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Short communication

Microstructure and piezoelectric properties of CuO-doped $0.95(K_{0.5}Na_{0.5})NbO_3$–$0.05Li(Nb_{0.5}Sb_{0.5})O_3$ lead-free ceramics

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Abstract

The effects of sintering temperature and the addition of CuO on the microstructure and piezoelectric properties of $0.95(K_{0.5}Na_{0.5})NbO_3$–$0.05Li(Nb_{0.5}Sb_{0.5})O_3$ were investigated. The KNN-5LNS ceramics doped with CuO were well sintered even at 940 °C. A small amount of Cu^{2+} was incorporated into the KNN-5LNS matrix ceramics and XRD patterns suggested that the Cu^{2+} ion could enter the A or B site of the perovskite unit cell and replace the Nb^{5+} or Li^+ simultaneously. The study also showed that the introduction of CuO effectively reduced the sintering temperature and improved the electrical properties of KNN-5LNS. The high piezoelectric properties of $d_{33} = 263$ pC/N, $k_p = 0.42$, $Q_m = 143$ and $\tan\delta = 0.024$ were obtained from the 0.4 mol% CuO doped KNN-5LNS ceramics sintered at 980 °C for 2 h.

Keywords: Lead-free; KNN; CuO addition; Low temperature sintering; Piezoelectric properties

1. Introduction

Among all lead-free piezoceramics $(KNa)_{0.5}NbO_3$ (KNN) has drawn much attention since the breakthrough made by Saito et al.[1] However, the piezoelectric coefficient, d_{33} of pure KNN is considerably low.[2,3] It seems undesirable that KNN ceramics only show a d_{33} of ∼100 pC/N by ordinary sintering,[4–6] and ∼160 pC/N by cold isostatic pressing which is the highest value reported to date,[7] indicating that experimental results concerning KNN still have a distance from theoretical values.[8,9]

Its low d_{33} of 100 and 160 pC/N obtained through conventional and cold isostatic pressing, respectively, seems undesirable and far away from the theoretically value.[4–9] As far as electrical properties are concerned, KNN ceramics seem to exhibit soft characteristics (high remnant polarization $P_r \sim 15$ pC/N, low coercive field $E_c \sim 1$ kV/mm and large loss value).[7] It appears difficult for them to be used for high-power device application. Copper oxide (CuO) has been proved to be an effective acceptor dopant to induce hardening features in KNN ceramics.[10] Moreover, doping of CuO could improve the densification, decrease the sintering temperature and hence enhance the properties of KNN ceramics. Besides, as the ionic radius of Cu^{2+} is 0.72 Å, it may substitute the B-site ions Nb^{5+} (0.69 Å) as an acceptor dopant. It is hence expected that, similar to the cases for MnO_2-doped $Pb((Zn_{1/3}Nb_{2/3})_{0.2}(Zr_{0.50}Ti_{0.5})_{0.8})O_3$[11] and MnO_2 or Fe_2O_3 doped $Pb(Ti, Zr)O_3$ ceramics,[12] high Q_m may be obtained in Cu-doped KNN ceramics.

Although the introduction of CuO can improve the sinterability of the KNN-based ceramics, previous research has also shown it would reduce the piezoelectricity of the ceramics to a certain degree.[13–17] Studies have suggested that employing the Sb^{5+} ion could increase the ferroelectricity of the KNN-based ceramics.[18] Therefore, in this work, Sb^{5+} ions were added in the CuO doped KNN-LN ceramics to maintain the piezoelectricity of the KNN-based ceramics. Wang et al. have reported that just Li-modified KNN lead-free piezoceramics can be sintered at a temperature as low as 950 °C, whose d_{33} value is up to 280 pC/N.[19,20] However, there are no details about the Q_m and $\tan\delta$ values of this system. The $0.95(K_{0.5}Na_{0.5})NbO_3$–$0.05Li(Nb_{0.5}Sb_{0.5})O_3$–$x$CuO ceramics elaborately designed by us, possess not only comparable piezoelectricity with that of Wang's,[19,20] but also better electric properties such as Q_m and $\tan\delta$, indicating this system is of great potential for industrial applications. Meanwhile, the

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doping with CuO can obviously reduce the sintering temperature and then the evaporation of alkali metals would be effectively prohibited.

In the present study, the ceramics of CuO doped $0.95(K_{0.5}Na_{0.5})NbO_3$–$0.05Li(Nb_{0.5}Sb_{0.5})O_3$ (abbreviated as KNN-5LNS-*x*Cu) solid solution were prepared by conventional sintering technique. The sintering behavior, microstructure evolution, and electrical properties will be discussed in detail.

2. Experimental procedure

A conventional ceramic fabrication technique was used to prepare the KNN-5LNS-*x*Cu ($x = 0$, 0.002, 0.004, 0.006, 0.008 mol) ceramics 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 (99.99%), and CuO (98%). These powders are all supplied by Sinopharm Chemical Reagent Co., Ltd. After being ball milled in a nylon jar with agate balls for 24 h and dried, the stoichiometric KNN-5LNS powder was synthesized at 760 °C for 5 h. After the calcination, KNN-5LNS and CuO powders were weighted according to the formula and re-milled for 24 h. Then the powders were dried and pressed into discs under a pressure of 60 MPa using polyvinyl butyral (PVB) as a binder. After PVB was burnt out, the pellets were respectively sintered in air at 940 °C, 980 °C, 1020 °C, 1060 °C for 2 h. Silver paste was fired on both sides of the samples at 600 °C for 20 min to form electrodes for the electrical measurements after polishing. The samples were poled in a 30–120 °C silicon oil bath by applying a direct current electric field of 4–6 kV/mm for 20 min. The electrical properties of all ceramics were measured after 24 h.

X-ray diffractometer (XRD) (D/MAX-2500, Rigaku) with a CuKα1 radiation ($\lambda = 0.15406$ nm) was utilized to identify the crystal structures. The as sintered surface of the samples was first polished and then scanned at 0.02° intervals of 2θ in the range 20–70°; the scanning speed was 6°/min. Grain morphology of the samples was examined by scanning electron microscopy (SEM, LEO-1530, Oberkochen, Germany). The fracture surfaces and the as sintered surfaces of the ceramics were coated using gold. Bulk densities were measured by the Archimedes method using distilled water as medium. The piezoelectric constant d_{33} was measured using a Berlincourt PiezoMeter system. The planar electromechanical coupling factor k_p and the mechanical quality factor Q_m were determined by the resonance-antiresonance method according to IEEE standards using an impedance analyzer (HP 4194A). Dielectric loss ($\tan\delta$) was measured using a LCR meter (TH2816, China) at 1 kHz.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of KNN-5LNS-*x*Cu sintered at 980 °C for 2 h. It was observed that all the samples were pure perovskite phase and no secondary phase was found. This suggested that KNN-5LNS based ceramics were well prepared, and the CuO completely diffused into the KNN-5LNS ceramic. Meanwhile, the doping of CuO induces the distortion of lattice, which is in the form of the slight changes in 2θ of different peaks.Table 1 presents the variations of the lattice parameters and the *c*/*a* ratio of the KNN-5LNS-*x*Cu ceramics sintered at 980 °C. Previous study showed that the possibility of Cu substitution to bigger A site cations such as K^+ and Na^+ would induce the shrinkage of lattice constants.[14] However, in this study, as shown in Table 1, the lattice parameter *c* and *a* changed slightly. The values of *c*/*a* ratio showed slight fluctuation while the content of CuO was below 0.006 mol, and did not show any remarkable change with further increasing CuO content, indicating that Cu^{2+} ions entered the KNN-5LNS ceramics and changed their lattice parameters slightly. The radius of Cu^{2+} ion (~0.72 Å) is similar to those of the Nb^{5+} (~0.69 Å) and Li^+ (~0.76 Å) ions, suggesting that the Cu^{2+} ion could enter the A or B site of the perovskite unit cell to replace the Li^+ or Nb^{5+}. However, the ratio of the substitution of A site and B site is difficult to be analyzed and more accurate data is necessary for detailed analysis. Because of the similarity of the ion radii of Cu, Nb and Li, whether Cu^{2+} replaced the Li^+ site or Nb^{5+} site, and the location of (0 0 2) peaks would not change considerably.

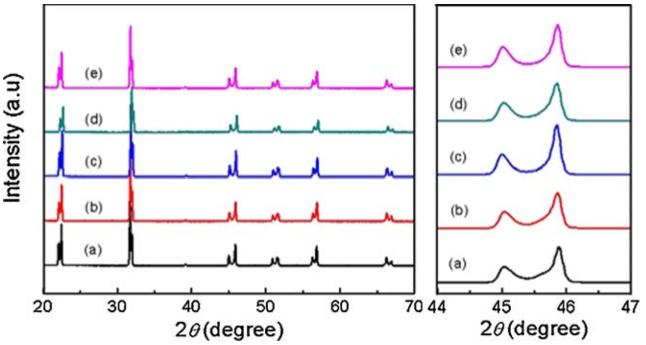

Fig. 1. X-ray diffraction patterns of the KNN-5LNS ceramics containing (a) 0.0, (b) 0.002, (c) 0.004, (d) 0.006, (e) 0.008 mol of CuO sintered at 980 °C for 2 h.

Fig. 2 shows the SEM images of the fracture surfaces of the KNN-5LNS-*x*Cu sintered at 940 °C, 980 °C, 1020 °C and 1060 °C for 2 h in air. As shown in Fig. 2, except a small amount of pores observed for the pure KNN-5LNS samples sintered at 940 °C and 980 °C, all of the KNN-5LNS-*x*Cu samples ($x \geq 0.004$) have highly dense microstructure at the sintering temperature between 940 °C and 1060 °C. With the further addition of CuO, the optimum sintering temperature for dense structure would be lowered. For the samples with 0.004 mol CuO, the sintering temperature for initial dense structure is

Table 1
Variations according to the CuO content of the lattice parameters and the *c*/*a* ratio of the KNN-5LNS-*x*Cu ceramics sintered at 980 °C for 2 h.

x (mol)	*c* (Å)	*a* = *b* (Å)	*c*/*a*
0	4.0224	3.9524	1.01771
0.002	4.0222	3.9542	1.0172
0.004	4.0256	3.9544	1.01801
0.006	4.024	3.9544	1.0176
0.008	4.024	3.9542	1.01765

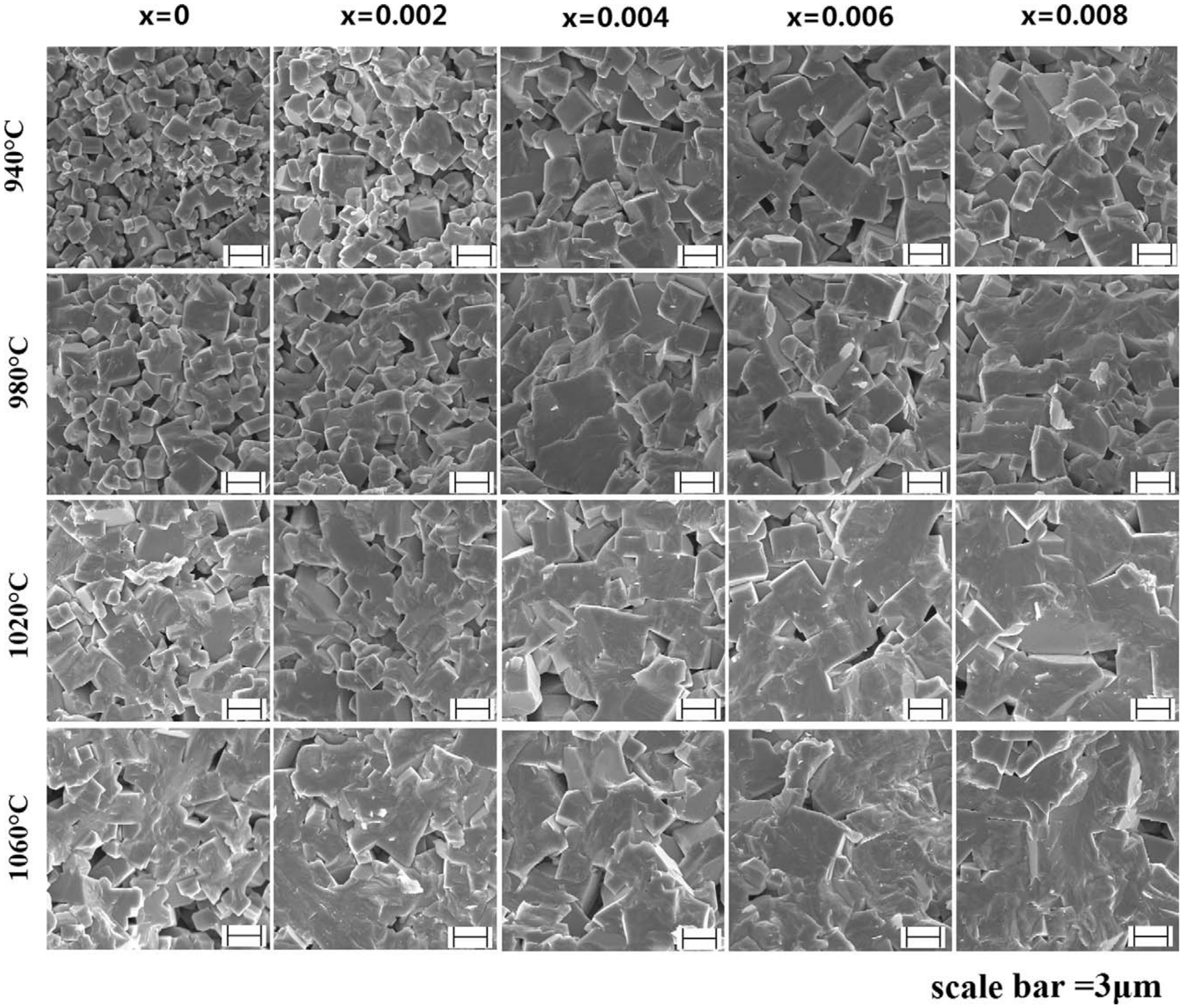

Fig. 2. SEM images of the fracture surfaces of the KNN-5LNS-*x*Cu ceramics sintered for 2 h at 940 °C, 980 °C, 1020 °C and 1060 °C.

1020 °C. Meanwhile, it is 980 °C for the samples with 0.006 mol CuO.

It is also observed that the more addition of CuO, the lower temperature, and earlier the appearance of some larger grains (about 8 μm) was achieved. Under the same sintering temperature, the average grain size increased and the microstructure became denser with the addition of CuO increasing. And the results above may be ascribed to the liquid-phase sintering. How-

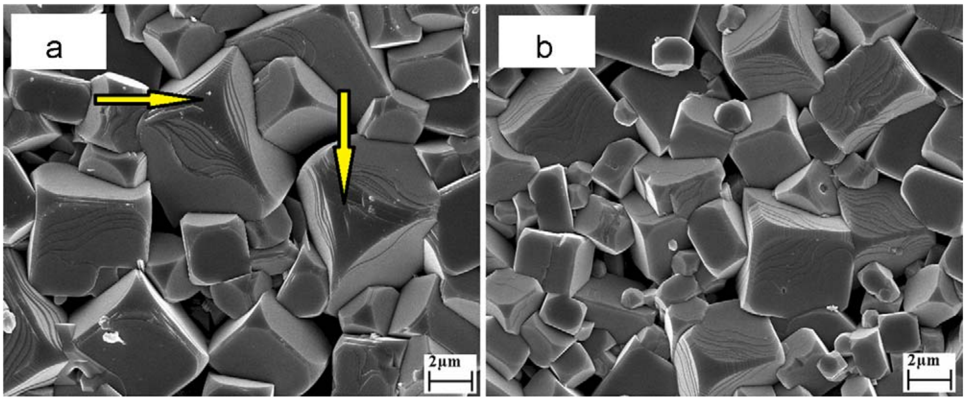

Fig. 3. The as-sintered surfaces of 0.004 mol CuO-added KNN-5LNS ceramics (a) sintered at 1020 °C and (b) at 940 °C.

ever, it was very difficult to find liquid phase, implying that the liquid phase formed during the sintering could easily dissolve in the KNN ceramics that led to its eventual disappearance with sintering time. Together with the SEM observation, it is clearly seen that a small amount of CuO doping can assist the densification effectively and improve the sintering performance of the KNN-5LNS ceramics.

The as sintered surface of specimen sintered at 1020 °C showed large grains, as indicated by the arrow in Fig. 3(a), and the enlarged grains were angular with a flat interface. An angular grain with a flat surface is typically observed in the abnormal grain growth in the presence of the liquid phase.[21] Therefore, it was considered that densification of the CuO-added KNN-5LNS ceramics might be explained by the liquid-phase sintering. Fig. 3(a) shows the 0.004 mol CuO-added KNN-5LNS ceramics sintered at 1020 °C, in which a dense microstructure with larger grains can be observed. Their relative density was approximately 95% of the theoretical density. On the other hand, for the specimen of this composition sintered at 940 °C (Fig. 3(b)), even though a few grains were enlarged with a flat interface, the development of grain was not completed and there still existed a large number of small grains. Moreover, their relative density was low, approximately 87% of the theoretical density. We can get the conclusion that the appropriate increase of sintering temperature could enhance the occurrence of the liquid phase, which prompts the dense structure for CuO doped KNN-5LNS ceramics.

Fig. 4 shows the variation of the relative density of KNN-5LNS-*x*Cu ceramics sintered at 940, 980, 1020 and 1060 °C. It can be seen that the sintering temperature with the maximum density of each composition is different within the sintering temperature range. This result indicates that the optimum sintering temperature of KNN-5LNS-*x*Cu ceramics is different.

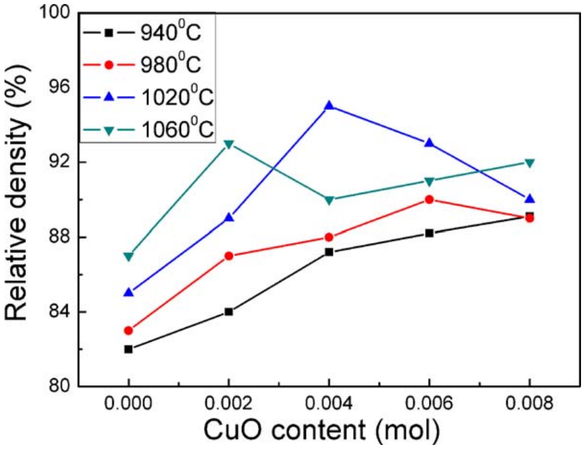

Fig. 4. The relative density variation of the KNN-5LNS-*x*Cu ($x = 0$–0.008) ceramics.

Except for the change in microstructure, the sintering temperature and the addition of CuO also significantly affect the electric properties of KNN-5LNS ceramics. Fig. 5 shows the d_{33}, k_p, Q_m and tan δ of KNN-5LNS versus the addition of CuO and the sintering temperature. The variations of d_{33} and k_p are very sensitive to the microstructure of those samples. Therefore, the changes of d_{33} with the sintering temperature and the addition of CuO increasing are resulted from the variations of the compact degree and the grain size of samples. Planar electromechanical coefficient, k_p showed a similar tendency. The increase of d_{33} may be attributed to the increase of density and grain uniformity, which lowers the leakage current and enhances

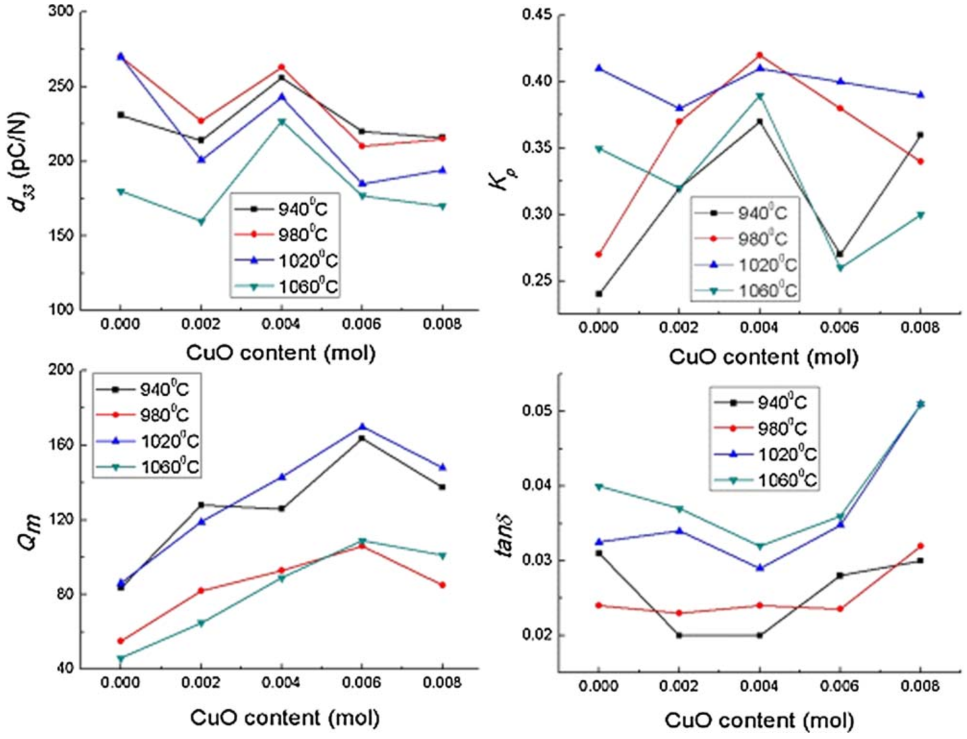

Fig. 5. Variations of the d_{33}, k_p, Q_m and tan δ of KNN-5LNS versus the addition of CuO and the sintering temperature.

the poling efficiency.[22,23] The changes of Q_m and $\tan\delta$ with the amount of CuO are also shown in Fig. 5. It was found that the addition of CuO was effective to increase the Q_m. Notable improvement (twice more than those of undoped ceramics) in mechanical quality was achieved at $x = 0.006$ and the maximum value of $Q_m = 170.9$ was obtained; however, this result is not as notable as in the KNN case.[15,24] The slight change of $\tan\delta$ can be interpreted by the change of the microstructure of the KNN-5LNS-*x*Cu. The denser the microstructure, and the lower the values of $\tan\delta$ are.

On the basis of analyses on crystal structure and electric properties, it is suggested that Cu ions reveal amphoteric doping behavior in KNN-5LNS ceramics. Two kinds of ion substitution exist as rivals at the same time. Just one kind of ion substitution is dominant under certain conditions. The reason of the excellent piezoelectricity may be related with this. As is known, the substitution of B site brings about oxygen vacancy and thus reduces the piezoelectricity of the ceramics. However, the substitution of A site does not cause above effects. At doping levels up to 0.006 mol, the Cu ions mainly substitute pentavalent B-site cations, acting as acceptors that generate O-vacancies to resultantly harden the ceramics. At doping levels above 0.006 mol, however, Cu ions predominantly play a role as donors by replacing monovalent A-site cations. It is suggested that there is a transition in the doping behavior of Cu ions in KNN-5LNS-*x*Cu ceramics. The change of Q_m in Fig. 5 could prove this point.

In summary, the addition of CuO reduces the piezoelectric property of the KNN-5LNS ceramics to a certain degree, but the d_{33} still possesses relative high value. Meanwhile, however, the other properties indicated in this paper are all improved by the addition of CuO comparing with these of pure KNN-5LNS ceramics. The optimized piezoelectric and other electric properties prove that the sintering temperature 980 °C is most suitable for the KNN-5LNS-*x*CuO ($0 < x < 0.008$ mol) ceramics. When the sintering temperature is further increased over 980 °C, the electric properties deteriorate obviously, owing to the severe volatilization of alkali metal during high-temperature sintering.[25] The result of this work revealed that CuO doped KNN-5LNS lead-free piezoceramics can be sintered at a temperature as low as 980 °C, whose d_{33} value is up to 263 pC/N. The research result shows that low-temperature sintering and high performance could be achieved together in high-performance KNN-5LNS-*x*Cu lead-free piezoceramics.

4. Conclusion

KNN-5LNS-*x*Cu lead-free ceramics have been prepared by a conventional ceramic fabrication technique, and their microstructure, piezoelectric, and other electric properties have been investigated in detail. All the ceramics possess a perovskite structure with tetragonal symmetry. The addition of CuO could decrease the sintering temperature and improve the densification of the ceramics effectively. XRD patterns indicate that there simultaneously exist two kinds of ion substitution, A site and B site. The KNN-5LNS-*x*Cu possessing the considerable well piezoelectricity could be ascribed to this reason. With CuO addition, the KNN-5LNS ceramics were well sintered even at 940 °C due to the liquid phase sintering. The k_p and Q_m values of the CuO-added KNN-5LNS ceramics were much higher than those of the pure KNN-5LNS ceramics because the dense microstructure and the suppression of the evaporation of alkali metals enhanced the piezoelectric properties. The high piezoelectric properties of $d_{33} = 263$ pC/N, $k_p = 0.42$, $Q_m = 143$ and $\tan\delta = 0.024$ were obtained from the 0.4 mol% CuO doped KNN-5LNS ceramics sintered at 980 °C for 2 h.

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