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Relaxor behavior and ferroelectric properties of $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$KNbO_3$ lead-free ceramics

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Lead-free ferroelectric ceramics of $(1-x)$ $[0.88Na_{0.5}Bi_{0.5}TiO_3\text{-}0.12K_{0.5}Bi_{0.5}TiO_3]$-$x$ $KNbO_3$ ($x =$ 0, 0.02, 0.04, and 0.06) were prepared by the conventional ceramic fabrication technique. The crystal structure, dielectric properties and *P-E* hysteresis loops were investigated. XRD data showed that all compositions could form pure perovskite structure. Temperature dependence of dielectric constant ε_r and dissipation factor tanδ measurement between room temperature and 500°C revealed that the compounds experience phase transitions that from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric in the range of x = 0–0.04. The frequency dependent dielectric constant showed these compounds were relaxor ferroelectric. At low frequency and high temperature, dielectric constant and dissipation factor increased sharply attributed to the superparaelectric clusters after the $KNbO_3$ doped. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

In recent years, lead-free piezoelectric ceramic has attracted considerable attention as an important piezoelectric material because of its outstanding advantages in free control atmosphere and no lead pollution. $Na_{0.5}Bi_{0.5}TiO_3$ composition (abbreviated as NBT) is one of the important lead-free piezoelectric materials with perovskite structure discovered by Smolenskii *et al.* in 1960. As NBT has a remanent polarization $P_r =$ 38 $\mu C/cm^2$, a coercive field $E_c = 7.3$ kV/mm and high Curie temperature $T_c = 320°C$ [1], it has been considered to be a good candidate of lead-free piezoelectric ceramics to replace the widely used lead-based piezoelectric materials. In addition, NBT is known as belonging to the family of relaxor ferroelectric because the Na^+ and Bi^{3+} ions are randomly distributed the space (coordination 12) between the corner-linked anion octahedral [2, 3]. At heating process, NBT presents an interesting temperature dependence phase transitions which varied from ferroelectric to anti-ferroelectric at 200°C and anti-ferroelectric to paraelectric at 320°C [4]. Recent investigations have revealed that some modifications such as Ba^{2+}, K^+, Pb^{2+} and Sr^{2+} are likely to influence both the temperature of phase transitions and the dielectric behaviors [5–7]. It has been already shown that $KNbO_3$ (KN) is a ferroelectric material with a Curie temperature $T_C = 415°C$. Ishii *et al.* [8] reported that $KNbO_3$ would form the morphotropic phase boundary (MPB) when 0.04 mol of NBT was added to it. In addition, there is no MPB when $KNbO_3$ is less than 0.35 mol in $(1-x)$ KBT-x KN system, where the maximum K_p can obtain at $x = 0.075$ mol [9]. Wang reported that the maximum remanent polarization P_r was located at $x = 0.13$ and the solid solution belongs to rhombohedral structure in $(1-x)$ NBT-x KBT system [10].

In this paper, the $0.88Na_{0.5}Bi_{0.5}TiO_3$-$0.12K_{0.5}Bi_{0.5}TiO_3$ (NKBTK0) was selected as a basic composition, different amount of $KNbO_3$ was added to form NBT-KBT-KN solid solution. The effects of $KNbO_3$ on crystal structure, relaxor behavior, phase transition characteristics and ferroelectric properties were investigated.

2. Experimental procedure

Reagent grade oxide or carbonate powders of Bi_2O_3, Na_2CO_3, K_2CO_3, TiO_2 and Nb_2O_5 were used as starting raw materials. A conventional powder synthesis technique was adopted to synthesize $0.88Na_{0.5}Bi_{0.5}TiO_3$-$0.12K_{0.5}Bi_{0.5}TiO_3$ (NKBTK0) and $KNbO_3$, respectively. Raw materials were mixed using planetary milling with agate media and alcohol. The mixed powders were calcined at 900°C for 2 h. According to $(1-x)$ NKBTK0-x KN with $x = 0$, 0.02, 0.04, and 0.06 (hereafter named NKBTK100x), different ratios of synthesized powders of NKBTK0 and KN were mixed

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using planetary milling with agate media and alcohol for 6 h. Then the mixed powders were pressed into a disk of 20 mm in diameter and about 1.5 mm in thickness. After binder burnout, these pressed disks were sintered at 1100–1150°C for 2 h in air. Silver paste was fired on both faces of the disks at 850°C as electrodes.

X-ray powder diffraction (XRD) patterns were taken on a D/MAX-III X-ray diffractometer with Cu K_α radiation (λ =1.5418 Å) and graphite monochrometer. The diffraction data were recorded for 2θ between 20 and 80°, with a resolution of 0.02°. The lattice parameters were refined by a least-square method using Si as an internal standard. The relative dielectric constant ε_r and dissipation factor (tanδ) at room and heating temperature were measured at 1, 10 and 100 kHz using TH2816 LRC meter. P-E hysteresis loops were obtained using a Radiant Precision Workstation ferroelectric testing system.

3. Results and discussion

3.1. Crystal structure

X-ray diffraction patterns are shown in Fig. 1 indicate that pure perovskite crystalline structure has formed in all specimens. The results reveal the solid solution samples without any secondary impurity phases can be found in the NBT-KBT-KN system. The lattice distortion in the NKBTK100x compounds was investigated in the 2θ range of 57–60°. The indices ($h\,k\,l$) of the reflecting planes of the NKBTK100x in the 2θ range were determined to be (211), $(21\bar{1})$ with respect to the rhombohedral axes. The inserted figure in Fig. 1 shows a change in the diffraction peaks of NKBTK100x compositions. It is found that up to 0.04 mol of KN, the NKBTK100x compounds still had a rhombohedral structure with a slight change in anxial length and angle parameters (Table I), which indicate the ferroelectric character would decrease with the more addition KN. The diffraction peaks in the stated 2θ ranges of NKBTK6 were altered. It is observed that the two peaks merge into a single peak which means the crystalline structure has become cubic symmetry. Thus, it can be concluded that no phase transition was observed for NKBTK100x with 0–0.04 mol KN. Moreover, the structure of NKBTK6 transformed to a cubic form.

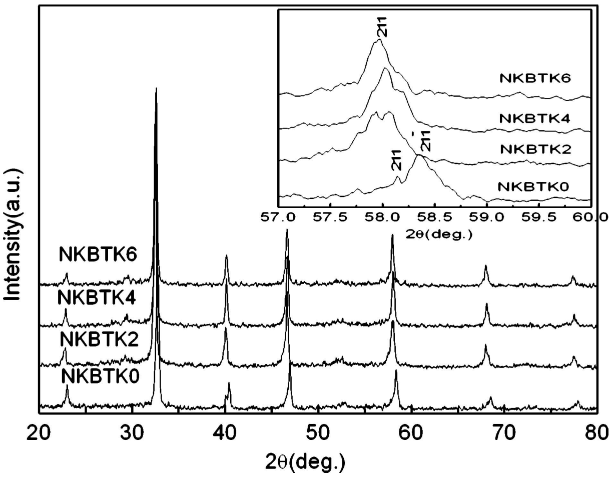

Figure 1 XRD patterns of NKBTK100x ceramics.

TABLE I Lattice parameter of NKBTK100x composition for x = 0–0.06

Specimens no.	x	a(Å)	α°	Structure
NKBTK0	0	3.898	89.68	Rhombohedral
NKBTK2	0.02	3.927	89.82	Rhombohedral
NKBTK4	0.04	3.933	89.88	Rhombohedral
NKBTK6	0.06	3.952	90	Cubic

3.2. Dielectric relaxor and ferroelectric properties

Fig. 2 shows the temperature dependence of the dielectric constant ε_r and the dissipation factor tanδ of NKBTK100x between room temperature to 500°C at 1, 10, and 100 kHz. From the dielectric constant versus

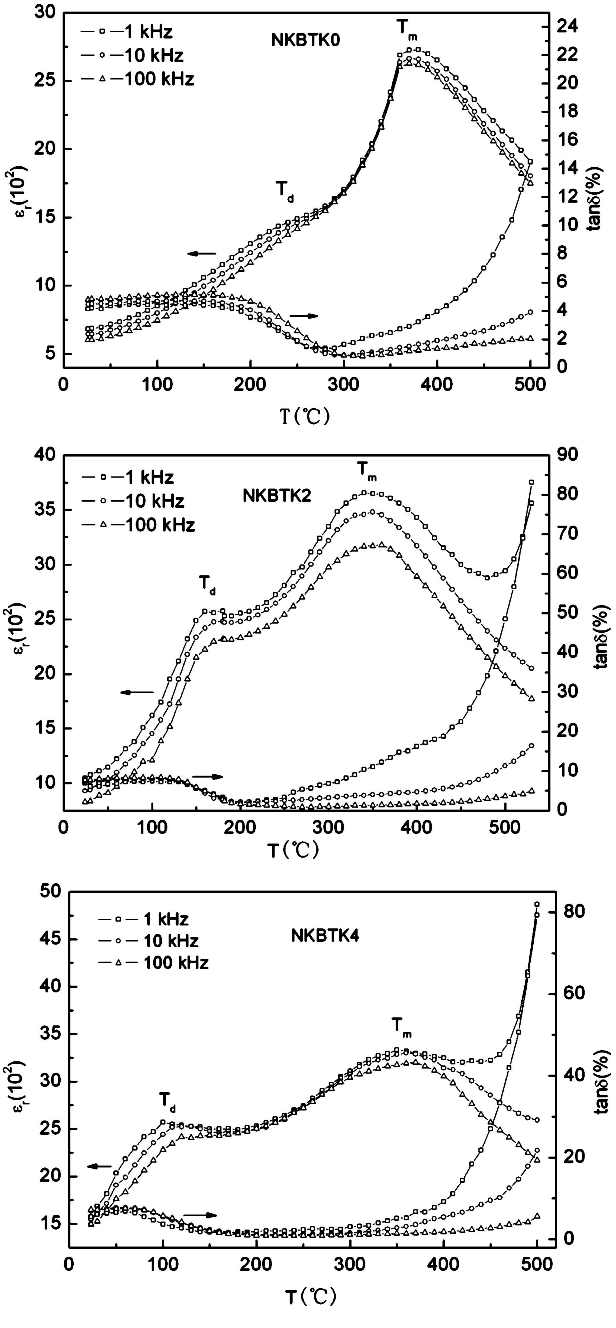

Figure 2 The dielectric constant ε_r and the dissipation factor tanδ of NKBTK100x ceramics as a function of temperatures at 1, 10 and 100 kHz.

temperature curves, it can be evidently seen that there are two dielectric peaks at the temperature range. The two dielectric abnormal peaks can attribute to the reason caused by the phase transitions from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric phase, which is consistent with the previous reports of NBT, NBT-BT, NBT-KBT lead-free ceramics systems [4–6]. Here, the low transition temperature is called as depolarization temperature (T_d) and the high temperature corresponding to relatively high dielectric constant named as T_m. Both T_d and T_m decrease with the increasing amount of $KNbO_3$.

The dissipation factor tanδ as a function of temperature plots shown in Fig. 2 indicates that all specimens only have one dielectric loss peak corresponding to T_d. The dissipation factor achieves the minimum value before the temperature T_m. In ferroelectric phase, the dissipation factor probably comes from domain wall movement. When phase transition from ferroelectric to anti-ferroelectric occurred at T_d, the domain wall movement enhancement brings to the dissipation factor peak. The reason that no second dissipation factor peak was observed is that the anti-ferroelectric macro-domain would soon break into micro-domains. Above T_m, the sharp dissipation factor increase was caused by the high conductivity of ceramics at high temperatures [3].

It can be also found from Fig. 2 that all samples have relaxor ferroelectric characteristics. The dielectric constant ε_r, dissipation factor tan δ, transition temperature T_d and T_m are strongly depended on the measurement frequency. The value of the relative dielectric constant ε_r decreases as the measuring frequency increases. Also, the fact that the T_d and T_m increase with measurement frequency increase shows the evidence of a diffusion phase transition with a frequency dispersion occurring around the temperature T_d and T_m. For most ABO_3-type perovskite ferroelectric, it has relaxor feature caused by A or B-site cations substitutions. These materials are characterized by the existence of local polarization to the temperatures much higher than that the one at which a remanent polarization can be sustained. This indicates that relaxor behavior arises due to the breaking of the translational invariance of the polarization, preventing the formation of normal micron-sized domains. Many compounds possessing various ions co-occupied at A or/and B-site(s) such as $PbBaMgNbO_3$, $(Pb,La)(Zr,Ti)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$ and doped $BaTiO_3$ have the perovskite structure [11–15], which would appear the ordered micropolar regions (microdomains) and correlations between them are essential for relaxor behavior [16]. In present work, K^+, Na^+ and Bi^{3+} substitute at A-site and Ti^{4+}, Nb^{5+} at B-site induce the ions disorder at lattice. However, because the ion radius of K^+ (r_{K^+} = 1.33 Å) is much larger than that of Na^+ and Bi^{3+} (r_{Na^+} = 0.97 Å, $r_{Bi^{3+}}$ = 0.98 Å), it would likely improve the ordered microdomain at a certain extent [17]. Therefore, these compounds were expected to relaxor behavior.

The dielectric constant and the dissipation factor presented in Fig. 2 also indicates another phenomenon that the dielectric constant and the dissipation factor increase at a low frequency and high temperature after $KNbO_3$ was added. The more the amount of $KNbO_3$ is, the more distinct the phenomenon is and the lower starting temperature is. This phenomenon was also observed by Tu [3] and Wang [18] and has been explained by Tu *et al.* [3] in terms of superparaelectric clusters existing in the tetragonal phase of the NBT ceramics. In the NBT-KBT-KN system ceramics, the Na^+, K^+ and Bi^{3+} are randomly distributed at the A sites, and the Nb^{5+} doped at B-site, causing randomly local electric fields and elastic distortions. As a result, the ferroelectric ordering of the ceramics as a whole is inhibited and the unit dipoles are divided into superparaelectric clusters. The reorientation of the cluster polarization in the applied electric field is governed by the relaxation time required for the redistribution of charge carries around the cluster. Accordingly, the cluster polarization is 'frozen' under a high-frequency electric field, whereas the reorientation of the cluster polarization under a low-frequency electric field is allowed, leading to a large dielectric constant value.

It is obvious that the temperature-dependent dielectric constant of NKBTK-100x ceramics does not follow the classical Curie–Weiss law at temperatures higher than T_m. At 100 kHz, however, they obey the law $1/\varepsilon - 1/\varepsilon_m = C(T - T_m)^\gamma$, as shown in Fig. 3 with $\gamma = 1.55$, 1.70 and 1.80 for NKBTK0, NKBTK2 and NKBTK4, respectively, where C is Curie constant and γ is called the diffusion coefficient which ranges from 1 to 2 for materials with a diffuse phase transition. That is to say, NKBTK100x ceramics undergo a diffuse phase transition at T_m. The addition of $KNbO_3$ does not change the transition mechanism but the relaxor characteristics becomes more distinctly.

Saturated P-E hysteresis loops at room temperature of all investigated specimens are plotted in Fig. 4. It reveals that all compounds except of NKBTK6 are ferroelectric corresponding to the XRD results. The remanent polarizations of NKBT0, NKBTK2 and NKBTK4 are 33.0, 20.6, and 16.1 $\mu C/cm^2$, respectively, which means that $KNbO_3$ doped would reduce the ferroelectric properties. However, the remanent polarization of

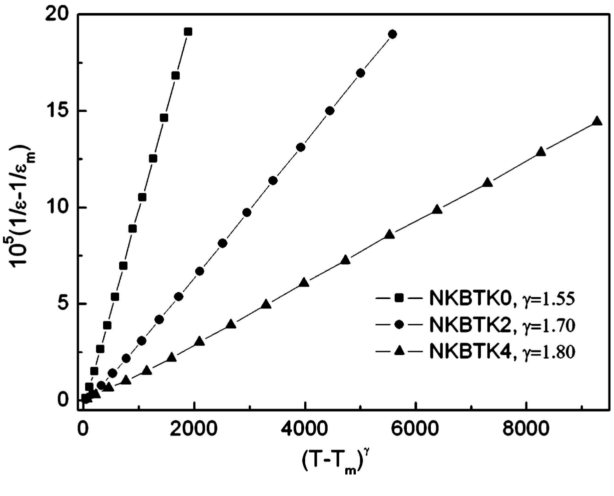

Figure 3 Reciprocal dielectric constant ($1/\varepsilon - 1/\varepsilon_m$) of NKBTK100$x$ ceramics as a function of ($T - T_m$) at 100 kHz.

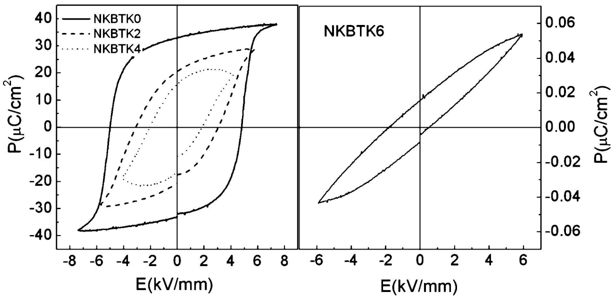

Figure 4 Saturated P-E hysteresis loops of the NKBTK100x ceramics at room temperature.

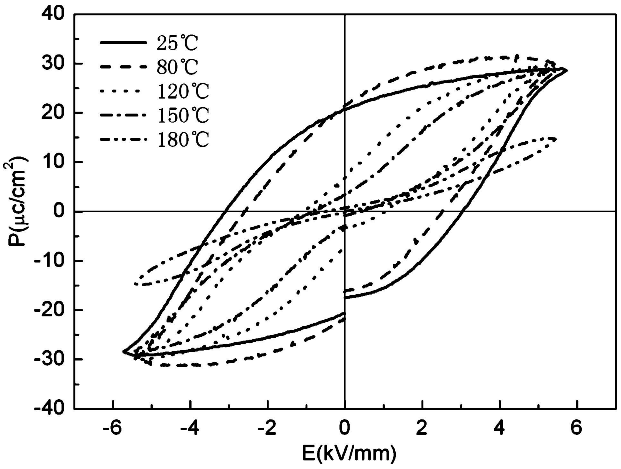

Figure 5 P-E hysteresis loops of NKBTK2 ceramic at different temperatures.

NKBTK6 only has 0.0094 μC/cm^2 which indicates the ferroelectric property disappears fully.

To examine occurring of the phase transition at the heating process, P-E hysteresis loops at different temperatures of NKBTK2 sample was obtained depicted in Fig. 5. It can be seen that ferroelectric state exists at the room temperature and 80°C. At 120°C, corresponding to T_d, the hysteresis loop becomes double loops which is an anti-ferroelectric feature. As the temperature increases, the double hysteresis loops become very narrow which means that the macrodomain anti-ferroelectric will soon break into microdomains. This result is also in agreement with the investigations previously published [4–6].

4. Conclusions

All compositions investigated in this work can form pure perovskite solid solution. Powder X-ray diffraction patterns can be indexed the crystalline structure that varies from rhombohedral to cubic with the increase concentration of KNbO$_3$. When the amount of KNbO$_3 x \leq 0.04$, the ceramic specimens undergo two phase transitions at the range of room temperature to 500°C which are ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric phase transitions. Both phase transition temperatures are lowered due to introduction of KNbO$_3$. The frequency dependent dielectric constant shows these compounds are relaxor ferroelectric. At low frequency and high temperature, the dielectric constant and the dissipation factor increase sharply which attribute to the superparaelectric clusters after the KNbO$_3$ doped.

Acknowledgements

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