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Microstructure, Piezoelectric and Dielectric Properties of Lead-Free Ceramics $K_{0.475}Na_{0.475}Li_{0.05}NbO_3$-$CaZrO_3$-CuO†

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The (1-x)$K_{0.475}Na_{0.475}Li_{0.05}NbO_3$-x$CaZrO_3$-2 % molCuO lead-free piezoelectric ceramics have been prepared by conventional technique at 1140 ºC and exhibit highly dense structure by SEM patterns observed. X-ray diffraction analysis shows that the ceramics possess a pure perovskite structure and only have tetragonal phases. The ceramic with x = 0.045 possess optimum electrical properties (d_{33} = 176 pC/N, k_p = 37 %, ε_r = 1083, tan δ = 2.4 %). This results indicate that the ceramic is a promising lead-free piezoelectric ceramic.

Key Words: Lead-free, Microstructure, Dielectric, Piezoelectric, Ceramics.

INTRODUCTION

Lead-based piezoelectric materials such as Pb(Zr, Ti)O_3 (PZT) ceramics are the most widely used, owing to their superior piezoelectric performances[1]. However, the toxicity of lead oxide, which contains more than 60 wt %, can cause damaging to the kidney, brain and nervous system[2]. Thus, many countries have required that all electronic equipment must be lead-free for human health and environmental protection in recent, which results in urgently developing with lead-free piezoelectric ceramics. ($K_{0.5}Na_{0.5}$)NbO_3(KNN)-based ceramics has been paid to a key attention owing to their superior piezoelectric properties, high Curie temperature (about 420 ºC) and environmental friendliness[1-4]. However, pure KNN ceramic is difficult to densify by conventional sintering technique because of the high volatility of alkaline elements at high sintering temperatures. Considering a better solution to above problems, many studies have been carried out to improve the electrical properties of KNN-based ceramics by forming new solid solutions with other perovskite or perovskite-like ABO_3 compounds. such as KNN-Bi($Zn_{0.5}Ti_{0.5}$)O_3[5], KNN-$LiTaO_3$[6], KNN-$BaTiO_3$[7].

In this work, the (1-x)$K_{0.475}Na_{0.475}Li_{0.05}NbO_3$-$_x$$CaZrO_3$-2 % mol CuO lead-free piezoelectric ceramics were fabricated and their structure, dielectric and piezoelectric properties also were investigated. Particularly, we put emphasis on the effect of CuO additives and substitution $CaZrO_3$ to phase structure and electrical properties of the ceramics.

EXPERIMENTAL

The (1-x)$K_{0.475}Na_{0.475}Li_{0.05}NbO_3$-$_x$$CaZrO_3$ (x = 0.000, 0.025, 0.045, 0.065, 0.085) [KNLN-CZ] ceramics with 2 % mol CuO doping were prepared by the conventional mixed oxide method. K_2CO_3, Na_2CO_3, Li_2CO_3, $CaCO_3$, Nb_2O_5 and ZrO_2 were used as starting raw materials. They were ball milled for 16 h with agate ball media and alcohol. After calcination at 860 ºC for 2 h, the calcined powders were milled again and pressed into disks of 1.2 cm in diameter and 1 mm in thickness under 20 MPa using PVA as a binder. The disk samples were sintered at 1140 ºC for 3 h in air. Silver paste was dried on both sides of the samples at 300 ºC for 5 h as the electrodes for the electrical measurements. The samples were poled in 120 ºC silicon oil bath by applying a DC electric field of 3-5 kV/mm for 30 min. The electrical properties of all ceramics were measured more than a day later. X-ray diffraction characterization of the ceramics was performed by using CuK_α radiation (Rigaku, Tokyo, Japan). The microstructure of the ceramics was studied by scanning electron microscope (JSM-6700F, Japan). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (ZJ-3A, China). The electromechanical coupling factor k_p and mechanical quality factor Q_m were 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).

RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns of the KNLN-CZ ceramics with 2 % mol CuO aids synthesized at 1140 ºC for

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3 h. As shown in Fig. 1(a), it is found that the ceramics show a pure perovskite structure and no secondary phase is detected, suggesting that the dopants were completely diffused into the $K_{0.475}Na_{0.475}Li_{0.05}NbO_3$ lattices, with Ca^{2+} entering the $(K_{0.475}Na_{0.475}Li_{0.05})^+$ sites as well as Zr^{4+} occupying the Nb^{5+} sites, to form a new homogeneous solid solution. It can be seen from Fig. 1(b), the enlarged XRD patterns of the ceramics in the range of 2θ from 44.5° to 47.0° also show that the ceramics only possess the tetragonal phase.

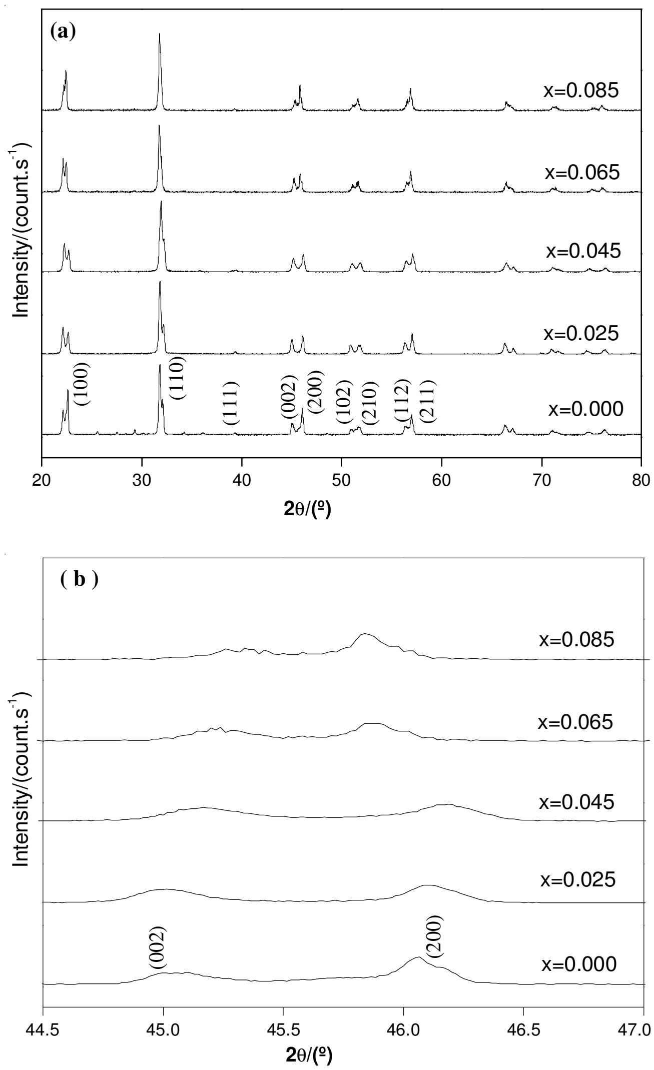

Fig. 1. (a) and (b) XRD patterns of the (1-x)KNLN-$_x$CZ ceramics as a function of x

Fig. 2. shows the SEM micrographs of the external and transect of the (1-x)KNLN-$_x$CZ ceramics at x = 0.045. As shown in Fig. 2(a), the ceramic has been well-sintered and possess clear grain boundary. Moreover, the ceramic possess relatively high density excepting the nonuniformity of grains and a little of cavitas among grains, which are shown in Fig. 2(b). Obviously, the dopants of CuO and $CaZrO_3$ are very effective to increase sintering ability and electrical properties of the ceramics.

Fig. 3. shows the d_{33}, k_p, ε_r and tanδ of the (1-x)KNLN-$_x$CZ ceramics as a function of x. It can be observed that the properties exhibit a compositional dependence from Fig. 3(a), the piezoelectric constant d_{33} and planar electromechanical coefficient k_p increased gently with increasing x and then decreased fastly, giving respectively a maximum value of 176 pC/N and 37 % at x = 0.045. Comparing with d_{33} and k_p, as shown in Fig. 3(b), the observed er and tand show similar dependences on x, reching a maximum values (ε_r = 1083 and tanδ = 2.4 %, respectively) at x = 0.045. The gradual increasing of electrical properties before maximum values could be included that the ceramics have transformed gradually from a normal ferroelectric to a relaxor ferroelectric. The diffuse phase transition may owing to the increase in the disorder degree of A- and B-site ions after the partial substitutions of Ca^{2+} for the A-site $(K_{0.475}Na_{0.475}Li_{0.05})^+$ and Zr^{4+} for the B- site Nb^{5+}. After maximum values, decreased properties due to increasing difficulties in ferroelectric domain inversion.

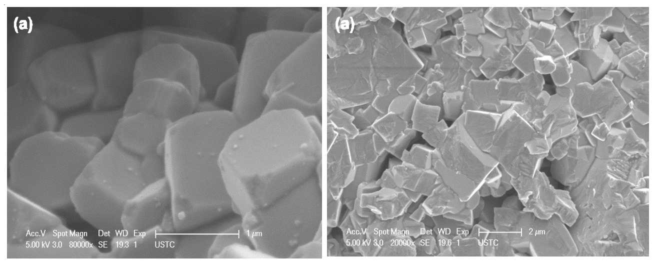

Fig. 2. SEM micrographs of the (1-x) KNLN-$_x$CZ (x = 0.045) ceramic (a) external; (b) transect

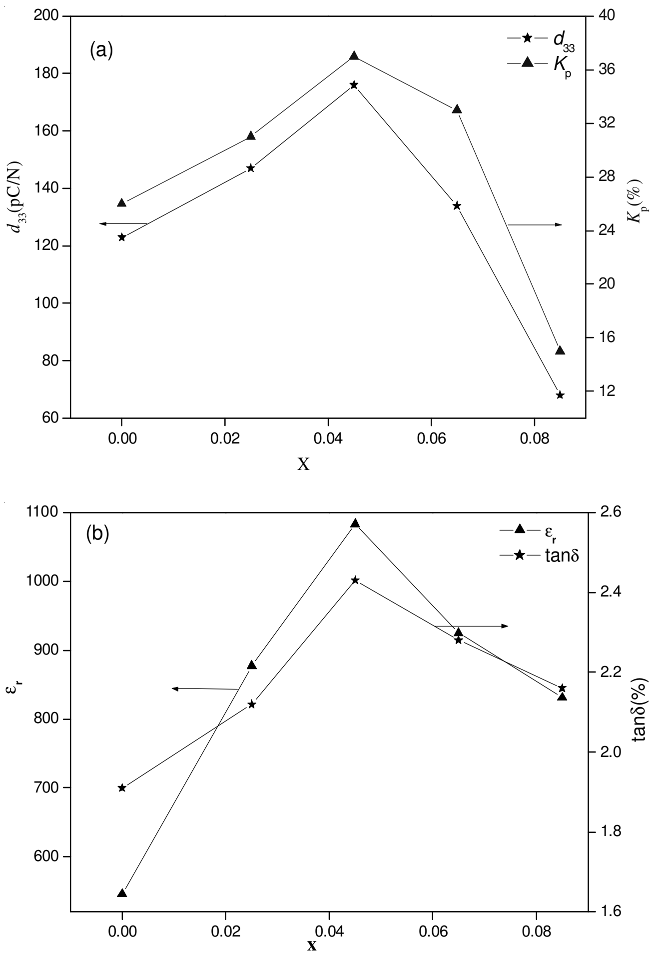

Fig. 3. (a) and (b) Variations of d_{33}, k_p, ε_r and tand with x for the (1-x)KNLN-$_x$CZ ceramics

Conclusion

In this study, the (1-x)$K_{0.475}Na_{0.475}Li_{0.05}NbO_3$-$_x$$CaZrO_3$-2 % mol CuO lead-free piezoelectric ceramics have been prepared by the conventional ceramics sintering technique at 1140 ºC and show highly density by SEM analysing. X-ray diffraction analysis shows that the ceramics possess a pure perovskite structure and only have tetragonal phases. The ceramic with x = 0.045 exhibits optimum electrical properties (d_{33} = 176 pC/N, k_p = 37 %, ε_r = 1083, tan δ = 2.4 %). These results indicate the dopants of CuO and $CaZrO_3$ are very effective way to increase sintering ability and electrical properties of the ceramics.

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