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Enhancement of Q_m in CuO-doped compositionally optimized Li/Ta-modified (Na,K)NbO_3 lead-free piezoceramics

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Abstract

The effects of CuO on electrical properties of compositionally optimized Li/Ta-modified (Na,K)NbO_3 (LT-KNN) piezoceramics were studied to develop LT-KNN with high mechanical quality factor Q_m and low dielectric loss tg δ as well as relatively high piezoelectric constant d_{33} for actuator applications. Both ''hard'' and ''soft'' effects were observed due to CuO addition, and the discussion related to high Li doping amount was presented to explain this phenomenon. By increasing CuO addition, the d_{33} gradually decreases while the Q_m increases significantly. Particularly, tg δ at 1 kHz can be reduced from ~2.7% for LT-KNN ceramics to ~0.8% for CuO-added LT-KNN ceramics. When the CuO addition is lower than 1 mol%, both high Q_m (~323) and relatively high d_{33} (>180 pC/N) can be obtained, in addition to a relatively high dielectric constant $\varepsilon_r \sim 500$.

Keywords: C. Piezoelectric properties; Lead free; KNN; Defect structure

1. Introduction

(Na,K)NbO_3-based ceramics have been extensively studied as one of the promising lead-free piezoelectric materials [1–4]. However, these ceramics have a drawback for power device applications due to some ''soft'' characteristics such as very low Q_m (~40–50) and high tg δ [5]. Previous reports revealed that high Q_m can be obtained in (Na,K)NbO_3-based piezoceramics doped with $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$, CuO or MnO_2, but their d_{33} usually was of a low level (<110 pC/N) [6,7]. Since Q_m and d_{33} are the same important for power device applications, enhancing Q_m while maintaining relatively high d_{33} are extraordinarily desired for (Na,K)NbO_3-based piezoceramics. Meanwhile, tg δ should also be lowered from the point view of reducing energy loss for the devices under working conditions.

In this work, we first prepared compositionally optimized Li/Ta-modified (Na,K)NbO_3 (LT-KNN) piezoceramics by the conventional sintering method. Then, based on this LT-KNN ceramic, CuO was introduced for the purpose of enhancing Q_m. The effects of CuO on dielectric, piezoelectric and ferroelectric properties of the LT-KNN ceramics were studied systematically.

2. Experimental

$(Na_{0.535}K_{0.485})_{0.93}Li_{0.07}(Nb_{0.942}Ta_{0.058})O_3 + x$ mol% CuO ($x = 0, 0.5, 1, 1.5$) ceramics were prepared by a conventional method as reported previously [3]. The optimized sintering temperature was 980 °C (for $x = 0$ and 0.5) and 960 °C (for $x = 1$ and 1.5). X-ray diffraction (XRD) characterization was performed using Cu$K\alpha_1$ radiation filter through Ni foil. The Curie temperature of sintered ceramics was evaluated by differential scanning calorimetry (DSC) analysis.

Room temperature dielectric constant and loss were measured using an Agilent 4194A precision impedance analyzer at 1 kHz. For piezoelectric and electromechanical measurements, the ceramic samples were poled at 130 °C for 30 min under an electric field of 3 kV/mm in silicone oil. The d_{33} was measured using a quasi-static piezoelectric constant testing meter (ZJ-3A). The k_p was determined by a resonance and anti-resonance method performed on the basis of *IEEE* standards using an impedance analyzer (Agilent 4194A). A ferroelectric test module (AixACCT TF Analyzer 1000, Germany) was employed to measure the polarization–electric

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field (P–E) hysteresis loops at the frequency of 1 Hz at room temperature for the poled samples.

3. Results and discussion

As shown in Fig. 1, the samples have a single perovskite phase regardless of the CuO doping up to 1.5 mol%, even though the sintering temperature is as low as 960–980 °C. The optimized sintering temperature for high CuO doping amounts ($x = 1$ and 1.5) was reduced to 960 °C from 980 °C for those without and with low CuO addition ($x = 0$ and 0.5), because CuO itself is a good sintering aid. For $x = 0$ and 0.5, the intensity of (2 2 0) and (0 0 2) peaks is close, indicating that the amount of orthorhombic and tetragonal phases is almost same. While for $x = 1$ and 1.5, the phase structure is more close to the orthorhombic symmetry, which can be deduced from the fact that (2 2 0) peak is slightly stronger than (0 0 2) peak. This phenomenon should be attributed to the following two reasons: the partially suppressed volatilization of alkali metal ions at low sintering temperature, in addition to the large CuO addition amount, as reported by Ahn et al. [8].

Fig. 2 shows the DSC heating curves of LT-KNN + x mol% CuO ceramics, while the inset gives the Curie temperature (T_c) determined by the endothermic peak of the DSC curves. A high T_c of 430 °C is obtained for the LT-KNN ceramics without CuO. By increasing CuO addition, the T_c linearly decreases to 417 °C for the LT-KNN ceramics with 1.5 mol% CuO.

Fig. 3 shows the d_{33}, k_p, and Q_m of LT-KNN + x mol% CuO ceramics as a function of CuO amount. The d_{33} and k_p gradually decrease with CuO addition. However, significant enhancement of Q_m can be observed due to CuO addition. Especially for the LT-KNN + 1 mol% CuO ceramics, Q_m can be enhanced to 323, which is nearly five times that of pure LT-KNN ceramics ($Q_m = 69$). On the other hand, the d_{33} value only decreases 26% from 250 pC/N for pure LT-KNN ceramics to 185 pC/N for the LT-KNN + 1 mol% CuO ceramics. The dielectric constant and loss of LT-KNN + x mol% CuO ceramics as a function of CuO amount is shown in Fig. 4. As the case of d_{33} and k_p, the ε_r also gradually decreases with increasing CuO amount. However, the tg δ has some different behavior, i.e., first decreases and then suddenly increases. It can be reduced to lower than 1.0% for the CuO addition $x \leq 1$.

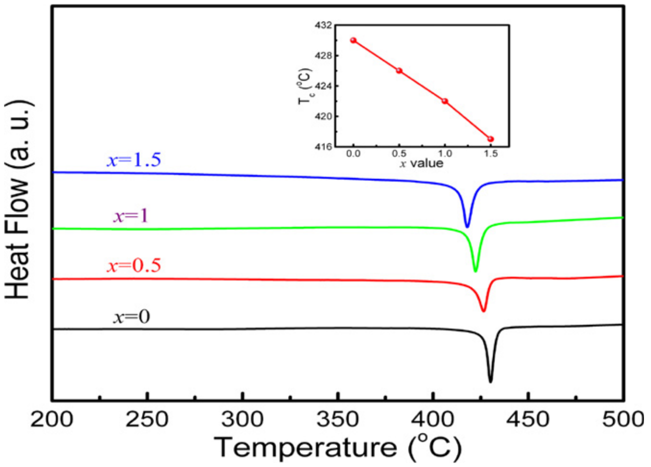

Fig. 2. DSC heating curves of LT-KNN ceramics containing x mol% CuO.

As shown in Fig. 5, well-saturated hysteresis loops can be obtained under an electric field of 40 kV/cm for all samples. Meanwhile, ranging over all CuO amount x values, the ceramics show strong ferroelectricity with remnant polarization $2P_r > 40$ μC/cm^2. However, the coercive field $2E_c$ significantly decreases by increasing CuO amount, reaching a nearly unchangeable value of 21.6 kV/cm when $x \geq 1$. In addition, as shown in Fig. 5(a), the P–E hysteresis loop of pure LT-KNN ceramic shows a symmetrical shape. However, it can be seen from Fig. 5(b–d) that CuO addition induces the P–E hysteresis loops shifting to negative or positive direction. This phenomenon indicates that an internal bias field E_i should exist in CuO-added LT-KNN ceramic samples. The frequency dependence of the impedance magnitude Z and phase angle θ at the planar-mode resonance for the present ceramics was also measured. For LT-KNN ceramic sample without CuO, the observed θ was approximately 70.5°, but significantly increased to 81° for $x = 1$, and then decreased somewhat with further CuO addition. This result indicates that the CuO addition improves the poling of the ceramics.

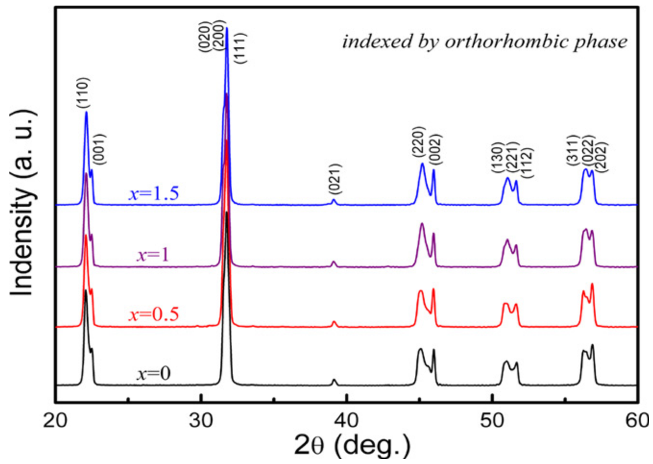

Fig. 1. XRD patterns of LT-KNN ceramics containing x mol% CuO.

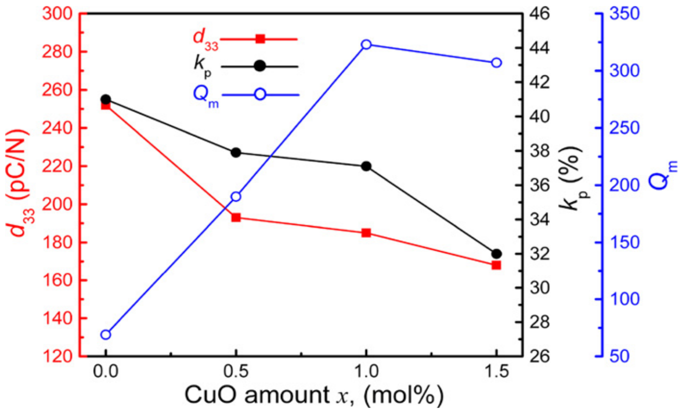

Fig. 3. d_{33}, k_p, and Q_m of the LT-KNN + x mol% CuO ceramics as a function of CuO amount.

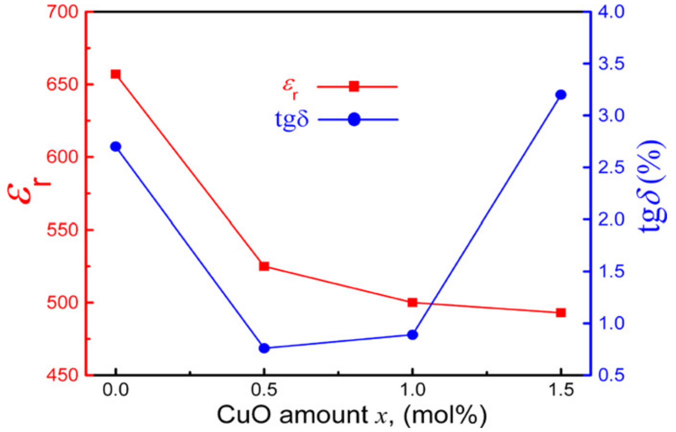

Fig. 4. Dielectric constant and loss of the LT-KNN + x mol% CuO ceramics as a function of CuO amount.

It has been widely accepted that the addition of CuO may cause hardening effects in KNN-based ceramics, because the ionic radius of Cu^{2+} is 0.72 Å, which may substitute the *B*-site ions Nb^{5+}(0.69 Å) and Ta^{5+}(0.68 Å) as an acceptor-type dopant, rather than the *A*-site ions Na^{+}(0.97 Å) and K^{+}(1.33 Å) as an donor-type one [9,10]. As stated by Li et al. [11], the Cu^{2+} ions incorporated into the *B*-site of the perovskite lattice acting as acceptors to increase oxygen vacancy concentration as follows:

$$\mathrm{Nb_{Nb}} + \frac{3}{2}\mathrm{O_O} + \mathrm{CuO} \rightarrow \mathrm{Cu_{Nb}'''} + \frac{1}{2}\mathrm{Nb_2O_5} + \frac{3}{2}\mathrm{V_O^{\bullet\bullet}} \qquad (1)$$

The charge defects, such as $\mathrm{Cu_{Nb}'''}$ and $\mathrm{V_O^{\bullet\bullet}}$, can form defect complexes with dipole character. Dipoles thus provide the pinning effect, which induces the KNN-based ceramics to show ''hard'' characteristics. According to the XRD results in Fig. 1, all ceramics show pure perovskite structure without secondary phase, and the DSC results from Fig. 2 revealed that the Curie temperature decreases with the CuO addition. These two respects indicate that CuO must enter into the lattice of LT-KNN ceramics within the added amount. Meanwhile, some acceptor-type ''hard'' effects induced by CuO addition can be found indeed, such as increment of Q_m, reduction of d_{33}, k_p, and ε_r, as shown in Figs. 3 and 4. On the other hand, from Fig. 5, the *P–E* hysteresis loops shift to negative or positive direction by doping CuO as reported by Li et al. [11]. The defects with negative and positive charges are easy to release electrons and holes, respectively, which can be equally named as space charges. These space charges are inclined to collect at domain boundaries, and then generate an internal bias field E_i. The E_i will align to the direction of the external field applied through the movements of space charges during poling. Therefore, for poled samples, under the external field applied in the hysteresis measurement, the field needed to switch the spontaneous polarization (P_s) in the negative or positive direction becomes higher due to the existence of E_i. This is the reason for the shift of the hysteresis loop to negative or positive direction for CuO-added LT-KNN ceramics. In addition, the shifting of the hysteresis loop to negative or positive side depends on the direction of the poled sample relative to the clamping jig for the hysteresis measurement.

Besides some acceptor-type ''hard'' effects induced by CuO addition were observed, interestingly some donor-type ''soft'' characteristics were also found. For example, the reduction of E_c, being indicative of ''soft'' effect, is observed in the samples

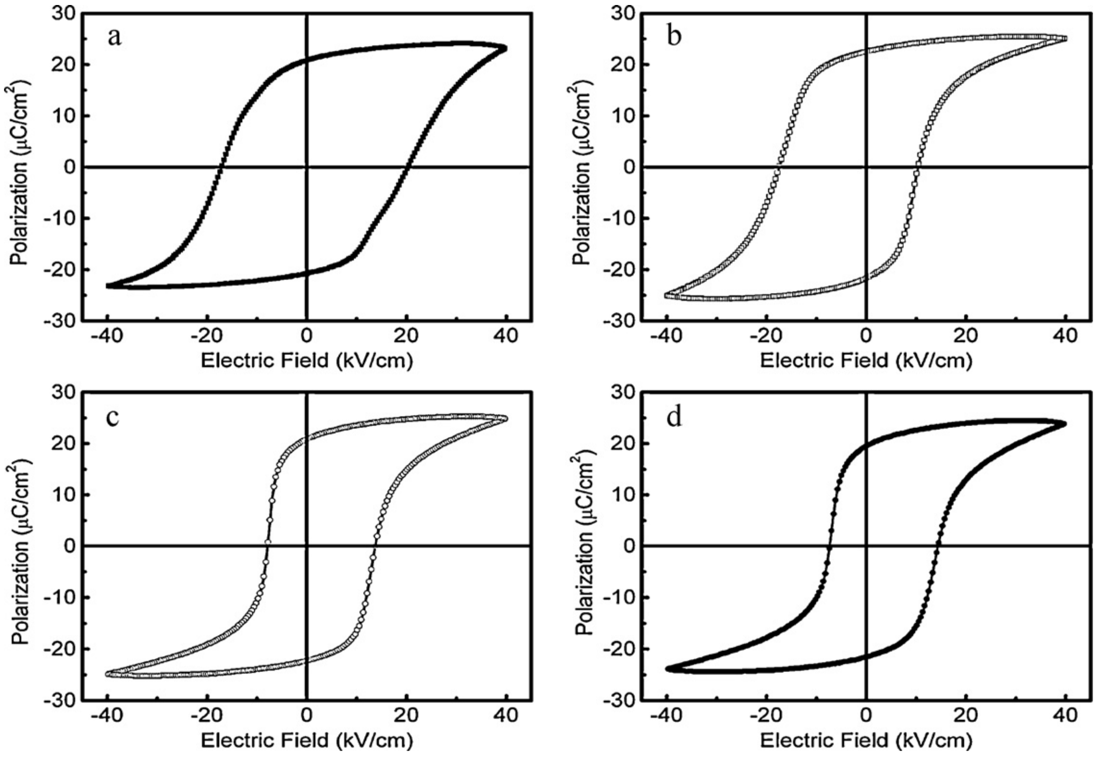

Fig. 5. *P–E* hysteresis loops of the LT-KNN + x mol% CuO ceramics: (a) $x = 0$, (b) $x = 0.5$, (c) $x = 1$, and (d) $x = 1.5$.

with $x < 1$ mol%. Meanwhile, as can be seen from the inset of Fig. 2, the T_c decreases by increasing CuO amount. Actually, in the case of $Pb(Zr,Ti)O_3$, the donor ions decrease T_c while the acceptor ions increase T_c [12]. Although the reasons of such "soft" effects induced by CuO addition are not yet well understood at present, we speculate that it should be related to high Li doping amount in this study.

$$CuO + 2Li_{Li} \rightarrow Cu_{Li}^{\bullet} + V'_{Li} + Li_2O \quad (2)$$

According to a previous work, for KNN-based ceramics without Li ions doped in *A*-site, CuO addition can improve Q_m significantly to over 1000, and even higher than 2000 [7]. These values are well above the highest Q_m value of 323 in this work. The reason of this phenomenon is that the ionic radius of Cu^{2+} is more close to the *B*-site ions Nb^{5+} and Ta^{5+} rather than the *A*-site ions Na^+ and K^+, so that such acceptor dopant will induce typical "hard" effects, and then significantly improve Q_m. However, it shows an alternative condition in high Li-containing KNN-based ceramics. As is known, although the ionic radius of Li^+ (0.68 Å) is smaller than Na^+ or K^+, Li^+ ions can still enter into *A*-site of perovskite lattice. In this case, for the CuO-added high Li-containing KNN-based ceramics, Cu^{2+} ions not only enter into *B*-site, but also have a chance to enter into *A*-site to substitute Li^+ as a donor dopant following the defect Eq. (2) because of their close ionic radius. Actually, according to the study on CuO-doped LF4 (Li-containing in *A*-site) ceramics by Li et al. [13], although they found that the CuO-doping changed the LF4 to "hard" piezoelectric ceramics with improvement of Q_m from 26 to 137, this Q_m improvement degree is largely inferior to that observed in CuO-doped KNN-based ceramics without Li ions doped in *A*-site. From their reported *P–E* hysteresis loops (see Fig. 6 in Ref. [13]), the E_c of all CuO-doped LF4 ceramics was also lower than that of pure LF4 ceramics, which shows "soft" characteristics inversely as compared to "hard" one of Q_m improvement. Meanwhile, from Fig. 4, the tg δ first decreases and then suddenly increases by increasing CuO amount, which also suggests complex "soft" and "hard" effects induced by CuO addition. Recently, Hagh et al. also found that Cu^{2+} could be substituted in both *A*- and *B*-sites for CuO-doped $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.1}Sb_{0.06})O_3$ ceramics [14].

4. Conclusions

The effects of CuO addition on the phase structure and electrical properties of LT-KNN ceramics have been investigated. Compared with pure LT-KNN ceramics ($Q_m = 69$ and $d_{33} = 250$ pC/N), Q_m increases nearly by five times while the d_{33} value only decreases by 26% for the LT-KNN + 1 mol% CuO ceramics ($Q_m = 323$ and $d_{33} = 185$ pC/N). The CuO addition not only induces some "hard" effects such as increment of Q_m, reduction of d_{33}, k_p, and ε_r, but also causes some "soft" one such as reduction of E_c and T_c. This phenomenon may be related to the high Li doping amount, 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.

Acknowledgments

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