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Dielectric and ferroelectric properties of lead-free $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ ferroelectric ceramics

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Abstract

Ceramics with compositions belonging to the $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ system were fabricated by conventional ceramics preparation technique. The dielectric constant of all compositions between room temperature and 500 °C shows a strong temperature and frequency dependent behavior. The dielectric constant decreases and its maximum are shifted towards high temperature as the frequency increases. In the high temperature range, the thermal variation of the dielectric constant is well described by the law $(1/\varepsilon) - (1/\varepsilon_m) = C(T - T_m)^\gamma$ with γ close to 1.5. Such a relaxation behavior is interpreted in terms of cations disorder due to Na^+, K^+, Bi^{3+} at A-site. The *P–E* hysteresis loops at different temperatures reveal the loops to deform at high temperature as a result of macrodomain breaks into microdomains corresponding to a phase transition from ferroelectric to anti-ferroelectric during the heating process. When the crystalline structure belongs to tetragonal symmetry, the material has anti-ferroelectric characteristic because of the loosely packed A-site cations.

Keywords: A. Powders: solid-state reaction; C. Electrical properties; D. Perovskite; Phase transformation

1. Introduction

Sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), is a kind of perovskite (ABO_3-type) ferroelectric discovered by Smlenskii et al. [1]. NBT is considered to be an excellent candidate of lead-free piezoelectric ceramics because it is rhombohedral symmetry with $a = 3.891$ Å and $\alpha = 89^\circ 36'$ at room temperature. It is ferroelectric with a relatively large remanent polarization, $P_r = 38\ \mu C/cm^2$, and a relatively large coercive field, $E_c = 7.3$ kV/mm [1]. NBT undergoes a series of temperature induced phase transitions: (i) the dielectric constant shows a flat, frequency-dependent hump assigned to ferroelectric (rhombohedral)-anti-ferroelectric (tetragonal) phase transition at ~230 °C, (ii) the symmetry changes to cubic symmetry at ~520 °C [2]. In addition, the maximum dielectric constant at ~320 °C is diffused and frequency dependent [3,4]. Appropriate cation modifications such as Ba^{2+}, Pb^{2+}, La^{3+}, K^+ are likely to influence both the temperature of phase transition and the dielectric behavior [5–9]. It has already been shown that the solid solution keeps the rhombohedral symmetry up to 16 mol% KBT, and the morphotropic phase boundary (MPB) is located at 16–20 mol% KBT in the $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ (NBT–KBT) system [8,9]. The changes of the dielectric behavior and ferroelectric properties of rhombohedral and tetragonal symmetry structure NBT–KBT solid solution compound were studied in this paper.

2. Experimental

The conventional solid state reaction method was used to prepare NBT, $(Na_{0.92}K_{0.08})_{0.5}Bi_{0.5}TiO_3$ (NKBT8) and $(Na_{0.70}K_{0.30})_{0.5}Bi_{0.5}TiO_3$ (NKBT30) ceramics. Reagent-grade metal oxide or carbonate powders of Bi_2O_3, TiO_2, Na_2CO_3 and K_2CO_3 were used as starting raw materials. The oxides were mixed in ethanol with agate balls by ball milling for 4 h. After being mixed, the dried powder was calcined at 850–900 °C for 2 h. The calcined powder was reground by

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ball milling for 6 h. The dried powder was mixed with polyvinyl alcohol and pressed at 150 MPa into pellets 20 mm in diameter and about 1.5 mm in thickness. The green compacts were sintered at various temperatures (1150–1200 °C) for 2 h in air atmosphere. Silver paste was fired on the surfaces of the disc as electrodes. Frequency dielectric measurements were carried out between room temperature and 500 °C at several frequencies from 1 to 100 kHz using a TH2816 LRC meter. The *P–E* hysteresis loops were obtained by a Radiant Precision Workstation ferroelectric testing system.

3. Results and discussions

3.1. Dielectric properties

NBT is rhombohedral and ferroelectric at room temperature. Fig. 1 shows the variations of the relative dielectric constant ε_r of NBT ceramics sample as a function of temperatures at 1, 10 and 100 kHz. A frequency-dependent behavior is observed with a hump between room temperature and ~210 °C (T_1) and a diffusion of the relative dielectric constant for temperature higher than ~320 °C (T_m). The increase of the dielectric constant at high temperature and low frequency is significant of space charge polarization and associated ionic conductivity. On cooling, these characteristic temperatures are shifted by 30–40 °C downwards.

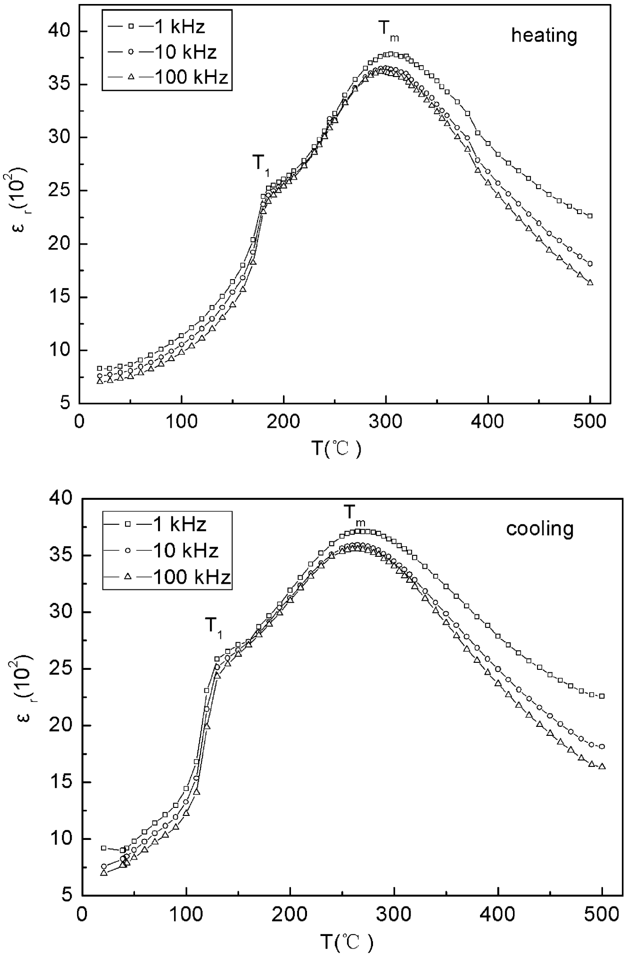

Fig. 1. Temperature dependence of the dielectric constant of NBT at heating and cooling for several frequencies.

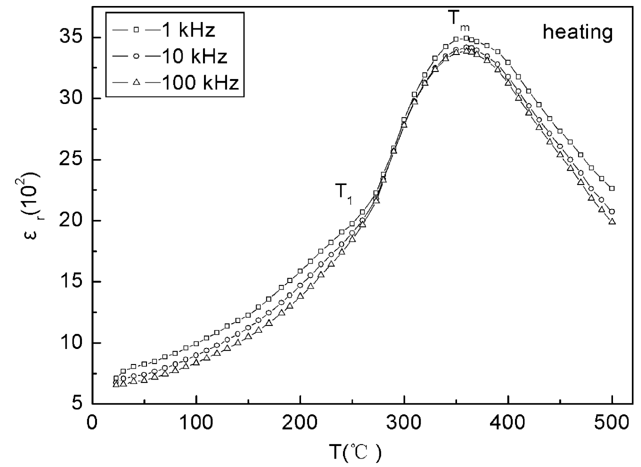

Fig. 2. Temperature dependence of the dielectric constant of NKBT8 at heating for several frequencies.

Temperature dependence of the relative dielectric constant ε_r of NKBT8 on heating for several frequencies is shown in Fig. 2. The hump at T_1 is softened and even disappeared, whereas T_m increases as the frequency increases in a way similar to that observed for relaxor material. As Na$^+$, K$^+$ and Bi^{3+} are randomly distributed in the 12-fold coordination sites, the relaxation behavior would reasonably be attributed to these cations disorder at A-site.

For temperature higher than T_m, the variation of the dielectric constant does not follow the classical Curie–Weiss law. Whatever the measurement frequency, the dielectric constant varies according to the law $(1/\varepsilon) - (1/\varepsilon_m) = C(T - T_m)^\gamma$ with γ equals to 1.5 as clearly shown in Fig. 3

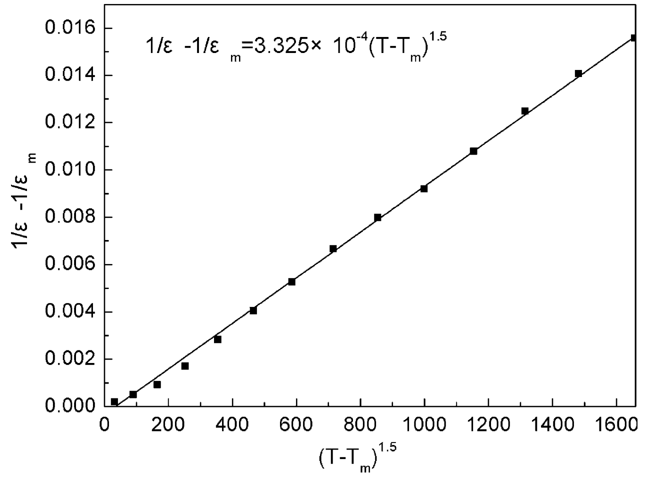

Fig. 3. Reciprocal dielectric constant of NKBT8 vs. T–T_m.

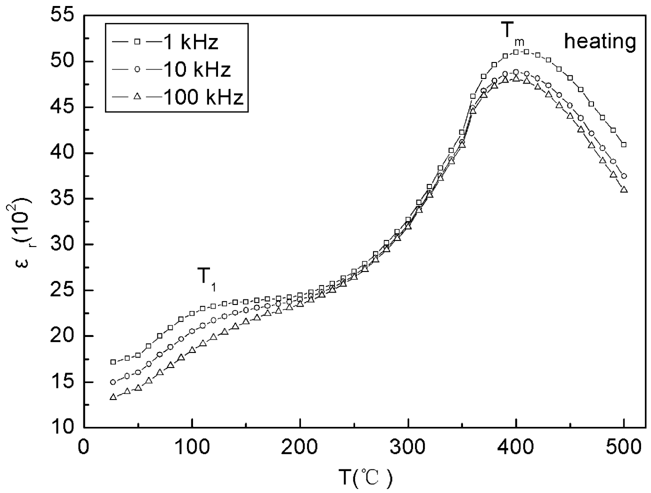

Fig. 4. Temperature dependence of the dielectric constant of NKBT30 at heating for several frequencies.

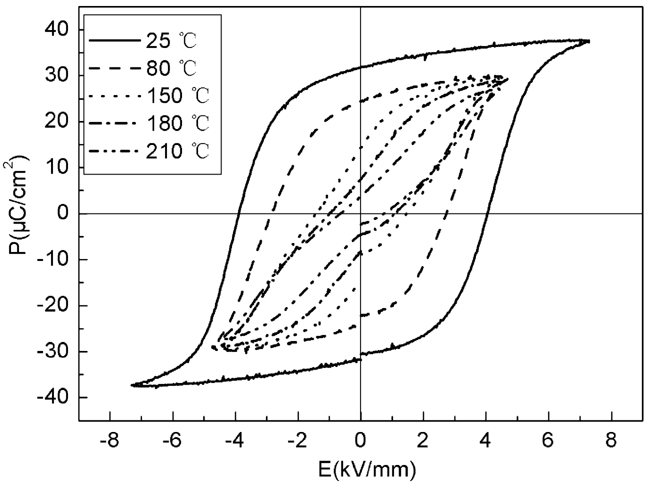

Fig. 5. Hysteresis loops of NKBT8 at different temperatures.

at 1 kHz. In this relation, γ acts as a diffusion coefficient and ranges between 1 and 2 for materials with a diffuse phase transition [10]. This behavior would be significant of a relaxation process due to A-site cations mixture.

For compositions above MPB, the behavior of the dielectric constant is strongly dependent on the KBT concentration. Fig. 4 shows the thermal variations for the relative dielectric constant ε_r of NKBT30 ceramics. A frequency dependence and a hump were observed between room temperature and ~130 °C (T_1), and a diffusion of the dielectric constant at temperatures higher than ~400 °C (T_m) was also found. The relaxor characteristic is more evident with the increase of the amount of KBT. This is believed that the higher concentration of K^+ ion substitute Na^+ ions, which distorts the unit cell, changes the dipolar moment, and induces strain in the lattice. It is generally accepted that the more cations co-occupy the same lattice of unit cell, the more the chemical composition and crystal structure are inhomogeneous at the nanometer scale, so the relaxation characteristic is more evident [10].

3.2. Ferroelectric properties

Fig. 5 shows the *P–E* hysteresis loops of NKBT8 ceramics at different temperatures. At room temperature, it is clearly seen that the shape of hysteresis loop is a typical ferroelectric phase. As the temperature increases, the shape of the hysteresis loops is narrower but still keeps the ferroelectric phase. However, the loops are deformed and become double *P–E* hysteresis loops above 180 °C which are characteristic of anti-ferroelectric phase. It can be concluded that there exists a transition from ferroelectric to anti-ferroelectric phase during heating. It was reported that phase transition of NBT ceramics from rhombohedral ferroelectric to tetragonal anti-ferroelectric is about 230 °C [1]. The cooperative long-range order of NKBT8 gradually vanished when temperature increases and the macropolar state broke into small polar region with rhombohedral symmetry and local spontaneous polarization. Additionally, small regions of tetragonal phase arise above 180 °C, as shown by a hump on the dielectric constant and double hysteresis loops. This loops features are very similar to the NBT-BT [5], NBT-PT [6], binary system.

Being the ionic radius of K^+ ($r_{K^+} = 1.33$ Å) considerably larger than that of Na^+ ($r_{Na^+} = 0.97$ Å), as previously described [11] K^+ substitution increased the size of unit cell. It is accepted that the material was subjected to tensile stress after substitution by K^+ which can cause the increase of the thermal hysteresis and narrow the temperature range of ferroelectric state of NKBT8.

The *P–E* hysteresis loops of NKBT30 at different temperatures shown in Fig. 6 are double hysteresis loops of the anti-ferroelectric phase at the measurement temperatures. Above 150 °C, the double hysteresis loops become very narrow. It might be assumed that the macrodomain breaks

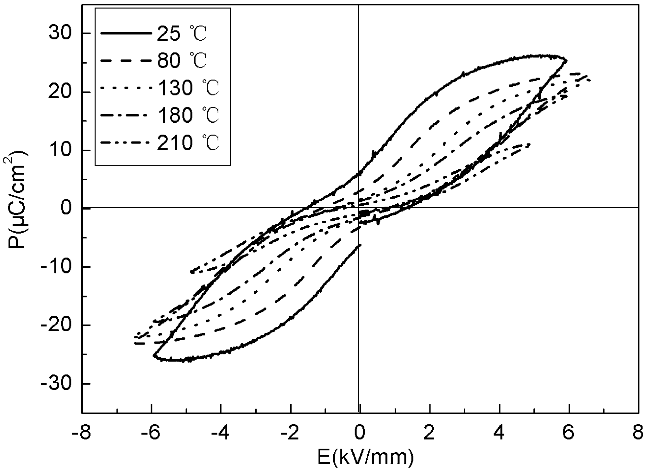

Fig. 6. Hysteresis loops of NKBT30 at different temperatures.

into microdomains with corresponding hump of the $\varepsilon(T)$ curve. The tetragonal symmetry of the crystalline structure of NKBT30 has been confirmed [8,9]. Thus, it can be concluded that the NBT–KBT ceramics with tetragonal structure symmetry is an anti-ferroelectric.

According to the theory of Palai [12], the ferroelectric polarization is due to the loose packing of the A and B cations in the structure, while anti-ferroelectric polarization is due to the loose packing of A cations only. Many ABO_3 compounds such as $PbZrO_3$, $PbHfO_3$, $CdTiO_3$, $NaNbO_3$, $NaTaO_3$, $Pb(Sc_{0.5}Ta_{0.5})O_3$ have distorted structure, and hence show an anti-ferroelectric phase transition. Due to the larger ionic radius of K^+ than that of Na^+ and the higher concentration of K^+ in NKBT30, the structure of NKBT30 is loose. The A cations are more free (loosely packed), the oxygen octahedra can be easily rotated without suffering any distortion, the oxygen atoms can contact with the A cations and form a distorted structure [13]. This distorted structure is in favor of forming the anti-ferroelectric state. This case is very similar to those of some B-site co-occupied $Pb(B'_{1/2}B''_{1/2})O_3$ compounds. It is often the case that $Pb(B'_{1/2}B''_{1/2})O_3$ compounds tend to form an anti-ferroelectric phase when the ionic radius of B' ion is much larger than that of B'' ion [14].

4. Conclusions

The dielectric and ferroelectric properties of lead-free ferroelectric NBT–KBT ceramics have been studied as a function of temperature and frequency. A relaxor behavior was observed and attributed to cations disorder in the 12-fold coordination sites. In the high temperature range, the thermal variation of the dielectric constant is well described by the law $(1/\varepsilon) - (1/\varepsilon_m) = C(T - T_m)^\gamma$ with $\gamma = 1.5$. *P–E* hysteresis loops at different temperatures during heating reveal the loops to deform at high temperature attributed the macrodomain breaks into microdomains corresponding to a phase transition from ferroelectric to anti-ferroelectric. When the crystalline structure is of tetragonal symmetry, the material has anti-ferroelectric characteristic because of the loosely packed A-site cations.

Acknowledgements

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