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Sintering and electrical properties of Cu-particle-dispersed (Na,K,Li)NbO_3

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Abstract

Cofiring of electroceramics with metals is receiving ever-increasing attention. In this paper, Cu-particle-dispersed $[(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}]NbO_3$ (NKLN/Cu) piezoelectric composites were fabricated by protective sintering in a nitrogen gas. The X-ray diffraction (XRD) results show that only perovskite NKLN and metallic Cu phases were detected in the composites. With increasing Cu content up to 30 vol%, the relative dielectric constant ε_r markedly increased from 121 for monolithic NKLN ceramics to 3938 for NKLN–30 vol% Cu composite. The piezoelectric constant d_{33} decreased from 171 pC/N to undetected and electromechanical coupling factor k_p decreased from 26% to undetected, showing a gradually changed profile of piezoelectric property. The decrease in piezoelectric properties with increasing Cu content was ascribed to non-piezoelectric effect of metallic phases and poling characteristics of piezoceramics/metal composites. The NKLN/Cu composites could be utilized to provide a central electrode of functionally graded microstructure (FGM) to modify conventional bimorph-type piezoelectric actuators.

Keywords: B. Composites; C. Piezoelectric properties; C. Dielectric properties; (Na,K)NbO_3

1. Introduction

Many electronic devices such as multilayer ceramic capacitors (MLCCs), multilayer ceramic actuators, and bimorph-type actuators need inner metal electrodes to supply electric power. In MLCCs and multilayer ceramic actuators, noble metals such as Pd or Ag–Pd alloys are directly cofired with dielectrics and piezoceramics to form the inner electrodes [1,2]. In conventional bimorph-type actuators, however, a central metal shim acting as the inner electrode is usually bonded with two piezoceramics plates by using organic agents [3]. The inherent defect in such actuators is interfacial stress concentration and bonding deterioration after a period of use [4,5]. Similar to multilayer ceramic actuators, the two piezoceramics plates in bimorph actuators could also be cofired with the central metal shim to achieve firmly metallurgical bonding. Nevertheless, stress concentration will still exist at the interface when the actuator is deflected, because the piezoceramics plate and metal shim naturally possess much different deformation ability.

To achieve harmonious deformation between piezoceramics plate and metal shim, the interface can be replaced by a compositionally graded layer in which the metal content is gradually altered following a designed profile [6]. Recently, lead zirconate titanate/Pt (PZT/Pt) [7] and PZT/Ag composites [8] were developed to modify the inner electrode of conventional bimorph-type actuators. The central metal shim is replaced by a piezoceramics/metal composite layer. When metal content gets to above a critical value, the composite becomes electrically conductive and serves as the inner electrode. There are also other composite layers between monolithic piezoceramics and the conductive layer. The metal content is gradually changed to adjust piezoelectric properties and thus deformation ability of the composites to form functionally graded microstructure (FGM) [9]. The harmonious deformation of composite multilayer effectively relieves stress concentration at interface and enables reliable performance of the modified bimorph actuator [5,10].

Expensive noble metals currently used is another concern of the inner electrode in electronic devices. Base metal electrode (BME) has become a hot issue for a long time [11]. The Ni electrode is commonly cofired with $BaTiO_3$-based dielectrics to produce BME MLCCs [12,13]. It is also reported that perovskite PZT films can be directly deposited onto base

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metal Cu foils [14,15] for microelectromechanical systems (MEMs) application. The processing atmosphere should be controlled in an appropriate oxygen partial pressure window in order to avoid oxidation of base metals [12–15]. In this study, we demonstrated that perovskite (Na,K)NbO_3-based (NKN) piezoceramics can also be cofired with base metal Cu in a protective atmosphere. It is noted that densification of metal-particle-dispersed piezoceramics composites is different from deposition of piezoelectric films. The sintering temperature of composites is much higher than the crystallization temperature of films. There are also much more piezoceramics/metal interfaces in composites than in films.

The objective of this paper is to clarify the effects of dispersing Cu particles on sintering characteristics and electrical properties of the NKN/Cu composites. The results could be beneficial for the understanding of production of BME-type bimorph actuators and multilayer ceramic actuators.

2. Experimental procedure

The starting materials were commercially available sodium carbonate (Na_2CO_3, purity: 99.8%, Beijing Chemical Industry, China), potassium carbonate (K_2CO_3, purity: 99.0%, Beijing Chemical Industry, China), niobium oxide (Nb_2O_5, purity: 99.4%, Yifeng Tantalum-Niobium Company, China), lithium carbonate (Li_2CO_3, purity: 99.5%, Beijing Chemical Industry, China), and copper powders (purity: 99.7%, average particle size: 45 μm, J & K Chemical, China). The Na_2CO_3, K_2CO_3, Li_2CO_3, and Nb_2O_5 were mixed with the nominal compositions of $[(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}]NbO_3$ (NKLN) by ball milling in an ethanol solution. The slurry was dried at 80 °C for 6 h and then calcined at 750 °C for 4 h in air to ensure the formation of single niobate phase. The synthesized NKLN powders were mixed with Cu powders by using an agate mortar and pestle at compositional ratios of 0–30 vol% Cu, with a small amount of poly-vinyl-alcohol (PVA) binder added. The mixtures were compacted by die pressing at 100 MPa in a Φ10 mm mold. The powder compacts were sintered at 1060 °C for 2 h in air, industrial N_2 gas (oxygen content ~0.5%), and high-purity N_2 gas (oxygen content ~3 ppm), respectively.

X-ray diffraction (XRD, Cu Kα, Rigaku, Japan) and scanning electron microscope (SEM, Cambridge S-360, UK) were respectively used to inspect phase structure and microstructure of the NKLN/Cu composites. For SEM observations, the samples were prepared by mechanical grinding and polishing, followed by thermal etching. The grain size was determined from SEM photographs by using the linear intercept method. The sample densities were measured by the Archimedes method. To evaluate the electrical properties, both surfaces of the disk-shaped samples were coated with silver pastes and baked at 520 °C for 30 min to form the electrodes. The coated samples were polarized under dc electric fields of 8–50 kV/cm for 20–60 min at 110–130 °C in a silicone oil bath. The dielectric properties were evaluated using an Agilent impedance analyzer (4294A, Hewlett-Packard, USA). The piezoelectric constant was measured using a quasi-static piezoelectric d_{33} meter (ZJ-3A, Institute of Acoustics, China).

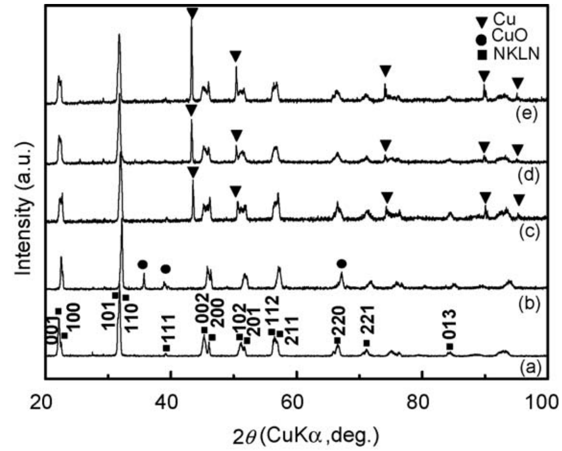

Fig. 1. X-ray diffraction patterns of the samples sintered at 1060 °C for 2 h: (a) monolithic NKLN ceramics sintered in air and NKLN–10 vol% Cu composites sintered in (b) air, (c) industrial N_2 gas, (d) high-purity N_2 gas, and (e) NKLN–30 vol% Cu composites sintered in industrial N_2 gas.

The planar electromechanical coupling factor k_p was calculated using the resonance–antiresonance method. The ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (RT6000 HVS, Radiant Technologies, Inc., USA).

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the monolithic NKLN ceramics sintered at 1060 °C for 2 h in air. The result suggests that pure perovskite structure was obtained for the NKLN ceramics. Fig. 1(b) shows the XRD pattern of the NKLN–10 vol% Cu composites sintered at 1060 °C for 2 h in air. The CuO phases were detected in the composites. Fig. 1(c) and (d) show the XRD patterns of the NKLN–10 vol% Cu composites sintered in industrial N_2 and high-purity N_2 gas, respectively. The NKLN and Cu phases were found, and no Cu oxides were detected. The diffraction peaks of Cu corresponded to $2\theta = 43.3°$, 50.4°, 74.1°, 89.9°, and 95.1°, respectively. The NKLN phase preserved the perovskite structure, as the same as the monolithic NKLN ceramics sintered in air. The results suggest that NKLN/Cu composites could be successfully produced in both industrial N_2 and high-purity N_2 gas. This is similar to the circumstance of PZT films directly deposited onto Cu substrate [14]. In this study, industrial N_2 gas was used as the sintering atmosphere to fabricate NKLN/Cu piezoelectric composites for the consideration of universal industry utilizations. Fig. 1(e) shows the XRD pattern of the NKLN–30 vol% Cu composites sintered at 1060 °C for 2 h in industrial N_2 gas. The intensity of diffraction peaks of Cu was found to increase with increasing Cu concentration from 10 to 30 vol%.

Fig. 2 shows the SEM micrographs of the monolithic NKLN ceramics and NKLN–10 vol% Cu composites sintered at 1060 °C for 2 h in air or in industrial N_2 gas. Comparing Fig. 2(a) with Fig. 2(b), the monolithic NKLN ceramics sintered in N_2 gas seemed a little porous than those sintered in air. The comparison indicates that the sintering atmosphere of N_2 gas has some effects on densification behavior of NKLN

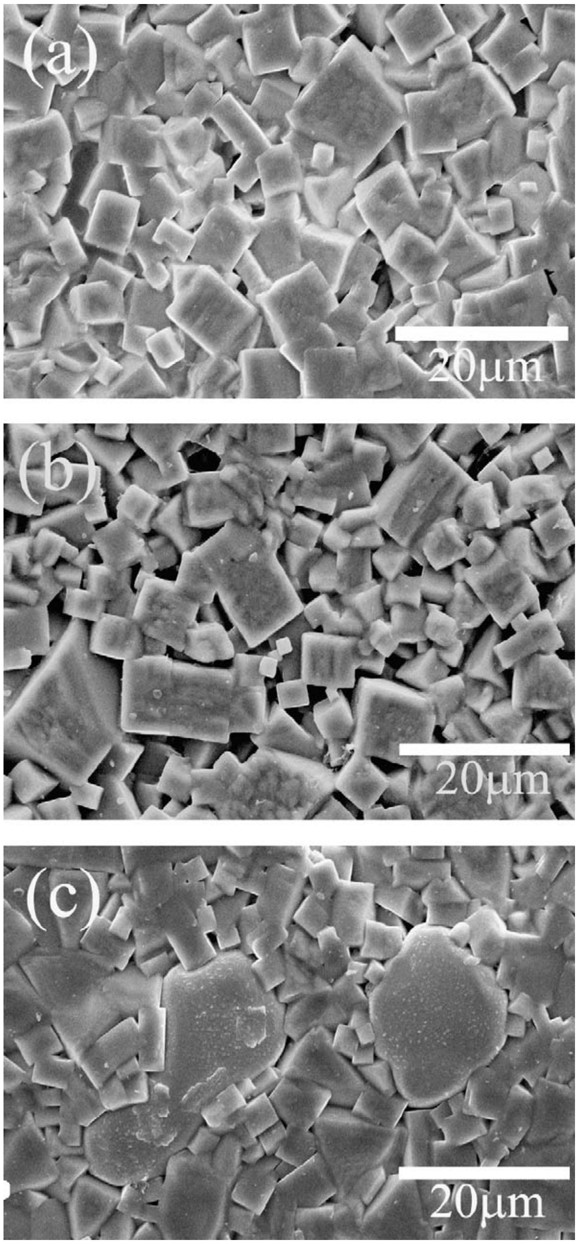

Fig. 2. SEM micrographs showing microstructure of the samples sintered at 1060 °C for 2 h: (a) monolithic NKLN ceramics sintered in air, (b) monolithic NKLN ceramics sintered in industrial N_2 gas, and (c) NKLN–10 vol% Cu composites sintered in industrial N_2 gas.

ceramics. This is consistent with reported results for Mn-doped $BaTiO_3$ ceramics fired in a reducing atmosphere of moist N_2 gas [16]. The authors has suggested that the length change of $BaTiO_3$ samples depends on the number of oxygen vacancies. Fig. 2(c) shows that the Cu particles were tightly contacted with the NKLN ceramic matrix. The relative density and grain size of the NKLN/Cu composites are shown in Table 1. It can be seen that the relative density was ranged from 87% to 93% assuming the theoretical density of NKLN to be 4.51 g/cm^3 for $(Na_{0.5}K_{0.5})NbO_3$ [17]. The grain size was a little increased due to the addition of Cu. The results suggest that Cu addition has promoted the sintering of NKLN matrix. As shown in Fig. 2, some pores were still observed in the composites. The low density could be the result of low oxygen partial pressure of N_2 atmosphere used. In addition, severe volatilization of alkali elements at high temperatures is partly responsible for the low density of NKLN/Cu composites. The composition of NKLN matrix could be optimized to enhance the sample density [18]. Some processing techniques such as cold isostatically pressing (CIP) could also be employed to densify the NKLN/Cu composites.

Table 1
Relative density, grain size and relative dielectric constant of the resultant NKLN/Cu composites in the range of 0–30 vol% Cu.

Cu content (vol%)	Relative density (%)	Grain size (μm)	ε_r [a]
0	87.1	1.9 ± 0.1	121
5	90.2	2.2 ± 0.2	392
10	92.2	2.3 ± 0.1	585
15	91.1	2.4 ± 0.1	706
20	92.1	2.4 ± 0.3	2261
25	92.6	2.3 ± 0.1	2683
30	93.0	2.5 ± 0.2	3938

[a] Measured at 1 kHz.

Fig. 3 shows the change in relative dielectric constant ε_r of NKLN/Cu composites with measuring frequency. The ε_r values decreased with increasing measuring frequency for all the NKLN/Cu composites. This is associated with some relaxation polarization mechanisms at high frequencies. The decrease in ε_r takes place when the jumping frequency of the electric charge carriers in the sample cannot follow the alternation of the applied electric fields beyond a certain critical frequency [19,20]. The relative dielectric constants measured at 1 kHz of the NKLN/Cu composites are shown in Table 1 as a function of Cu concentration. The ε_r values increased remarkably from 121 for monolithic NKLN ceramics to 3938 for NKLN–30 vol% Cu composite. The increase in dielectric constant could be ascribed to effective dielectric fields developed between Cu particles dispersed in NKLN matrix [21]. With increasing Cu concentration the conducting particles apparently shorten the electrode distance, thereby increasing the effective electric field in the dielectric NKLN phase [22].

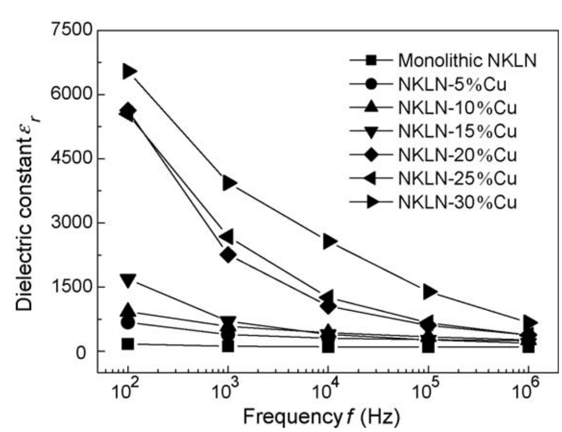

Fig. 3. Dependence of relative dielectric constant upon measuring frequency for the NKLN/Cu composites sintered at 1060 °C for 2 h in industrial N_2 gas.

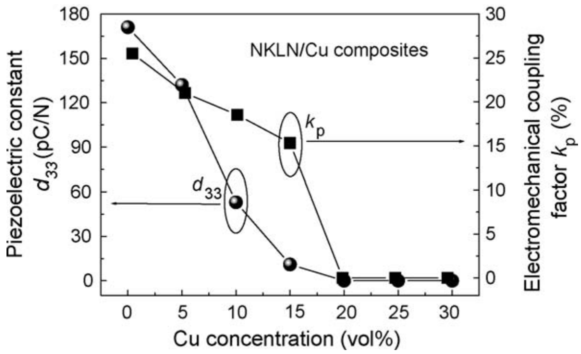

Fig. 4. Piezoelectric constant d_{33} and planar electromechanical coupling factor k_p as functions of Cu concentration for the NKLN/Cu composites sintered at 1060 °C for 2 h in industrial N_2 gas.

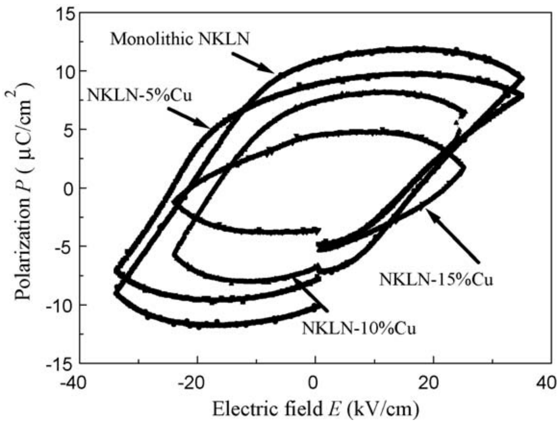

Fig. 5. *P–E* hysteresis loops of the NKLN/Cu composites sintered at 1060 °C for 2 h in industrial N_2 gas.

Fig. 4 shows the dependence of piezoelectric properties of the NKLN/Cu composites on Cu concentration. The piezoelectric constant was found to gradually decrease with increasing Cu concentration. The d_{33} values decreased from 171 pC/N to undetected when more than 20 vol% Cu was added to NKLN ceramics. The varying trend of electromechanical coupling factor k_p with Cu concentration was similar to that of d_{33}. The k_p values decreased from 26% to undetected for >20 vol% Cu concentrations. The results reveal that gradually changed piezoelectric properties can be obtained by altering metal content in the NKLN/Cu composites.

The decrease in piezoelectric property shown in Fig. 4 is expected because Cu is a non-piezoelectric phase [7]. Furthermore, the NKLN/Cu composites with >10 vol% Cu are difficult to adequately polarize under electric fields applied. It was found that lower electric fields were allowed to apply to composite samples with increasing Cu concentration. Insufficient deflection of ferroelectric domains will degrade the piezoelectric properties of NKLN phase [23]. This result partly explains why the piezoelectric properties of NKLN/Cu composites were nonlinearly decreased with increasing Cu concentration. So far there is no reasonable theory dealing with the influence of metal-particle dispersion on polarization of piezoceramics composites. Therefore, we are still unable to provide further explanation to the quantitative relationship between piezoelectric property and Cu volume fraction of NKLN/Cu composites.

Fig. 5 shows the *P–E* hysteresis loops of NKLN/Cu composites sintered at 1060 °C for 2 h in industrial N_2 gas. As shown in Fig. 5, the remnant polarization P_r values were 10.7, 8.8, 7.3, and 4.5 μC/cm^2 for the samples with Cu concentrations of 0 vol%, 5 vol%, 10 vol%, and 15 vol%, respectively. The varying trend of P_r value was similar to that of d_{33} and k_p with respect to Cu concentration, since higher P_r values tend to attain higher piezoelectric properties [8,23]. The change in coercive field E_c was somewhat irregular with increasing Cu concentration. The hysteresis loops for >15 vol% Cu composites cannot be obtained in the present experiments, and the reason could be explained as follows. A pair of Cu particles and NKLN phase enclosed between the two Cu particles could be regarded as a micro-capacitor. The total conductance of NKLN/Cu composite is the sum of all these micro-capacitors. The increase in Cu concentration could directly lead to the decrease in spacing between Cu particles. Due to the percolation effect [24], decreasing Cu particle spacing causes the increase in conductivity. When Cu concentration is >15 vol%, the NKLN/Cu composites could have too high a conductivity to be electrically applied to acquire a ferroelectric hysteresis loop.

4. Conclusion

The $[(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}]NbO_3$/Cu composites with Cu content up to 30 vol% were successfully sintered at 1060 °C in industrial N_2 gas. The Cu particles were uniformly dispersed in the NKLN matrix. The relative dielectric constant increased, the remnant polarization and piezoelectric constant decreased with increasing Cu content for the NKLN/Cu composites. The graded change in electrical properties of NKLN/Cu composites could be used to develop modified bimorph actuators with an inner electrode of functionally graded microstructure.

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