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The phase structure and electric properties of low-temperature sintered (K, Na)NbO_3-based piezoceramics modified by CuO

Jia-Jun Zhou[a], Li-Qian Cheng[b], Ke Wang[b,*], Xiao-Wen Zhang[b], Jing-Feng Li[b], Hong Liu[a], Jing-Zhong Fang[a]

[a]*Institute of Optics and Electronics, Chinese Academy of Sciences, Chengdu 610209, China*

[b]*State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

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Abstract

0.25 wt% CuO-doped (Li,K,Na)(Nb,Ta)O_3–$AgSbO_3$ lead-free piezoceramics with pure perovskite structure were successfully prepared at a sintering temperature below 1000 °C. The sintering temperature of KNN-based piezoceramics was effectively reduced by about 100 °C due to the enhanced densification process induced by the addition of CuO. Besides, the acceptable sintering temperature window was broadened by the addition of CuO. It is found that the CuO-doped samples show slightly higher tetragonal–orthorhombic phase transition point (T_{T-O}) but a lower Curie point (T_c), compared to undoped ones. The KNN-based piezoceramics became "hard" as CuO was added, supported by an increase of Q_m. Fairly good electrical properties of d_{33}^*=383 pm/V, ε_r=860, Q_m=188 and T_c=215 °C could be obtained in dense CuO-modified KNN-based piezoceramics sintered at 970 °C, demonstrating promising potential in practical applications.

Keywords: C. Piezoelectric properties; D. Perovskites; D. Niobates; Lead-free

1. Introduction

Traditional lead-based piezoceramics have been widely used in sensors, transducers, actuators, and other important devices for decades. As an increasing concern of the toxicity of lead in traditional Pb(Zr,Ti)O_3-based piezoceramics, lead-free piezoceramics have drawn much attention recently [1–3]. Among various kinds of lead-free piezoceramics systems, (K,Na)NbO_3 (KNN)-based ceramics show relatively high Curie point as well as attractive piezoelectric activity comparable to PZT-based ceramics; therefore, they are considered as one of the most promising lead-free candidates for the substitution of PZT-based ceramics [4–8].

KNN-based piezoceramics fabricated by conventional methods are normally sintered at high temperatures above 1000 °C, resulting in several problems. Firstly, the inevitable volatilization of alkaline elements during high temperature firing leads to compositional deviation, which greatly increases the difficulty in reproducibility of sample preparation, since the amount of alkaline elements has a significant influence on the phase structure as well as electrical properties [9,10]. Secondly, the high sintering temperature is very close to the liquid–solid phase transition line of this system, easily leading to compositional segregation and abnormal grain growth [11,12]. Thirdly, for applications in multilayer-structured devices, low-temperature sintering of the piezoceramics will reduce the cost significantly, since the expensive Ag–Pd inner electrode normally used for high temperature sintering (above 1000 °C) can be replaced by inexpensive electrode materials such as copper [13]. Therefore, it is of great necessity to develop the low temperature sintering technology for KNN-based piezoceramics.

In our previous work, excellent piezoelectric performance with d_{33}^*=598 pm/V (E_{max}=1 kV/mm) was obtained in 0.95$Li_{0.02}$($Na_{0.53}K_{0.48}$)$_{0.98}Nb_{0.8}Ta_{0.2}O_3$–0.05$AgSbO_3$ (LKNNTAS) lead-free piezoceramics, which will serve as the base material in the present work [14]. On the other hand, CuO has been proved as an effective sintering aid for many kinds of piezoceramics. But it is also reported that the addition of a large amount of CuO will induce undesirable secondary phases, which deteriorates piezoelectric properties [15–17]. According to the above considerations, proper

*Corresponding author. Tel.: +86 10 62784845; fax: +86 10 62771160.
E-mail address: wang-ke@tsinghua.edu.cn (K. Wang).

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amount of CuO (0.25 wt%) was selected to lower the sintering temperature of LKNNTAS piezoceramics without the introduction of secondary phase. The phase structure and electrical properties of CuO-modified LKNNTAS piezoceramics were systematically studied in the present work.

2. Experimental procedure

KNN-based lead-free piezoceramics exhibiting high piezoelectric performance with the composition of $0.95Li_{0.02}(Na_{0.53}K_{0.48})_{0.98}Nb_{0.8}Ta_{0.2}O_3$–$0.05AgSbO_3$ were prepared by the solid-state reaction method, according to the Ref. [14]. Then, 0.25 wt% of CuO was added to previously synthesized LKNNTAS powders (abbreviated as LKNNTAS–CuO) by ball milling for 24 h in ethanol using ZrO_2 balls. After the slurry was dried, the mixed powders were pressed into small disks of 10 mm in diameter, followed by a cold isostatic pressing at 200 MPa. The sintering temperature was optimized according to the shrinkage curves.

The shrinkage curves of LKNNTAS and LKNNTAS–CuO piezoceramics were measured by a dilatometer (Netzsch DIL 402 PC, Germany) at a heating rate of 5 °C/min. The crystal structure of the sintered samples was determined by X-ray diffraction (XRD) characterization with monochromatic Cu $K_{\alpha1}$ radiation (Rigaku, D/Max 2500, Tokyo, Japan). The as-sintered sample surfaces were observed by field emission scanning electron microscopy (FESEM, S-7001F, JEOL, Japan). The piezoelectric properties were determined by the strain–field method, using the piezo-testing system (aixACCT TF Analyzer 1000, Germany). The converse piezoelectric constant d^*_{33} was calculated as S_{max}/E_{max}. Evaluation of dielectric temperature stability was measured at 1 kHz in a temperature-regulated chamber, which was connected with Agilent 4194 (Hewlett-Packard, Palo Alto, CA, USA) at 1 kHz.

3. Results and discussion

Fig. 1 shows the shrinkage and shrinkage rate curves of LKNNTAS and LKNNTAS–CuO piezoceramics, respectively. The LKNNTAS sample shows the peak shrinkage rate around

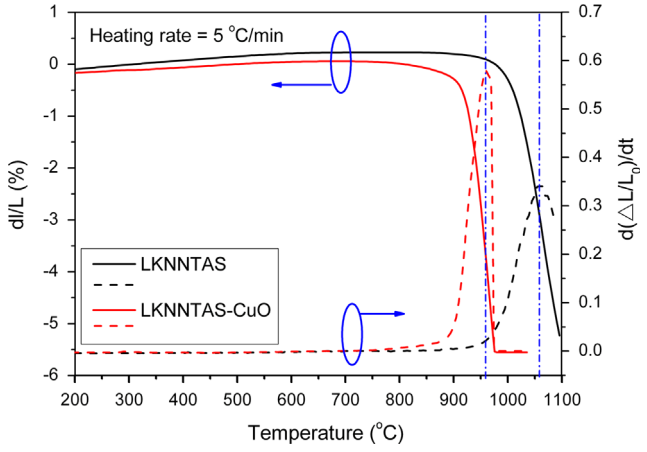

Fig. 1. The shrinkage and shrinkage rate curves of LKNNTAS and LKNNTAS–CuO piezoceramics, respectively.

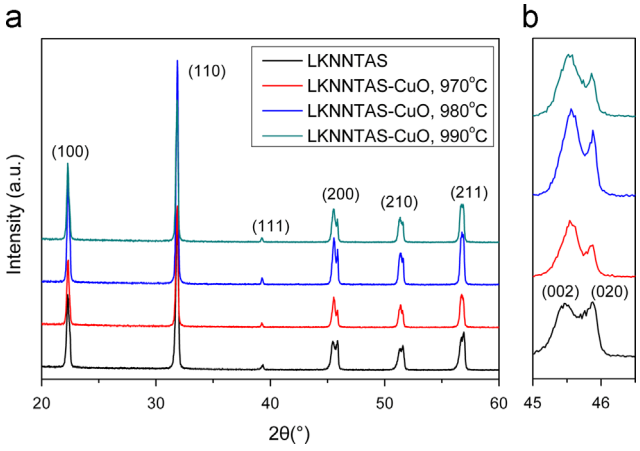

Fig. 2. XRD patterns of LKNNTAS and LKNNTAS–CuO piezoceramics.

1060 °C and the optimal sintering temperature for the ceramics is about 1080 °C with a holding time of 2 h. With the addition of CuO, the temperature corresponding to the peak shrinkage rate is significantly reduced to about 960 °C. It can be speculated that the liquid phases is formed below 900 °C, ruling out the possibility of CuO itself as the liquid phase (the melting point of CuO is 1326 °C). The sintering temperature for LKNNTAS–CuO was selected in the range of 970–990 °C.

Fig. 2 shows the XRD patterns of LKNNTAS and CuO-modified LKNNTAS ceramics sintered at different temperatures in the 2θ range from 20° to 60°. All the compositions demonstrate pure perovskite phases, and no trace of second phase is found due to the reasonable content of CuO. This result indicates that a small amount of Cu^{2+} may incorporate into the lattice of KNN matrix. The relative intensity of (002)/(020) peaks around $2\theta=45°$ changes obviously, according to the enlarged area in Fig. 2(b). It is well known that KNN-based piezoceramics usually show orthorhombic and/or tetragonal symmetry at room temperature, which can be identified by the following details in the XRD patterns [18]. When the material is of orthorhombic phase with cell parameters $a \approx c > b$, $I_{(002)}/I_{(020)}$ roughly equals 2 and the (002) peak appears at a smaller Bragg angle, but the $I_{(002)}/I_{(020)}$ decreases to 0.5 for a tetragonal phase with $a=b<c$ [19,20]. In the present study, the $I_{(002)}/I_{(020)}$ of LKNNTAS piezoceramics is about 1, indicating the coexistence of orthorhombic and tetragonal phases in LKNNTAS samples. With the addition of CuO, the $I_{(002)}/I_{(020)}$ increases, implying that orthorhombic phase becomes dominant in LKNNTAS–CuO ceramics. It is thus concluded that the addition of 0.25 wt% CuO favors the phase transformation from tetragonal to orthorhombic in LKNNTAS lead-free piezoceramics at room temperature. It is also observed that the differences in the investigated sintering temperature range have little influence on the phase structure of LKNNTAS–CuO ceramics which is probable due to the suppressed violation of alkali elements at the low temperature sintering.

Fig. 3 shows the SEM images of the as-sintered surfaces of LKNNTAS and LKNNTAS–CuO piezoceramics. Pure LKNNTAS ceramics sintered at 1080 °C show a relatively

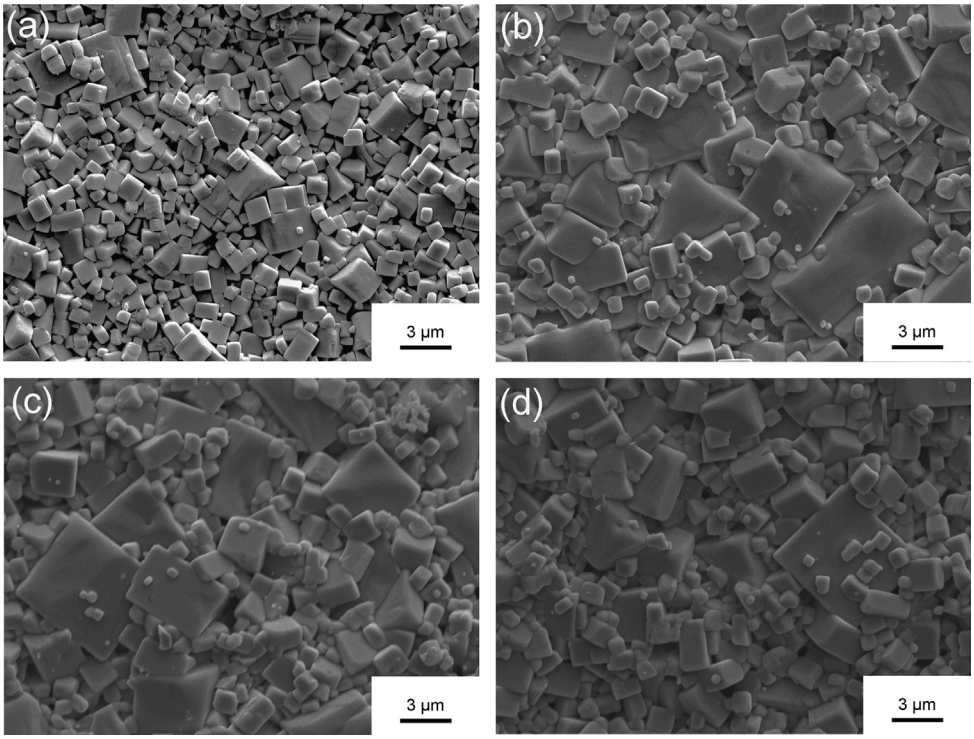

Fig. 3. SEM images of the as-sintered surfaces of LKNNTAS and LKNNTAS–CuO piezoceramics, (a) LKNNTAS, (b) LKNNTAS–CuO sintered at 970 °C, (c) LKNNTAS–CuO sintered at 980 °C, (d) LKNNTAS–CuO sintered at 990 °C.

uniform distribution of grain size, with some larger grains of 2–3 μm and smaller grains of 1 μm. The average grain size of LKNNTAS increases with the addition of CuO, which is possibly attributed to the appearance of liquid phases during the sintering process. However, the addition of CuO strengthens the bimodal distribution of grain size. For LKNNTAS–CuO ceramics sintered at 970 °C, it is observed that large grains up to 4–5 μm and small grains of 1 μm coexist. This phenomenon is probable a consequence of the inhomogeneous distribution of liquid phase, while the liquid phases only promote growth of local grains [21]. Meanwhile, there is a tendency that the average grain size of LKNNTAS–CuO piezoceramics decreases as the sintering temperature increases, which implies that the distribution of liquid phases becomes more homogeneous as the sintering temperature increases.

Fig. 4 shows the temperature dependence of the relative dielectric constant of CuO doped and undoped LKNNTAS piezoceramics measured at 1 kHz during the heating process (2 °C/min). Considering the similar phase structures of LKNNTAS–CuO piezoceramics sintered at different temperatures, only the sample sintered at 970 °C was provided here. Both the LKNNTAS and LKNNTAS–CuO ceramics undergo orthorhombic–tetragonal phase transition (T_{T-O}) and tetragonal–cubic phase transition (T_c) during the measured temperature range. The pure LKNNTAS ceramics possess T_c and T_{T-O} of 235 °C and 30 °C, respectively. With the addition of CuO, the T_c of LKNNTAS slightly decreases to 215 °C, while the T_{T-O} increases to 60 °C. The increased T_{T-O} of LKNNTAS–CuO piezoceramics indicates that the orthorhombic phase is dominant at room temperature, in consistent with the analysis of XRD patterns. The dielectric properties of LKNNTAS piezoceramics decrease with the addition of CuO, showing similar tendency to the previous work [15–17].

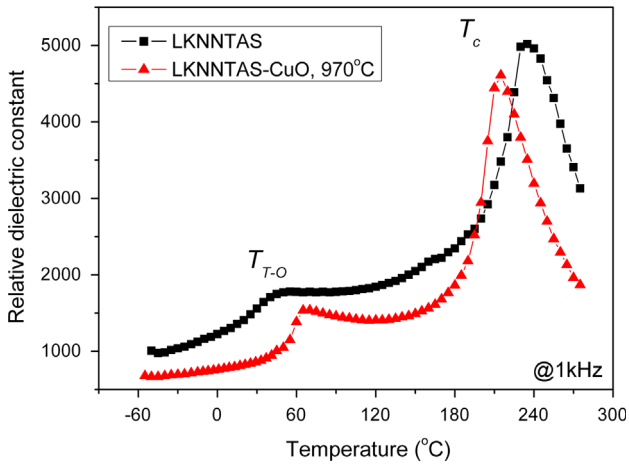

Fig. 4. Temperature dependence of the relative dielectric constant of LKNNTAS and LKNNTAS–CuO (sintered at 970 °C) piezoceramics.

Fig. 5 shows the representative *P*–*E* loops of LKNNTAS and LKNNTAS–CuO piezoceramics measured at a frequency of 1 Hz. Well-saturated hysteresis loops are obtained for all the compositions. LKNNTAS piezoceramics possess the P_r and E_c of 14.2 μC/cm^2 and 7.8 kV/cm, respectively. The LKNNTAS–CuO piezoceramics sintered at 970 °C and 980 °C nearly have the same ferroelectric properties, that coercive fields E_c are 6.1 kV/cm for both samples, while the remnant polarizations

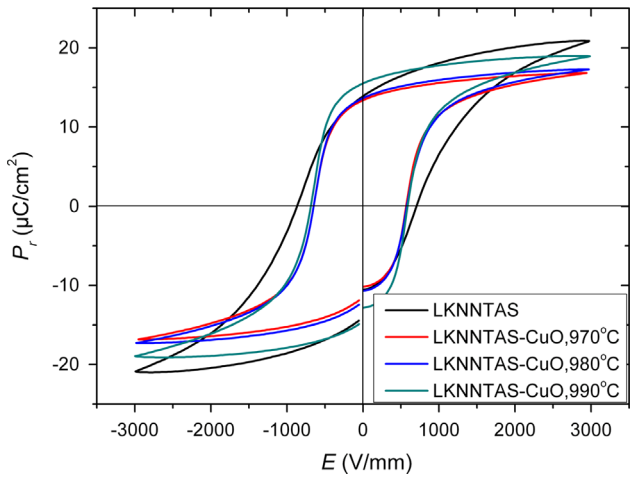

Fig. 5. *P–E* loops of LKNNTAS and LKNNTAS–CuO piezoceramics.

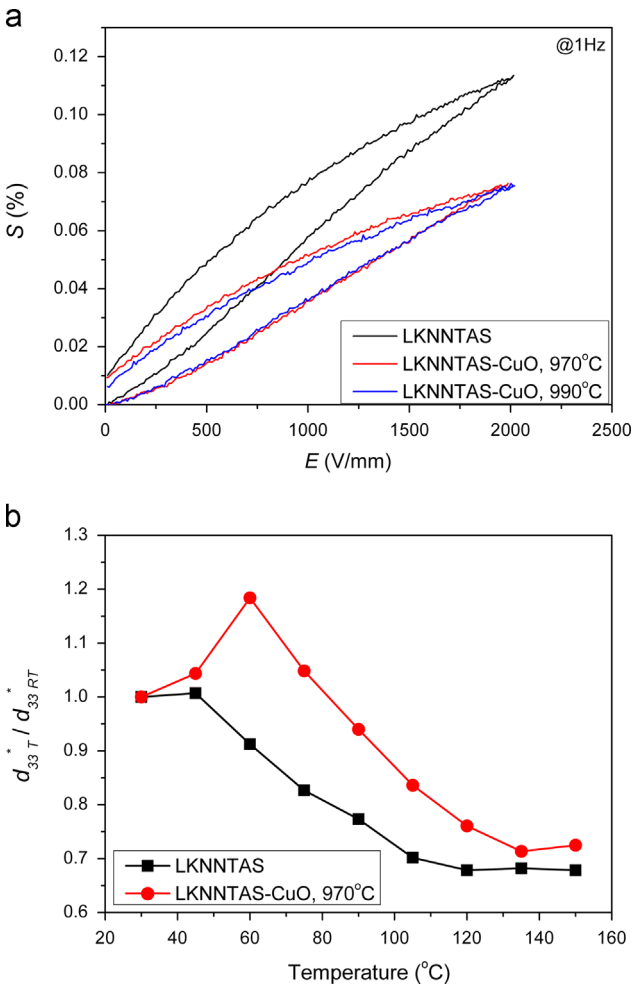

Fig. 6. Room-temperature *S–E* curves (a), and temperature dependent d^*_{33}/d^*_{RT} (b) of LKNNTAS and LKNNTAS–CuO piezoceramics.

P_r are 12.6 μC/cm^2 and 13.0 μC/cm^2, respectively. The LKNNTAS–CuO piezoceramics sintered at 990 °C possess slightly higher E_c of 6.4 kV/cm and P_r of 15.2 μC/cm^2 than the other two samples. The E_c of LKNNTAS piezoceramics decreases obviously with the addition of CuO, which seems to be contradictive with the increase of Q_m. Similar results have also been found in CuO-doped KNN-based piezoceramics in previous reports [22,23], which can be attributed to the complex substitution of Cu^{2+} to A/B-sites in KNN matrix.

Fig. 6 shows the representative *S–E* curves and temperature dependence of d^*_{33T}/d^*_{33RT} of LKNNTAS and LKNNTAS–CuO piezoceramics. The converse piezoelectric constant d^*_{33} was calculated from *S–E* curves. All the compositions show typical linear *S–E* curves of ferroelectric ceramics. With the addition of CuO, the field-induced strains of LKNNTAS piezoceramics decreases from 0.11% to 0.076% under the electric field of 2 kV/mm at room temperature, which is mainly attributed to the following two reasons. Firstly, the addition of 0.25 wt% CuO increases the T_{T-O} of LKNNTAS piezoceramics from room temperature to around 60 °C, so the room-temperature piezoelectricity will decrease as a result of significantly weakened polymorphism phase transition (PPT). Secondly, the Cu^{2+} can act as an acceptor into KNN matrix and most likely occupies B-site (Nb^{5+}), which leads to the "hardening" effect [21–23]. This behavior will lower the extrinsic contribution of strains under electric field. It should be noted that the LKNNTAS–CuO ceramics sintered at 970 °C and 990 °C almost have the same piezoelectric constant, demonstrating a broader sintering temperature window than the undoped samples. The d^*_{33} of LKNNTAS piezoceramics varies as the temperature changes and decreases ~32% (from 560 to 380 pm/V) when the temperature increases from room temperature (30 °C) to 150 °C. However, the d^*_{33} of LKNNTAS–CuO piezoceramics firstly increases with the rising temperature and shows a peak value of 452 pm/V at 60 °C, then decreases ~28% at the temperature of 150 °C. The peak value of d^*_{33} of LKNNTAS–CuO around T_{T-O} (60 °C) is mainly attributed by the PPT effect in which polarization switching will become easier under the same electric field.

Table 1 shows the room-temperature electrical properties of LKNNTAS and LKNNTAS–CuO piezoceramics. The d^*_{33}, k_p and ε_r of LKNNTAS piezoceramics decreases with the addition of CuO due to the combined influences of the significantly weakened PPT effect and the "hardening" effect. At the same time, LKNNTAS–CuO ceramics show higher Q_m and lower tan δ than the undoped LKNNTAS ceramics. Differences in sintering temperatures have little influence on the electrical properties of LKNNTAS–CuO ceramics, indicating that a broader sintering temperature window was achieved. Sintered at a low temperature of 970 °C, the LKNNTAS–CuO sample shows the electrical properties of d^*_{33} ~ 383 pm/V, k_p ~ 33.3%, ε_r ~ 860, demonstrating fairly good piezoelectric performance in KNN-based piezoceramics [15–17,21].

4. Conclusions

The phase structure and electrical properties of CuO-modified LKNNTAS piezoceramics sintered at a low temperature have been systematically investigated. Dense LKNNTAS sample with pure perovskite phase sintered below 1000 °C was achieved by the addition of proper amount of CuO.

Table 1
Electrical properties of LKNNTAS and LKNNTAS–CuO piezoceramics at room temperature.

Composition	Sintering temperature (°C)	d_{33}^* (pm/V)	k_p (%)	ε_r (1 kHz)	Q_m	tan δ (%) (1 kHz)
LKNNTAS	1080	560	43	1560	35	3.9
LKNNTAS–CuO	970	383	33.3	860	188	0.8
LKNNTAS–CuO	990	377	33.8	980	160	1.3

The addition of CuO increases the T_{T-O} of LKNNTAS ceramics, while decreases its T_c slightly. The sintering temperature window becomes broader with the addition of CuO. A large increase of Q_m is induced by CuO-doping. LKNNTAS–CuO piezoceramics sintered at the temperature as low as 970 °C exhibit attractive electrical properties of d_{33}^*∼383 pm/V, ε_r∼860, Q_m∼188 and T_c∼215 °C, demonstrating very promising potential in practical applications.

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