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Effect of CuO on dielectric and piezoelectric properties of $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.87}Ta_{0.06}Sb_{0.07})O_3$ ceramics

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ABSTRACT

In this paper, the effects of CuO addition on microstructure and electrical properties of $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.87}Ta_{0.06}Sb_{0.07})O_3$ (abbreviated as KNLNST) ceramics were studied to develop KNLNST with high mechanical quality factor Q_m and low dielectric loss $\tan\delta$. The results of this work suggest that both "hard" and "soft" effects were observed due to CuO addition, which enhanced the Q_m and planar mode electromechanical coupling factors k_p, and reduced the piezoelectric coefficient d_{33}, coercive field E_c, dielectric constant ε_r and $\tan\delta$. High dielectric and piezoelectric properties of $\varepsilon_r = 1304$, $d_{33} = 241$ pC/N, $k_p = 0.437$ and $Q_m = 138$ were obtained for the specimens containing 1 mol% CuO. Particularly, $\tan\delta$ at 1 kHz can be reduced from 0.038 for KNLNST ceramics to 0.0087 for 1 mol% CuO-added KNLNST ceramics.

1. Introduction

In recent years, $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based ceramics have been extensively studied as one of the promising lead-free piezoelectric materials for replacing $PbTiO_3$-$PbZrO_3$ (PZT) based piezoelectric ceramics [1–3]. The densification of pure KNN ceramics is problematic but it can be improved by substituting Nb for Ta or Sb, Na and K for Li [4–7]. However, these ceramics have a drawback for power device applications due to some "soft" characteristics such as very low Q_m (30–50) and high $\tan\delta$ [8]. Previous researches revealed that high Q_m can be obtained in KNN-based piezoceramics doped with $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ [9], MnO_2 [10,11], $CuNb_2O_6$ [12] or CuO [13,14]. For example, M. Matsubara et al. [9] reported that a high Q_m value of 680 was achieved for 0.23 mol% $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$-added $(K_{0.5}Na_{0.5})(Nb_{0.7}Ta_{0.3})O_3$ ceramics. Lin et al. [10] explored the effects of MnO_2 doping on electromechanical properties of $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3$ lead-free ceramics, and the Q_m values increased from 6 to 123 with MnO_2 content increasing form 0 to 0.5 mol%. Alkoy and Papila [13] reported that piezoelectric properties of $d_{33} = 120$ pC/N, $k_p = 0.27$ and $Q_m = 772$ were obtained from the 1.5 mol% CuO-added KNN ceramics produced by the conventional solid state reaction method. Moreover, CuO itself is a good low-temperature sintering aid.

The present study is a continuation of our previous work [15]. The $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.87}Ta_{0.06}Sb_{0.07})O_3$ ceramics were prepared by the conventional sintering method in the work. However, the usage of the ceramics system is undesirable for high power transducer applications, due to its low mechanical quality factor ($Q_m = 39$) and high dielectric loss ($\tan\delta = 0.038$). Therefore, CuO (0.5–2 mol%) were added to the KNN-based ceramics to enhance Q_m and reduce $\tan\delta$, and the microstructure and electromechanical properties were systematically investigated.

2. Experimental

A conventional ceramic fabrication technique was used to prepare $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.87}Ta_{0.06}Sb_{0.07})O_3$ ceramics using analytical-grade metal oxides or carbonate powders: K_2CO_3 (99%), Na_2CO_3 (99.8%), Li_2CO_3 (98%), Nb_2O_5 (99.5%), Ta_2O_5 (99.99%), and Sb_2O_3 (99.5%). The stoichiometric powders were mixed by ball-milling in ethanol for 12 h and then dried and calcined at 900 °C for 5 h. After the calcination, KNLNST and CuO (99%) powders were weighted according to the formula of KNLNST + x mol% CuO (x = 0.5, 1, 1.5 and 2) and ball milled for 12 h and dried. The obtained powders were mixed with 3 wt% polyvinyl alcohol (PVA) solution, and then uniaxially pressed into pellets with a diameter of 1.5 cm under 300 MPa pressure, subsequently, sintered in air at 1040–1120 °C for 3 h.

The densities of the sintered samples were obtained by the Archimedes method. The crystal structure was determined using X-ray powder diffraction (XRD) with a Cu Kα radiation (Bruker D8 Advance). The microstructure was observed by using a scanning electron microscope (SEM, JSM-6300). The average grain size was determined using Fullman's method. For the measurement of dielectric and piezoelectric properties, silver paste electrodes were formed at the two circular surfaces of the disk-shaped specimens after firing at 550 °C for 10 min. Dielectric properties as a function of temperature and frequency were measured by an impedance analyzer (HP4294A). Polarization versus electric field hysteresis loops were measured using a ferroelectric test system (TF Analyzer 2000). Before measuring the relevant electrical

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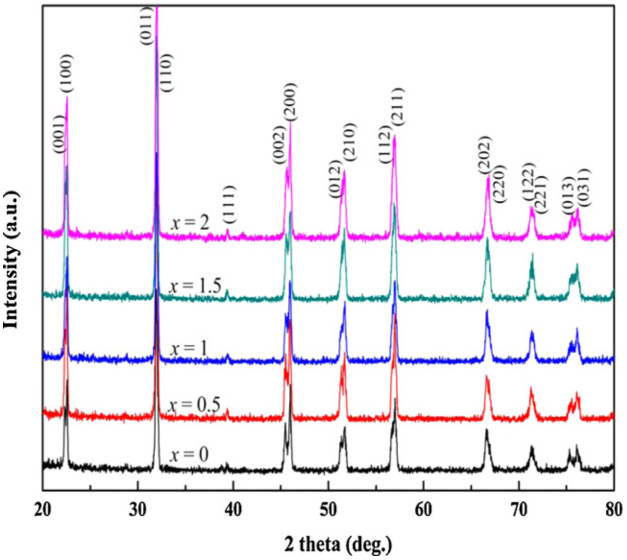

Fig. 1. X-ray diffraction profiles of KNLNST + *x* mol% CuO ceramics.

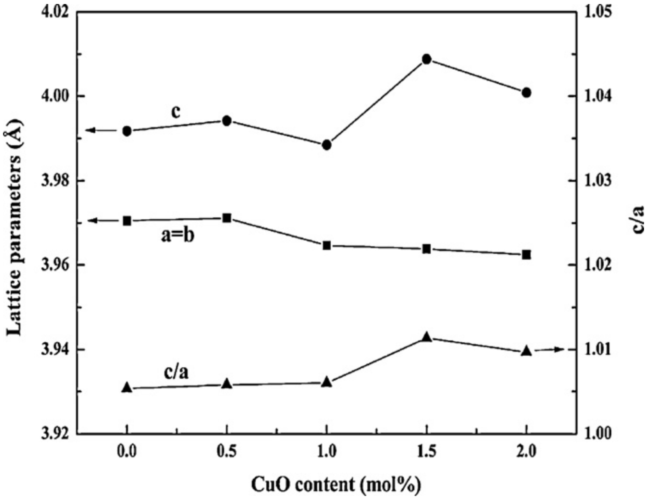

Fig. 2. Lattice parameters and *c*/*a* ratio of KNLNST + *x* mol% CuO ceramics.

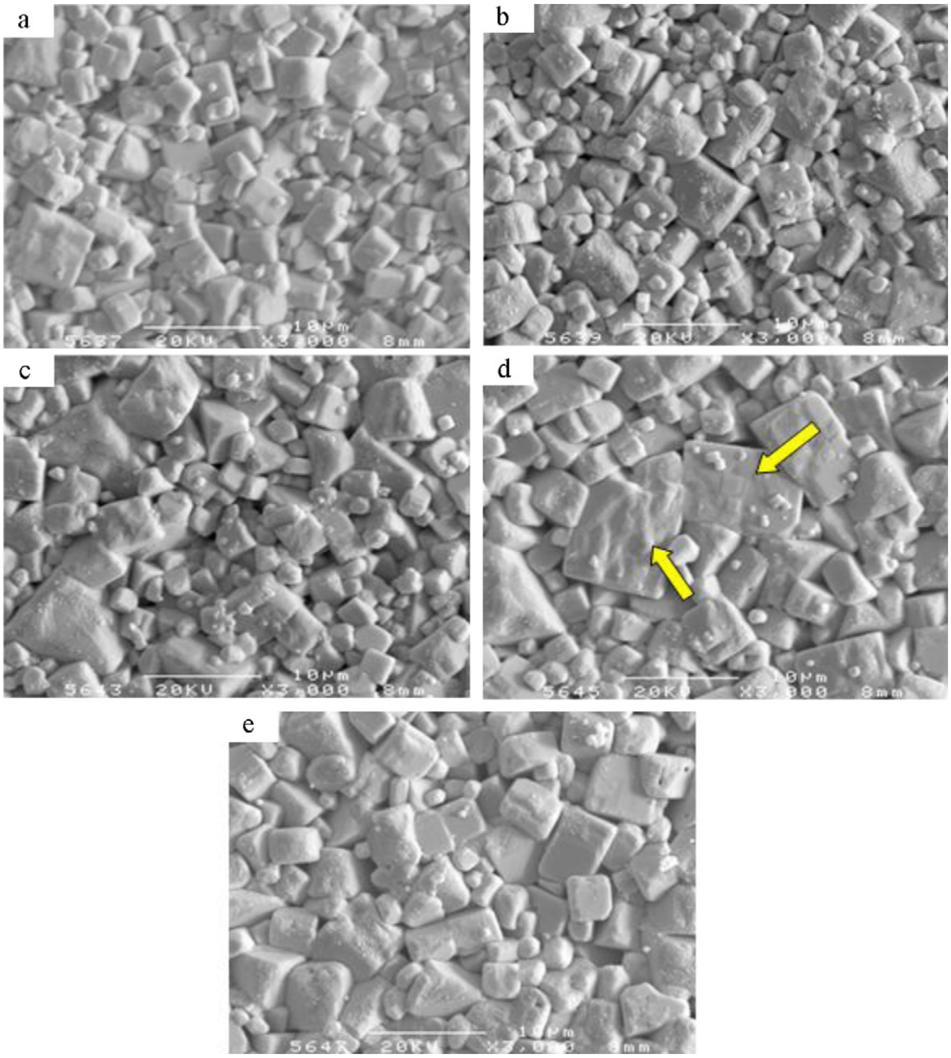

Fig. 3. SEM micrographs of the surface of KNLNST + *x* mol% CuO ceramics, (a) *x* = 0, sintered at 1120 °C for 3 h, (b) *x* = 0.5, (c) *x* = 1, (d) *x* = 1.5, (e) *x* = 2, sintered at 1080 °C for 3 h.

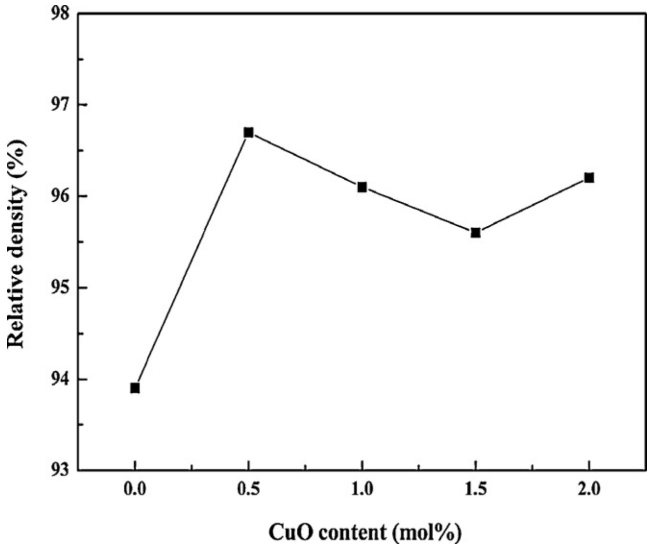

Fig. 4. The relative densities of KNLNST + x mol% CuO ceramics.

properties, the sintered samples were poled under 3 kV/mm bias at 110 °C in a silicone oil bath for 30 min and then aged at room temperature for 24 h after poling. The electromechanical coupling factors k_p and mechanical quality factor Q_m were determined by the resonance-antiresonance method according to the IEEE Standards using an impedance analyzer (HP4294A). The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric constant testing meter (ZJ-3A).

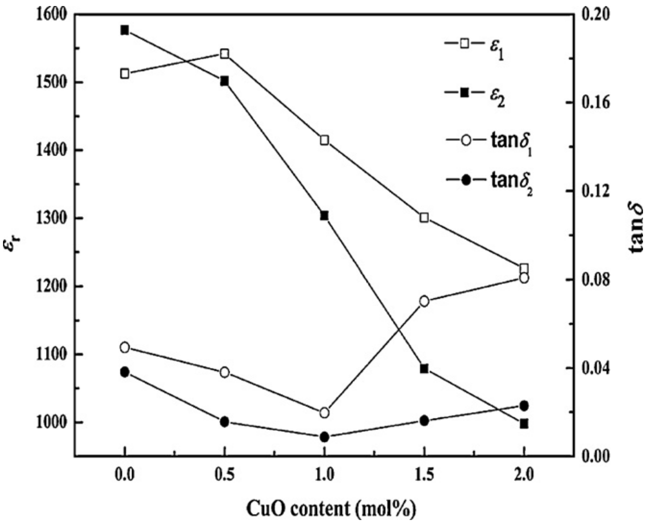

Fig. 5. Dielectric constant and dielectric loss of KNLNST + x mol% CuO ceramics before (ε_1, $\tan\delta_1$) and after (ε_2, $\tan\delta_2$) poling.

3. Results and discussion

Fig. 1 shows X-ray diffraction profiles of the KNLNST + x mol% CuO ceramics, with $x = 0$ sintered at 1120 °C for 3 h, and $0.5 \leq x \leq 2$ sintered at 1080 °C for 3 h. It can be seen that all samples with

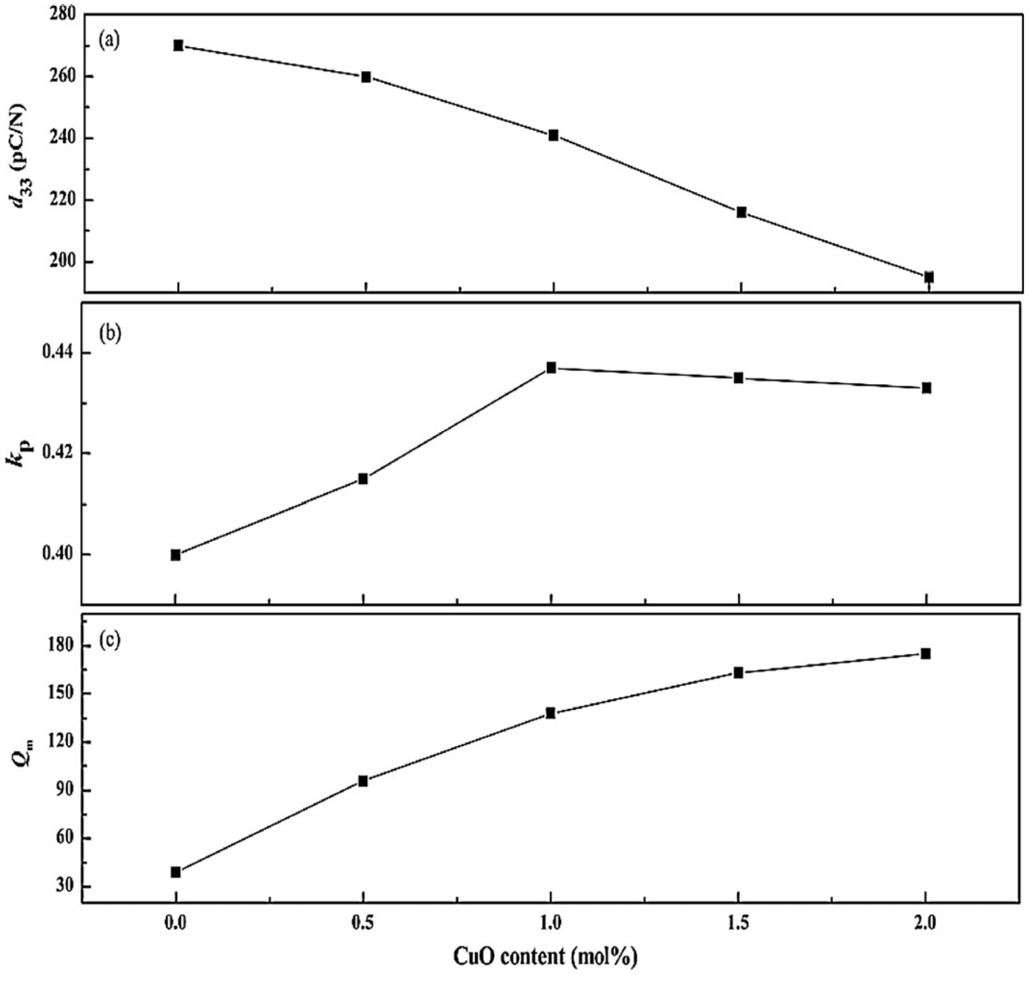

Fig. 6. Variations of d_{33}, k_p, Q_m of KNLNST + x mol% CuO ceramics.

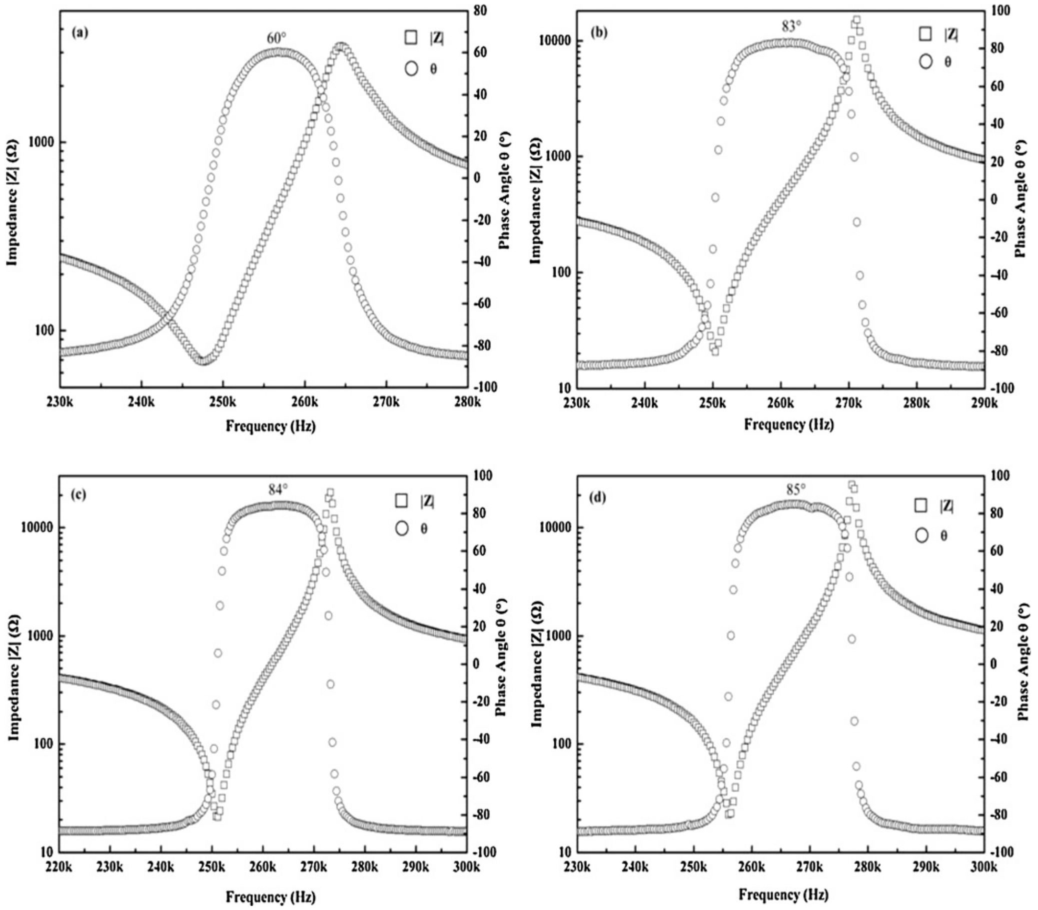

Fig. 7. Impedance $|Z|$ and phase angle θ as functions of frequency for KNLNST + x mol% CuO ceramics in the k_p mode (a) $x = 0$, (b) $x = 1$, (c) $x = 1.5$, (d) $x = 2$.

the studied composition range exhibit a tetragonal phase without a secondary phase. This suggests that CuO has diffused into the KNLNST lattices to form a new homogeneous solid solution. Cu^{2+} may replace both A and B sites, because of the ionic radius of Cu^{2+} (0.73 Å) is smaller than A-site ions (K^+: 1.38 Å, Na^+: 1.02 Å, Li^+: 0.76 Å) and larger than B-site ions (Nb^{5+}: 0.64 Å, Ta^{5+}: 0.64 Å, Sb^{5+}: 0.60 Å) [16] of KNLNST ceramics. However, Li et al. [17] reported the presence of second phase $K_4CuNb_8O_{23}$ in the CuO added $(K_{0.44}Na_{0.52}Li_{0.04})(Ta_{0.1}Sb_{0.04}Nb_{0.86})O_3$ ceramic when the CuO addition exceeded 0.1 wt%. The disparity in results could be attributed to the slight compositional difference, different powder precursors, different processing procedure, and different amounts of CuO [18]. Fig. 2 illustrates lattice parameters and c/a ratio as a function of the amount of CuO content. The calculation for lattice parameters was done from a tetragonal primitive cell. The tetragonality (c/a ratio) of the ceramics increased with increasing x form 0 to 1.5. Qualitatively, these changes implied that the CuO doping induced a lattice distortion of the KNLNST ceramics.

Fig. 3 shows the microstructures of KNLNST ceramics doped with different amounts of CuO ($x = 0$, 0.5, 1, 1.5 and 2). All the ceramics show a bimodal distribution with many fine grains being located at the boundaries of coarse grains. A homogeneous microstructure with a small grain size (3–4 μm) was formed in pure KNLNST ceramics. With CuO addition, the enlarged grains was developed and the specimens with $x = 1.5$ showed abnormally grown grains, as indicated by the arrow in Fig. 3(d). An angular grain with a flat surface is typically observed in the abnormal grain growth in the presence of the liquid phase [19]. In order to identify the composition, the small grains and abnormal grains of KNLNST + 1.5 mol% CuO ceramics underwent energy-dispersive spectroscopy (EDS) analysis, and the results of the composition analysis are shown in Table 1, which shows the two types of grain own similar chemical composition. The concentration and the distribution of Li cannot be detected by the EDS technique. Densities of ceramics were also increased with CuO-doped, which might be explained by the liquid-phase sintering. The relative densities of KNLNST + x mol% CuO ceramics are shown in Fig. 4. All samples were fully densified and relative densities up to 95% after the addition of CuO. In addition, the small grain size (4–5 μm) of the specimens with $x = 2$ could be attributed to the increased liquid phase, which was explained by the impingement of the grains in the early stage of the grain growth, leading to the development of a microstructure with small grains [20]. However, it was very difficult to find liquid phase, implying that the liquid phase formed during the sintering could be a transient liquid phase, with a high solubility in the KNLNST ceramics that led to its eventual disappearance with sintering time [21]. Moreover, grain morphology changed from sharp-cornered cubical grains with smooth surfaces to cut-cornered grains with rough surfaces, because of introducing the Cu^{2+} might alter the growth behavior of the grains by decreasing the surface energy [18].

Fig. 5 shows the values of dielectric constant and dielectric loss of the ceramics before (ε_1, $\tan\delta_1$) and after (ε_2, $\tan\delta_2$) poling as a function of CuO content at 1 kHz. Both ε_1 and ε_2 values decreased with increasing x. ε_2 decreased compared with ε_1 at $0.5 \le x \le 2$, however, after poling treatment, the pure KNLNST ceramics showed a larger dielectric constant than that of the unpoled sample. The dielectric constant ε_2 decreased monotonically from 1577 to 998 as x increases from 0 to 2. While both $\tan\delta_1$ and $\tan\delta_2$ values firstly decreased with increasing x, and then it began to increase on further increasing x to 2. All the $\tan\delta_2$ values

Table 1
Chemical composition of small grains and abnormal grains of KNLNST + 1.5 mol% CuO ceramics from EDS spectra (at.%).

Element	K	Na	Nb	Sb	Ta	Cu	O
Small grains	7.81	12.62	21.21	0.99	1.82	1.23	54.32
Abnormal grains	8.55	10.16	20.38	1.26	1.55	1.63	56.47

decreased compared with the tan δ_1 values. The minimum value of 0.0087 of dielectric loss tan δ_2 was obtained at $x = 1$, which was a quarter of that of undoped ceramics. Furthermore, with increasing CuO content, the difference between that of a poled sample and an un-poled sample increased. This result indicates that the crystallographic anisotropy of KNLNST ceramics increased with increasing CuO content [22].

Fig. 6 shows the variations of d_{33}, k_p, Q_m with x for KNLNST + x mol% CuO ceramics. After the addition of CuO, The d_{33} values decreased gradually from 270 to 195 pC/N with increasing x form 0 to 2. The decrease in piezoelectric coefficient could be due to the "hard" effect of CuO, which lowers the piezoelectric coefficient and the dielectric loss. The k_p values slightly increased and then decreased with increasing CuO content, giving a maximum value of 0.437 at $x = 1$, which may have been due to the improvement in densification. The increased grain size as shown in Fig. 3 might also have contributed to the increased k_p values because the domain rotation was eased for large-grained specimens [23]. The Q_m values increased monotonically with increasing CuO content to 175 for the KNLNST ceramic containing 2 mol% CuO. However, Q_m was only 39 for the pure KNLNST ceramics. The improvement of Q_m value may be due to the "hard" effect of the Cu^{2+}. The rise of Q_m was accompanied by the decline of dielectric loss tan δ_2 as shown in Fig. 5, which may be because of the addition of Cu^{2+} has reduced the energy loss of the KNLNST system by restricting the domain wall motions. The high Q_m is desirable especially for high power ultrasonic applications, where the energy loss and generated heat are critical factors affecting the performance of transducer.

Fig. 7 shows the impedance magnitude $|Z|$ and phase angle θ as functions of frequency for the KNLNST + x mol% CuO ceramics with $x = 0$, 1, 1.5, and 2 at the planar-mode resonance. It has been known that θ will have a value of 90° in the frequency range between the anti-resonance and resonance frequencies under the ideal poling state. For the KNLNST ceramics, the observed θ was low, approximately 60°. After the addition of CuO, the observed θ for the KNLNST + x mol% CuO ceramics became larger than 83°, indicating that it is easier to pole successfully the ceramics. The doping of CuO can improve the poling state of the ceramics. In addition, the resonance impedance of KNLNST + x mol% CuO ceramics were 80 Ω when $x = 0$ and 20 Ω when $x = 2$, however, the Q_m value is inversely proportional to the resonance impedance, which can be seen from the increased Q_m values with increasing CuO content as shown in Fig. 6(c).

Temperature dependence of relative permittivity and dielectric loss (measured at 10 kHz) of KNLNST + x mol% CuO ceramics are shown in Fig. 8. There were two anomalisms within the measured temperature range from room temperature to 400 °C. These anomalisms are considered to correspond to the two phase transitions from orthorhombic phase to tetragonal phase at lower temperature ($T_{\text{O-T}}$) and from tetragonal phase to cubic phase at higher temperature (T_C), respectively. As can be seen from Fig. 8(a), both $T_{\text{O-T}}$ and T_C slightly shifted toward higher-temperature regions by increasing the content of CuO. The $T_{\text{O-T}}$ and T_C were 59 °C and 258 °C at $x = 0$, and were 75 °C and 265 °C at $x = 2$. After the addition of CuO, all the ceramics had lower dielectric loss compared to the undoped ceramic at temperature <250 °C. While at the temperatures >250 °C and particularly above T_C, the addition of CuO resulted in a sharp increase in dielectric loss values. That may be due to a decrease in bulk resistivity of KNLNST ceramics at higher temperatures, where the ceramic becomes electrically conductive. Moreover, we noticed that a peculiar inconsistency between the $T_{\text{O-T}}$ values obtained in dielectric measurement and the actual crystalline structure revealed by the XRD profiles. As shown in Fig. 8(a), it indicated that all the ceramics should be orthorhombic phases at room temperature, whereas the XRD profiles actually showed that their dominant phases were the tetragonal structures as shown in Fig. 1. Similar phenomenon has also been observed in the ceramics doped with Li [24,25]. The inconsistency may arise from the coexistence of two phases as indicated by the peak broadened corresponding to $T_{\text{O-T}}$, but needs to be further clarified.

In order to characterize the ferroelectricity, polarization-field (P–E) hysteresis loops of KNLNST + x mol% CuO ceramics were evaluated at room temperature as shown in Fig. 9. As shown in Fig. 9(a), samples prepared with additions of CuO exhibited well saturated P–E hysteresis loops with reducing hysteresis loop areas, which shows the amount of dissipated energy in the form of heat. The larger the area of hysteresis loop, the higher the energy required to reverse dipoles. The results of P–E hysteresis loops were in good agreement with the dielectric loss measurements as shown in Fig. 5. Fig. 9(b) shows the effect of CuO on remanent polarization (P_r) and coercive field (E_c). Both P_r and E_c decreased gradually with increasing CuO content from 0 to 2 mol%. The decrease of E_c may be due to the decrease of oxygen vacancies pinning the domain wall motion. When KNLNST ceramics were modified by Cu^{2+} ions as donor ions

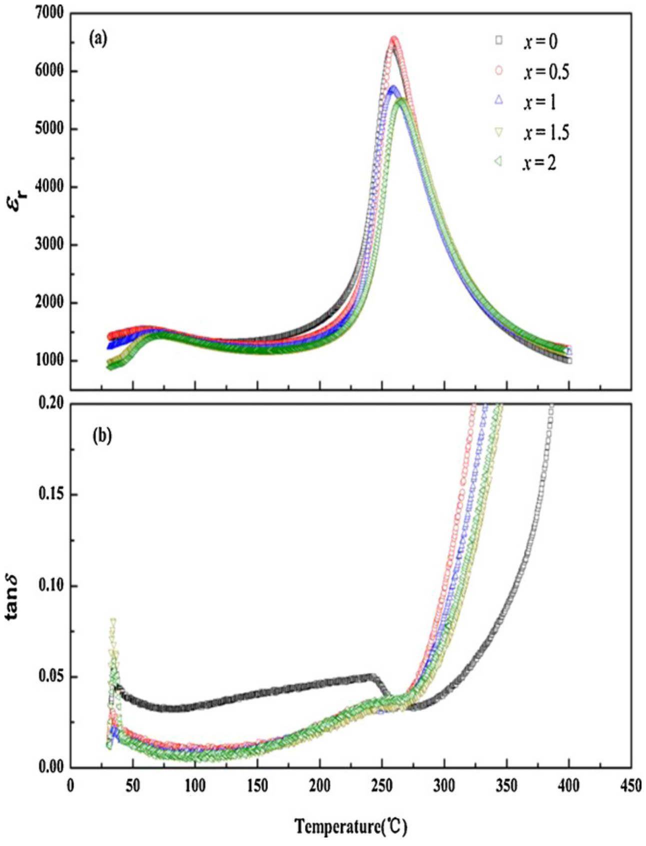

Fig. 8. Temperature dependence of relative permittivity (ε_r) and dielectric loss (tan δ) of KNLNST + x mol% CuO ceramics, measured frequency: 10 kHz.

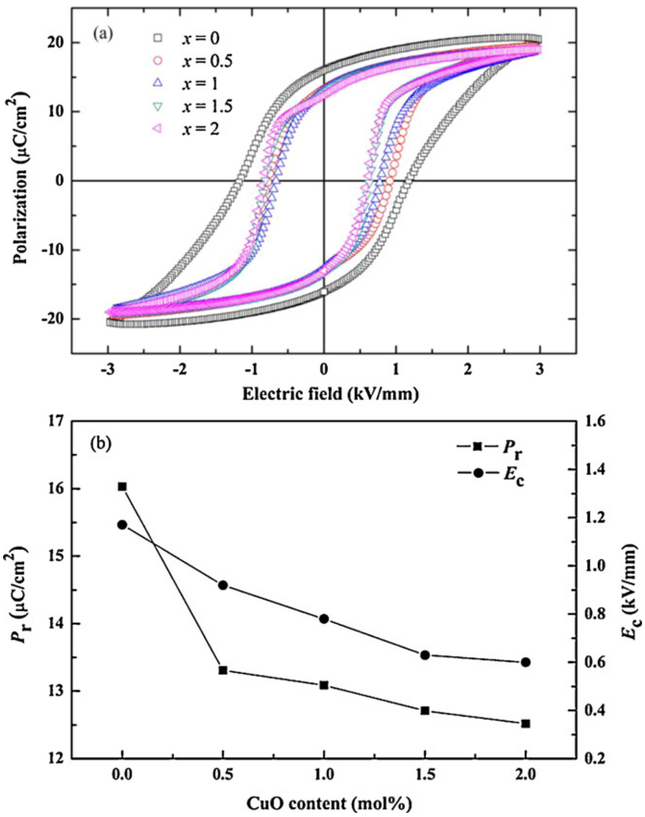

Fig. 9. (a) Polarization-field response of KNLNST + x mol% CuO ceramics, and (b) remanent polarization (P_r) and coercive field (E_c) as a function of the amount of CuO added.

(A-site replacement), oxygen vacancies were reduced to keep the charge neutrality [17]. However, the high Q_m values as shown in Fig. 6(c) were assumed to be responsible for “hardening” effect of the Cu^{2+}-doped KNLNST ceramic, which could increase E_c by B-site acceptor substitution. In contrast, the improvement of Q_m and the decline of E_c implied that Cu^{2+} could be substituted in both A- and B-sites. Shen et al. [26] considered that this phenomenon may be attributed to the doping of Li^+, and a portion of Cu^{2+} ions can enter into A-site to substitute Li^+ as a donor dopant because of their close ionic radius.

4. Conclusions

In this study, the effects of CuO doping (0.5–2 mol%) on microstructure, dielectric, ferroelectric and piezoelectric electromechanical properties of $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.87}Ta_{0.06}Sb_{0.07})O_3$ system were investigated. Addition of CuO to KNLNST structure increased the grain size and modified the morphology of grains from sharp-cornered cubical grains with smooth surface to cut-cornered grains with rough surfaces. Compared with pure KNLNST ceramics ($Q_m = 39$, $k_p = 0.40$, $\tan\delta = 0.038$, $\varepsilon_r = 1577$, $d_{33} = 270$ pC/N), Q_m increased more than three times while the d_{33} value only decreased by 10.7% for the KNLNST + 1 mol% CuO ceramics ($Q_m = 138$, $k_p = 0.437$, $\tan\delta = 0.0087$, $\varepsilon_r = 1304$, $d_{33} = 241$ pC/N). The results of this study suggest that the CuO addition not only induces some “hard” effects such as increment of Q_m, reduction of d_{33} and ε_r, but also causes some “soft” effects such as increment of k_p and reduction of E_c.

Acknowledgments

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