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Short communication

Synthesis and electrical properties of lead free $(Bi_{0.5}K_{0.5})TiO_3$–$BaTiO_3$–$Bi(Zn_{0.5}Ti_{0.5})O_3$ ceramics

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Abstract

Lead free ferroelectric materials with high Curie temperature in $(x)[(Bi_{0.5}K_{0.5})TiO_3]-(1-x)[0.5Bi(Zn_{0.5}Ti_{0.5})O_3–0.5BaTiO_3]$ or (x)BKT–$(1-x)$[BZT–BT] ternary system, where $x = 0.4$, 0.5, 0.6 and 0.8, were synthesized. The single phase perovskite for all ceramics were formed at 900 °C for 6 h in air. The ceramic compositions with $x = 0.5$ and 0.6 exhibited the dielectric properties with relaxor-like phase transition behavior, while the ceramic with $x = 0.8$ showed the dielectric behavior of normal ferroelectric materials. From room temperature $P–E$ measurement, the maximum remnant polarization (P_r of 2.75 μC/cm^2) and coercive field (E_c of 12.41 kV/cm) were obtained in the composition with $x = 0.6$. In addition, the T_C, P_r and E_c were found trend to increase with increasing BKT content.

Keywords: Ferroelectric; Dielectric; Relaxor-like behavior; High Curie temperature

1. Introduction

Pb-based perovskite ferroelectric ceramics and single crystals have been extensively investigated for piezoelectric applications [1–5]. However, due to environmental concern, the replacement of toxic Pb in piezoelectric materials which shows comparable electric properties with Pb-based piezoelectric materials was critically needed. While Bi-based perovskite is a good candidate due to the similar electronic structure with Pb [3], smaller size of Bi cation limited the stability of perovskite structure. Therefore, another end member who has stable perovskite is required. $BaTiO_3$ and $Bi_{1/2}K_{1/2}TiO_3$ are both good candidates due to high degree of solid solution with other perovskites and their tetragonal structure at room temperature [6–14]. Recently, the high Curie temperature $[Bi(Zn_{1/2}Ti_{1/2})O_3]_x–[BaTiO_3]_{1-x}$ or (BZT–BT) perovskite has been discovered at composition of $x \leq 0.3$ [13], while the morphotropic phase boundary (MPB) between tetragonal and rhombohedral was observed at 0.1BZT–0.9BT [13]. On the other hand, bismuth potassium titanate, $(Bi_{1/2}K_{1/2})TiO_3$ (BKT) is a well-known typical lead free ferroelectric material with tetragonal symmetry at room temperature and relatively high Curie temperature; T_C of 380 °C [14]. However, in the case of the BKT ceramic, it is difficult to prepare a dense ceramic because potassium carbonate easily reacts with humidity (H_2O) in air, resulting in low density and porous ceramics [15]. On the basis of the above mentioned statements, solid solutions of BZT–BT and BKT are expected to synergistically combine the properties of both the high Curie temperature ferroelectric (BZT–BT) and lead free ferroelectric (BKT), which could exhibit electrical properties that are better than those of the BZT–BT and BKT end members [6–14]. Interestingly, there have been no systematic studies on physical and electrical properties of solid solution of the high Curie temperature of BZT–BT and lead free BKT ferroelectric material in $(x)[(Bi_{1/2}K_{1/2})TiO_3]–(1-x)[0.5Bi(Zn_{1/2}Ti_{1/2})O_3–0.5BaTiO_3]$ or (x)BKT–$(1-x)$[BZT–BT] ternary system. Therefore, the overall purpose of

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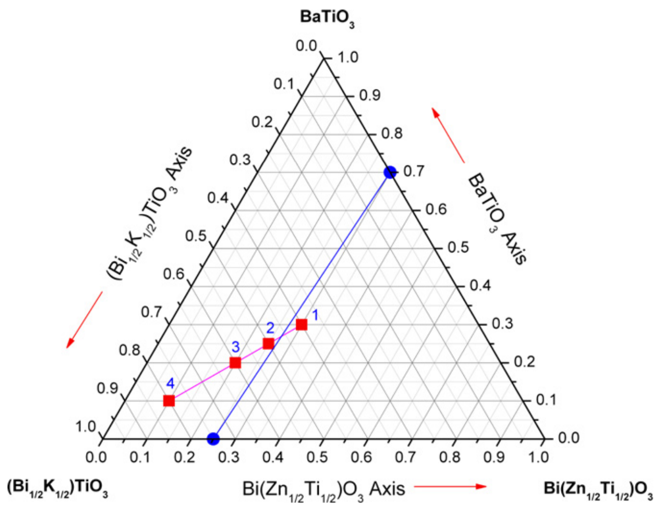

Fig. 1. BKT–BT–BZT ternary system.

this study is to examine the effects of BKT addition on phase formation, dielectric and ferroelectric properties of ceramics in a (x)BKT–$(1-x)$[BZT–BT] ternary system.

2. Experimental procedure

Samples of the $(x)[(Bi_{1/2}K_{1/2})TiO_3]$–$(1-x)[0.5Bi(Zn_{1/2}Ti_{1/2})O_3$–$0.5BaTiO_3]$, where $x = 0.4$, 0.5, 0.6 and 0.8 solid solutions, as shown in Fig. 1, were prepared by a conventional mixed oxide technique. Stoichiometric mixtures of starting reagent-grade oxides of $BaCO_3$ (98.5%), Bi_2O_3 (99.9%), K_2CO_3 (99.9%), ZnO (99.9%) and TiO_2 (anatase-structure) (99.9%) were ball milled in ethanol with yttria-stabilized zirconia balls for 24 h. To achieve phase homogeneity, the powders were calcined in a cover alumina crucible at a temperature of 900 °C for 6 h. The calcined powders were then uniaxially cold-pressed at 2500 psi into disc-shaped pellets with a diameter of 10 mm and a thickness of 1 mm with 3 wt.% poly (vinyl alcohol) (PVA) added as a binder. Following binder burnout at 500 °C, the pellets were sintered at 1025 °C for 2 h with a heating/cooling rate of 5 °C/min. The phase structure of the ceramics was analyzed via X-ray diffraction (XRD; Philips XPert Pro). Density was determined by Archimedes method. The dielectric properties of the sintered samples were measured using an automated measurement system with an Agilent 4284A LCR meter over a wide temperature range in a NorECS ProboStat high temperature measurement cell. The room temperature ferroelectric properties were examined using a simple Sawyer–Tower circuit at fixed measuring frequency of 50 Hz.

3. Results and discussions

The phase formation behaviors of ceramics in (x)BKT–$(1-x)$[BZT–BT] ternary system, where $x = 0.4$, 0.5, 0.6 and 0.8, are revealed by the XRD method. The XRD patterns of the samples are shown in Fig. 2, indicating that the single phase perovskite is presented at composition between $0.5 \leq x \leq 1$, while the pyrochlore phase (▼) of $Bi_xTi_xO_x$ is observed at composition less than $x = 0.5$. However, the phase of these

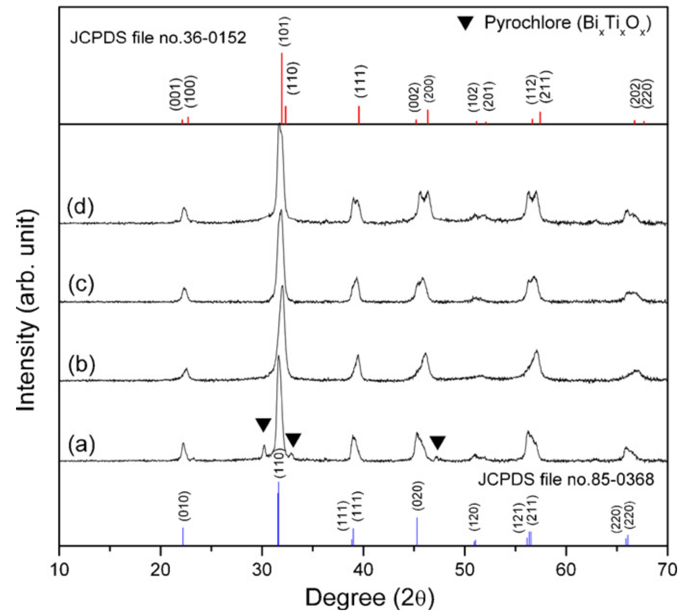

Fig. 2. XRD pattern of BKT–BT–BZT ternary system.

single phase perovskite samples, noticeably changes from the rhombohedral-like structure of BZT–BT (JCPDS file No. 85-0368) to the tetragonal-like structure of BKT (JCPDS file No. 36-0152) with increasing BKT content. In addition, the c/a ratio of the samples varies from 0.98 to 0.99, as shown in Table 1. This similar behavior is observed in other systems with BKT additions in BT–BKT [16], KNN–BKT [17], and BKT–BS–PT [18]. The effect of BKT modification on density of BZT–BT ceramics in (x)BKT–$(1-x)$[BZT–BT] systems (which $x = 0.5$, 0.6 and 0.8) was also examined. As listed in Table 1, it is clearly evident that the density of the ceramics decreased with increasing BKT content. This is likely due to that fact that generally in ceramic systems with high BKT content it is difficult to prepare the dense ceramics because start powders of potassium carbonate can easily react with humidity (H_2O) in air, resulting in low density and porous ceramics [14,15].

The characteristic temperature and frequency dependences of the dielectric properties (ε_r and tan δ) of the single phase (x)BKT–$(1-x)$[BZT–BT] ternary system with $x = 0.5$, 0.6 and 0.8 are displayed in Fig. 3(a)–(c). The results in Fig. 3(a) and (b) show board peaks in dielectric constant with strong frequency dependence. With increasing frequency, the maximum dielectric constant decreases (while the maximum dielectric loss increases) and the temperature of maximum dielectric constant shifts toward high temperature, indication of the relaxor-like ferroelectric behavior [19]. However, the maximum transition temperature (T_m) increases with increasing BKT content, most

Table 1
Physical and electrical properties of BKT–BT–BZT ternary system.

x	c/a ratios	Density (g/cm^3)	T_C at 10 kHz	P_r ($\mu C/cm^2$)
0.5	0.981	6.1712	212	0.98
0.6	0.985	6.1667	236	2.99
0.8	0.994	5.1128	327	–

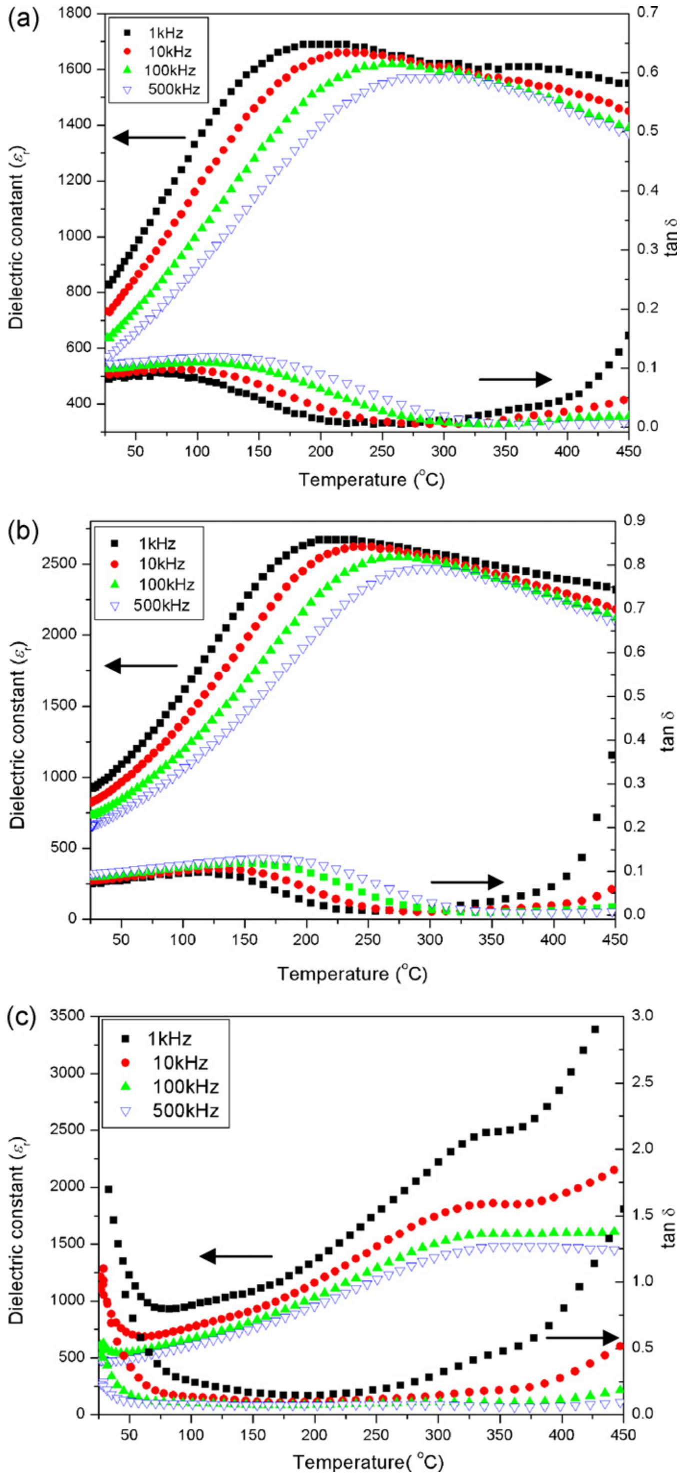

Fig. 3. Dielectric properties of pure (x)BKT–$(1-x)$[BZT–BT] ceramics, (a) $x = 0.5$, (b) $x = 0.6$ and (c) $x = 0.8$.

likely due to change of the c/a ratio of the materials from 0.98 to 0.99 and also from high T_C of BKT itself, as confirmed with XRD results in Fig. 2 and illustrated in Table 1. This result suggests that the transition temperature of (x)BKT–$(1-x)$[BZT–BT] system can be varied over a range from 212 to 327 °C by controlling the BKT content in the system [6–14], as shown in Table 1. This similar behavior is observed in other BKT-based systems; such as BT–BKT [16], KNN–BKT [17], and BKT–BS–PT [18]. While $x = 0.8$ as shown in Fig. 3(c), the slightly frequency dependence was found in this composition most likely normal ferroelectric behavior. However, which is rather lossy possible due to the lowest density is observed, as illustrated in Table 1. As well as the other features, like high and stable dielectric constant at high temperatures which might be good for high temperature capacitor applications [1–5].

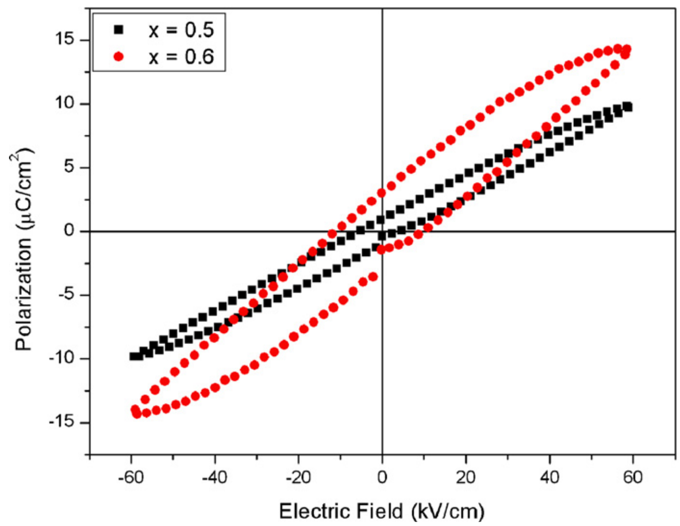

Fig. 4. Ferroelectric properties of (x)BKT–$(1-x)$[BZT–BT] ceramics.

Since BKT is the lead free ferroelectric materials [14], it is thus of interest to assess its effect on the ferroelectric characteristics of lead free BZT–BT ceramics. Fig. 4 shows room temperature P–E relations for compositions with $x = 0.5$ and 0.6 at the same electric field of 60 kV/cm (while $x = 0.8$ is too lossy to obtain P–E loop). However, (x)BKT–$(1-x)$[BZT–BT] ceramics are expected to have very high coercive field (E_c), hence it is very difficult to fully obtain the saturated P–E loops, as in other lead-free systems [9–14]. In the other hand of pure BZT–BT and BKT, the P–E characteristic showed a slim-type loop with low remnant polarization and coercive field [13,14]. The results show that P_r and E_c slightly increase with increasing BKT content. The maximum remnant polarization (P_r of 2.75 μC/cm^2) and coercive field (E_c of 12.41 kV/cm) are presented at composition of $x = 0.6$, while the P–E loop of the composition $x = 0.8$ cannot be measured possible due to its high dielectric loss, as shown in Fig. 3(c). Interestingly, the ferroelectric properties of high Curie temperature BZT–BT ceramics can be controlled by addition of BKT. This similar behavior is also observed in other systems with BKT additions in BNT–BKT [11], BT–BKT [16], KNN–BKT [17], and BKT–BS–PT [18].

4. Conclusion

In this study, lead free ferroelectric materials with high Curie temperature in $(x)[(Bi_{1/2}K_{1/2})TiO_3]$–$(1-x)[0.5Bi(Zn_{1/2}Ti_{1/2})O_3$–$0.5BaTiO_3]$ or BKT–BZT–BT ternary system were synthesized by conventional solid state reaction. It has been indicated that the single phase perovskite was formed at 900 °C for 6 h in air at compositions with $x = 0.5$, 0.6 and 0.8. The compound undergoes a phase transition at 212, 236 and 327 °C with $x = 0.5$, 0.6 and 0.8, respectively. The dielectric properties (ε_r and tan δ) are observed to show the relaxor-like ferroelectric behavior at composition of $x = 0.5$ and 0.6. The optimal remnant polarization P_r of 2.75 $\mu C/cm^2$ with a coercive field E_c of 12.41 kV/cm are obtained at $x = 0.6$. In particular, P_r and E_c slightly increase with increasing BKT content.

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