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 $(1-x)K_{0.475}Na_{0.475}Li_{0.05}NbO_3$ - $xCaZrO_3$ -2 % molCuO lead-free piezoelectric ceramics have been prepared by conventional technique at 1140 °C 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, $k_p = 37$ %, $\epsilon_r = 1083$, $\tan \delta = 2.4$ %). 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 performances¹. However, the toxicity of lead oxide, which contains more than 60 wt %, can cause damaging to the kidney, brain and nervous system². 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 °C) and environmental friendliness¹⁻⁴. 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-LiTaO₃⁶, KNN-BaTiO₃⁷.

In this work, the $(1-x)K_{0.475}Na_{0.475}Li_{0.05}NbO_3$ - $xCaZrO_3$ -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 $(1-x)K_{0.475}Na_{0.475}Li_{0.05}NbO_3$ - $xCaZrO_3$ ($x = 0.000, 0.025, 0.045, 0.065, 0.085$) [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 °C 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 °C for 3 h in air. Silver paste was dried on both sides of the samples at 300 °C for 5 h as the electrodes for the electrical measurements. The samples were poled in 120 °C 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 °C 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 $\text{K}_{0.475}\text{Na}_{0.475}\text{Li}_{0.05}\text{NbO}_3$ lattices, with Ca^{2+} entering the $(\text{K}_{0.475}\text{Na}_{0.475}\text{Li}_{0.05})^+$ 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 $(1-x)\text{KNLN}_x\text{CZ}$ ceramics as a function of x

Fig. 2. shows the SEM micrographs of the external and transect of the $(1-x)\text{KNLN}_x\text{CZ}$ 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 $\tan\delta$ of the $(1-x)\text{KNLN}_x\text{CZ}$ 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 ϵ_r and $\tan\delta$ show similar dependences on x , reaching a maximum values ($\epsilon_r = 1083$ and $\tan\delta = 2.4\%$, 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 $(\text{K}_{0.475}\text{Na}_{0.475}\text{Li}_{0.05})^+$ 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 $(1-x)\text{KNLN}_x\text{CZ}$ ($x = 0.045$) ceramic (a) external; (b) transect

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

Conclusion

In this study, the $(1-x)\text{K}_{0.475}\text{Na}_{0.475}\text{Li}_{0.05}\text{NbO}_3\text{-}x\text{CaZrO}_3\text{-}2\%$ mol CuO lead-free piezoelectric ceramics have been prepared by the conventional ceramics sintering technique at 1140 °C 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, $k_p = 37\%$, $\epsilon_r = 1083$, $\tan \delta = 2.4\%$). 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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