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Letter

Effects of sintering temperature and poling conditions on the electrical properties of $Bi_{0.50}(Na_{0.70}K_{0.20}Li_{0.10})_{0.50}TiO_3$ piezoelectric ceramics

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ABSTRACT

In this work, effects of sintering temperature and poling condition on the electrical properties of $Bi_{0.50}(Na_{0.70}K_{0.20}Li_{0.10})_{0.50}TiO_3$ (BNKLT) ceramics were systematically investigated, and these ceramics were prepared by the normal sintering. A pure perovskite phase is demonstrated for these ceramics sintered at 1040–1140 °C. The poling temperature and poling electric field strongly affect the piezoelectric properties of BNKLT ceramics, and an enhanced piezoelectric behavior of $d_{33} \sim 215$ pC/N and $k_p \sim 33.8\%$ is demonstrated for the ceramic sintered at 1100 °C when poled at a temperature of ~15 °C and ~5.68 kV/mm. The electric field-induced depolarization temperature of BNKLT ceramics is clearly observed by measuring the temperature dependence of the dielectric loss of these ceramics poled at different electric fields, and this value increases with an increase in poling electric field. These underlying physical mechanisms were addressed.

1. Introduction

Lead-based materials have been widely used for various ferroelectric and piezoelectric applications, for example, Pb(Zr,Ti)O_3, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ [1,2]. However, the use of lead-based materials has resulted in serious human health and environmental issues because of the loss of PbO during their preparation and processing. Moreover, these electronic devices with Pb element will be banned in the future in view of the environmental protection. Therefore, it is necessary to develop lead-free piezoelectric materials with compatible properties to those of lead-based ceramics [3–11].

$Bi_{1/2}Na_{1/2}TiO_3$ (BNT) ceramic is one kind of important candidates for lead-free piezoelectric materials because of its strong ferroelectricity at room temperature and a high Curie temperature of ~320 °C [12,13]. However, BNT ceramics have serious drawbacks of a high coercive field ($E_c \sim 73$ kV/cm) and a high conductivity, making them difficultly poled [12,13]. It has been reported that Li and K-modified BNT ceramics exhibit a high piezoelectric constant (d_{33}) of >200 pC/N [14–16], together with a decrease of their E_c value (~40 kV/cm). It is well known that a composition deviation from optimally designed one easily happens for BNT-based ceramics when sintered at a high temperature, resulting in a degradation of their d_{33} values [17]. Therefore, the use of an optimum sintering temperature can well maintain the material composition for further enhancing the d_{33} of Li and K-modified BNT ceramics. Moreover, piezoelectric properties of lead-free ceramics could be modified by tailoring the poling condition, where an enhanced piezoelectric behavior is demonstrated at an optimum poling electric field and a poling temperature [18,19]. However, there are no reports on the systematical investigation of the effect of the poling condition on the electrical properties of Li and K-modified BNT ceramics, and the effect of poling electric field on their depolarization temperature (T_{PEF}) value is also few involved.

In the present work, we importantly studied the effect of sintering temperature and poling condition on the electrical properties of $Bi_{0.50}(Na_{0.70}K_{0.20}Li_{0.10})_{0.50}TiO_3$ (BNKLT) lead-free ceramics prepared by the conventional solid state method under different sintering temperatures. An improvement of piezoelectric properties could be obtained by selecting an optimum sintering temperature, a poling electric field, and a poling temperature. The poling electric field not only results in the formation of T_{PEF} but also affects the T_{PEF} value of BNKLT ceramics, and these underlying physical mechanisms were also addressed.

2. Experimental procedure

$Bi_{0.50}(Na_{0.70}K_{0.20}Li_{0.10})_{0.50}TiO_3$ ceramics were prepared by the conventional ceramic processing. In this work, all raw powders were provided by the Sinopharm Chemical Reagent Co., Ltd. Raw materials of TiO_2 (99%), Bi_2O_3 (99%), Na_2CO_3 (99.8%), K_2CO_3 (99%), and Li_2CO_3 (98%) were mixed in a polyethylene jar by using a horizontal ball mill in ethanol with zirconia balls for 24 h, calcined at ~850 °C for 6 h, and then these powders were milled again for 24 h. After drying, these powders were manually pressed into 10 mm in diameter pellets and 1.0 mm in thickness by a uniaxial pressure of 10 MPa, and sintered at 1040–1140 °C for 2 h in air. Silver pastes were fired at 700 °C for 10 min on both sides of these samples as electrodes for electrical

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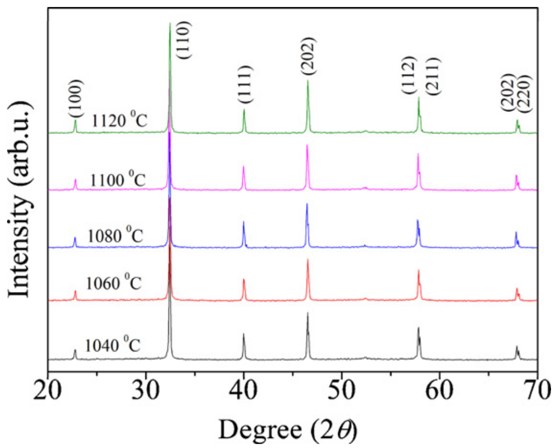

Fig. 1. XRD patterns of BNKLT ceramics as a function of sintering temperature.

measurements. These ceramics were poled at a room temperature of 15–100 °C in a silicone oil bath under a dc field, and their electrical properties were measured after 24 h.

The phase structure in these ceramics was measured by the X-ray diffraction (XRD) using the Cu Kα (wavelength ~0.15406 nm) source operated at the running conditions of 40 kV and 20 mA (DX-1000, PR China). Their dielectric behavior as a function of the measurement temperature was obtained in a tube furnace by using an LCR meter (HP 4980, Agilent, USA), and the heating rate is 3 °C/min. The d_{33} value of these ceramics was measured by using a piezo-d_{33} meter (ZJ-3A, China).

3. Results and discussion

Fig. 1 shows the XRD patterns of BNKLT ceramics as a function of sintering temperature. All ceramics have a pure perovskite phase, and no secondary phases are detected in the measurement range of XRD machine. These results indicate that the different sintering temperature does not change the crystalline structure of BNKLT ceramics in this work.

Fig. 2(a)–(f) shows the surface morphologies of SEM patterns of BNKLT ceramics as a function of sintering temperature. The sintering temperature obviously affects the surface morphologies of BNKLT ceramics, as shown in Fig. 2(a)–(f). Some pores and smaller grain sizes are demonstrated for these BNKLT ceramics sintered at <1080 °C, while these ceramics sintered at >1080 °C have a denser microstructure and a larger grain size. Therefore, the optimum sintering temperature helps to improve the microstructure of BNKLT ceramics in this work.

Fig. 3(a)–(d) plots the temperature dependence of the dielectric constant (ε_r) and dielectric loss (tan δ) of BNKLT ceramics sintered at 1040 °C, 1060 °C, 1100 °C, and 1140 °C, measured at 1, 10, 100, and 1000 kHz. In this measurement, all ceramics were poled at a room temperature of ~15 °C and the electric field of ~4.10 kV/mm. All ceramics exhibit two phase transitions, and the first one is assigned to the depolarization temperature (T_d) corresponding to the phase transition from ferroelectric to antiferroelectric, and the second one is assigned to the temperature at maximum ε_m (T_m) corresponding to a phase transition from antiferroelectric to paraelectric order [20].

Fig. 4(a) shows the temperature dependence of the ε_r of BNKLT ceramics sintered at 1040 °C, 1060 °C, 1100 °C, and 1140 °C, measured at 10 kHz. The T_m value of BNKLT ceramics almost keeps unchanged with sintering temperature. Moreover, it is observed that the ceramic sintered at 1100 °C has a higher dielectric constant (ε_m) as compared with those of these ceramics sintered at 1040 °C, 1060 °C, and 1140 °C. In this work, the ε_m value of BNKLT ceramics gradually increases with increasing sintering temperature from 1060 to 1100 °C because of an involvement of larger grain sizes [Fig. 2], and reaches maximum when sintered at 1100 °C, and then decreases with further increasing sintering temperature because of the loss of bismuth during sintering. Therefore, the enhancement in ε_m of BNKLT ceramics could be attributed to an optimum sintering temperature. In this work, one method of the temperature dependence of the tan δ is used to define the depolarization temperature (T_d). Fig. 4(b) plots the temperature dependence of the tan δ of BNKLT ceramics sintered at different temperature, measured at 10 kHz. All ceramics have a tan δ peak which is identified as the T_d, and their tan δ peak position is similar (~46 °C). However, a broader tan δ peak is demonstrated for these ceramics sintered at 1040 °C and 1060 °C, and these ceramics sintered at 1100 °C and 1140 °C have a sharper tan δ peak, as shown in the inset of Fig. 4(b). This broader tan δ peak should result in a dramatic decrease in d_{33} value, which will be discussed later.

Fig. 5 plots the density of BNKLT ceramics as a function of sintering temperature. These ceramics have a low density when sintered at a low or high temperature, while a highest density is demonstrated for the ceramic sintered at 1100 °C. Fig. 6 plots the piezoelectric properties of BNKLT ceramics with different sintering temperature. These ceramics sintered at ≤1060 °C have a low d_{33} value because of their broader tan δ peaks. In this work, the broader tan δ peak located at the depolarization temperature is similar to the “relaxor” behavior of ferroelectrics, as shown in Fig. 4(b). Therefore, a lower d_{33} value is observed for these ceramics

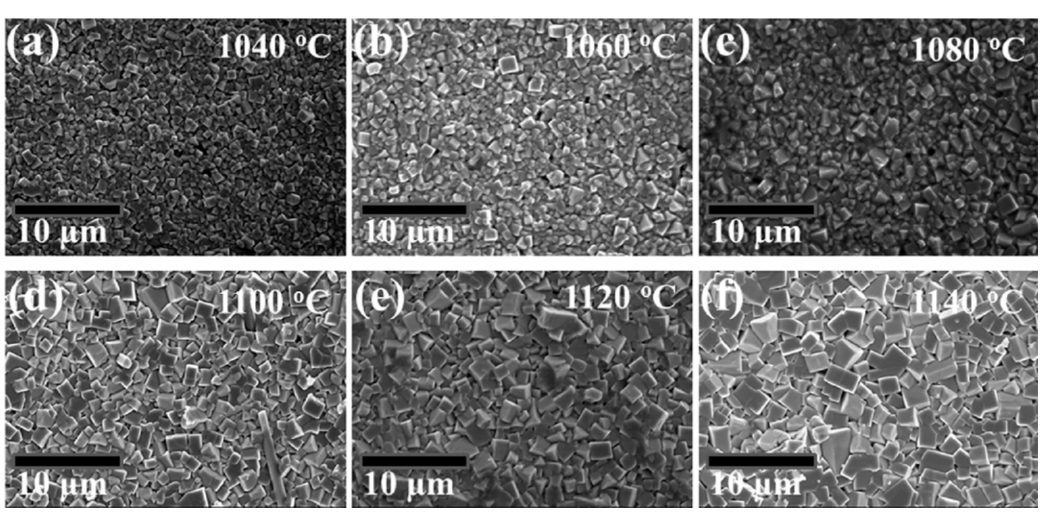

Fig. 2. SEM patterns of BNKLT ceramics as a function of sintering temperature: (a) 1040 °C, (b) 1060 °C, (c) 1080 °C, (d) 1100 °C, (e) 1120 °C, and (f) 1140 °C.

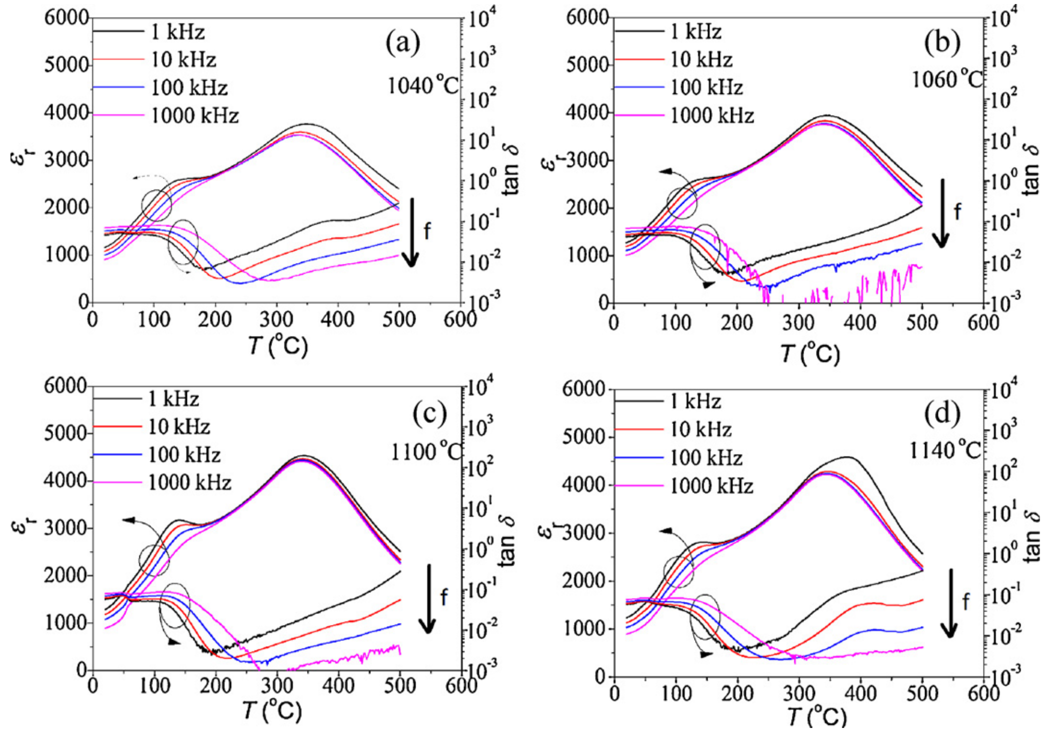

Fig. 3. Temperature dependence of the dielectric properties of BNKLT ceramics sintered at (a) 1040 °C, (b) 1060 °C, (c) 1100 °C, and (d) 1140 °C.

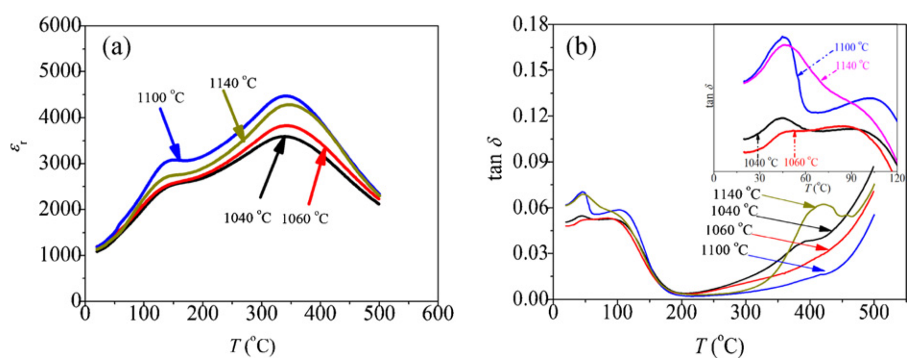

Fig. 4. Temperature dependence of the (a) dielectric constant and (b) dielectric loss of BNKLT ceramics sintered at different temperature, measured at 10 kHz, where the inset in (b) is expanded temperature dependence of the dielectric loss of BNKLT ceramics sintered at different temperature.

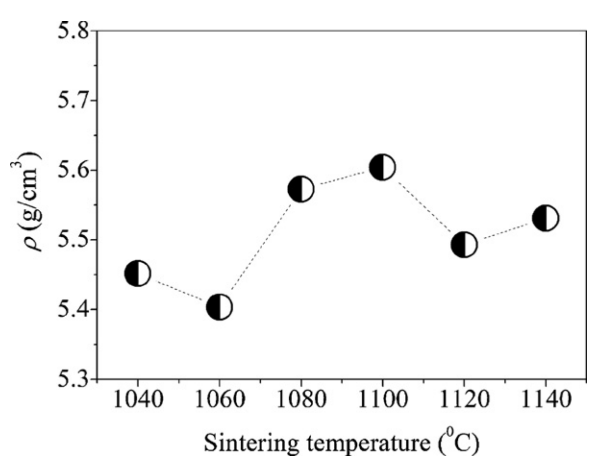

Fig. 5. Density of BNKLT ceramics as a function of sintering temperature.

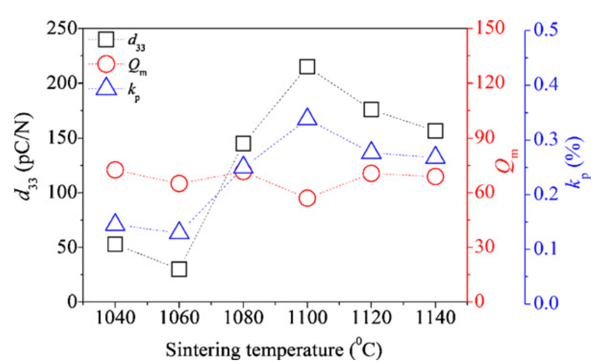

Fig. 6. Piezoelectric properties of BNKLT ceramics as a function of sintering temperature.

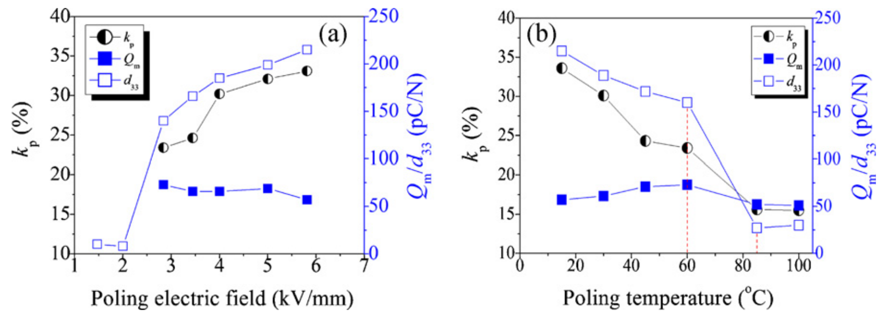

Fig. 7. (a) Poling electric field and (b) poling temperature-induced piezoelectric properties of BNKLT ceramics sintered at 1100 °C.

sintered at ≤1060 °C. A maximum d_{33} value is demonstrated for the ceramic sintered at 1100 °C, together with a highest k_p value, owing to a highest density. With further increasing sintering temperature (≥1120 °C), their d_{33} value decreases because of the loss of Bi during such a high processing temperature. However, the mechanical quality factor (Q_m) value of BNKLT ceramics is in the range of 57–73 for all ceramics sintered at different temperature.

Fig. 7(a) shows the dependence of the poling electric field (E_p) on the piezoelectric properties of BNKLT ceramics sintered at 1100 °C. It can be observed that the E_p significantly affects the piezoelectric properties of BNKLT ceramics. The d_{33} value of BNKLT ceramics is close to zero at $E_p < \sim 2.8$ kV/mm because of the incomplete switching of the domain at $E_p < E_c$, and gradually increases with an increase in the E_p value due to the complete switching of the domain at $E_p > E_c$. The domain switching and rotation of BNKLT ceramics could be induced by the poling electric field, making these ceramics exhibit a piezoelectric behavior. In a low electric field, a 180° domain can be easily switched, while the 90°, 120°, 180° domains are also switched at a higher poling electric field [21]. A threshold field is ∼2.8 kV/mm for the BNKLT ceramic in this work. Similar phenomenon has been demonstrated for the BNT ceramic [22]. However, the Q_m value of BNKLT ceramics is slightly changed with increasing E_p value. Fig. 7(b) shows the dependence of the poling temperature (T_p) on the piezoelectric properties of BNKLT ceramics sintered at 1100 °C. The d_{33} value of BNKLT ceramics decreases with increasing T_p value, and decreases to zero at $T_p > 60$ °C because of the involvement of a below T_d value at this point [23].

Fig. 8 indicates the temperature dependence of the tan δ of BNKLT ceramics sintered at 1100 °C, poled at a room temperature of ∼15 °C and different electric fields and measured at 10 kHz. A tan δ peak cannot be observed for these ceramics poled at a low E_p value, gradually forms at a high E_p value. However, a stronger

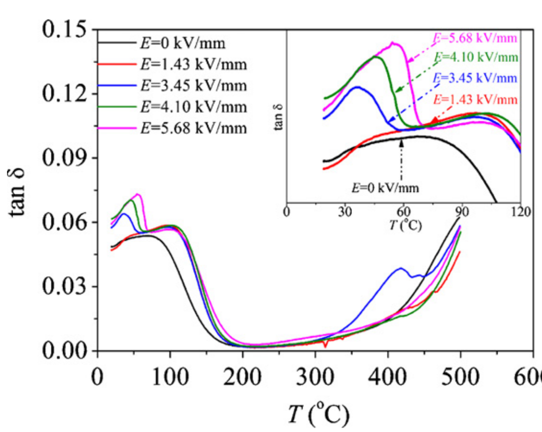

Fig. 8. Temperature dependence of the dielectric loss of BNKLT ceramics sintered at 1100 °C, poled at room temperature and different electric fields, where the inset is their expanded temperature dependence of the dielectric loss.

and sharper tan δ peak is demonstrated for these ceramics poled at $E = 5.68$ kV/mm, as shown in the inset of Fig. 8. Therefore, it is confirmed that the T_{PEF} of BNKLT ceramics is induced by the poling electric field in this work. Moreover, it is of great interest to note that the T_{PEF} value of BNKLT ceramics is dependent on the poling electric field, and gradually increases with increase electric field, as shown in the inset of Fig. 8.

Sapper et al. [24] reported that the T_d value of $(1-x)Bi_{1/2}Na_{1/2}(Ti_{0.995}Mn_{0.005})O_3$–$xBa(Ti_{0.995}Mn_{0.005})O_3$ is affected by the external bias during the temperature-dependent measurement of dielectric properties, and has a notable dependence on the external field. This finding can be attributed to the crystal structure if there are two different types of polar nanoregions (PNRs) which differ in their reaction to the applied field. In this work, the shift of T_d in BNKLT could be attributed to a local structural change, such as the stabilization of the macroscopic polarization by the external field during the poling process. Similar phenomenon has been observed elsewhere [24,25]. Moreover, the T_d value of BNKLT ceramics increases with an increase with poling field because these ceramics are not sufficiently well poled [26]. It was reported that two ways (the temperature-dependent measurement of dielectric properties and the temperature-dependent of piezoelectric constant) are to determine the T_d value of BNT-based ceramics [27]. In this work, the ceramic could be fully poled when the electric field is equal to be ∼5.68 kV/mm, as shown in Figs. 7 and 8.

4. Conclusion

$Bi_{0.50}(Na_{0.70}K_{0.20}Li_{0.10})_{0.50}TiO_3$ (BNKLT) ceramics were prepared by the normal sintering at different temperature and poled at different electric field and temperature, and effects of sintering temperature and poling condition on their electrical properties were systematically investigated. A pure perovskite phase is demonstrated for these ceramics, independent on the sintering temperature of 1040–1140 °C. An enhanced piezoelectric behavior of $d_{33} \sim 215$ pC/N and $k_p \sim 33.8\%$ is observed for the ceramic sintered at 1100 °C when poled at an optimum poling electric field of ∼5.68 kV/mm and a poling temperature of 15 °C. The poling temperature and poling electric field strongly affect the piezoelectric properties of BNKLT ceramics because of the switching of domain wall. The formation of T_{PEF} in BNKLT ceramics is determined by using the applied electric field, and its T_{PEF} value increases with increasing electric fields. Therefore, the investigation of the sintering temperature and the poling condition helps to improve the electrical properties and widen the application temperature of BNKLT ceramics.

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