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Dielectric and Piezoelectric Properties of CuO-Doped $(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}NbO_3$ Lead-Free Ceramics†

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$(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}NbO_3$-x (mol %) CuO ceramics were prepared by a solid state reaction approach and their dielectric and ferroelectric properties were evaluated by conventional methods. The high piezoelectric properties of d_{33} = 115Pc/N, k_p = 0.259, ε_r = 697, tan δ = 2.9 % were obtained for the $(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}NbO_3$ ceramics containing 1 mol % CuO sintered at 1035 ºC for 2 h. Therefore, the $(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}NbO_3$ ceramics containing a small amount of CuO are a good candidate material for lead-free piezoelectric ceramics.

Key Words: Ceramics, Ferroelectric, Piezoelectric, Solid state reaction.

INTRODUCTION

Ceramics based on lead zirconate titanate (PZT) system are the most important and the most widely used piezoelectric materials because of their outstanding piezoelectric performance. However, the toxicity caused by lead evaporation leads to environmental pollution. Recently, lead-free piezoelectric materials have been attracting increasing attention as new materials in place of PZT materials for the sake of environmental protection. Recently, significant progresses have been made in $(K_xNa_{1-x})NbO_3$-based (KNN-based) ceramics, which show that KNN-based ceramics are promising candidates as the lead-free piezoelectric materials[1-5].

In order to further enhance the properties of KNN-based ceramics and meet the requirements for practical uses, it is necessary to develop new KNN -based ceramic. In the present work, $(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}NbO_3$-x mol % CuO (KNNL·xCuO) ceramics are prepared and the dielectric and ferroelectric properties has been further investigated by conventional methods.

EXPERIMENTAL

KNNL·xCuO ceramics (with x = 0.00, 0.50, 1.00, 1.50, 2.00, 2.50, respectively) were prepared by the conventional solid-state reaction technique in ambience, using starting materials of K_2CO_3 (99.0 %), Na_2CO_3 (99.8 %), Li_2CO_3 (99.9 %) and Nb_2O_5 (99.5 %). The raw materials were dried in a vacuum oven at 120 ºC for at least 8 h to remove the absorbed moisture. After this procedure, they were weighed according to the stoichiometric ratio, ball-mixed in alcohol for 12 h and calcined at 860 ºC for 8 h. After re-milling with CuO additive, the powders were dried and pressed into discs under a pressure of 60 kgf/cm^2 and sintered at different temperatures for 2 h in air.

The microstructure of sintered ceramics was studied by scanning electron microscope. The densities of the sintered specimens were measured by a water-immersion technique. For dielectric and piezoelectric characterization, specimens were coated with silver paint on both surfaces and fired at 700 ºC for 15 min and poling was accomplished in silicon oil using a dc power supply under the dc field strength of 5.0 kV/mm at 120 ºC for 0.5 h. The piezoelectric constant d_{33} was measured using a d_{33} meter (ZJ-3A, China). The electromechanical coupling factor k_p was determined by the resonance method using an impedance analyzer (HP4294A). The dielectric constant and dissipation factor of the ceramics were examined with a LCR analyzer (TH2816). Ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (Trek 609B, Radiant Technologies, Inc., Albuquerque, NM).

RESULTS AND DISCUSSION

Fig. 1 shows the SEM micrograph of the fracture surface of the KNNL·xCuO piezoelectric ceramics with the different sintering temperature. It can be seen from Fig. 1(a) that many

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distinct pores exist in the grain boundary of KNNL-1.00 CuO ceramics sintered at 1000 ºC for 2.0 h. The microstructure is inhomogeneous and the fracture surface is the typical transgranular fracture mode for the sample sintering at 1000 ºC. This result demonstrates that the grains of KNNL-1.00 CuO ceramics sintered at 1000 ºC do not grow sufficiently. With the sintering temperature increases, the pores significantly decrease. The microstructure of the sample sintering at 1035 ºC is much uniform and fine, the average grain size is about 0.5-3.0 μm as seen in Fig. 1(b). This result indicates that KNNL-1.00 CuO grains of the sample sintered at 1035 ºC grow sufficiently and the atomic binding force is greater than intergranular force. The relatively density of the KNNL ceramics doped with CuO sintered at 1035 ºC for 2.0 h are generally larger than 96 %. These clearly show that the doping of CuO is effective in promoting the densification of the ceramics[6-8]. Take into account above results, it can be concluded that the optimum sintering temperature for KNNL·xCuO ceramics should be 1035 ºC.

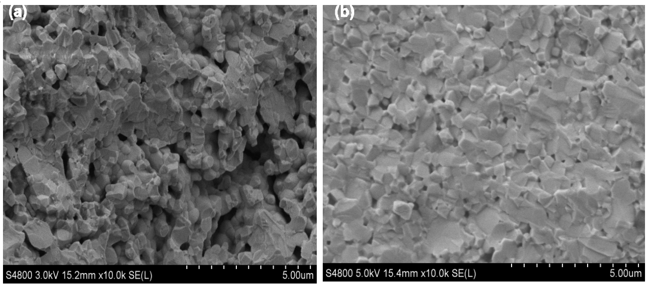

Fig. 1. SEM images of the fractured surface of the KNNL-1.00 CuO ceramics sintered at various temperatures: (a) 1000 ºC, (b) 1035 ºC

Fig. 2 show the piezoelectric constant d_{33} and the planar electromechanical coefficient k_p of KNNL·xCuO ceramics sintered at 1035 ºC for 2.0 h as a function of x. The d_{33} increases with the increasing x and reaches maximum (115pC/N) at x = 1.00, then it drops with further increasing x. Similar to d_{33}, it is also found that the k_p increases with the increasing x and reaches maximum (k_p = 25.9 %) at x = 1.00, then it decreases with further increasing x. These results indicate that the KNNL-1.00 CuO ceramics possess good electrical properties at room temperature, *i.e.*, the piezoelectric constant d_{33} of 115 pC/N and planar electromechanical coefficient k_p of 25.9 %. Over this boundary (x = 1.00), the electrical properties decrease with the increasing x. So it is found that the MPB plays an important role in improving the piezoelectric properties of KNNL-1.00 CuO ceramics[9-11].

Fig. 3 shows the dielectric constant er and dielectric loss tand at room temperature of KNNL·xCuO ceramics sintered at1035 ºC for 2 h as a function of x. The dielectric constant ε_r increases with increasing CuO fraction up to x = 1.00 with ε_r = 697, then decreases. while the dielectric loss tand decreases with increasing x and reaches minimum (tan δ = 2.9 %) at x = 1.00, then it increases with further increasing x.

In order to characterize the ferroelectric properties, the P-E hysteresis loops of KNNL·xCuO ceramics were measured. Fig. 4 shows typical P-E hysteresis loops of KNNL·xCuO (0.00 ≤ x ≤ 2.00) ceramics. From the P-E hysteresis loops in Fig. 4, well saturated hysteresis loops were observed over a wide composition range. Usually, the existence of P-E hysteresis loops is considered as evidence that material is ferroelectrics[11]. In this work, the saturated P-E hysteresis loops confirm good ferroelectric nature of the KNNL·xCuO ceramics.

Conclusion

Effect of the content of CuO and the sintering temperature on the microstructure and piezoelectric properties of

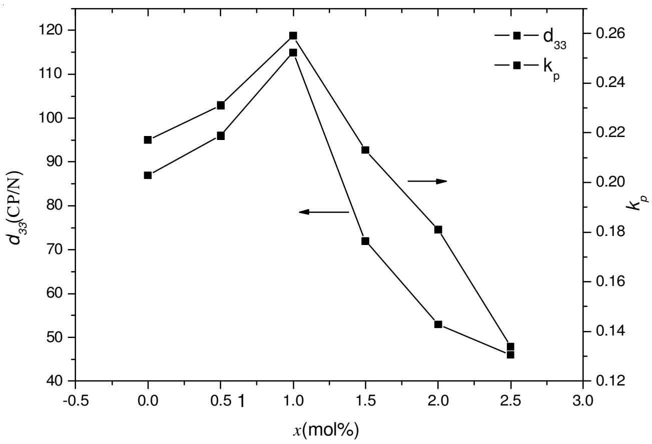

Fig. 2. Piezoelectric constant d_{33} and planar electromechanical coefficient k_p of KNNL·xCuO ceramics as a function of x

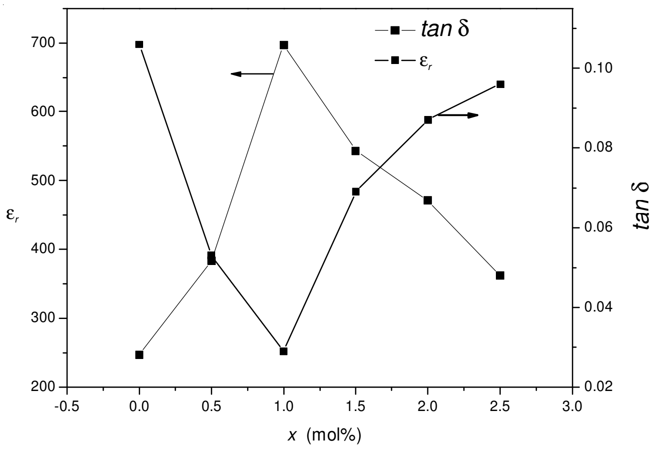

Fig. 3. Dielectric constant ε_r and dielectric loss tan δ of KNNL·xCuO ceramics as a function of x

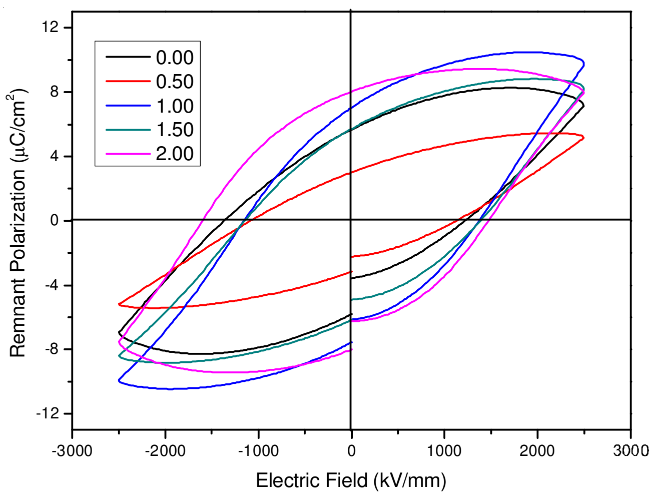

Fig. 4. Polarization *versus* electric field curves for KNNL·xCuO ceramics sintered at 1035 ºC for 2 h

$(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}NbO_3$ ceramics were investigated. The results are summarized as follows:

1. Lead-free piezoelectric ceramics KNNL·xCuO have been synthesized by a solid state reaction approach. CuO can effective in promoting the densification of the ceramics, the optimum sintering temperature for KNNL·xCuO ceramics should be 1035 ºC.

2. The optimum composition for KNNL·xCuO ceramics is KNNL-1.00 CuO. Piezoelectric properties of KNNL-1.00 CuO ceramics under condition the optimum composition and sintering temperature are piezoelectric constant d_{33} of 115 pC/N, planar electromechanical coupling factor k_p of 25.9 % and the dielectric constant ε_r of 697 and dielectric loss tand of 2.9 %, respectively. The results show that KNNL-1.00 CuO is an excellent candidate for lead-free piezoelectric ceramics.

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