However, it requires a much longer collection time (>6 hour for each sample for NS) compared to the XRS measurement (~30 mins). In terms of sensitivity between NS and XRS on structural identification, there is not much difference to assign the space group for NBT, such as monoclinic, tetragonal and rhombohedral. However, the NS data will provide more clear information on the superlattice reflections, such as $\{1/2, 3/2, 3/2\}_p$.²²

For example, a short-range monoclinic distortion was identified in NBT by local structure analysis, based on cation displacements. Under application of an electric field, much enhanced peak intensities, along with changes in the total-scattering function, $S(Q)$, were observed for $E > 35 \text{ kV cm}^{-1}$, confirming an electric field-induced phase transformation from short-range monoclinic to long-range rhombohedral structure.²³ Furthermore, the local off-centre displacement of Bi relative to the Ti atoms in NBT- $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics was also studied by Goetzee-Barral and co-workers using *in-situ* electric poling XRS.²⁴ In the present work, we take advantage of the high-energy synchrotron XRS method and PDF analysis to employ local structural characterisation of the solid solution $(1-x)\text{NBT}-x\text{KN}$, with $x=0-0.07$. Instead of electric-field poling, *in-situ* thermally-induced local structural transformations in NBT- x KN ceramics are studied, which are correlated with temperature-dependent physical property measurements to gain further understanding of the structure property relationships in this lead-free relaxor ferroelectric material.

Experimental procedures

Ceramics were prepared using the conventional solid-state method and sintered at 1150 °C for 2h. Disk-shaped ceramic pellets with relative densities >95% were coated with silver electrodes (Gwent, UK) on both parallel surfaces, followed by a firing procedure at 550 °C for 2h prior to electrical measurements. The capacitance of the ceramics was measured in the temperature range from 50 °C to 440 °C, at frequencies of 1, 10 and 100 kHz, using a HP 4284A LCR meter, with a heating rate of 2 °C min⁻¹. Temperature-dependent dielectric permittivity, ϵ_r -T, and loss, $\tan\delta$ -T, data were plotted after geometrical correction.^{21,25,26} Temperature-

dependent synchrotron x-ray scattering experiments were performed in Diamond light source, beamline I15-1, with x-ray energy of 76.69 keV (wavelength of 0.161669 Å). The sintered pellets were crushed into fine powders, followed by annealing at 550 °C for 2h to eliminate residual stress induced during manual crushing. Then, the powder samples were loaded into glass capillaries of 0.3 mm inner diameter. The samples were heated up to 410 °C using both a cryojet and hot-blower with a ramp rate of 5 °C min⁻¹. After temperature stabilisation, total scattering patterns were recorded on a Perkin Elmer XRD 4343 CT detector with a collection time of 600 s while the glass capillary was spinning. The G(r) PDF patterns were obtained from the S(Q) after background subtraction, normalisation and Fourier transformation using PDFgetX3.²⁷ To obtain appropriate PDF analysis, the maximum scattering vector ($Q_{\max}$) used for Fourier transform is 25 Å⁻¹.^{28, 29} *In-situ* temperature-dependent PDF analysis provides the opportunity to closely examine the structural transformations in NBT-xKN ceramics over a range of length scales, by carrying out the “box-car” analysis. A 10 Å range of the PDF was investigated at different points along the PDF to obtain structural information in the different ranges. Here, the “box-car” method was applied over the r ranges of 2-12, 2-22, 2-32, 2-42 and 2-52 Å to compare the structure from the local- to medium-range. PDF patterns were refined with PDFGui using the least-squares minimisation method.³⁰

Results and discussion

The dielectric data in the temperature range from 50 to 430 °C for all compositions of the NBT-xKN (x=0.01-0.07) ceramics are presented in Figure 1. Both ϵ_r -T. and $\tan\delta$ -T. curves exhibit frequency dispersion, indicating a relaxor behaviour. The abrupt increase on $\tan\delta$ value for NBT-xKN at elevated temperature (~300 °C) was mainly due to the ionic conductivity.⁴⁻⁷ Two anomalies, $T_1 \sim 130$ °C and $T_m \sim 320$ °C, were observed for NBT-0.01KN ceramics, which are similar to those observed in other reports on NBT. T_1 is commonly identified as the depolarisation temperature (T_d) or phase transition temperature from rhombohedral to tetragonal (T_{R-T}), while T_m is often reported to be the Curie temperature, T_c . With increasing KN concentration, T_m drops slightly to ~295 °C and T_1 shifts gradually toward lower temperatures, reaching ~90 °C for NBT-0.07KN. Meanwhile, the ϵ_r -T curve is observed to be much flatter for NBT-0.07KN, compared to the other three compositions. Similar suppression of the temperature-dependent dielectric properties has previously been reported in other NBT-based solid solutions, e.g. NBT-0.09KN and NBT-0.10NN, which are recognised as potential capacitor materials with low temperature coefficient of capacitance (TCC).^{21, 31} Here, the observed changes in the ϵ_r -T characteristics, such as the reduced T_1 and general suppression of the permittivity values with increasing KN concentration, are attributed to co-doping with K⁺ and Nb⁵⁺ on the A- and B-sites of the perovskite NBT lattice, indicating possible changes on the local scale due to disrupted ferroelectric coupling or structural transformations. Wang and co-workers recently described the structure of NBT-xKN as pseudo-cubic with slight rhombohedral distortion up to 225 °C using SXPD.²¹ Thus, the structure for NBT-xKN materials across the transition temperatures T_1 and T_m needs to be investigated further.

Figure 1. Temperature-dependent ϵ_r -T. and $\tan\delta$ -T. curves for (a) NBT-0.01KN (b) NBT-0.03KN (c) NBT-0.05KN (d) NBT-0.07KN ceramics.

Figure 2a shows the results of “box-car” analysis for NBT-0.01KN for different PDF ranges. Five different structural models were used for refinement: Cubic $Pm\bar{3}m$, Tetragonal $P4bm$, Tetragonal $P4mm$, Rhombohedral $R3c$ and Monoclinic $C1c1$, as they all have been reported for NBT-based materials. For local-range boxes ($r < 25$ Å), Monoclinic $C1c1$ yielded best fits with $R_w=11.46\%$ over rhombohedral $R3c$ ($R_w=12.01\%$) and other symmetries (Figure S1, Supplementary information). Significantly less-pronounced peaks were observed at higher r range compared to the local range ($r < 25$ Å), where more medium and long range correlation were reflected. The best fitting for higher r range was obtained using the $R3c$ model with $R_w=11.81\%$. These results are in agreement with the TEM study that has been performed by Levin and Reaney, where the monoclinic phase was only observed at a very local scale due to unique in-/out-phase octahedral tilting and cation displacement within ABO_3 perovskite structure.¹²

Figure 2. (a) “Box-car” fitting for NBT-0.01KN ceramics in a r range of 2-52 Å at room temperature (b) The rhombohedral inter-axial angle for NBT- x KN ceramics.

It is critical to investigate the atom-atom coherence length at the local- and medium-range for lead-free electroceramics to understand the nature of relaxor behaviour, which has been considered as the distinct

feature for realizing promising electrical and mechanical performance, e.g. electrostrain, piezoelectric coefficient and energy density.³²⁻³⁹ Thus, converted PDF data for all compositions of the NBT-xKN (x=0.01-0.07) ceramics were refined using the “box-car” method to identify local- and medium-range structural information, as presented in Figure 2b. Here the centre of the range, R ($r/2$, 7-27 Å), has been determined to represent the r range at 2-12, 2-22, 2-32, 2-42 and 2-52 Å to compare the structure from the local- to medium-range. To facilitate comparison with the cubic structure, results obtained using the $R3c$ model for all ranges were chosen and converted into the pseudo-cubic setting using the method described in the supplementary information. The inter-axial angles at the lowest r range was found to be $\sim 89.5^\circ$ for NBT-0.01KN and 89.2° for NBT-0.07KN, as more KN incorporating into NBT-KN solid solution. The ionic size difference on the A-site, between $\text{Na}^+/\text{Bi}^{3+}$ and K^+ , and the B-site, between Ti^{4+} and Nb^{5+} , could cause more cation displacement and octahedral tilting at the local scale with increasing KN concentration. Then α_{pc} for all compositions approaches to 90° with increasing r length, indicating that the different size of local-range polar nano-cluster (PNCs) are embedded into medium-range pseudo-cubic matrix. At high r range, highest inter-axial angle $\sim 89.9^\circ$ was obtained for NBT-0.07KN, very close to 90° . The average structure this composition is thus more likely to be identified as pseudo-cubic structure using conventional XRD technique. The size of these PNCs are expected to be below 5 nm. At the contrast, inter-axial angle for NBT-0.01KN and NBT-0.03KN are found to be much lower $\sim 89.7^\circ$ even in the medium r range, suggesting a much larger distorted PNCs. The inter-axial angle at highest r range are found to be similar to the average structure reported in the previous work.²⁶

Here, the calculated size of the PNCs provides another insight to distinct ergodic-relaxor (ER) and non-ergodic relaxor (NE) behaviour. In general, the difference between an ER and NE relaxor depends on whether it can reversibly or irreversibly transform to the metastable ferroelectric phase after poling. Based on the previous studies, both NBT-0.01KN and NBT-0.03KN were identified as NE due to the observed irreversible electric field-induced transformation from pseudo-cubic to rhombohedral. However, compositions with 5% KN or above were shown to exhibit ER behaviour with pseudo-cubic structure.²⁶ Combined with the PDF results, the reason for these changes in behaviour for different KN contents can be interpreted to be the atom-atom coherence length at the local range, which is equivalent to the size of PNCs. The medium- or long-range PNCs (for example, >5 nm) are able to merge into micro-domains and retain after poling, for example in NBT-0.01KN and NBT-0.03KN where an average rhombohedral structure can be observed at poled state.²⁶ On the other hand, much smaller PNCs with $r < 25$ Å are found for higher KN concentrations, which cannot be correlated under the application of an electric field, resulting in a long-range pseudo-cubic symmetry.^{21, 26}

T_m in ϵ_r - T data has been commonly considered as T_c , where phase transition to paraelectric cubic phase (following Curie-Weiss law), for typical ferroelectric materials. However, it is not applicable for NBT-based materials due to the relaxor nature, which is presence of local PNCs within a pseudo-cubic matrix. For example, a mixture of $R3c$ and $P4bm$ PNCs were identified above T_m for NBT-0.06BT ceramics, as reported by Jo.¹⁶ We therefore investigated the local structural behaviour for NBT-0.01KN from 20 to 410 °C by performing *in-situ* temperature PDF analysis. Figure 3 shows the *in-situ* temperature-dependent PDF patterns for NBT-xKN (x=0.01-0.07) from 50 to 410 °C. On the local scale ($r < 25$ Å), the peaks become broad and less distinct with increasing temperature due to thermal motion producing an increase in the distribution of atom-atom distances. For the medium range ($r > 25$ Å), shifting of the peak positions to higher r become evident due to thermal expansion.

Figure 3. The PDFs $G(r)$ data from 2 to 42 Å for NBT- x KN ($x=0.01-0.07$) for a series of temperatures from 50 to 410 °C.

The refinement of the temperature-dependent PDF data for NBT-0.01KN was focused on the local structure ($r < 25$ Å) using five different models: Tetragonal $P4bm$, Tetragonal $P4mm$, Cubic $Pm\bar{3}m$, Rhombohedral $R3c$ and Monoclinic $C1c1$, at temperatures ranging from 20 to 410 °C, shown in Figure 4.

Figure 4. The PDF refinement ($r < 25 \text{ \AA}$) using five different models for NBT-0.01KN at temperature of (a) 150 °C (b) 250 °C (c) 360 °C (d) 410 °C.

The temperatures between anomalies in the ϵ_r -T data were intentionally selected to investigate potential structural transformations. The best refinement was obtained using both Monoclinic $C1c1$ profile for all temperatures. At 410 °C, which is much higher than the T_m (as shown in Figure 2a) for NBT-0.01KN ceramics, the local structure is still identified as distorted Monoclinic $C1c1$ rather than Cubic $Pm\bar{3}m$. At local length scales ($r < 25 \text{ \AA}$), the PNCs, which cannot be readily identified using conventional characterisation methods, are randomly distributed in a large-scale undistorted matrix, determined on average as a pseudo-cubic symmetry previously.²¹

The crystallographic parameters were obtained after refinement using the $R3c$ model for all compositions in the temperature range from 20 to 410 °C, as displayed in Figure 5. The pseudocubic lattice parameters a_{pc} for all compositions increase at a relatively uniform rate up to 410 °C because of thermal expansion. The inter-axial angle α_{pc} remains approximately constant at 89.6° with temperature (variation $< 0.1\%$), suggesting that local distortion cannot be eliminated until 410 °C, which is much higher than T_2 . With increasing KN concentration, both A- and B-site ionic sizes enlarge due to the larger ionic radii of K^+ (1.64 Å) and Nb^{5+} (0.64 Å) relative to Na^+ (1.39 Å), Bi^{3+} (1.03 Å) and Ti^{4+} (0.605 Å), which results in an increase of lattice parameter (a_{pc}) from approximately 3.89 Å to 3.93 Å.⁴⁰ Furthermore, α_{pc} decreases from approximately 89.6° to 89.2° with increasing KN concentration at the local-range scale, indicating a possible change of octahedral tilting within the perovskite structure induced by chemical dopants. Thus it can be confirmed that T_m is not the Curie temperature and the structure after T_m is not a conventional paraelectric phase for NBT-KN ceramics.

Figure 5. The temperature-dependent lattice parameters and inter-axial angle for (a) NBT-0.01KN (b) NBT-0.03KN (c) NBT-0.05KN (d) NBT-0.07KN ceramics at the local length scale.

Conclusions

In summary, the local structure of NBT-xKN ceramics was examined in the temperature range from 20 to 410 °C using high-energy synchrotron x-ray scattering and the PDF data was analysed using the “box-car” method. At room temperature, the local structure ($r < 25 \text{ \AA}$) was identified as monoclinic $C1c1$ for all compositions. With increasing KN concentration, the distortion of local PNCs becomes more significant due to changes in the mismatch of ionic size. Using the “box-car” method, the local inter-axial angle gradually increases toward 90° with increasing r range for all compositions, suggesting that these local PNCs are embedded within a medium- or large-range pseudo-cubic matrix. It was also noted that the nature of relaxor

for NBT-KN can be correlated with the size of PNCs at local/medium scale. For example, large local distorted PNCs (>5 nm) tend to perform irreversible transformation from NE relaxor (pseudo-cubic) into metastable ferroelectric (rhombohedral) under application of electric field.

At elevated temperatures, the *in-situ* PDF analysis produces a new conclusion for NBT-based materials in that there is no local structural transformation, as commonly stated in previous reports (based on ϵ_r -T curves), up to the maximum dielectric peak (T_m). Instead, local PNC of $C1c1$ symmetry exist from 20 to >410 °C with similar distortion. This study provides a unique insight to combine local structural characterisation with electrical results, which can be used for other types of ferroelectrics or relaxor-ferroelectrics.

Acknowledgement

We thank Diamond Light Source for access to beamline I15-1 (proposal number EE17691-1) that contributed to the results presented here and support from the Functional Materials and Devices group at the University of Sheffield. We also wish to acknowledge the Henry Royce Institute for Advanced Materials, funded through EPSRC grants EP/R00661X/1, EP/S019367/1, EP/P02470X/1 and EP/P025285/1, for the financial support at The University of Sheffield,

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