

Dielectric Investigations of 0.945(Bi_{0.5}Na_{0.5})TiO₃-0.055BaTiO₃

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Abstract—Dielectric properties of 0.945(Bi_{0.5}Na_{0.5})TiO₃-0.055BaTiO₃ (BNBT5.5) (a composition close to the rhombohedral-tetragonal morphotropic phase boundary) ceramics are studied. It is shown that BNBT5.5 is a relaxor with a characteristic relaxation time that follows Vogel-Fulcher's law. The following Vogel-Fulcher parameters of the relaxation time were calculated: $\tau_0 = (2.0 \pm 2.4) \cdot 10^{-14}$ s, $E/k_B = (1620 \pm 270)$ K, $T_0 = (262 \pm 9)$ K.

I. INTRODUCTION

IN recent years, lead-free piezoelectric ceramics have drawn an increasing amount of attention as lead-containing materials, which have dominated industrial applications for years, became an object of very strict environmental regulations, e. g., European Union (EU) directives on waste from electrical and electronic equipment (WEEE), restrictions of hazardous substances (RoHS), and end-of-life vehicles (ELV). One concern is that lead-free ceramics have not yet overcome the electromechanical characteristics of traditional Pb(Zr,Ti)O₃-based materials, although the differences diminish if higher Curie temperatures are considered [1]). However, the possibility of sintering in air atmosphere and the reduced hazard to the environment from production to final disposal make research into lead-free alternatives very worthwhile.

Bismuth sodium titanate (Bi_{0.5}Na_{0.5})TiO₃ (BNT) and its solid solutions are considered among the best candidates for replacing PZT. At room temperature, BNT is ferroelectric, passing into an antiferroelectric phase at 473 K and to a paraelectric cubic phase at 593 K [2]. BNT has a rhombohedral symmetry at room temperature. This allows for a possible morphotropic phase boundary (MPB) when mixed with a perovskite-type ferroelectric of tetragonal or orthorhombic symmetry, such as bismuth potassium titanate (BKT), barium titanate (BT), sodium niobate (NN), or potassium sodium niobate (KNN). From a practical point of view, MPB solid solutions are most important because the electromechanical properties are greatly enhanced compared with the individual constituents. So far, many binary (such as BNT-BKT [3]), ternary (BNT-NN-BT [4]), or even quaternary systems (BNT-BT-KNN [5], [6]) have been investigated.

It has been reported that (Bi_{0.5}Na_{0.5})TiO₃-BaTiO₃ solid solution ceramics possess an MPB as the BT content approaches 6 mol% [2], [7]. For 5 mol% BT concentration, a paraelectric-antiferroelectric transition at 548 K and antiferroelectric-ferroelectric transition at 423 K are observed. A relatively large remnant polarization of about 20 to 40 $\mu\text{C}/\text{cm}^2$ at room temperature has been reported [2], [8]. Surprisingly, the dielectric dispersion has not been investigated for near-MPB BNT-BT so far, despite the fact that knowledge about the dielectric behavior is crucial to understanding the different phase transitions in this material. To remedy this lack, this paper studies the dielectric dispersion of 0.945BNT-0.055BT (or simply BNBT5.5) ceramics with a concentration of barium titanate slightly below the MPB.

II. EXPERIMENT

A conventional powder solid-state reaction method was used to prepare the samples: weighted powders of TiO₂, BaCO₃, Bi₂O₃, and Na₂CO₃ (at least of 99.8% purity) were ball-milled in ethanol suspension for 24 h, dried, hand-milled with mortar and pestle, calcined at 1073 K for 2 h, and ball-milled again. Then the powder was pressed into pellets of 10 mm diameter and sintered at 1423 K in air atmosphere for 2 h.

The measurements were performed using an HP4284A precision LCR meter (Hewlett Packard, Palo Alto, CA), covering frequencies from 20 Hz to 1 MHz. Silver electrodes were applied on polished samples to provide good electrical contact. The measurements were performed during the cooling cycle at a cooling rate of 1 K/min from 700 K to 330 K.

III. RESULTS AND DISCUSSION

The temperature dependence of the real and imaginary parts of the dielectric constant is shown in Fig. 1. The real part shows 2 anomalies: one large broad peak at about 543 K and a "bump" at about 393 K. The large peak corresponds to the paraelectric-antiferroelectric phase transition. The bump, however, should not be related to the antiferroelectric-ferroelectric phase transition, as one can clearly observe a pronounced anomaly in the imaginary part of the dielectric spectra, which has the features of a typical relaxor: the maxima cover a wide temperature range, the peak temperature strongly depends on the measurement frequency, the curves do not intersect one an-

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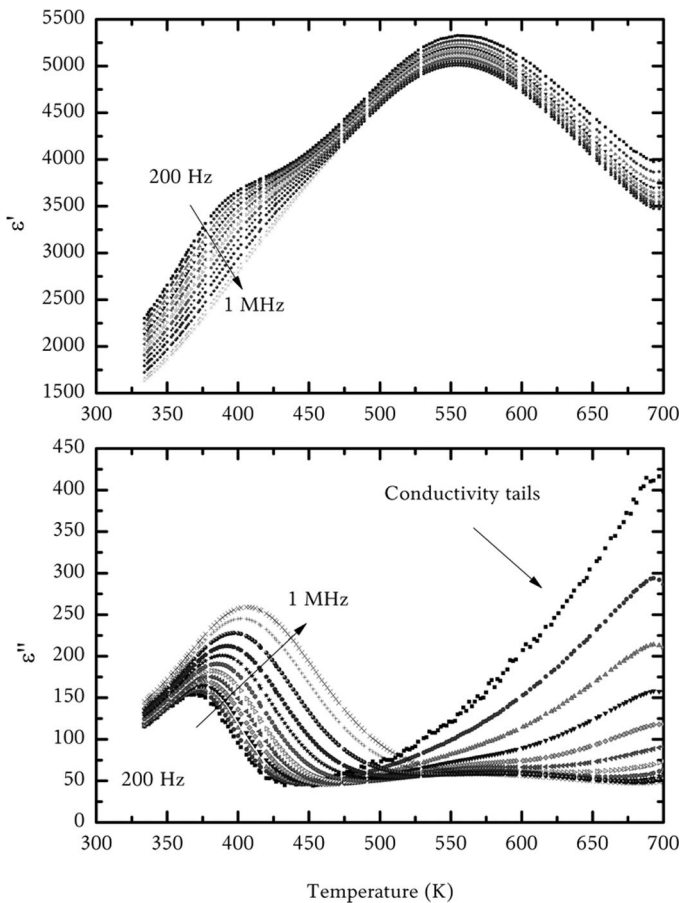


Fig. 1. Dielectric spectra of BNB5.5.

other as they do in glasses, and they coincide nearly to one curve at low temperatures. Thus, the dielectric dispersion observed in the temperature range from 330 K to 473 K is due to polar nanoregions, and all the ferroelectric and antiferroelectric properties are related to the remaining bulk volume in which these abovementioned nanoregions emerge.

For higher temperatures and lower frequencies, ionic conductivity starts influencing the results. The imaginary dielectric constant increases dramatically. However, this phenomenon falls beyond the scope of this paper. Finally, at the paraelectric-antiferroelectric phase transition temperature, we observe a slight increase of the imaginary part (see the bottom contour of the imaginary part of dielectric constant in Fig. 1) of the dielectric constant, which only indicates the beginning of the dielectric dispersion that lies at much higher frequencies, probably in the terahertz range. This transition is very difficult if not impossible to investigate using dielectric spectroscopy, because the primitive cell doubles during the transition. Thus, the soft mode softens at the edge of the first Brillouin zone, while the dielectric spectroscopy probes only the center, which remains mostly unaffected during the paraelectric-antiferroelectric phase transition. In dielectric spectroscopy, only a step of the dielectric constant should be present, but in this case, it is masked by relaxor behavior.

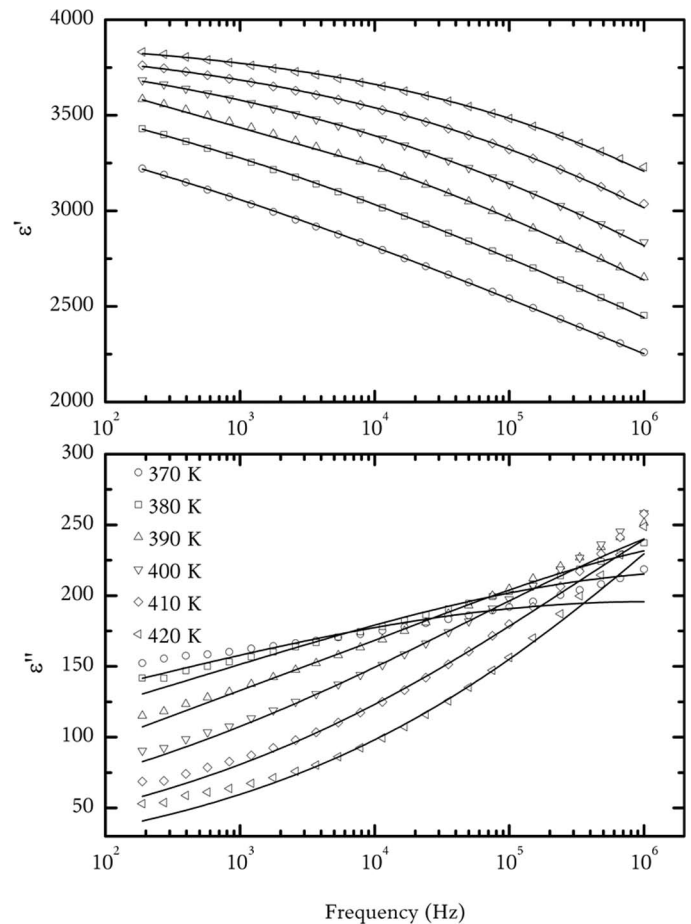


Fig. 2. Cole-Cole function fits of real and imaginary parts of dielectric constant for selected temperatures.

Polar nanoregions in relaxors cannot be characterized by a single relaxation time; instead, there is a wide distribution of different relaxation times. In the Cole-Cole relaxation model, the relaxation time distribution is introduced by adding the additional parameter $0 \leq \alpha \leq 1$ to Debye's law:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^{1-\alpha}} = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + i\omega\tau)^{1-\alpha}}, \quad (1)$$

where ε_∞ is the permittivity at the high frequency limit and ε_s is the static permittivity. If $\alpha = 0$, then the Cole-Cole equation simplifies to Debye's equation.

The dielectric spectra of BNB5.5 were fitted using the Cole-Cole equation. The plots are shown in Fig. 2 and Fig. 3, and the exact values of parameters are given in Table I. It should be noted that the Cole-Cole equation assumes a *symmetrical* relaxation time distribution (defined by parameter α), while the actual distribution might be far from symmetrical [9], [10]. However, even though validity of fitted Cole-Cole parameters has to be the object of discussion, its dependence on temperature is probably correct.

The most important Cole-Cole equation parameter is the polar nanoregion relaxation time τ , which represents

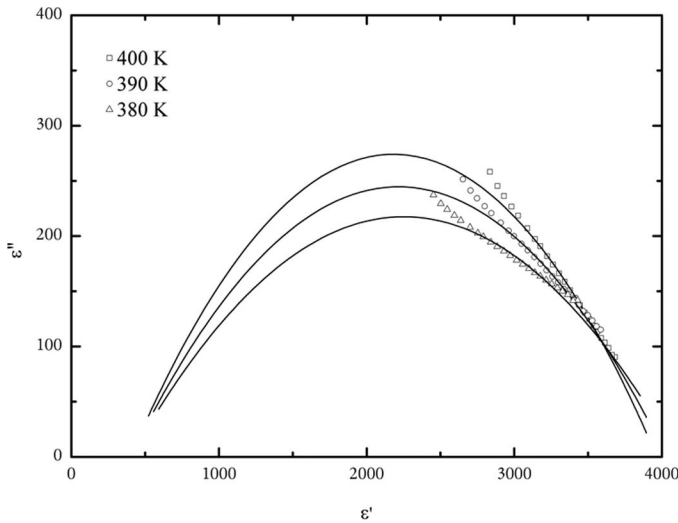


Fig. 3. Cole-Cole plots for selected temperatures.

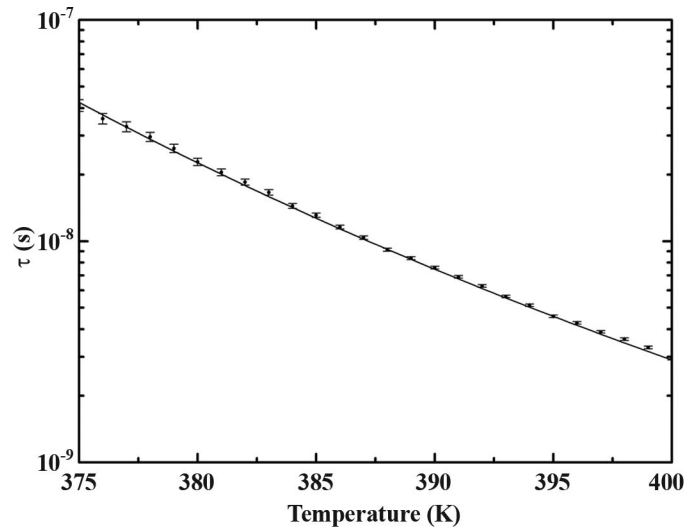


Fig. 4. Vogel-Fulcher fit for relaxation times temperature dependence.

TABLE I. COLE-COLE PARAMETERS FOR SELECTED TEMPERATURES.

Temperature	τ	$\Delta\epsilon$	α	ϵ_{∞}
370K	$(1.49 \pm 0.20) \cdot 10^{-7}$ s	3689 ± 37	0.865 ± 0.002	400
380 K	$(4.04 \pm 0.29) \cdot 10^{-8}$ s	3703 ± 24	0.851 ± 0.002	400
390 K	$(1.34 \pm 0.30) \cdot 10^{-8}$ s	3631 ± 14	0.829 ± 0.002	400
400 K	$(3.74 \pm 0.10) \cdot 10^{-9}$ s	3566 ± 10	0.806 ± 0.002	400
410 K	$(1.56 \pm 0.07) \cdot 10^{-9}$ s	3524 ± 7	0.778 ± 0.003	400
420 K	$(7.75 \pm 0.70) \cdot 10^{-10}$ s	3525 ± 7	0.753 ± 0.004	400

the *mean* relaxation time of all nanoregions. Its development with temperature is shown in Fig. 4. It can be fitted using the Vogel-Fulcher law [11]:

$$\tau = \tau_0 e^{E/[k_B(T-T_0)]}, \quad (2)$$

where T_0 is the “freezing” temperature of the polar nanoregions, indicating the point where the dynamics of the nanoregions slow down to infinitely low frequencies. E is the activation energy, and k_B is Boltzmann’s constant. The activation energy is often expressed in units of E/k_B , resulting in the activation temperature.

For BNBT5.5, the fitted Vogel-Fulcher parameters are $\tau_0 = (2.0 \pm 2.4) \cdot 10^{-14}$ s, $E/k_B = (1620 \pm 270)$ K, and $T_0 = (262 \pm 9)$ K. Again, all these parameters reflect only the averaged properties of the real polar nanoregions.

IV. CONCLUSIONS

Dielectric measurements revealed that a solid solution 0.945BNT-0.055BT is quite a complex material, showing a phase transition from the paraelectric to an antiferroelectric phase at 543 K, followed by a relaxor phase and another phase transition from the antiferroelectric to a ferroelectric phase. From the dielectric measurements it looks as if the steplike behavior at the antiferroelectric-ferroelectric phase transition is covered by the additional contribution of polar nanoregions. For the exact evaluation of the antiferroelectric-ferroelectric phase transition,

temperature measurements at much higher frequencies are needed, where the contribution of the polar nanoregions is completely suppressed. Only in this case can the antiferroelectric-ferroelectric phase transition be clearly identified. Otherwise other methods, such as X-ray diffraction (XRD), have to be used. As a relaxor, BNBT5.5 is characterized by very broad dielectric dispersion, especially at temperatures lower than 373 K. This feature is typical for relaxors. Nevertheless, a mean relaxation time could be obtained from the dielectric spectra. Its temperature dependence follows the Vogel-Fulcher law with the parameters: $\tau_0 = (2.0 \pm 2.4) \cdot 10^{-14}$ s, $E/k_B = (1620 \pm 270)$ K, and $T_0 = (262 \pm 9)$ K. We can conclude that the most of polar nanoregions freeze at this temperature. There is still the open question of the Burns temperature, the upper limit where the polar nanoregions start to appear. The paraelectric-antiferroelectric phase transition at 543 K might be triggering the appearance of the polar nanoregions, or they might be present already even in the paraelectric phase. It is not possible to get conclusive evidence to answer this question from the present measurements; additional investigations such as neutron scattering, piezoforce microscopy, or synchrotron radiation are needed.

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S. Greicius, J. Banys, R. Zuo, and T. Granzow biographies and photographs not available at time of publication.