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Effects of CuO doping on the piezoelectric properties of KNLNS–BZ ceramics

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Abstract Lead-free piezoelectric ceramics with 0.96 $(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{1-x}Sb_xO_3$–0.04$BaZrO_3$ ($0.07 \leq x \leq 0.09$) and 1 mol% CuO (KNLNSx–BZ–CuO) compositions were prepared with hard characteristics for possible application on piezoelectric transformers. The results showed that good piezoelectric properties were found for ceramics with $x = 0.07$ and 0.08 (d_{33}, d_{31} and k_p were similar for both compositions). The higher mechanical quality factor (Q_m) corresponds to $x = 0.07$, which was close to 770. This combination of properties make the KNLNSx–BZ–CuO compositions promising materials for high power applications.

1 Introduction

The lead titanate-zirconate (PZT) materials still dominate the market of piezoelectric ceramics because of its excellent electrical properties [1]. However, the use of lead-based piezoelectric materials has serious environmental problems, due to the high volatilization of lead oxide during the production process. In recent years, some alternative piezoelectric materials have been investigated; among them, alkali niobates, sodium–bismuth titanates and other systems [2–9] have potential applications.

The $K_{0.5}Na_{0.5}NbO_3$ (KNN) lead-free solid solution has received much attention as one possible replacing material for lead titanate-zirconate ceramics. KNN has good piezoelectric and electromechanical properties [6, 10]. It was found that doping can improve the piezoelectric properties of KNN ceramics [2, 3, 11–13]. Nevertheless, high temperatures are required for sintering KNN-based ceramics with high density. Furthermore, for high power applications some dopants are being added. Some of these dopants that have enhanced the mechanical properties of KNN and related compositions are CuO, MnO, NiO [4, 10, 14–17]. These dopants can increase the density and decrease the sintering temperature.

For the above-mentioned applications, in addition to the high mechanical properties, also good piezoelectric constants (d_{33}, d_{31} and k_p) are required. For improving these properties usually *A* and *B* ions are added in the KNN perovskite structure. Recently, very high piezoelectric properties have been obtained in Li–Bi–Sb–$BaZrO_3$ doped KNN (KNLNS–BZ) ceramics processed by conventional solid state method [12, 18–20].

The main features of these new compositions include lowering the Curie temperature close to 200 °C for compositions with the highest properties. The enhancement of piezoelectric performance was attributed to the coexistence of rhombohedral–tetragonal crystalline structures at room temperature [12, 19]. The obtained results are comparable with those of some soft PZT materials, and demonstrate that piezoelectric properties of KNN related compounds can be controlled modifying the chemical composition [18, 20].

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Considering the high piezoelectric performance of KNLNS–BZ ceramics, it can be expected that doping with CuO or another hardening cation will result in piezoelectric ceramics for high power applications. Then, in this work 1 mol% CuO was used as sintering aid to improve the mechanical quallity factor of $0.96(K_{0.48}Na_{0.52})_{0.95}$-$Li_{0.05}Nb_{1-x}Sb_xO_3$–$0.04BaZrO_3$ (KNLNSx–BZ), maintaining the high piezoelectric properties. The structural and physical properties of CuO-doped KNLNSx–BZ ceramics were investigated.

2 Experimental

$0.96(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{1-x}Sb_xO_3$–$0.04BaZrO_3$ ($0.07 \leq x \leq 0.09$) with 1 mol% CuO ceramics were prepared by solid state method. The synthesis was carried out using Nb_2O_5, Sb_2O_5, Li_2CO_3, K_2CO_3, Na_2CO_3, $BaCO_3$, ZrO_2 and CuO as raw materials. The reagents were weighed according to the stoichiometric chemical formula, dried, and mixed in an agate mortar with acetone until complete dryness. After that, the powders were calcined at 850 °C for 4 h, cooled to room temperature and ball milled for 12 h using ethanol as medium. The resulted powders were uniaxially pressed into disks of 13 mm in diameter and 1.5 mm thick under 300 MPa and then sintered at 1100 °C for 4 h.

The structural analysis was determined by X-ray diffraction (XRD) with Cu Kα radiation (D8 Advance, Bruker). The microstructures of the samples were observed by a scanning electron microscope (JEOL JSM IT300). The density of ceramic samples was determined by the Archimedes method.

For piezoelectric and dielectric measurements the samples were polished, and silver electrodes were painted on both sides. The electroded samples were heat treated at 600 °C for improving electrode adhesion. Polarization was carried out in silicone oil bath at room temperature under a DC electric field of 4 kV/mm for 30 min. The piezoelectric constant d_{33} was measured using a d_{33}-meter (PIEZOTEST). The relative permittivity (ε) and the dielectric loss (tan δ) were obtained using an impedance analyzer (Agilent 4294A). The electromechanical coupling factor k_p was determined by an iterative method [21], and the mechanical quality factor Q_m was calculated by the following equation [22]

$$Q_m = \frac{1}{2\pi f_r\left(1-(f_r/f_a)^2\right)RC}$$

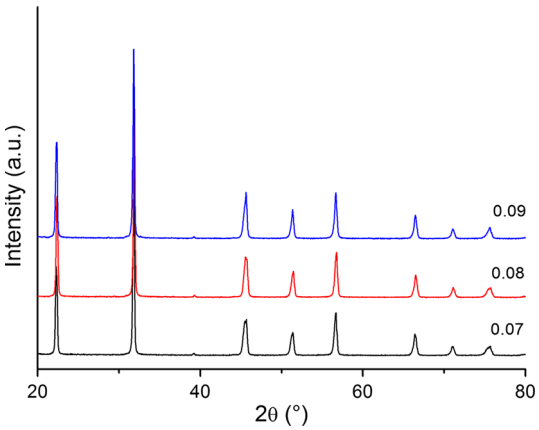

Fig. 1 XRD results of CuO doped KNLNSx–BZ ceramics sintered at 1100 °C for 4 h

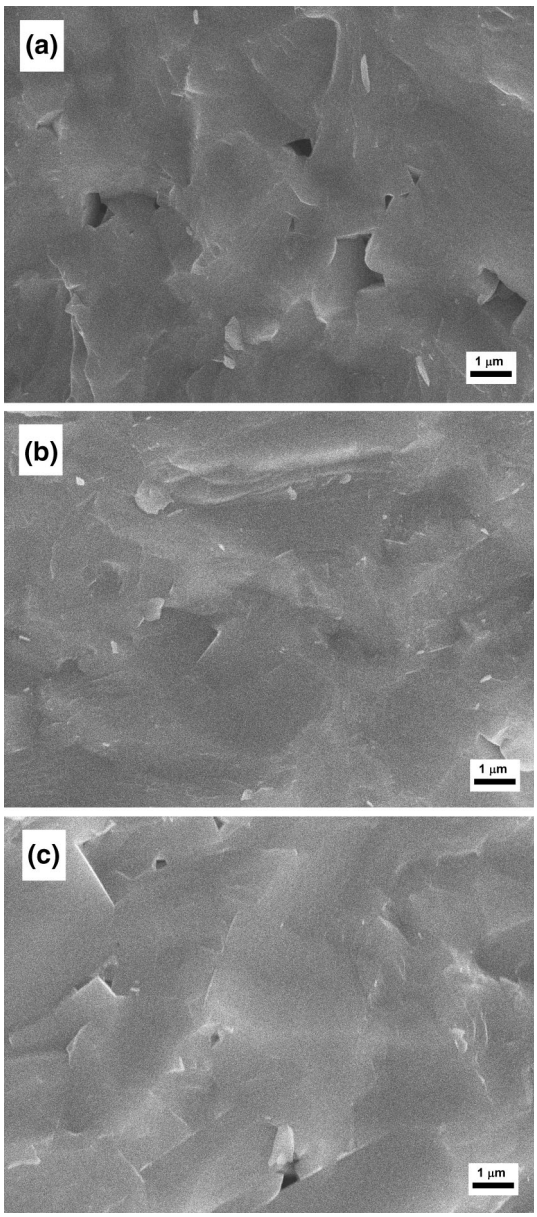

Fig. 2 SEM images of KNLNSx–BZ–CuO sintered at 1100 °C for 4 h: **a** x = 0.07, **b** x = 0.08 and **c** x = 0.09

where Q_m is the mechanical quality factor, f_r and f_a are the resonant and antiresonant frequency, respectively. *R and C* are the resonant resistance and capacitance at 1 kHz, respectively.

The ferroelectric loops were measured in a Radiant ferroelectric tester.

3 Results and discussion

Figure 1 shows the XRD patterns of CuO doped KNLNSx–BZ ceramics sintered at 1100 °C. It can be seen that pure perovskite phase was obtained for all compositions. Which suggest that there is no change in the crystal structure of KNLNS–BZ ceramics with Cu substitution in a small amount.

This is because the ionic radius of Cu^{2+} (0.73 Å) is similar to that of Nb^{5+} (0.64 Å) and could substitute it into the *B* site of the perovskite structure [23, 24]. Furthermore, the substitution on *B* site is energetically more favorable than the *A* site [24].

Figure 2 shows the SEM images of CuO doped KNLNSx–BZ samples sintered at 1100 °C. The images were taken over fractured samples, so that few pores are observed. In general, high density was achieved for all compositions, with more than 94 % of theoretical value (4.51 g/cm^3 was taken as reference). Also, chemical analysis was done over the samples, looking for secondary phases, because in these materials is common to find non-desirable phases resulting from volatilization of sodium/potassium. The most common secondary phase is a potassium rich with tungsten–bronze crystal structure [2]. The results from the EDS analysis and chemical mapping is shown in Fig. 3 for the sample with x = 0.07. The chemical mapping revealed a homogeneous distribution of elements, which confirm the pure perovskite phase encountered by DRX. Moreover, the analysis was similar for all CuO-doped compositions studied.

In Fig. 4, the ferroelectric loops are observed. From this image it is clearly seen that the remnant polarization decreases with the increasing amount of Sb^{5+}.

This behavior would be the result of the shift of the rhombohedral–tetragonal (*R–T*) phase transition from room temperature. Also, the E_C was found to decrease in the same manner. As the *R–T* coexistence shifts, the polarizability of the CuO doped KNLNSx–BZ ceramics becomes much harder.

In Fig. 5, the permittivity and dielectric losses (tan δ) versus temperature are shown. Considering the XRD, and seeing the dielectric curves, it is possible to observe that

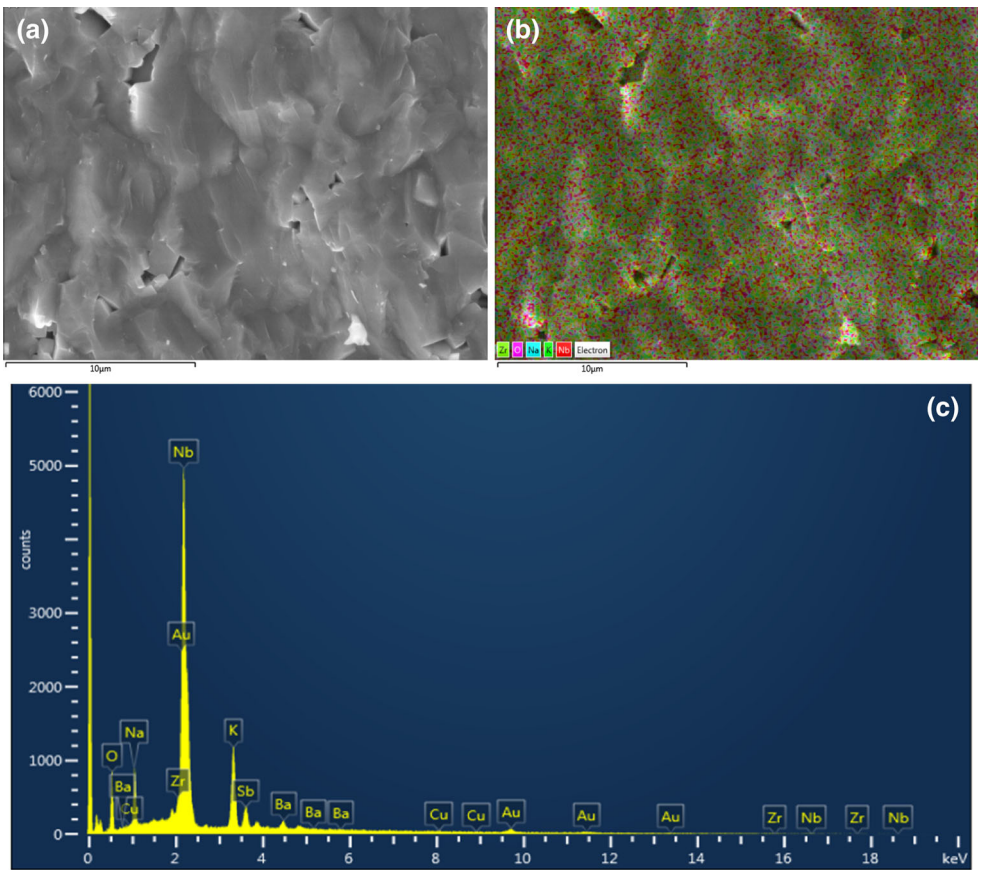

Fig. 3 **a** SEM area analyzed, **b** chemical mapping results and **c** EDS graph for sample with 0.07 of Sb^{5+}

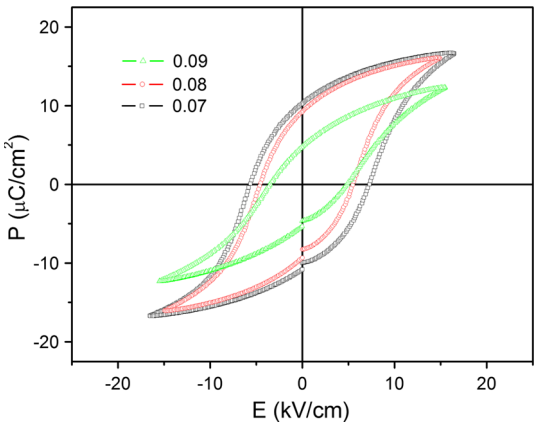

Fig. 4 Ferroelectric loops for KNLNSx–BZ–CuO ceramics sintered at 1100 °C for 4 h

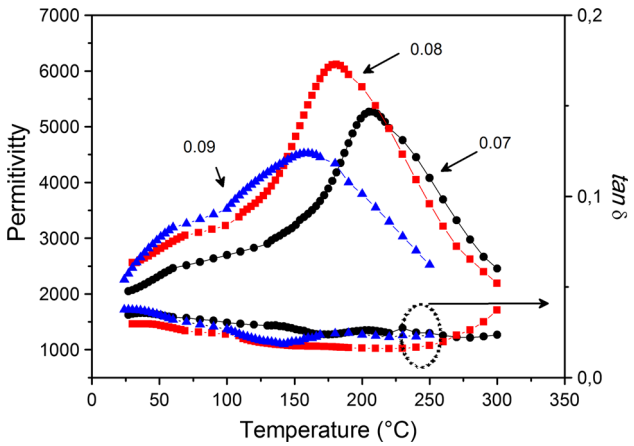

Fig. 5 Permittivity and dielectric losses for CuO doped KNLNSx–BZ ceramics sintered at 1100 °C for 4 h

there are two phase transitions for x = 0.07, the coexistence of rhombohedral–tetragonal (*R–T*) polymorphic phase transition near room temperature. This has been identified in other similar compositions [12, 25], and the Curie temperature (T_C) close to 210 °C. As the amount of Sb^{5+} increases the T_C diminishes and reach 160 °C for x = 0.09. On the other hand, the dielectric losses remain low along the temperature range (tan δ < 3 %) for all compositions.

The piezoelectric properties for CuO doped KNLNSx–BZ ceramics are summarized in Table 1. Analyzing the results and comparing them with other reports, the piezoelectric constant d_{33} for KNLNSx–BZ–CuO, is higher compared with KNN derived solid solutions doped with CuO [5, 14–16]. Moreover, comparing the combined d_{33} and mechanical quality factor (Q_m), the KNLNSx–BZ–CuO have better properties. For example, LS–CuO doped KNN has slightly better d_{33} (~260 pC/N) but much more lower Q_m (~140) [26]. Also, the KNLNSx–BZ–CuO has better

Table 1 Piezoelectric properties of KNLNS–BZ–CuO ceramics

Composition	d_{33} (pC/N)	$-d_{31}$ (pC/N)	k_p (%)	Q_m	ρ (g/cm^3)
0.07	241	88	37.5	776	4.26
0.08	240	93	35.3	740	4.24
0.09	147	56	20.5	740	4.25

performance than KNN doped with CuO, $LiNbO_3$, $LiSbO_3$ and $BiScO_3$ [14, 27, 28]. Then, the properties obtained in the KNLNSx–BZ–CuO ceramics with 0.07 and 0.08 of Sb^{5+} are promising materials for high power applications.

4 Conclusions

$BaZrO_3$–Sb–Cu co-doped KNN ceramics with perovskite structure were prepared via conventional solid state method. CuO addition on KNLNSx–BZ ceramics has promoted the enhancement of Q_m, which is almost ten times higher than in pure KNLNSx–BZ. Furthermore, high piezoelectric properties were obtained for KNLNSx–BZ with x = 0.07 and 0.08 of Sb^{5+} doping. These good properties makes these materials suitable for high power applications like piezoelectric transformers.

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