Morphotropic phase boundary and electrical properties of lead-free $(K_{0.5}Bi_{0.5})TiO_3–Bi(Ni_{0.5}Ti_{0.5})O_3$ relaxor ferroelectric ceramics

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Abstract

Lead-free relaxor ferroelectric ceramics $(1-x)(K_{0.5}Bi_{0.5})TiO_3–xBi(Ni_{0.5}Ti_{0.5})O_3$ were prepared by a conventional solid-state route, the phase transition behavior and corresponding electrical properties were investigated. A typical morphotropic phase boundary (MPB) between rhombohedral and tetragonal ferroelectric phases was identified to be in the range of $0.05 < x < 0.07$ where the optimum piezoelectric and electromechanical properties of $d_{33} = 126$ pC/N and $k_P = 18\%$ were achieved. Most importantly, a high Curie temperature ~ 320 °C, around which the material shows a typical relaxor ferroelectric behavior characterized by the presence of diffuse phase transition and frequency dispersion, was obtained in MPB compositions, significantly higher than those of some existing MPB lead-free titanate systems. These results demonstrate a tremendous potential of the studied system for device applications.
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Keywords: C. Electrical properties; Lead-free ceramics; Phase transition; Relaxor ferroelectrics

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT) based ceramics have been widely used in industry owing to their excellent dielectric and piezoelectric properties close to a typical morphotropic phase boundary (MPB). Although a lot of studies on alternative lead-free ceramics were done [1–5], the currently focused lead-free systems were found to own some drawbacks as far as their device applications are concerned. The piezoelectric properties of pure $BaTiO_3$ (BT) ceramics were significantly enhanced [4], yet obviously reduced Curie temperatures ($T_c \sim 90$ °C) tend to seriously limit their applications. The $(Na_{0.5}Bi_{0.5})TiO_3$ based systems were reported to have a traditional rhombohedral (R)–tetragonal (T) MPB and relatively good piezoelectric properties, i.e. piezoelectric constant ($d_{33}) \sim 230$ pC/N and planar electromechanical coupling factor ($k_p) \sim 40\%$ [1], yet all these compositions have a rather low depolarization temperature ($T_d < 100$ °C) owing to a ferroelectric–antiferroelectric phase transition. By comparison, (Na, K)NbO$_3$ (NKN)-based ceramics exhibited fascinating properties ($d_{33} \sim 400$ pC/N and

$k_p \sim 50\%$) and high T_c values (> 160 °C) [5]. A polymorphic phase boundary (PPB), rather than a typical MPB, has been considered as a main cause of the poor thermal stability of this system [6].

A challenging task would be then to synthesize a lead-free material with acceptable electrical properties simultaneously with a high T_c and a traditional MPB. To the authors' knowledge, this situation seems not yet to be improved currently. The key issue is to achieve two perovskite ferro-electrics with a single T symmetry and a single R symmetry below T_c, together with a relatively high T_c value for the construction of MPB piezoelectric solid solutions. In comparison with lead-free BT and NKN, $(K_{0.5}Bi_{0.5})TiO_3$ (KBT) has a single T symmetry below its T_c, a relatively large tetragonality and a high T_c value (~ 380 °C) [7]. A few KBT-based solid solutions were prepared afterwards, such as KBT–Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ [8], KBT–KNbO$_3$ [9] and KBT–BiFeO$_3$ [10], in which no traditional MPB was obtained. As an important member of BiMeO$_3$ family, Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$ (BNT) was reported to be a simple R ferroelectric and have a high Curie point [11]. It formed an MPB solid solution with T-phase PT, which owns good piezoelectric properties ($d_{33} \sim 260$ pC/N) and a relatively high T_c of 400 °C [12]. Unfortunately, nearly

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50 wt% PbO still exists in the composition. However, it would be of much interest to know what is going on if PT is replaced by KBT?

The purpose of this study is to thus investigate the phase transition behavior of $(1-x)$KBT–xBNT solid solutions and explore the composition-dependent piezoelectric properties. Experimental results demonstrated that a new lead-free piezoelectric solid solution ceramic was successfully manufactured, which owns a traditional MPB and a relatively high T_c and a certain piezoelectric properties. This work seems to open up a way for synthesizing new potential piezoelectric materials.

2. Experimental

The $(1-x)$KBT–xBNT ($(0 \leq x \leq 0.4$, in mol) ceramics were synthesized by a conventional solid-state reaction method using high-purity ($> 99\%$) Bi_2O_3, TiO_2, K_2CO_3 and NiO as raw-materials. The weighed powders were ball-milled in ethanol and zirconia media for 4 h. The dried powders were calcined twice between 900–950 °C for 3 h in air, and then ball-milled for 6 h. The uniaxially pressed pellets were sintered in a sealed crucible between 1030–1075 °C for 3 h. For electrical measurements, silver paste was coated on major sides of the samples and then fired at 650 °C for 30 min. The samples were poled under a dc field of 5~6 kV/mm at 120 °C for 30 min in silicone oil.

The crystal structure was examined by an X-ray diffractometer (XRD, D/Max-RB, Rigaku, Japan). The dielectric constant was measured as a function of temperature and frequency by an LCR meter (Agilent E4980A, Santa Clara, CA). Polarization versus electric field (P–E) hysteresis loops were measured using a ferroelectric measuring system (Precision LC, Radiant Technologies Inc., Albuquerque, NM). The d_{33} value was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The k_p value was determined by a resonance–antiresonance method with an impedance analyzer (PV70A, Beijing Band ERA Co., Ltd. China).

3. Results and discussion

The full XRD patterns of $(1-x)$KBT–xBNT solid solutions are shown in Fig. 1(a). It can be seen that most compositions form solid solutions with a single perovskite structure except for those with $x > 0.20$. The secondary phase was identified as $K_4Ti_3O_8$ marked with stars. The possible reason can be attributed to both a low solubility limit of BNT in the KBT lattice and a smaller tolerance factor of BNT ($t = 0.95$). Moreover, the crystal structure of the solid solutions gradually changes from T to R symmetry with increasing x, as manifested by the splitting of (200) peaks. Refined scanning results of (200) diffraction lines are shown in Fig. 1(b). These (200) diffraction lines were fitted by using a Pearson function. It is obvious that pure KBT ceramics had a T symmetry as evidenced by the splitting of the $(002)_T/(200)_T$ peaks. However, the lattice distortion of the T symmetry gradually diminishes with increasing the BNT content. Meanwhile, an R symmetry starts to appear as $x > 0.05$. The integrated

intensities of $(200)_R$ increase while the intensities of $(002)_T/(200)_T$ decrease remarkably. These changes can also be observed from the variation of the lattice parameters of $(1-x)$KBT–xBNT ceramics, as shown in Fig. 2. The least-square refinements were performed on the XRD data for different compositions. The c/a value for pure KBT is 1.019 ($a = 3.9221$ Å, $c = 3.9970$ Å) and agrees well with the reported values ($a = 3.9250$ Å, $c = 3.9930$ Å and $c/a = 1.018$) [13], which declines as more BNT is added. As $x \geq 0.08$ the c/a value becomes 1 and the materials own a single R phase. Therefore, a traditional MPB could be identified to be in the range of $x = 0.05 \sim 0.07$, around which the R and T ferroelectric phases coexist. Clearly, the formation of the phase boundary here was not realized by a shift of any kind of polymorphic phase transitions which used to be observed in BT- and NKN-based materials [2–4].

The dielectric constant at 100 kHz of $(1-x)$KBT–xBNT ceramics as a function of temperature is shown in Fig. 3. It can be observed that the phase transition temperature (T_m) at the dielectric maxima decreases from 373 °C for pure KBT ceramics to 289 °C for the $x = 0.2$ sample. The samples with $x = 0.06$ approximately have a T_m value of 325 °C at 100 kHz. A decline in the phase transition temperature is usually ascribed to a decrease of the tetragonality for a couple of

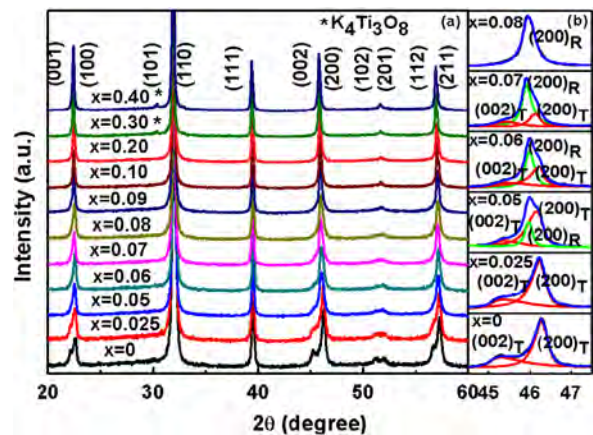
Fig. 1. (a) Powder X-ray diffraction patterns of $(1-x)$KBT–xBNT ceramics as indicated and (b) the locally refined scanning of (200) diffraction lines.
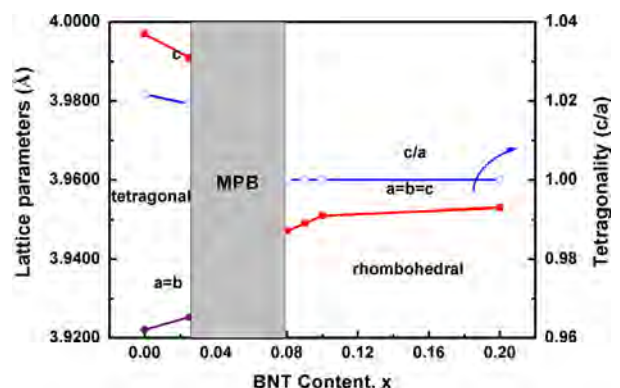

Fig. 2. The lattice parameters and tetragonality c/a values of $(1-x)$KBT–xBNT ceramics as indicated.

perovskite solid solution ceramics. In combination with the XRD data, a phase diagram of $(1-x)$KBT–xBNT ceramics can be roughly plotted (see inset of Fig. 3). Similar to the PZT binary system, a narrow hatching area corresponds to the coexistence zone of R and T ferroelectric phases. Moreover, the ferroelectric–paraelectric phase transition temperature decreases with increasing the BNT content.

The dielectric constant of $(1-x)$KBT–xBNT $(0 \leq x \leq 0.2)$ ceramics was measured as a function of temperature and frequency. The 0.94KBT–0.06BNT sample was taken as an example, as shown in Fig. 4. It can be seen that the ceramics exhibit broad and frequency-dependent dielectric peaks, typical of a relaxor ferroelectric. Furthermore, the substitution of BNT for KBT tends to increase the relaxor behavior, as characterized by both the diffuseness of the phase transition and the degree of relaxation. The former one could be described by an empirical parameter $\Delta T_{dif} = T_{0.9\varepsilon m(100\ kHz)} - T_{\varepsilon m(100\ kHz)}$ where $T_{0.9\varepsilon m(100\ kHz)}$ is the temperature corresponding to 90% of the maximum dielectric constant (ε_m) at the high temperature side and $T_{\varepsilon m(100\ kHz)}$ is the T_m value at 100 kHz.

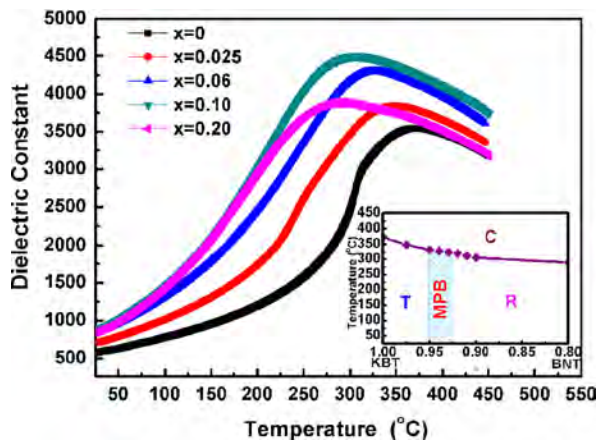Fig. 3. Temperature dependence of the dielectric constant of $(1-x)$KBT–xBNT ceramics as indicated; the inset is the phase diagram of $(1-x)$KBT–xBNT solid solutions where the R(T)−C phase transition temperature was determined by the T_m value at 100 kHz for each sample.
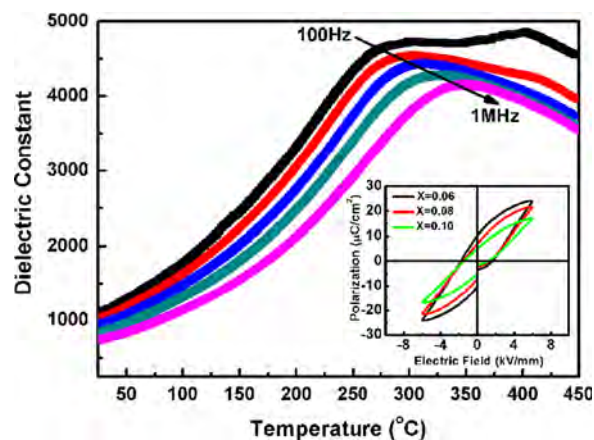

Fig. 4. Frequency dependence of the dielectric constant for 0.94KBT–0.06BNT ceramics; the insets are the curves of the polarization versus electric field for $(1-x)$KBT–xBNT ceramics as indicated.

Moreover, the frequency dispersion can be described by a parameter $\Delta T_{fre} = T_{m(100\ kHz)} - T_{m(100\ Hz)}$ [14]. For a relaxor ferroelectric, a modified Curie–Weiss law was proposed as follows [15]: $1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma / C$, where γ is the degree of relaxation ranging between 1 for a normal ferroelectric and 2 for an ideal relaxor ferroelectric, and C is assumed to be a constant. According to Fig. 4 (other samples were also included), the calculated parameters are listed in Table 1. It is clear that all three parameters become significantly large with increasing x. Generally speaking, relaxor ferroelectrics are a special type of polar materials characterized by the disorder on one (or more) lattice sites and the short-range polar order. Yang et al. [16] reported that the relaxor behavior of KBT ceramics can be attributed to the positional disorder between K^+ and Bi^{3+} cations on A sites. Our experimental results would suggest that the BNT addition enlarged the disorder degree of the KBT lattice on A and/or B sites. At the same time, the BNT addition would also promote the formation of chemically ordered regions [17], and result in an increase in the number of the polar nanoregion, impeding the development of long-range polar ordering and making the phase transition around T_m more diffuse. The feature of a typical relaxor can be also seen from its P–E loops. A slim loop can be observed for $(1-x)$KBT–xBNT compositions, particularly for the composition with higher BNT content (see inset of Fig. 4). From these loops, a relatively small remanent polarization P_r can be found $(\sim 10\ \mu C/cm^2$ for the $x=0.06$ sample and $\sim 5\ \mu C/cm^2$ for the $x=0.2$ sample). Although the normal ferroelectric state with long-range dipoles in a relaxor ferroelectric can be excited by electric field [18], yet it cannot be maintained after the external electric field is released. As a result, the sample finally exhibits a lower P_r. It is also believed that the absence of long-range dipoles not only restricts the polarization but also tends to induce the formation of polar nanodomains [19].

Fig. 5 shows the composition-dependent piezoelectric and electromechanical properties for poled $(1-x)$KBT–xBNT ceramics. It can be seen that the properties exhibit a strong compositional dependence near the MPB. Poled specimens show peak values of $d_{33} = 126$ pC/N and $k_p = 18\%$ for the sample with $x=0.06$. This phenomenon is similar to that observed in conventional Pb-based piezoelectric ceramics. The coexistence of two ferroelectric phases provides more spontaneous polarization directions, leading to higher piezoelectric activity. However, both values decrease sharply with the addition of more BNT mainly owing to the weakening of ferroelectricity. The as-achieved piezoelectric properties seem not very exciting, probably owing to the difficulty in sintering of such potassium-containing systems. It is still reasonably expected that they could be improved either by promoting the

Table 1
The calculated parameters for $(1-x)$KBT–xBNT ceramics.

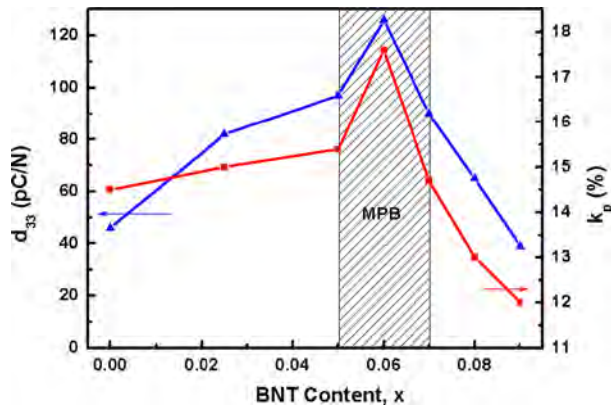| x	0	0.025	0.06	0.10	0.20
ΔT_{dif} (°C)	77	84	88	103	113
ΔT_{fre} (°C)	17	23	46	58	74
γ	1.82	1.83	1.87	1.90	1.96

Fig. 5. Piezoelectric and electromechanical properties of poled $(1-x)$KBT–xBNT ceramics.

densification behavior or by doping some donor dopants such as La^{3+} and Nb^{5+}.

4. Conclusions

Lead-free $(1-x)$KBT–xBNT solid solution ceramics were fabricated by a conventional solid-state reaction method. A typical MPB between R and T ferroelectric phases was identified in the composition range of $x=0.05\sim0.07$, in which the samples exhibit optimum electrical properties of $d_{33}=126$ pC/N and $k_p=18\%$ together with a relatively high T_c of $\sim320\,^\circ$C. The relaxor behavior of the solid solution was enhanced distinctly with increasing the BNT content. These results demonstrate that $(1-x)$KBT–xBNT solid solution system could be a new promising lead-free piezoelectric material for possible device applications.

Acknowledgments

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