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Letter

$BiScO_3$-modified $(K_{0.475}Na_{0.475}Li_{0.05})(Nb_{0.95}Sb_{0.05})O_3$ lead-free piezoelectric ceramics

Xuhai Li, Jiliang Zhu*, Mingsong Wang, Yuansheng Luo, Wei Shi, Lihua Li, Jianguo Zhu, Dingquan Xiao

Department of Materials Science and Engineering, Sichuan University, Chengdu, Sichuan 610064, China

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ABSTRACT

The $BiScO_3$-modified $(K_{0.475}Na_{0.475}Li_{0.05})(Nb_{0.95}Sb_{0.05})O_3$ lead-free piezoelectric ceramics were prepared using normal sintering technique. The effects of the $BiScO_3$ on the phase structure and electrical properties of the ceramics were systematically studied. These results show that the $BiScO_3$-modified $(K_{0.475}Na_{0.475}Li_{0.04})(Nb_{0.95}Sb_{0.05})O_3$ lead-free piezoelectric ceramics form stable solution with tetragonal structure, and the Curie temperature and the polymorphic phase transition of the ceramics decreased with increasing x. Furthermore, the effect of the polarization temperature (T_p) on the piezoelectric properties of the ceramics was also discussed. These results show that the piezoelectric properties of the ceramics strongly depend on the T_p. The ceramics with $x = 0.005$ poled at 30 °C exhibit optimum piezoelectric properties ($d_{33} = 280$ pC/N, $k_p = 49\%$, $\varepsilon_r = 1432$, and $\tan\delta = 3.7\%$). These results indicate that the ceramic is a promising candidate material for lead-free piezoelectric ceramics.

1. Introduction

Lead-based piezoceramic is widely used because it has excellent piezoelectric properties. However, because of environmental issues associated with lead, the development of lead-free piezoceramic has attracted much attention recently. The $(K,Na)NbO_3$ (KNN) lead-free ceramics have been widely investigated as a replacement for the $Pb(Zr,Ti)O_3$-based ceramics because of their high Curie temperature, low dielectric constant and relatively favorable piezoelectric properties [1,2]. However, the major draw back for KNN ceramics is the difficulty of obtaining high density by conventional preparation and ordinary sintering in air, because the phase stability is limited to 1140 °C for potassium sodium niobate. In addition, slight changes in stoichiometry lead to the formation of extra phases which make the final sample disintegrate quickly once exposed to humidity [3].

To improve the densification and piezoelectric properties of KNN ceramics, a number of studies have been carried out to improve the sinterability and electrical properties. These include the formation of solid solutions of KNN with other ABO_3-type ferroelectrics or non-ferroelectrics (e.g., $LiSbO_3$, $LiTaO_3$, $BaTiO_3$, $CaTiO_3$) [4–13]. The enhancement in piezoelectric properties of the modified KNN-based ceramics is generally attributed to the polymorphic phase transition (PPT) temperature near or at room temperature [13]. This PPT limits their implementation greatly because of the property variation and domain instability during thermal cycling between the two ferroelectric phases [14]. Thereupon the key approach for enhancing the thermal stability is to lower the PPT temperature, to shift the tetragonal–orthorhombic phase transition below room temperature [15,16].

The addition of $CaTiO_3$ into KNN was found to shift PPT well below room temperature [17]. As bismuth scandium, $BiScO_3$ (BS), is a rhombohedral ferroelectric below its Curie temperature (~480 °C). Moreover, $BiScO_3$ has been used to modify the sintering and electrical properties of KNN ceramics, the PPT was shifted to near room temperature, and therefore possess high piezoelectric properties [9,11]. Therefore, it is reasonable to anticipate that addition of BS could improve the piezoelectric stability of KNN-based ceramics around room temperature by shifting the PPT to below room temperature. In this work, $BiScO_3$-modified $(K_{0.475}Na_{0.475}Li_{0.05})(Nb_{0.95}Sb_{0.05})O_3$ lead-free piezoelectric ceramics were prepared by ordinary solid-state sintering technique, their dielectric, piezoelectric and ferroelectric properties were studied, and the effect of the poling temperature on the piezoelectric properties of the ceramics was also investigated.

2. Experiment

A conventional ceramic fabrication technique was used to prepare the $(1-x)(K_{0.475}Na_{0.475}Li_{0.05})(Nb_{0.95}Sb_{0.05})O_3$–$xBiScO_3$ [$(1-x)$KNNLS–xBS] ($x = 0$, 0.005, 0.010, 0.015, and 0.020) ceramic using analytical-grade metal oxides or carbonate powders: Na_2CO_3 (99%), K_2CO_3 (99.8%), Nb_2O_5 (99.5%), Li_2CO_3 (99%), Sb_2O_3 (98%), Bi_2O_3 (99%), Sc_2O_3 (99.99%) and $MnCO_3$ (98%). The stoichiometric powders were ball milled in a nylon jar with ZrO_2 balls for 24 h and dried. After the calcinations at 850 °C for 6 h, the powders were pressed into disks under a pressure of 20 MPa using polyvinyl alcohol (PVA) as a binder. After burning off PVA, the pellets were sintered in air in the temperature range of 1050–1140 °C for 3 h. After polishing, silver paste

* Corresponding author. Tel.: +86 28 85432078; fax: +86 28 85432078.
E-mail address: jlzhu167@yahoo.com.cn (J. Zhu).

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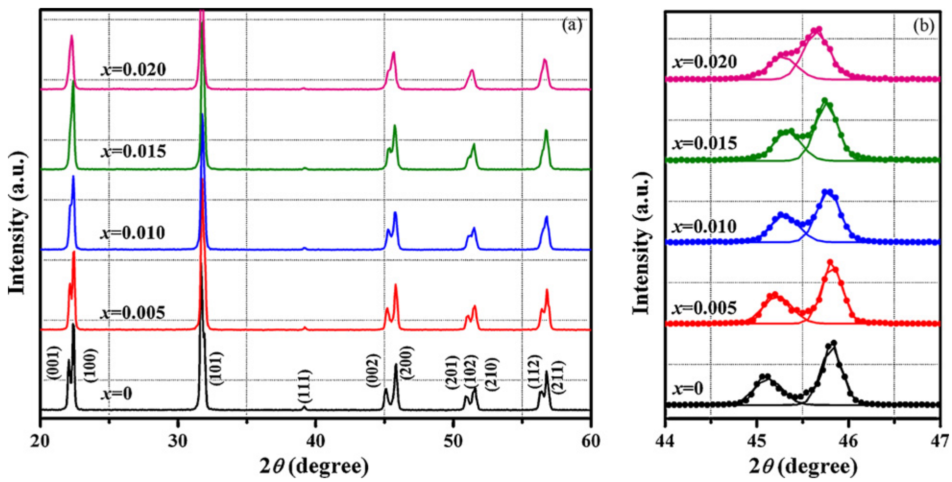

Fig. 1. XRD patterns of the $(1-x)$KNNLS–xBS ceramics as a function of x.

was fired on both sides of the samples at 700 °C for 10 min to form electrodes for the electrical measurements. The samples were poled in a 30–135 °C silicon oil bath by applying a direct current electric field of 4 kV/mm for 20 min.

X-ray diffractometer (XRD) (DX1000, Fangyuan Inc., Dandong, China) with a Cu Kα radiation was utilized to identify the crystal structures. The temperature dependence of the dielectric constant of the ceramics was measured using an impedance analyzer (Agilent E4980A). The piezoelectric constant was measured using a piezo-d_{33} meter (ZJ-3A, Institute of Acoustics Academic Sinica, Beijing, China). The electromechanical coupling factor k_p was determined by the resonance method using an impedance analyzer (HP 4294A). The polarization versus electric field (P–E) hysteresis loops of the ceramics was observed using a Radiant Precision Workstation (Radiant Technologies Inc., Albuquerque, NM).

3. Results and discussion

The X-ray diffraction patterns of $(1-x)$KNNLS–xBS ceramics with various x values are shown in Fig. 1(a). It can be seen that the pure perovskite phase with tetragonal symmetry could be obtained in $(1-x)$KNNLS–xBS ceramics throughout the research composition range ($x = 0$–0.02), which suggests that Bi^{3+} could substitute A sites and Sc^{3+} substitute B sites of perovskite structure, respectively. The enlarged and simulated XRD patterns of the ceramics [Fig. 1(b)] in the 2θ range of 44–47° also show that the crystal structure of the ceramic possesses a tetragonal structure.

The temperature dependence of the dielectric constant (ε_r) for the $(1-x)$KNNLS–xBS ceramics measured at 100 kHz is shown in Fig. 2(a). As shown in Fig. 2(a), the tetragonal and cubic phase transition temperature (T_C) and the PPT are observed in the pure KNNLS ceramics, while the PPT of the ceramics almost disappears (below room temperature) with the addition of BS. Fig. 2(b) shows the T_C of the $(1-x)$KNNLS–xBS ceramics as a function of x. The BS decreases the T_C of the ceramics, and the observed T_C of the ceramics decreases linearly from 353 to 257 °C as x increases from 0 to 0.02. As a result, the BS decreases the Curie temperature of the $(1-x)$KNNLS–xBS ceramics and shifts the PPT below room temperature. The PPT below room temperature is very helpful to improve the temperature stability of KNN-based ceramics [6,16,17].

Fig. 3 shows the d_{33}, k_p, ε_r and $\tan\delta$ of the ceramics as a function of x. It can be seen that the d_{33} value increases with increasing x, reaches a maximum (280 pC/N) at $x = 0.005$, and then decreases as x increases further. Similar to the d_{33} value, the k_p value also reaches a maximum value (49%) at $x = 0.005$. Besides, the ε_r value increases with increasing x, and the $\tan\delta$ value of the ceramics shows almost no change with increasing x. These results indicate the ceramics with $x = 0.005$ possess optimum piezoelectric and dielectric properties at room temperature ($d_{33} = 280$ pC/N, $k_p = 49\%$, $\varepsilon_r = 1432$, and $\tan\delta = 3.7\%$).

It is generally believed that the key approach for improving the piezoelectric properties of KNN-based ceramics is to make the PPT around room temperature. However, for these KNN-based ceramics' PPT depend not only on the compositions but also on the temperature. Thus, it is necessary to study the effect of the poling temperatures on the piezoelectric properties of KNN-based ceramics [6,8,17]. Fig. 4 shows the piezoelectric properties of the ceramics with $x = 0$ and 0.005 as a function of poling temperature (T_p). As

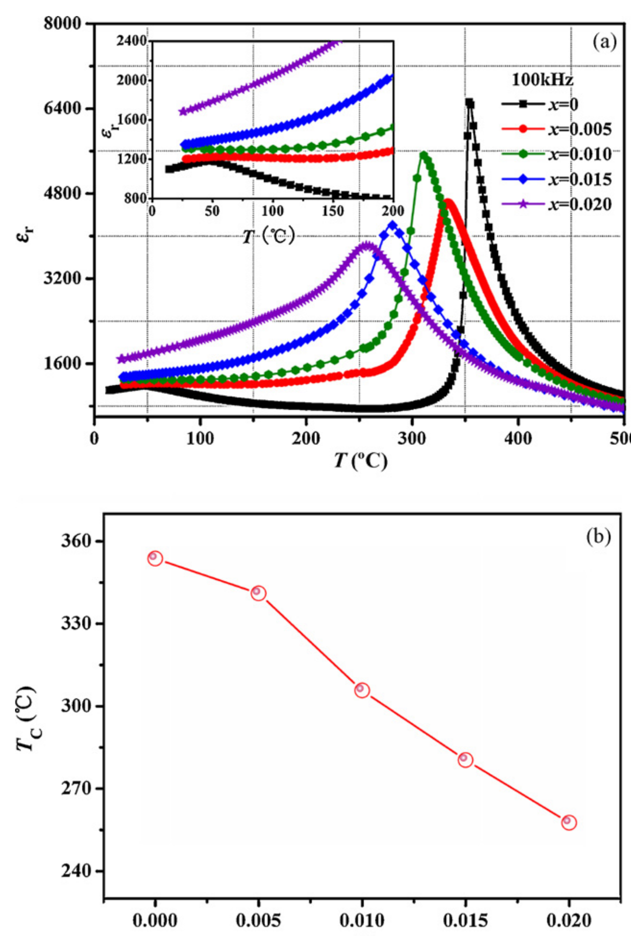

Fig. 2. (a) Temperature dependence of the dielectric constant for $(1-x)$KNNLS–xBS ceramics at 100 kHz; (b) T_C of the ceramics as a function of x.

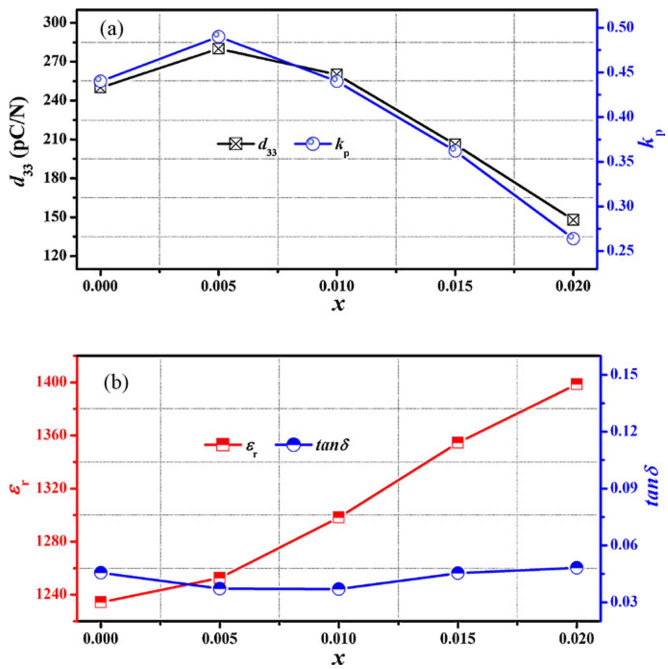

Fig. 3. Piezoelectric and dielectric properties of the $(1-x)$KNNLS–xBS ceramics with x.

shown in Fig. 4, T_p has obvious effect on the piezoelectric properties of the ceramics. For the unmodified ceramics [Fig. 4(a)], the d_{33} was found to be 225 pC/N at $T_p = 30\,^{\circ}$C, increasing to 250 pC/N at around 45 °C and then decreasing to 180 pC/N at 135 °C, a peak corresponding to the PPT was formed. For the ceramics with $x = 0.005$ [Fig. 4(b)], as the T_p decreases from 135 to 30 °C, the value of d_{33} increases from 185 to 280 pC/N. As a result, the T_p plays an significant role in improving the piezoelectric properties of $(1-x)$KNNLS–xBS ceramics. When T_p lies in the PPT region, the domain volume fractions could be more easily switched during poling, resulting in the coexistence of tetragonal and orthorhombic polarized domains [8]. However, the PPT value of the ceramics was far below room temperature, whereas the ceramics can be poled fully at a T_p that is closer to PPT. Therefore, the 0.995KNNLS–0.005BS ceramics with the PPT below room temperature (Fig. 2) in this work possess good temperature stability along with improved piezoelectric properties.

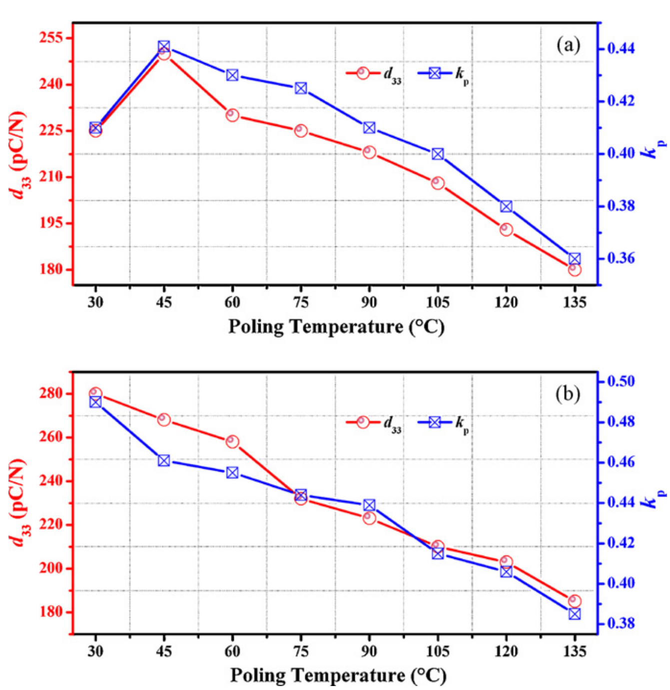

Fig. 4. Piezoelectric properties of the $(1-x)$KNNLS–xBS ceramics (a) $x = 0$ and (b) $x = 0.005$ as a function of poling temperature.

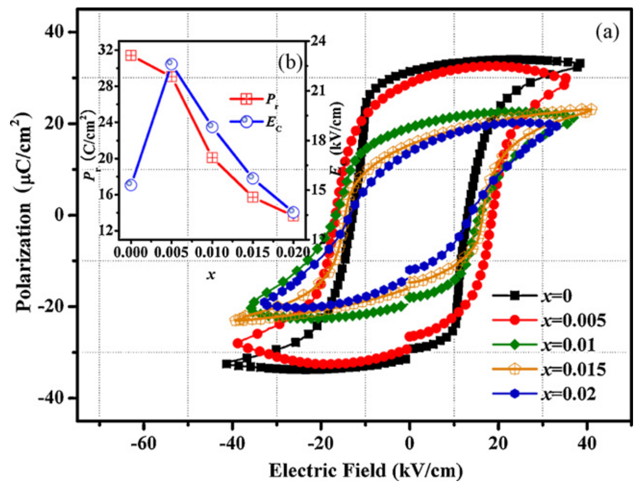

Fig. 5. (a) P–E hysteresis loops of the ceramics with $x = 0$, 0.005, 0.01, 0.015, and 0.02. (b) P_r and E_C of the ceramics as a function of x.

Fig. 5(a) shows the P–E loops of KNLNS–BS–x ceramics with $x = 0$, 0.005, 0.01, 0.015, and 0.02. Well-saturated hysteresis loops were observed over a wide composition range. Fig. 5(b) shows the P_r and E_C values of the KNLNS–BS–x ceramics as a function of x. It can be observed from Fig. 5(b) that the ceramics with the modifying BS tend to reduce the remnant polarization, while the E_C firstly increases with the increase of BS, and then decreases with further increase of BS. E_C is a parameter characterizing the difficulty of the domains switches. This may depend on the type of domain structures to a certain degree. 90° domains predominantly existing in a tetragonal phase switches with an electric field more difficult than 180° domains probably appearing in an orthorhombic phase [7]. In the tetragonal zone, the tetragonal phase increases with increasing x [Fig. 1]. The increase in E_C can be attributed to the increasing tetragonal phase which may induce the formation of more 90° domains. These results suggest that BS weakens the ferroelectric properties of KNN-based ceramics.

4. Conclusions

In summary, $BiScO_3$ modified $(K_{0.475}Na_{0.475}Li_{0.05})(Nb_{0.95}Sb_{0.05})O_3$ lead-free ceramics with enhanced electrical properties were prepared by conventional sintering technique. The effects of the $BiScO_3$ on the phase structure, piezoelectric and ferroelectric properties were detailedly studied. The experimental results show that the polymorphic phase transition of the ceramics was shifted to below room temperature with the modification of $BiScO_3$. The ceramics with $x = 0.005$ possess good temperature stability along with improved piezoelectric properties. These results indicate that BS modified KNNLS lead-free ceramics are potential candidates for high performance lead-free piezoelectric applications.

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