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**Enhanced piezoelectric properties and electrocaloric effect in novel lead-free
(Bi_{0.5}K_{0.5})TiO₃-La(Mg_{0.5}Ti_{0.5})O₃ ceramics**

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Abstract

The crystal structure, electromechanical properties and electrocaloric effect in novel lead-free $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3\text{-La}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramics were investigated. A morphotropic phase boundary (MPB) between the tetragonal and pseudocubic phase was found at $x=0.01\sim 0.02$. In addition, the relaxor properties were enhanced with increasing the $\text{La}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ content. In situ high temperature X-ray diffraction patterns and Raman spectra were characterized to elucidate the phase transition behavior. The enhanced electrocaloric effect ($\Delta T=1.19$ K) and piezoelectric coefficient ($d_{33}=103$ pC/N) were obtained for $x=0.01$ at room temperature. Meanwhile, the temperature stability of the ECE was considered to be related to the high depolarization temperature and relaxor characteristics of the BKT-based ceramics. The above results suggest that the piezoelectric and ECE properties can be simultaneously enhanced by establishing an MPB. These results also demonstrate the great potential of the studied systems for solid-state cooling applications and piezoelectric-based devices.

Key words: $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ ceramic; Lead-free; Dielectric relaxor; Piezoelectric; Electrocaloric effect.

1. INTRODUCTION

Perovskite-type bismuth-based ferroelectric ceramics are promising candidates to replace the hazardous lead-containing ceramics in sensors, actuators and transducers applications.¹ $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) and $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT) are two typical bismuth-based ferroelectric ceramics. Since ferroelectric-relaxor transition induced excellent strain properties were discovered in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-(K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ systems, eco-friendly

BNT-based ferroelectric ceramics have attracted global research interest.² However, only a few studies have been focused on BKT-based ceramics to date. In contrast to BNT with typical rhombohedral structure, BKT exhibits a tetragonal symmetry and presents high tetragonality $c/a=1.02$ ($a=3.925 \text{ \AA}$ and $c=3.993 \text{ \AA}$) at room temperature. The structural difference between BNT and BKT is suggested to originate from the large ionic radius of K^+ that contributes to the appearance of long-range ferroelectric order.³ BKT exhibits two successive phase transitions, i.e., from tetragonal to pseudocubic at 260°C and from pseudocubic to cubic at 380°C .^{4,5} The piezoelectric coefficient d_{33} of the pure BKT ceramic is estimated to be only 69.8 pC/N , which is not sufficient for practical applications.⁶ Generally, MPB has been used to enhance the piezoelectric and ferroelectric properties and a number of BKT-based solid solutions have been prepared, including the BKT-Bi($\text{Ni}_{0.5}\text{Ti}_{0.5}$) O_3 and BKT-Bi $_{0.5}$ Na $_{0.5}$ Zr O_3 systems.^{7,8} The MPB separating the tetragonal and rhombohedral/pseudocubic phases facilitates domain rotations and extensions and thus enhances the piezoelectric properties.⁹ This behavior indicates the potential to explore high electromechanical performances by establishing MPB in BKT-based systems.

With the application or removal of an electric field in the polar crystals, the adiabatic entropy/temperature change will take place, and this phenomenon is called electrocaloric effect (ECE).^{10,11} The research of the ECE has renewed interest since giant ECEs were obtained in ferroelectric and organic thin films.^{12,13} Afterwards, the ECE was extensively explored and much progress has been made on both experimental and theoretical sides.¹⁴⁻¹⁶ However, in thin films, large ECE was usually acquired by applying high electric field, which leads to a low ECE efficiency ξ ($\Delta T_{\text{max}}/\Delta E$). Therefore, it is essential to explore large ECEs in bulk ceramics to establish macroscopic cooling cycles. BaTiO $_3$ -based single crystals and ceramics with optimal ECEs have been developed. However, the typical first-order phase transition results in a narrow and sharp peak on heating process, predicting the temperature instability of the ECE properties.^{17,18} Taking this into consideration, relaxor ferroelectrics characterized by diffuse phase transitions are expected to display a broad temperature range, as previously reported in Bi $_{0.5}$ Na $_{0.5}$ TiO $_3$ -based systems.¹⁹ In particular, the alignment of polar nanoregions (PNRs) in relaxor ferroelectrics also contributes to the ECE.²⁰ Regarding the ECE measurement for relaxor ferroelectric ceramics, the directly measured ECE method is

essential because the Maxwell relations can be only applied to equilibrium states.²¹ For example, in $\text{Ba}(\text{Zr,Ti})\text{O}_3\text{-(Ba,Ca)TiO}_3$ and Aurivillius relaxor ferroelectric ceramics, large discrepancies have been observed between the direct and indirect ECE measurements.^{22,23} Therefore, the direct measurement of ECE is essential to disclose the cooling ability of the BKT-based relaxor ferroelectric ceramics.

La-containing complex compound perovskites are one kind of fundamental material that is used in applications of microwave resonators. $\text{La}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (LMT) is usually considered as a typical low-loss microwave material and is also an promising end member to modulate electromechanical properties.^{24,25} In this work, novel lead-free BKT-LMT ceramics are investigated and the MPB region is the focus. The composition dependent phase structure, and the dielectric, piezoelectric, ferroelectric and ECE properties of the ceramics are discussed in detail.

2. EXPERIMENTAL PROCEDURE

Conventional solid-state reaction method was used to fabricate the $(1-x)\text{BKT-xLMT}$ ($x=0\sim 0.03$) ceramics. High-purity chemicals Bi_2O_3 , K_2CO_3 , TiO_2 , La_2O_3 and $4[\text{MgCO}_3]\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ ($\geq 99.0\%$, Sinopharm Chemical Reagent Co. Ltd., China) were used as raw materials. The K_2CO_3 raw powder was desiccated in the oven at $140\text{ }^\circ\text{C}$ for 12 h as it is susceptible to moisture in the air. The mixing powders were first milled with zirconia media in ethanol for 6 h, and the milled powder were calcined twice in a covered alumina crucible at $930\text{ }^\circ\text{C}$ for 2 h. After second calcination, the powders were milled again for another 12 h. The dried powders were mixed with 5 wt% PVA binder, and then pressed into pellets with 1 mm in a thickness and 10 mm in diameter. After removing the PVA binder, the pellets were sintered over the range of $1060\text{ }^\circ\text{C}\text{--}1080\text{ }^\circ\text{C}$ depending on the LMT content. All pellets were covered with the corresponding sacrificial powders to reduce the loss of K and Bi elements during sintering. The obtained pellets were polished and the silver pastes were covered on the both sides of the pellets for electrical characterizations. The samples were poled at $120\text{ }^\circ\text{C}$ for 15 min by applying a dc field of 5 kV/mm in silicon oil and finally cooled to room temperature with electric-field. The crystal structures were monitored by an X-ray

diffraction patterns were measured using a X-ray diffractometer (XRD, Bruker D8 Advance, Karlsruhe, Germany) with CuK α 1 radiation. Raman spectra were acquired by Raman scattering spectrometer (Horiba Jobin-Yvon HR800, France) with a 532 nm laser and was equipped with a Linkam THMSE 600 heating stage. The microstructure of the ceramics was observed using a scanning electron microscope (SEM, JEOL JSM-6490LV, Tokyo, Japan). The temperature dependence of dielectric properties was measured with an LCR meter (Agilent E4980A, Santa Clara, CA). Polarization-electric field (P-E) hysteresis loops was measured by using a ferroelectric test system (Precision LC, Radiant Technologies, Inc. Albuquerque, NM). The piezoelectric coefficient was measured using a quasi-static d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). The temperature variation was detected by a thermistor that was adhered to the samples. A Cu conductive paste was used to connect the sample with high-voltage power amplifier and the signals outputted from the thermocouple was recorded by the computer.

2. RESULTS AND DISCUSSION

3.1 Room-temperature composition-dependent phase structural evolution and microstructure

The XRD patterns of the BKT-xLMT ($x=0\sim 0.03$) solid solutions at room temperature are shown in Fig. 1(a). It can be seen that all samples form main perovskite phases with a minute trace of the second phase $K_4Ti_3O_8$ (PDF#41-0167), which might be ascribed to the volatilization of elemental Bi during the sintering process.²⁶ To clearly demonstrate the evolution of the crystal structure of the BKT-xLMT ceramics, the locally magnified (111) and (200) peaks are shown in Figs. (b1-b4) and (c1-c4), and the (200) peak is fitted by a Gaussian peak shape function using PeakFit software (SeaSolve Software Inc.). The pure BKT ceramic exhibits a tetragonal phase that is characterized by a single (111) peak and the splitting of the (002)/(200) diffraction peaks. The transition from the tetragonal to the pseudocubic phase is detected and the content of the pseudocubic phase gradually increases with increasing LMT content. For $x=0.01$ and 0.02 , the (002)_T/(200)_T and (200)_{pc} peaks can be simultaneously detected, which indicates the formation of an MPB region with coexistence of the tetragonal and pseudocubic phases. The single (111) and (200) peaks in the

ceramic with $x=0.03$ are attributed to pseudocubic symmetry. This finding is also supported by the Raman spectrum discussed below. Therefore, the addition of LMT content tends to decrease the lattice distortion of the tetragonal phase matrix and finally the pseudocubic phase dominates. This result is considered to be related with the decoupling between the A-site of $\text{Bi}^{3+}/\text{La}^{3+}$ and the B-site of $\text{Ti}^{4+}/\text{Mg}^{2+}$ ions. The electro-negativity of La^{3+} (1.1) and Mg^{2+} (1.2) is much weaker than Bi^{3+} (1.9) and Ti^{4+} (1.5), the addition of the LMT component will weaken the coupling of the A- and B-site ions, while the angle of the BO_6 tilt decreases. Moreover, the absence of a shift in the (111) peaks indicates that the inter-planar spacing d of the BKT-xLMT ceramics remain nearly unchanged for all studied compositions. This behavior is probably due to the combined effects of the relatively smaller ionic radius of La^{3+} than that of Bi^{3+} and K^+ in the A-sites ($\text{CN}=12$, $R_{(\text{Bi}^{3+}/\text{K}^+)}^{2+}=1.525 \text{ \AA} > R_{\text{La}^{3+}}=1.22 \text{ \AA}$), and the larger ionic radius of Mg^{2+} ($\text{CN}=6$, $R_{\text{Mg}^{2+}}=0.72 \text{ \AA}$) than that of Ti^{4+} in the B-sites ($\text{CN}=6$, $R_{\text{Ti}^{4+}}=0.605 \text{ \AA}$).²⁷

Raman spectroscopy is known as an effective technique to probe the short-range order and phase transitions in perovskites. It can be seen that the Raman bands of the BKT-xLMT ceramics are relatively broad and diffuse. This behavior is mainly due to the random occupancy of ions in both the A-sites (Bi^{3+} , K^+ and La^{3+}) and B-sites (Mg^{2+} and Ti^{4+}).^{28,29} To better identify the band position and the full width at half maximum (FWHM), the diffusive peaks are deconvoluted by seven Lorentzian peaks (labelled A~F) in the range of 150~700 cm^{-1} , as shown in Fig. 2(a). Unlike the typical $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based ferroelectric ceramics, the E(1TO) mode at approximately 115 cm^{-1} and the A1 mode at approximately 141 cm^{-1} are clearly observed in the BKT-xLMT ceramics, these modes can be assigned to Bi-O and K-O bonding, respectively.³⁰ The intensity of both modes are enhanced for $x=0.02$ and suddenly degenerates for $x=0.03$, which suggests a variation in the local structure for the A-site cations in the BKT-xLMT ceramics. The 200-400 cm^{-1} region characterized by the A, B and C bands, is closely related to the B-O vibrations in the perovskites. The D, E and F bands in the range of 400~700 cm^{-1} correspond to the BO_6 octahedral vibrations.^{31,32} Variations in the band position and the FWHMs for B-O bond and BO_6 octahedral vibrations can provide useful information regarding the structural changes and their evolutions as a function of LMT content are plotted in Figs. 2(b-d). It can be seen that the C and F bands exhibit a redshift

with increasing LMT content. The redshift of the B-O bonds can be ascribed to the enhanced structural disorder and the reduced polarity of the unit cell.^{32,33} In addition, the sudden increase in the FWHM for the B and F bands is believed to be an indication of the phase transition. On the basis of the Raman spectra of $x=0.03$, the cubic phase should be ruled out because first-order Raman modes are not allowed in the P_{m-3m} space group.³⁴ Therefore, with increasing LMT content, the structural change occurs in the compositions of $x=0.01\sim 0.02$, and the $x=0.03$ ceramics exhibits a pseudocubic phase.

Figure 3(a-d) shows the cross-section morphology of the BKT-xLMT samples. All ceramics are well sintered at the proper temperature. The microstructure exhibits a homogeneous state for all compositions and no apparent porosity is detected. The addition of the LMT content has a minor effect on the grain shape and size and the grain size is in the vicinity of $0.45\pm 0.05\ \mu\text{m}$ for all compositions.

3.2 Evolution of the dielectric properties in the BKT-xLMT ceramics

The temperature dependence of the dielectric properties for the unpoled and poled BKT-xLMT ($x=0\sim 0.03$) ceramics was measured at 1, 10 and 100 kHz over a range of 25 °C-500 °C, as shown in Figs. 4(a-d). The temperature of the dielectric maxima (T_m) shows a frequency dispersion in all samples, thus exhibiting the characteristics of relaxor ferroelectrics.³⁵ For the virgin BKT ceramic, the temperature corresponding to the dielectric maxima T_m (1 kHz) is approximately 362 °C, and gradually decreases to 336 °C, 311 °C and 299 °C for $x=0.01$, 0.02 and 0.03 (virgin state), respectively. Another low temperature dielectric anomaly T_d (~274 °C) is observed for the unpoled BKT, corresponding to the spontaneous phase transition from the tetragonal to pseudocubic phase. Once poled (shown by red lines), interestingly, the T_d is enhanced and reaches 279 °C, both are also indicated by a hump in the $\tan\delta$ curves, as shown by arrows in Fig. 4(a). More obvious changes can be detected between the poled and unpoled states for $x=0.01$ ceramics. Compared to the BKT ceramic, the dielectric anomaly T_d of $x=0.01$ sample is approximately 187 °C and it can be only observed for the poled states. The application of electric field leads to an increment in the tetragonal phase proportion and the appearance of long-range polar order, which results in

an enhancement ($x=0$) or the appearance ($x=0.01$) of T_d . However, T_d is not detected above the room temperature for the poled $x=0.02$ and 0.03 ceramics. The dielectric permittivity at T_m is suppressed for the poled $x=0.02$ samples, as clearly shown in the inset of Fig. 4(c). As is known, the dielectric permittivity is affected by the domain wall mobility and density, and the variation in the dielectric permittivity for the unpoled and poled ceramics may signify the existence of polar nanoregions (PNRs).³⁶ Moreover, the size and dynamics of the PNRs are considered as an crucial factor in determining the performance for relaxor ferroelectric ceramics.³⁷⁻³⁹ The degeneration of the dielectric permittivity for the poled $x=0.02$ sample is due to the coalescence of the PNRs. For the $x=0.03$ sample, as shown in the inset of Fig. 4(d), no obvious changes are detected between the unpoled and poled states, which can be ascribed to the characteristics of the ergodic relaxor phase. Moreover, with increasing content of LMT, the relaxor properties of the BKT-xLMT ceramics are enhanced, as described in Supplementary data (Fig.S1).

3.3 In situ high temperature characterization of the XRD patterns and Raman spectra

To disclose the phase transition within the MPB region, in situ high-temperature X-ray diffraction from 25 °C to 400 °C is performed for the $x=0.01$ and 0.02 ceramics, and the XRD patterns are listed in Fig.S2. The structural parameters, calculated by the fitted diffraction peak profile, are shown in Figs. 5(a1-a2). The lattice constant c_T and tetragonality c/a gradually decreases with increasing temperature as a whole. The lattice constant a_T gradually increases with increasing temperature in the MPB. Once the temperature reaches their respective T_d values (180 °C for $x=0.01$ and 120 °C for $x=0.02$), the coexistence of the two phases finally transform into the pseudocubic phase, and the lattice parameter a_{PC} continuously increases with further increasing temperature. Notably, the T_d for the $x=0.02$ ceramic is not detected from the dielectric curves.

Additionally, the local structural evolution of the $x=0.01$ and 0.02 samples are analyzed by in situ temperature dependent Raman spectra, and special attention is paid to the boundary across from the coexistence of the tetragonal and pseudocubic to the single pseudocubic phase, as shown in Fig. S3. The evolution in the wavenumber, FWHM and intensity of the

typical B, C and F bands for the $x=0.01$ and 0.02 samples is plotted in Fig. 6 (a1-c3). Significant discontinuities in the wavenumber, FWHM and intensity for the B, C and F bands can be detected for $x=0.01$ and 0.02 when the temperature approaches their respective T_d , which is an indication of phase change. The B and C bands gradually soften until T_d is approached, which is closely correlated with the weakening of the Ti-O bond. The continual weakening of the Ti-O bond will induce structural transitions in the local scale, as indicated by the hatching area. It is also evidenced by the FWHM of the Ti-O bond and TiO_6 octahedra that they both sharply decrease in the vicinity of T_d , $180\text{ }^\circ\text{C}$ for $x=0.01$ and $120\text{ }^\circ\text{C}$ for $x=0.02$, which is also in accordance with the in situ XRD analysis. This result can be ascribed to a decrease in the coherence length of the Ti-O bond, as witnessed in $Bi_{0.5}Na_{0.5}TiO_3$ -based systems.⁴⁰ The intensity of the bands C and F gradually decreases with an increase in the temperature, and the discontinuity occurs around their respective T_d , which is related to the gradual evolution in the tetragonal phase to the pseudocubic phase. Moreover, the two studied samples possess the first-order Raman spectra even far above T_d , thus explaining that the phase structure is still pseudocubic. The underlying mechanism may be related to the doubling of the unit cell and the polar nanoregions in the BKT-xLMT ceramics.⁴¹

3.4 Ferroelectric and piezoelectric properties of the BKT-xLMT ceramics

Figure 7(a~d) shows the room-temperature P-E hysteresis loops and corresponding J-E curves for all compositions at a frequency of 10 Hz. It can be seen that, unsaturated P-E loops with flat J-E curves are obtained for the pure BKT ceramic, indicating that the tetragonal domains are not fully switched under $E=6\text{ kV/mm}$. However, the P-E loops gradually evolve to a saturated shape with a relatively large maximum polarizations P_{max} and the remnant polarizations P_r with a single sharp current density peak J1 when x increases to 0.01. For $x=0.02$ composition, the ferroelectricity is reduced with a weak J1 hump. A further increase in the LMT content to $x=0.03$ leads to slim P-E loops with a current density platform. Furthermore, the current density value for $x=0.01$ and 0.02 is larger than that of $x=0$ and 0.03 , which confirms the higher domain switching degree within the MPB zone.⁴² As shown in Fig. 7(e), in the pure BKT ceramics, the P_{max} and P_r values are $\sim 6\text{ }\mu\text{C/cm}^2$ and $3\text{ }\mu\text{C/cm}^2$,

respectively. For $x=0.01$, the highest values of $P_{\max} \sim 17 \mu\text{C}/\text{cm}^2$ and $P_r \sim 9 \mu\text{C}/\text{cm}^2$ are obtained. The further addition of LMT leads to a decrease in the P_{\max} and P_r . Moreover, the d_{33} value increases from 70 pC/N in pure BKT ceramic to the maximum value of 103 pC/N for $x=0.01$, and then it gradually decreases with a further increase in the LMT content, namely, 82 pC/N and 42 pC/N for $x=0.02$ and 0.03, respectively. The coexistence of tetragonal and pseudocubic phases provides easier domain switching, thus leading to better piezoelectric coefficients and ferroelectric properties. The d_{33} value of the 0.99BKT-0.01LMT composition is higher than in the BKT-BiScO₃⁴³ and BKT-BiFeO₃⁴⁴ ceramics and comparable to the BKT-Bi(Ni_{0.5}Ti_{0.5})O₃⁷ and BKT-Bi(Mg_{2/3}Nb_{1/3})O₃ systems.⁴⁵

3.5 Directly measured electrocaloric effect of the BKT-xLMT ceramics

Figure 8(a) shows the temperature change in the 0.99BKT-0.01LMT ceramic in response to the removal of the electric field. The black circles represent the measured data and the red line denotes the fit according to Eq.(1). Then, the ΔT can be precisely determined.⁴⁶

$$T(t) = T_{\text{bath}} + \Delta T e^{-t/\tau} \quad (1)$$

where T_{bath} is the surrounding temperature and t is the heat transfer time.

It can be seen that the temperature sharply decreases when electric field is released. This result effectively confirms that the BKT-xLMT ceramics exhibit a positive ECE. Fig. 8(b) shows the variation in ΔT as a function of the electric field at RT. It can be seen that ΔT almost linearly increases with an increasing electric field from 1 to 4 kV/mm, which is ascribed to the increasing entropy change at higher electric field strengths. The ΔT value is also enhanced in the vicinity of the MPB region, ΔT increases from 0.88 K for $x=0$ to 1.19 K for $x=0.01$ and then gradually decreases when deviated from the MPB. As shown in Fig. 8(c), ΔT for $x=0.01$ is 1.19 K at room temperature. When the temperature increases to 100 °C, ΔT is up to 1.26 K under $E=4$ kV/mm. In view of practical applications, the temperature stability is also very important. The instability η , defined as:

$$\frac{\Delta T_{\max} - \Delta T}{\Delta T_{\max}} \times 100\% \quad (2)$$

is adopted to evaluate the temperature stability of the ECE.⁴⁷ As plotted in Fig. 8(d), the instability is lower than 10% over the range 25 °C~120 °C for $x=0.01$. The parameter ξ is also utilized to evaluate the performance of different materials under the unit of electric field. The ξ of the ceramic with $x=0.01$ approaches 0.3 K·mm/kV, which is competitive with the ECE efficiency of the other relaxor ferroelectric ceramics, as shown in Table 1.⁴⁸⁻⁵³ With respect to the ECE, aside from the polarization contribution, the diffuse phase transition and the existence of PNRs also play an important role in the temperature stability of the ECE. The alignment of the PNRs will be easily induced by the external electric field, which is beneficial for the enhancement of the ECE. Moreover, the diffuse phase transition with high T_d will lead to the stability of the ECE in the studied temperature range.

4. CONCLUSIONS

The crystal structure, dielectric, ferroelectric, and piezoelectric properties, and electrocaloric effect of the BKT-xLMT binary solid solutions were discussed in detail. The introduction of LMT decreased the tetragonality of the BKT ceramic and an MPB region was formed at $x=0.01\sim 0.02$. The 0.99BKT-0.01LMT ceramic showed an enhanced piezoelectric coefficient ($d_{33}\sim 103$ pC/N) and ECE ($\Delta T=1.19$ K) at room temperature. The ΔT value of the $x=0.01$ ceramic exhibited a good temperature stability and the temperature instability η is lower than 10 % over 25°C~120 °C, which is clarified by in situ high-temperature XRD patterns, Raman spectra. The good thermal stability is attributed to the diffuse phase transition with high T_d and the existence of polar nanoregions. The BKT-LMT solid solution system demonstrates the potential of lead-free ceramics in piezoelectric-based devices and solid-state cooling applications.

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SUPPLEMENTARY DATA

See supplementary material for variation of ΔT_{fre} and γ values, in situ high-temperature XRD patterns and Raman spectra.

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Figures Captions

Figure 1. Room-temperature XRD patterns for (1-x)BKT-xLMT ceramics ($x=0\sim 0.03$); (b1)~(b4) the locally magnified (111) peaks and (c1)~(c4) the (200) diffraction peaks fitted using a Gaussian peak shape function.

Figure 2. (a) The Raman spectra for (1-x)BKT-xLMT ($x=0\sim 0.03$) ceramics and (b)-(d) wavenumber and FWHM for B, C and F band as a function of LMT content.

Figure 3. Cross-section morphology of the (a) $x=0$; (b) $x=0.01$; (c) $x=0.02$ and (d) $x=0.03$ ceramics.

Figure 4. (a)-(d) Temperature dependence of dielectric constant and loss tangent for poled (red line) and unpoled (black line) (1-x)BKT-xLMT ($x=0\sim 0.03$) ceramics measured at 1, 10 and 100 kHz.

Figure 5. The variation of lattice parameter and tetragonality as a function of temperature.

Figure 6. The variation of wavenumber (a1, b1 and c1), FWHM (a2, b2 and c2) and intensity (a3, b3 and c3) as a function of temperature.

Figure 7. (a-d) P-E loops with J-E curves of the (1-x)BKT-xLMT ceramics at room temperature and (e) variation of P_{\max} , P_r and d_{33} as a function of LMT content.

Figure 8. (a) A temperature signal versus time measured directly for the 0.99BKT-0.01LMT ceramics at room temperature as a representative (solid dots). The red line is the fitting function of the exponential decay due to the heat losses to the surroundings. The blue line represents the applied field. (b) The room-temperature adiabatic temperature change ΔT as a function of the electric field; the inset shows the variation of ΔT as a function of LMT content; (c) temperature dependence of ΔT and (d) temperature instability η for BKT-xLMT ($x=0\sim 0.03$) ceramics.

Table 1 Comparison of ECE properties of the 0.99BKT-0.01LMT ceramic in this work with those reported in the literature.

Material	T (°C)	ΔT (K)	ΔE (kV/mm)	ξ (K·mm/kV)	Reference
BCZT	85	0.6	4	0.15	48
Ce-SBN	30	0.6	2.8	0.21	49
BNKT	160	0.73	2.2	0.33	50
Reactive PMN-PT	70	0.558	2.4	0.23	51
KTN	RT	0.42	2	0.21	52
KNN	80	0.41	2	0.2	53
BKT-LMT	RT	1.17	4	0.29	This work











