Thermal evolution of polar nanoregions identified by the relaxation time of electric modulus in $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ system

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Abstract – The correspondence between the temperature dependence of phase structures and the experimental physical properties was made clear for the first time in $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ system according to in situ XRD, in situ Raman and impedance spectroscopy. XRD profiles show pseudo-cubic symmetry independent of temperature, while one of the Raman models disappears near 620K, indicating that the local symmetry increases. The temperature dependence of the main relaxation time of the electric modulus spectra can be divided into four regions, characterizing the thermal evolution of polar nanoregions (PNRs) with different symmetries and a phase transition between rhombohedral and tetragonal symmetry. Therefore, the relaxation times of the electric modulus provide a way to estimate the local phase transition and the thermal evolution of $R3c$ and $P4bm$ PNRs.

I. Introduction. - $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ (BNT)-based ferroelectric relaxors show strong potential in replacing lead-based piezoceramics due to their large strains. Great improvement in piezoelectric properties have been achieved in BNT-BaTiO₃ (BT),[1] BNT-K_{0.5}Na_{0.5}NbO₃ (KNN),[2] and BNT- $\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3$ (BKT).[3] Very large strains have been obtained in ternary systems such as BNT-BT-BKT [4] and BNT-BT-KNN. [5] The mechanism for enhancement of strain was attributed to incipient piezoelectricity of the relaxors where a phase transformation takes place under high electric fields. [6-9]

In most BNT based relaxor ferroelectrics, [10-12] there are two dielectric anomalies in the temperature- dependent permittivity data. The first anomaly appears at lower temperatures and shows typical relaxor behavior with frequency dispersion. [13] The second anomaly occurs as a dielectric maximum at higher temperatures. Researchers gave different explanations for this phenomenon. Jo *et. al* [14] proposed that 0.94BNT-0.06BT has a cubic symmetry at room temperature with rhombohedral $R3c$ and tetragonal $P4bm$ polar nanoregions (PNRs). A mixture of $R3c$ and $P4bm$ PNRs at low temperatures undergo a thermal evolution, resulting in the first anomaly. The second local maximum in the

temperature-dependent dielectric permittivity results from a mixed contribution from $R3c$ -to- $P4bm$ transition and a thermal evolution of $P4bm$ PNRs. Later, in the BNT-BT-KNN system,[15] they pointed out that low-temperature PNRs with rhombohedral symmetry are responsible for the first anomaly (relaxor behavior), and high-temperature PNRs with tetragonal symmetry contribute to the second anomaly. In addition, the phase transition between the two PNRs makes less contribution to the overall permittivity. Unfortunately, the exact mechanism associated with the dielectric behavior of relaxor materials has not been established yet, the structure change is too small to detect exactly. A possible method to identify the thermal evolution of PNRs is based on their relaxation times, however, in the BNT-based system, relaxation peaks of the imaginary part of the dielectric permittivity often do not show up in the frequency range from 1 Hz to 1MHz.

It is known that impedance spectroscopy (IS) is a powerful tool to investigate electroceramics, especially for electrically heterogeneous ceramics. [16,17] IS analysis on the dielectric relaxation is critical for better understanding the dynamics of PNRs, which gives rise to all the unique relaxor properties in relaxor ferroelectrics. [18] Our previous work reported large

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strain and a relaxor-antiferroelectric coherence in 90BNT-10SrTiO₃ with addition of up to 5% KNN as a replacement for SrTiO₃ (ST). [19] It was found that the temperature dependence of the dielectric permittivity can be fitted quite well with three consecutive events by an empirical equation. The fitting parameters for each event are reasonable, however, the polarization processes are not clear. In this paper, the temperature dependence of the relaxation time of 0.90Bi_{1/2}Na_{1/2}TiO₃–0.05SrTiO₃–0.05K_{0.5}Na_{0.5}NbO₃ (90BNT-5ST-5KNN) ceramic was confirmed according to electric modulus (M'') spectra. The three processes can clearly be seen based on the thermal evolution of PNRs and the phase transition between rhombohedral and tetragonal for the first time. The transition points were observed in the temperature dependence plot of the relaxation time, which agrees with the deconvolution of the dielectric spectra and XRD/Raman results.

II. Experimental Procedure. - The preparation of 90BNT-5ST-5KNN ceramic has been shown in Ref. 16 in detail. The annealed ceramic powder was characterized by XRD with Cu K α 1 radiation, in a Panalytical X'Pert Pro MPD (Panalytical B.V., Almelo, Netherlands) operating at 45 kV and 40 mA, at temperatures between 300K and 753K in intervals of 30K. The furnace used was an Anton Paar HTK16 (Anton Paar, Graz, Austria) with a Pt heating filament. Full profile Rietveld refinements were performed using FULLPROF.[20] The peak profile shape was described by a pseudo-Voigt function.[21] A Thermo Scientific DXR Raman microscope optimized for dispersive Raman measurements was employed. Raman spectra were measured with a 532 nm laser and an effective power of 5.0 mW. Temperature-dependent (in situ) Raman experiments were performed in the range of 300–753 K by means of a Linkam MDS600 (Linkam, Tadworth, UK) heating-cooling stage. Raman peak positions and full width at half maximum (FWHM) were extracted from fits according to multiple Gaussian-Lorentzian peak functions. Electrodes were fabricated with fired-on silver paste at about 873K for 30 min. The temperature and frequency dependence of the dielectric permittivity was measured from room temperature to 850K, by applying an alternating voltage of 500mV amplitude with frequencies in the range of 100Hz-1MHz, using an LCR meter (Agilent, 4294A, Hyogo, Japan) connected to a tube furnace with controlled temperature. Impedance spectroscopy was collected using an impedance analyzer (Agilent 4294A, Hyogo, Japan) in the 40 Hz-1 MHz frequency range from room temperature up to 850K. The heating rate was 5 K/min.

III. Results and Discussion.- The room temperature structure of 90BNT-5ST-5KNN has already been investigated and described.[19] However, the structural data of the sample upon heating and the exact transition behavior remains unclear. Therefore, a detailed examination of the development of the crystallographic structure of the ceramic powder upon heating was carried out using *in situ* XRD measurements. The temperature evolution of the XRD patterns of the sample upon

heating in the temperature range from 300 to 753K is represented in Fig. 1(a). It is found that all patterns can be described as a single perovskite phase with cubic symmetry, since the polymorphism of the sample is that $R3c$ and $P4bm$ symmetries coexist as nano-scale entities throughout the temperature regime of a common interest on a long-range $Pm-3m$ symmetry as a matrix [14]. Close inspection of the patterns indicates that no characteristic peak splitting or super structure reflections appear. However, cubic symmetry should be broken by weak rhombohedral or tetragonal distortions.[12-24] In order to conveniently observe the average structure change, the patterns were Rietveld-refined using $Pm-3m$ space group. The refined unit cell volumes for the measured temperatures are schematically represented in Fig. 1(b) for the primitive perovskite unit cell. The cell volume increases with increasing temperature, however, the increase in the unit cell volume is not linear. The main changes in the unit cell parameters take place near 500K. This could correspond to a phase transition from rhombohedral to tetragonal symmetry.

Fig. 1 (a) Rietveld refined X-ray diffraction data of 90BNT-5ST-5KNN ceramic powder upon heating in the temperature range between 300K and 753K (Symbols are the observed patterns and red solid lines are calculated patterns). (b) Temperature evolution of the refined reduced unit cell volume. The solid line is merely a guide to the eyes.

Furthermore, in order to more directly observe local structural modifications, the temperature evolution of the lattice vibrational modes was studied by Raman spectroscopy. Fig. 2(a) shows the temperature dependence of the Raman spectrum of 90BNT-5ST-5KNN in the range 300–753K. The Raman spectrum is characterized by a strong broadening of the Raman modes in pseudocubic BNT-based ceramics, which might underline the presence of second order effects or non- $k=0$ modes activated by local disorder, therefore, the traditional mode assignment based on group theory is challenging.[25] Spectral deconvolution was performed according to 9 Gaussian peak functions by means of a best-fitting algorithm. The spectrum could be linked to a mixed rhombohedral- tetragonal crystal structure, evident by the two

distinct splitting bands in the mode corresponding to Ti-O vibration centered around 250 cm^{-1} . [8,9] The spectrum undergoes broadening and the modes at 130 cm^{-1} and 590 cm^{-1} decrease in intensity with increasing temperature, indicating that a loss of polarity of the unit cell occurs. [26-28] Generally, a steady phonon softening with change of intensity of the modes is expected in the absence of phase transition. [29] In order to better illustrate the local temperature dependent phase transition behavior for the 90BNT-5ST-5KNN ceramic, the temperature dependence of the peak position and FWHM of the related modes are plotted in Fig. 2(b1-b3) and 2(b4-b5), respectively. The anomaly induced by the phase transition from $R3c$ to $P4bm$ is a change in the phonon wavenumber or FWHM which takes place in both the A-site related modes (at 120 and 135 cm^{-1}) and B-site related modes (at 280 cm^{-1} , 320 cm^{-1} , 480 cm^{-1} and 520 cm^{-1}) at around 500K . Another anomaly near 620K could be related to the $R3c$ phase disappearing or the transition to a region of fluctuating nanoregions, this is consistent with the temperature dependence of the octahedral and the B-site modes. [26] Since they are influenced by the dynamics of the nanodomain phase, influencing the Ti-O bonds and the octahedral vibrations, [30] this behavior is compatible with a diffuse phase transition (DPT) marking the beginning of the region of fluctuating nanoregions. This was confirmed by the following temperature dependence of the dielectric permittivity.

Fig. 2 (a) Raman spectrum of 90BNT-5ST-5KNN as a function of temperature. The spectra were deconvoluted according to 9 Gaussian peak functions (Green lines). The assignment of the spectral modes to particular lattice vibrations is also indicated. (b) Temperature dependence the peak position (b1-b3) and FWHM (b4 and b5) of selected modes of the 90BNT-5ST-5KNN spectrum. The dashed lines connecting the experimental points are merely guides to the eye. The locations of the anomaly points (near 500K) are indicated by the red vertical lines.

A discrete frequency spectrum, such as the temperature dependence of the dielectric permittivity at several frequencies, does not include additional details on the frequency dependence of the dielectric behavior. In order to

overcome these limitations, impedance spectroscopy with a broader and more continuous frequency spectrum is often employed in unpoled BNT-based ceramics. The complex electric modulus (M^*) is defined in terms of the complex dielectric constant (ϵ^*) and is represented as $M^* = (\epsilon^*)^{-1}$. Effects of electrode polarization and the electrical conductivity can be suppressed using electric modulus formalism. The imaginary part of the modulus (M'') at different temperatures are calculated for the 90BNT-5ST-5KNN ceramic and depicted in Fig. 3 (a-d). M'' is indicative for the energy loss under electric field. The M'' peak rapidly shifts to higher frequencies with increasing temperature from 300K to 390K , as shown in Fig. 3(a). Then it is independent of temperature in the region of 400 - 520K [Fig. 3(b)]. With further increasing temperature (530 - 610K), the peak slowly moves to lower frequencies. Finally, it again shifts to higher frequencies with increasing temperature from 620K to 850K . The electric modulus physically corresponds to the relaxation of the electric field in the materials while the electric displacement remains constant, so that the electric modulus represents the real dielectric relaxation process. [31] Consequently, the four dependencies could attribute to different relaxation mechanisms.

Fig. 3 Frequency dependence of the imaginary part of the electric modulus for 90BNT- 5ST- 5KNN measured at various temperatures. (a) 300 - 390K , (b) 400 - 520K , (c) 530 - 610K , (d) 620 - 850K .

Figure 4(a) shows the temperature dependence of the main relaxation time (τ). It is similar to, but more complex than, the time distribution of a $\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.80}\text{Ti}_{0.20})_{0.98}\text{O}_3$ ferroelectric ceramic. [32] In addition, the temperature dependence of the dielectric permittivity for 90BNT-5ST-5KNN at 100 kHz is shown in Fig. 4(b) in the same temperature region to understand the relaxation processes. Smolenskii, [33] Kirillov and Isupov [34] suggested that the total number of relaxators contributing to the dielectric response near the permittivity peak is temperature dependent and the temperature distribution of this number can be described by a Gaussian function with a mean value T_0 and a standard deviation δ :

$$\frac{\epsilon_0}{\epsilon - \epsilon_\infty} = \exp\left[\frac{(T - T_0)}{2\delta^2}\right] \quad (1)$$

where ϵ_∞ is the dielectric permittivity at high frequency close to the infrared (IR) region, and ϵ_0 is the static dielectric permittivity. The curve can be deconvoluted from three Gaussian functions, which agrees with Jo's assumption in poled 94BNT-6BT ceramics.[14] During heating, three consecutive events are expected to occur. The initially existing *R3c* PNRs undergo a thermal evolution resulting in a dielectric maximum, followed by a phase transition of *R3c* to *P4bm*, and then finally all the *P4bm* symmetry undergoes a thermal evolution giving rise to a broad dielectric maximum.

Fig. 4 (a) Temperature dependence of the main relaxation time according to the M'' peak. The purple line is the Vogel-Fulcher fitting. (b) Temperature dependence of dielectric permittivity for 90BNT-5ST-5KNN ceramics at 100 kHz. The black symbols are experimental data; the red lines represent the fitting results, the green lines are the fitted dielectric permittivity peaks based on the Gaussian function.

For ferroelectric relaxors, the relaxation time of clusters or polar nanoregions (PNRs) increases during the cooling process and hence the correlation among them increases.[35,36] It is difficult for some PNRs to orient in an external electric field. The decrease of τ at temperatures below T_f [in Fig. 4(b)] could be associated with the freezing of *P4bm* PNRs, which provides the frustration of the cooperative interactions and then only a few PNRs could couple with the electric field. In fact, the relaxation process prefers showing the DPT, as mentioned in the Raman spectra, rather than the typical relaxor behavior because the temperature dependence of the relaxation does not follow the Vogel-Fulcher law:

$$\tau = \tau_0 \exp\left[\frac{E_a}{k(T - T_f)}\right] \quad (2)$$

where E_a , k , τ_0 and T_f are the activation energy, the Boltzmann constant, Debye time and freezing temperature, respectively. It suggests that the high-temperature relaxation process can be associated with domain wall movements with increasing temperature (domain/polar cluster size shrinking). A broad minimum is observed for τ , which is in agreement with the phase transition between *R3c* and *P4bm*. The temperature of the minimum near 480K is very close to the phase transition temperature identified by XRD and Raman (Fig. 1 and Fig. 2). The increase in τ at lower temperatures could be associated with the increase in the size of *R3c* PNRs during cooling.[37] Noted that the relaxation process follows the Vogel-Fulcher

law as shown in Fig. 4a. The E_a is 0.025 ± 0.003 eV, τ_0 is $(3.2 \pm 1.0) \times 10^{-5}$ s and T_f is 252 ± 2 K. The activation energy is similar to $\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.80}\text{Ti}_{0.20})_{0.98}\text{O}_3$ ferroelectric ceramic, however, the Debye time is too long compared with typical relaxors. A possible mechanism explaining the longer-time-response of the PNRs is the side-ways motion of their boundaries without a change of orientation (just change volumes),[38] which should attribute to the distortion structure and heterovalent ions are displaced at both A site and B site in BNT-based ceramics.[39] The long relaxation time and the small change in them ($10^{-5} \sim 10^{-2}$ s) in the studied temperature range suggest: (i) a mixture of the time response of the *R3c* and *P4bm* polarization mechanisms (ii) minor changes in the size of the PNRs [40] and (iii) large size of the PNRs. Our previous work[40-42] reported that a coexistence of *R3c* and *P4bm* phase was evident in BNT-KNN ternary systems. Both *R3c* and *P4bm* phases are present on a nanoscale level and show a high thermal stability. Therefore, the discussion for the polymorphism in 90BNT-5ST-5KNN ceramic based on relaxation time, average structure and local structure is reasonable.

IV. Conclusions.- The average and local structure and dielectric relaxation of 90BNT-5ST-5KNN ceramic were investigated. Three consecutive events were identified by relaxation time of electric modulus spectra and by deconvoluting the temperature dependence of the dielectric permittivity using a phenomenological model. Reasonable results can be obtained by the characteristic relaxation time, whose temperature dependence can be obtained according to the electric modulus spectra. The exact temperature region of the phase transition between *R3c* and *P4bm* is obtained based on *in situ* XRD and Raman, which agrees with the result from the characteristic relaxation time. In comparison with the classical perovskite relaxor, $\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.80}\text{Ti}_{0.20})_{0.98}\text{O}_3$, the *R3c* PNRs show the same activation energy but larger size. Based on the XRD and Raman measurements, it is proposed that 90BNT-5ST-5KNN at room temperature has a pseudocubic symmetry with rhombohedral *R3c* PNRs. and the mid-temperature local maximum in the temperature-dependent dielectric permittivity arises from a phase transition from *R3c* to *P4bm*, and the high-temperature dielectric anomaly can be associated with the thermal evolution of *P4bm* PNRs.

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