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Re-entrant-like relaxor behaviour in the new $0.99\text{BaTiO}_3\text{--}0.01\text{AgNbO}_3$ solid solution

Chao Lei and Zuo-Guang Ye¹

Department of Chemistry and 4D LABS, Simon Fraser University, 8888 University Drive, Burnaby, BC, V5A 1S6, Canada

E-mail: zye@sfu.ca

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Online at stacks.iop.org/JPhysCM/20/232201**Abstract**

A new solid solution of $0.99\text{BaTiO}_3\text{--}0.01\text{AgNbO}_3$ was prepared by a solid state reaction. Its structural, dielectric and ferroelectric properties were investigated. Besides the three phase transitions associated with pure BaTiO_3 , the dielectric permittivity shows an additional peak around 100°C . This peak exhibits a dielectric relaxation satisfying the Vogel–Fulcher law, indicating typical relaxor behaviour. The relaxor state occurs after the paraelectric to ferroelectric phase transition upon cooling, i.e., inside the ferroelectric phase, indicating a re-entrant-like phenomenon. This unusual phase transition sequence has never been reported in canonical lead-based ferroelectrics. Moreover, the relaxor state arises from a tetragonal phase rather than from a cubic phase as observed in conventional complex perovskite relaxors.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Conventional lead-based perovskite solid solutions, such as $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) and relaxor-based $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}\text{PbTiO}_3$ (PMN–PT), have been widely used in various applications thanks to their outstanding piezoelectric and ferroelectric (FE) properties [1, 2]. However, the search for new lead-free materials with a high piezoelectric performance and high Curie temperature (T_C) has become an urgent task for obvious environmental reasons [3]. Consequently, barium titanate, BaTiO_3 (BT), a well-known normal ferroelectric material, has attracted renewed interest in the last few years. A great deal of work has been carried out on the modification of BT-based systems [4–8]. Theoretical calculations were also performed to predict possible high performance lead-free piezoelectric systems. It was recently predicted, by density functional theory calculations, that $(1-x)\text{BaTiO}_3\text{--}x\text{AgNbO}_3$ (BT–AN) solid solution would have two morphotropic phase boundaries at $x = 12.5\%$ and 37.5% , respectively, and it would exhibit good piezoelectric properties with a high T_C [9].

However, no compounds of this solid solution have been prepared experimentally.

In both canonical and lead-free relaxors, a strong frequency dispersion is usually observed on the low temperature slope of the dielectric peak, and the peak temperature (T_m) shifts to higher temperatures with increasing frequency, following the characteristic Vogel–Fulcher law [10–13]. Upon cooling, the succession of phase transitions in such solid solutions is from a paraelectric to an ergodic relaxor state, and then to a nonergodic relaxor or to a long-range ordered FE state, i.e. the relaxor state always appears before a FE phase [11]. On the other hand, this thermodynamically favorable phase sequence may be very different in some magnetic materials. In fact, Sherrington and Kirkpatrick predicted the ‘re-entrant’ disordered phase [14], which was found in many amorphous metallic magnets and magnetic spin glass (SG) alloys [15]. The term ‘re-entrant’, sometime a misnomer, means here that the cluster-glass state ‘re-enters’ the disordered phase from the ferromagnetic (FM) state, since the re-entrant SG (RSG) does not re-enter the normal (i.e. paramagnetic) state at the FM–SG phase transition temperature (T_{xy}) [16]. Indeed, recent results

¹ Author to whom any correspondence should be addressed.

reveal that the FM order does not collapse across T_{xy} , leading to coexisting FM and SG orderings [15]. Despite the cases in magnetic materials, no equivalent phenomenon has been found in (di)electrically disordered materials, except for the $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ solid solution, which shows a similar phase transition sequence [17], but no clear indication of re-entrant behaviour was pointed out. Also no equivalent example has been reported for the canonical lead-based relaxors.

In this work, we have synthesized a new solid solution of $0.99\text{BaTiO}_3-0.01\text{AgNbO}_3$ and found that it indeed exhibits the re-entrant phenomenon, which means that the more disordered state appears from a more ordered one upon cooling, in other words, the relaxor state occurs inside the ferroelectric phase. Moreover, the relaxor state arises from a tetragonal phase rather than from a cubic phase as observed in conventional relaxors. Thus, the BT-AN system provides a unique and interesting example of re-entrant relaxor behaviour.

2. Experimental details

Ceramics of the $0.99\text{BaTiO}_3-0.01\text{AgNbO}_3$ solid solution were prepared in a pure perovskite phase by solid state reactions. The complex dielectric permittivity was measured as a function of frequency (1 Hz–1 MHz) in the temperature range from 300 °C to –150 °C using a computer-controlled Alpha dielectric/impedance analyzer (NovoControl). The measurement field strength was about 1 V mm⁻¹. The structural change was studied within the temperature range of 10–300 °C using a Siemens x-ray diffractometer. The ferroelectric property was characterized by the measurement of the polarization as a function of the bipolar electric field, $P(E)$, in the temperature range from 200 to –150 °C using a Standard Ferroelectric Testing System RT66A (Radiant Tech.).

3. Results and discussion

The temperature dependences of the real part of the dielectric permittivity (ϵ'), measured at different frequencies upon cooling, for the 0.99BT-0.01AN ceramics are shown in figure 1. A sharp permittivity peak appears at $T_m = 119.9 \pm 0.2$ °C for all frequencies, which is slightly lower than the Curie temperature $T_C (\approx 127.5$ °C) of pure BT, indicating that the Ag^+ and Nb^{5+} ions have indeed diffused into the BT lattice to form a solid solution of BT-AN. Upon cooling, three more anomalies occur at lower temperatures: around 100 °C, 25 °C and –40 °C, respectively. The latter two temperatures correspond to the tetragonal/orthorhombic and orthorhombic/rhombohedral phase transitions in pure BT, respectively.

The reciprocal of dielectric constant ($1/\epsilon'$) at 100 kHz as a function of temperature is also shown in figure 1. It can be seen that the permittivity follows the Curie–Weiss (C–W) law [18, 19],

$$\epsilon' = \epsilon_0 + C/(T - T_{CW}) \quad (T > T_C) \quad (1)$$

with fitting parameters of $T_{CW} = 104.3$ °C and $C = 9.14 \times 10^4$ K. The temperature T_d , below which ϵ' starts to deviate

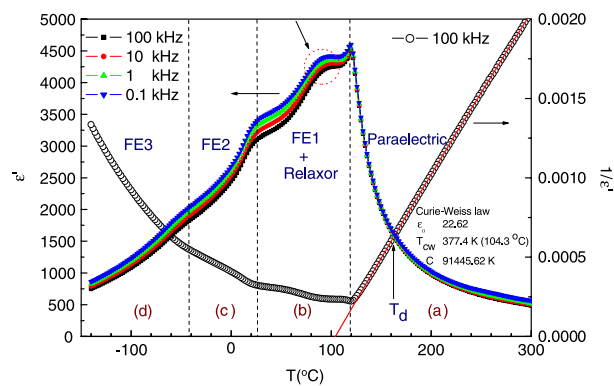


Figure 1. Temperature dependence of the real part of the dielectric permittivity (ϵ') of the $0.99\text{BaTiO}_3-0.01\text{AgNbO}_3$ ceramic measured at different frequencies upon cooling, and the reciprocal of the dielectric constant ($1/\epsilon'$) as a function of temperature at 100 kHz. Solid line is the fit to the Curie–Weiss law, equation (1).

from the C–W law, is found to be 166 °C, as indicated in figure 1. The temperature gap between T_d and T_C is found to be 46 °C, which is close to the value found for pure BT ceramics (about 50 °C) [12].

As the frequency increases, the dispersed permittivity peak at 100 °C decreases and its local peak temperature (T_{max}) shifts to higher temperatures, indicating a relaxor behaviour. The empirical Vogel–Fulcher (V–F) law,

$$f = f_0 \exp[-E_a/k(T_{max} - T_{VF})], \quad (2)$$

is thus used to characterize the frequency dispersion of T_{max} [20, 21], where f is the measurement frequency, and E_a , T_{VF} and f_0 are the parameters. In order to locate the accurate local T_{max} , a downward parabolic curve, $\epsilon'(f, T) = a(f)(T - T_m(f))^2 + b(f)$, where $a(f)$ and $b(f)$ are the fitting parameters, was used to fit the lower temperature slope of this dielectric anomaly. In the frequency range of 1.0×10^6 to 390.6 Hz, the data can be well fitted into the V–F relationship with the parameters $f_0 = 9.02 \times 10^9$ Hz, $E_a = 0.0096$ eV and $T_f = 364.6$ K. However, the same parameters cannot fit the data in the lower frequency range (244.1–1 Hz). This deviation from the V–F relationship is attributed to some other polarization contributions, such as ionic hopping, usually occurring at low frequencies and high temperatures.

Differential scanning calorimetry (DSC) analysis was carried out on the 0.99BT-0.01AN and pure BT ceramics (for comparison), as shown in figure 2. Only two thermal anomalies were found in the 0.99BT-0.01AN sample, with the onset temperatures of 121.6 °C and 23.3 °C upon cooling, corresponding to the cubic/tetragonal and tetragonal/orthorhombic phase transitions in BT, respectively. This is consistent with the results of the dielectric measurements. The thermal anomalies in 0.99BT-0.01AN are much weaker than those in pure BT, confirming that a solid solution is formed and the first order phase transitions in BT have been significantly impaired when only 1% AN was introduced. It is worth noting the absence of thermal peak around 100 °C which confirms that no macroscopic structural change takes place across the relaxor

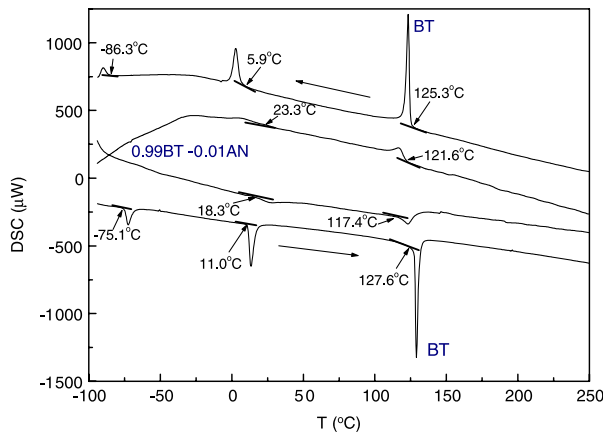


Figure 2. DSC curves of 0.99BT–0.01AN and BT as a function of temperature upon heating and cooling.

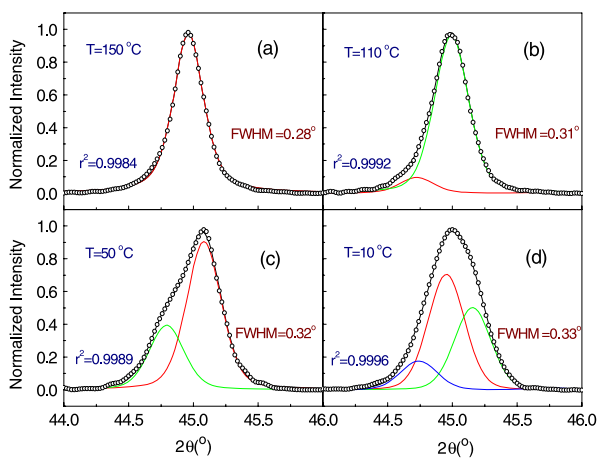


Figure 3. Powder XRD patterns of the (200) peak in 0.99BT–0.01AN ceramics at selected temperatures, and the deconvolution of the peak profile with different phase components: cubic (a), tetragonal (b) and (c) and orthorhombic (d).

peak. The orthorhombic–rhombohedral transition associated with the broad permittivity anomaly around -40°C in 0.99BT–0.01AN becomes thermally too weak to be detected in DSC.

Figure 3 shows the experimental XRD pattern (open circles) of the {200} reflection at selected temperatures (10, 50, 110 and 150°C). The overlapping {200} reflection peaks were then deconvolved into different phase components using Peakfit software, as shown in figure 3. Above T_m (i.e. $T = 150^\circ\text{C}$), the {200} reflection appears as a single peak, indicating a cubic structure (figure 3(a)). As the temperature decreases, the {200} reflection becomes asymmetrical. A slight tetragonal distortion was revealed at 110°C (figure 3(b)), and upon further cooling the tetragonal character increases across the temperature of the relaxor permittivity maximum, T_{max} (figure 3(c)). The {200} reflection at 10°C consists of three peaks, arising from the orthorhombic splitting, which confirms that the permittivity anomaly around 25°C is related to the structural phase transition between the tetragonal and orthorhombic phases, consistent with the DSC results.

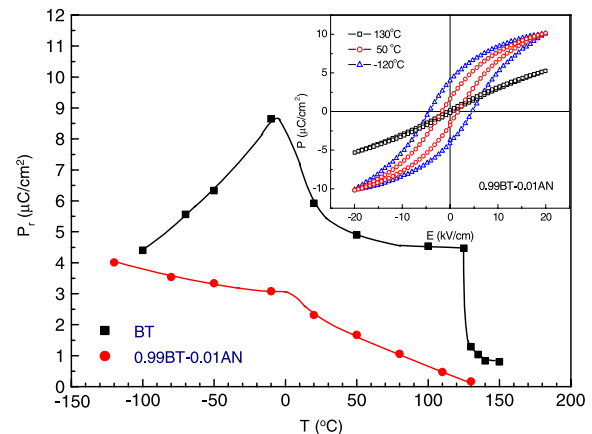


Figure 4. Remnant polarization of 0.99BT–0.01AN and BT ceramics as a function of temperature. The inset shows the hysteresis loops of 0.99BT–0.01AN at selected temperatures.

The variation of the remnant polarization (P_r) of 0.99BT–0.01AN and pure BT ceramics as a function of temperature is shown in figure 4. The ferroelectric hysteresis loops of 0.99BT–0.01AN at 130 , 50 and -120°C are displayed in the inset of figure 4. In contrast to the sharp increase in BT, the polarization in 0.99BT–0.01AN starts to appear at 120°C , and increases smoothly upon further cooling. It can be seen once again that the first order paraelectric to ferroelectric phase transition in pure BT has been significantly impaired when only 1% AN is introduced.

Based on the above analysis, the structural, dielectric and relaxor properties of 0.99BT–0.01AN in the temperature range of 300°C to -150°C can be divided into four regions with different kinds of behaviour, as shown in figure 1. Region (a) corresponds to the paraelectric phase with a cubic structure, in which the C–W law is observed and the $P(E)$ response is linear. In region (b), it changes into a ferroelectric state with a tetragonal structure. Interestingly, the relaxor state occurs within the tetragonal ferroelectric phase, not the cubic phase as in conventional complex perovskite relaxors. The smooth increase of P_r in 0.99BT–0.01AN upon cooling below 120°C (figure 4) suggests that the FE order is established gradually, in a similar way to a RSG system, in which FM ordering is not destroyed below T_{xy} . The exchange frustration between FM and antiferromagnetic exchange interactions is believed to be a characteristic of RSG [14], which results in a random non-collinear ordering, the SG state below T_{sg} and the freezing of transverse spin components occurring spontaneously. In the present case, pure AN has a tilted perovskite structure at room temperature with a tolerance factor of 0.95 [9]. Nb^{5+} has almost the same size as Ti^{4+} , while the size of Ag^{1+} is much smaller than Ba^{2+} . Therefore, the substitution of AgNbO_3 for BaTiO_3 may induce structural distortion, which impairs the cubic-to-tetragonal phase transition, as revealed by the slightly lower T_C and the relatively small tetragonality just below T_C . As the temperature decreases, the tetragonality increases and so does the spontaneous polarization. It is believed that the relaxor state arises from the partial breaking of the FE long-range

ordering (in BT) by the coupled substitutions of the Ag^{1+} and Nb^{5+} ions of different sizes and charges for the Ba^{2+} and Ti^{4+} ions, respectively, thus giving rise to the chemically disordered regions and the polar nano-structures responsible for the observed dielectric relaxation. In regions (c) and (d), the solid solution is in a ferroelectric state, with orthorhombic and rhombohedral structures, respectively.

4. Conclusions

In conclusion, the structural, dielectric and ferroelectric properties of the new $0.99\text{BaTiO}_3-0.01\text{AgNbO}_3$ solid solution ceramic have revealed some peculiar aspects. Besides the three phase transitions associated with pure BaTiO_3 , the dielectric permittivity shows an additional peak around 100°C . This peak exhibits a dielectric relaxation satisfying the Vogel–Fulcher law, indicating a typical relaxor behaviour. The relaxor state occurs after the paraelectric to ferroelectric phase transition upon cooling, i.e., inside the ferroelectric phase, indicating the re-entrant phenomenon. This unusual phase transition sequence has never been reported in canonical lead-based ferroelectrics. Moreover, the relaxor state arises from a tetragonal phase rather than from a cubic phase as observed in conventional relaxors.

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