DIELECTRIC, FERROLECTRIC AND PIEZOELECTRIC PROPERTIES OF Sb-DOPED KNLN LEAD-FREE PIEZOELECTRICS CERAMICS

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Abstract:

The $(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{1-x}Sb_x)O_3$ + 0.25wt.% CuO (KNLNxS) piezoelectric ceramics, where x = 0.0, 0.01, 0.03, 0.05 and 0.07 have been fabricated successfully by the conventional solid-state reaction method. The effect of Sb on the structure, microstructure and electrical properties of KNLNxS ceramics were studied. Experimental results showed that with the doping of Sb, the physical properties of KNLN ceramics have been improved. The ceramic samples containing 0.05 mol Sb sintered at 950˚C showed the good electrical properties: the density of 4.21g/cm^3; the electromechanical coupling factor, $k_p = 0.36$ and $k_t = 0.43$; the dielectric constant, $\varepsilon = 360$; the piezoelectric constant (d_{33}) of 151 pC/N.

Key Words: Lead-Free, Structure, Microstructure, Ferroelectric, Piezoelectric

INTRODUCTION

Over the past half century, piezoelectric ceramics have been manufactured and applied mainly are PZT-based ceramic systems [1]. They contain a large amount of lead, the high toxicity and volatility of lead oxide during manufacture have polluted the environment and affect human health. In order to protect the environment, many countries have made the requirement that all new electronic products must not contain lead [2]. It is therefore necessary to develop lead-free piezoelectric ceramics with perfect ferroelectric and piezoelectric properties so that can be replaced the lead-based piezoelectric ceramics in a variety of devices.

In general, there are many lead-free piezoelectric ceramic systems with ABO_3 perovskite structure have been investigated, Among them, the piezoelectric ceramics on the basis of (Na, K)NbO_3 (KNN) are attracting much attention of researchers due to its strong ferroelectricity, high Curie temperature (around 420ºC) and environmentally friendly, are capable of replacing lead-based ceramics [3–5]. However, due to the high volatility of alkaline elements at high sintering temperature, it is very difficult to manufacture KNN ceramics with high density, good electrical properties by conventional sintering technique. Therefore, the problem of controlling the evaporation of the alkaline elements by lowering the sintering temperature of the ceramics or modifying the KNN ceramics by appropriate impurities is expected to improve the density and electrical properties of KNN based ceramics.

The most common method to reduce the sintering temperature of KNN based ceramics is to add sintering agents such as ZnO [6], CuO [7–9], $K_4CuNb_8O_{23}$ (KCN) [10]. Among them, copper oxide (CuO) has been shown to be effective in reducing the sintering temperature, improving the density and enhancing the properties of ceramics. In previous work [11], we studied the effect of CuO addition on the sintering behavior and physical properties of $0.96(K_{0.5}Na_{0.5})NbO_3$-$0.04LiNbO_3$ (KNLN) + xwt.% CuO piezoelectric ceramics, where x = 0.0, 0.1, 0.2, 0.25, and 0.30. The experimental results have shown that with CuO doping, the KNLN ceramics have been well sintered at a low temperature (950ºC) and density has improved. Park *et al*. [9] successfully sintered [(Na0.5K0.5) NbO3 + 1.5 mol% CuO] ceramics at a temperature of 960°C. The properties of the ceramics obtained as follows: $k_p = 0.37$, $Q_m = 844$, $\varepsilon = 229$.

Although CuO can improve the sintering behavior of KNN based ceramics, however studies have shown that it will reduce the piezoelectricity due to the hardening of Cu^{2+} in the KNN crystal lattice. Therefore, in some studies, Sb impurities were added to the KNN ceramics to improve the electrical properties of the ceramics. Jiagang Wu et al. [12] clarified the role of Sb^{5+} in increasing the electrical properties of the ceramic system $(K_{0.48}Na_{0.52})(Nb_{1-x}Sb_x)O_3$ ($0 \le x \le 0.16$). This research has shown that doping with Sb^{5+} can simultaneously move their orthorhombic–tetragonal phase transition temperature (T_{O-T}) and rhombohedral–orthorhombic phase transition temperature (T_{R-O}) forward to room temperature. The coexistence of rhombohedral and orthorhombic phases was established in the Sb^{5+} composition range of 0.07–0.09. Their dielectric, ferroelectric, and piezoelectric properties are strongly dependent on the antimony content, with x = 0.07, the ceramics has the best piezoelectric properties: d_{33} = 210pC/N, k_p = 0.45.

In this study, we present the effect of Sb on the electrical properties of the $(K_{0,48}Na_{0,48}Li_{0,04})(Nb_{1-x}Sb_x)O_3$ + 0.25 wt.% CuO ceramics.

EXPERIMENTAL

The $(K_{0,48}Na_{0,48}Li_{0,04})(Nb_{1-x}Sb_x)O_3$ + 0.25 wt.% CuO (KNLN*x*S) piezoelectric ceramics, where x = 0.0, 0.01, 0.03, 0.05 and 0.07, were synthesized by a conventional mixed-oxide method. K_2CO_3, Na_2CO_3, Li_2CO_3, and oxide CuO, Nb_2O_5 (purity ≥ 99%) were used as starting materials. Before being weighed, the K_2CO_3 and Na_2CO_3 powders were dried in an oven at 200°C for 2 hour to minimize the effect of moisture. Mixed powder was milled for 20 hour with the ZrO_2 balls in ethanol. Two calcinations at temperature 850 °C for 2 hour were performed to obtain the single phase formation. Thereafter the calcined powders were ball milled again for 16 hour. The ground materials were pressed into disk 12 mm in diameter and 1.5 mm in thick under 1.5T/cm^2 and then were sintered at temperatures of 950 °C for 2 hours.

The crystal structure of the ceramic samples was examined by X-ray diffraction (XRD, D8 ADVANCE) with CuK_α radiation of wavelength 1.5405 Å at room temperature. The microstructure of the samples was examined by using a scanning electron microscope (SEM) (Hitachi S-4800). The densities of samples were measured by Archimedes method. Temperature dependence of dielectric constant was determined using RLC HIOKI 3532 with automatic programming. The samples were poled in a silicone oil bath at 90 °C by applying electric field of 40 kV/cm for 30 min. They were aged for 24h prior to testing. The d_{33} piezoelectric constant were determined using a d_{33} meter (YE2730A, Sinoceramics, Inc., China) and electromechanical coupling factor were determined from the resonance and antiresonance frequency using an impedance analyzer (HP 4193A and RLC HIOKI 3532). The ferroelectric property was measured by Sawyer-Tower method.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns in the range of 2θ from 20° to 80° for the KNLN*x*S ceramics sintered at 950°C. It can be seen that all the ceramic samples are of the perovskite phase, no secondary phase was detected. All the components have a double peak (220)/(020) with an relative intensity ratio of I_{220}/I_{002} = 2/1 around 2θ = 45.5°, according to work of Fang-Zhou Yao [13], with an orthorhombic symmetry, the ideal ratio of I_{220}/I_{002} equals to 2:1, while it evolves to 1:2 for a tetragonal phase. So, all samples exhibit a single perovskite structure with an orthorhombic symmetry over the whole composition range. This result has shown that Sb^{5+} ions have been diffused into the KNLN crystal lattice to form a homogeneous solid solution, with Sb^{5+} entering the Nb^{5+} sites due to the radius of the Sb^{5+} ion (0,62 Å) is similar to that of the Nb^{5+} ion (0.69 A°) [14].

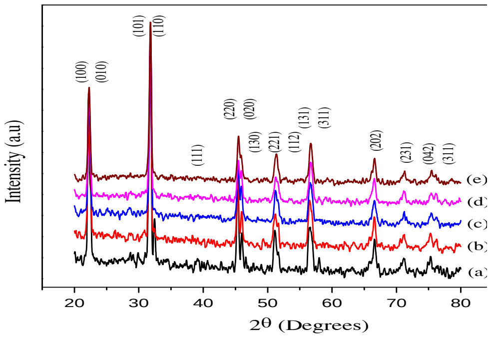

Figure 1. X-ray diffraction patterns of the KNLN*x*S ceramics sintered at 950°C: (a) *x* = 0.0; (b) *x* = 0.01;(c) *x* = 0.03; (d) *x* = 0.05; (e) *x* = 0.07

For further analysis of the effect of Sb on the phase structure of the ceramics, the X-ray diffraction spectra of the ceramic system were investigated in the ranges of 2θ from 44.5° to 46.5° (Fig. 2). With increasing of the Sb content, it was found that the diffraction peaks (220) and

(020) characteristic of the orthorhombic structure have shifted towards the higher diffraction angles, according to the Bragg's equation (2dsinθ = nλ), the inter-planar distance decreases gradually, suggesting that the crystal lattice volume has decreased with Sb substitution. As noted above, the ionic radius of Sb^{5+} is smaller than those of Nb^{5+} ion, when entering the lattice, it will replace Nb^{5+} at the B-sites of the perovskite unit cell, resulting in decreased the crystal lattice volume. This result is consistent with the works [12, 14]

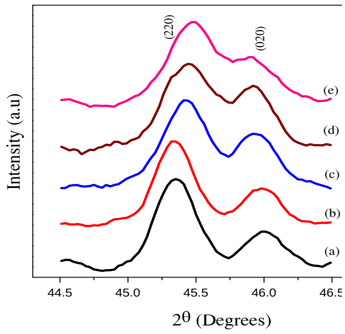

Figure 2. X-ray diffraction patterns of the KNLN*x*S ceramics in the ranges of 2θ from 44.5° to 46.5°

Figure 3a shows the densities of KNLN*x*S ceramics as a function of different amounts of Sb additive sintered at temperature 950°C. As shown in Fig. 3a, with increasing of Sb content, the density the ceramic samples strong increase and reaches the highest value of 4.21g/cm^3 at 0.05mol Sb concent, then decreases. This result is consistent with the microstructure of fracture surfaces of KNLN*x*S ceramic samples as shown in figures 3(b) – 3(f). Figure 3b shows that undoped ceramics had a porous microstructure, the distribution of discrete grains, the average size of the grains is abnormally large, 3.67 μm. When a small amount of Sb (0.01mol) was added, the average size of the grains decreases, (2,65μm), microstructure of the ceramics consists of relatively more uniform grains with rectangular shapes, however, there are still many porous holes, maybe this is the reason for low density (3.94g/cm^3). Further increasing the Sb content from 0.03 to 0.05mol (Fig. 3(d)–3(e)), the average grain size of the ceramics continued to decrease from 1,17μm to 0,76μm, respectively, amount of porous decreased markedly, the microstructure of samples becomes denser, corresponding to high density. When the amount of Sb increases to 0.07mol, the average grain size of ceramics decreases (0,4μm), and porous microstructure (Fig. 3f). Thus it has been shown that Sb inhibits the growth of particles. These results are consistent with the works of Qian Zhang [15] Jiagang Wu [12]. Such as the 0.05mol Sb added ceramics, the highly dense and homogeneous microstructure was obtained, which may expect improved electrical properties of ceramics.

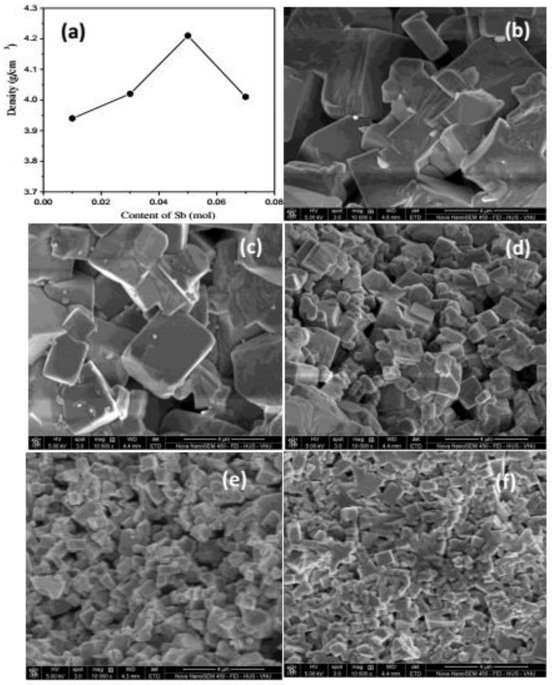

Figure 3: (a) The density of KNLN*x*S ceramics as a function of the Sb content and the SEM micrographs of KNLN*x*S ceramics with (b) *x* = 0, (c) *x* = 0.01, (d) *x* = 0.03, (e) *x* = 0.05 and (f) *x* = 0.07°C sintered at temperatures 950°C.

Figure 4 shows the room temperature dielectric constant ε and the dielectric loss was measured at 1kHz frequency of KNLN*x*S ceramics sintered at 950°C as a function of the Sb content. The dielectric constant ε increases with the Sb content increases and reaches the highest value (ε = 360) at $x = 0.05$. However, when $x > 0.05$, the dielectric constant ε decreased. Conversely, when the Sb concentration increases, the value of the dielectric loss tanδ decreases to the smallest value (tanδ = 0.025) at x = 0.05, then increases. This is related to density and microstructure of ceramics.

Figure 5 shows the temperature dependence of dielectric constant ε and dielectric loss tanδ was measured at a 10 kHz frequency of KNLN*x*S ceramics sintered at 950°C. As seen, all the ε(T) curves of the ceramic samples has two obvious peaks: a peak at low temperature (in the range of 67 - 134ºC), which is the peak corresponding to the orthorhombic-tetragonal ferroelectric phase transition temperature ($T_{O\text{-}T}$), the second peak at higher temperatures (in the range of 238 and 435ºC), corresponding to the ferroelectric-paraelectric phase transition temperature (T_C).

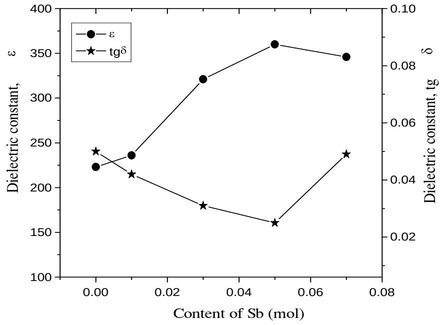

Figure 4. Room-temperature dielectric constant ε and the dielectric loss tanδ of KNLN*x*S ceramics with different amounts of Sb

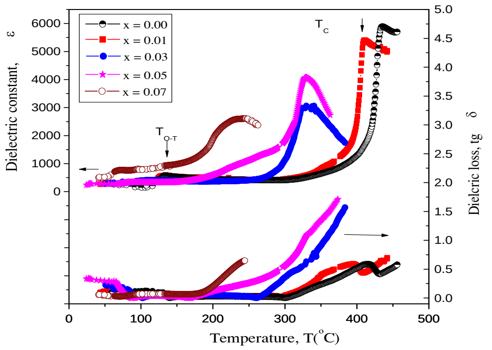

Figure 5. Temperature dependence of dielectric constant ε and dielectric loss tan*δ* of the KNLN*x*S ceramics sintered at 950°C.

As seen from figure 6, with the Sb concentration increases from 0 to 0.07mol, both T_C temperature and the $T_{O\text{-}T}$ orthorhombic - tetragonal transition temperature significantly reduced from 435 °C to 238 °C and 134 °C to 67°C, respectively. This is consistent with the decrease of the unit cell size when the Sb^{5+} ions with small size replace Nb^{5+} at the B-sites of the ABO_3 perovskite structure. These results are consistent with the work of F. Jiagang Wu [12] and Xuming Pang [14]. From figure 5 also shows that with the samples have low Sb concentration (x = 0 - 0.01), the peak of the sharp dielectric constant, indicating that the ceramics are a normal ferroelectric. However, with increasing of the Sb concentration (x = 0.03 -0.07), the peak of the dielectric constant was extended corresponding to the diffusion phase transition characteristic of relaxor ferroelecric [16]

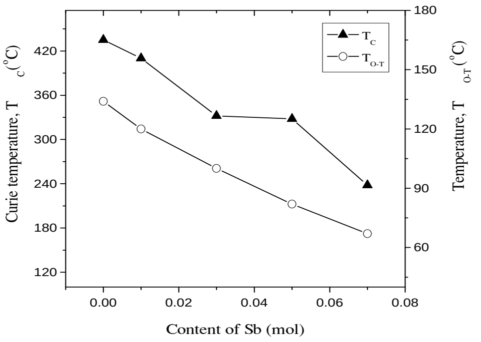

Figure 6. The T_C and $T_{O\text{-}T}$ temperatures of KNLN*x*S ceramics with changing the content of Sb.

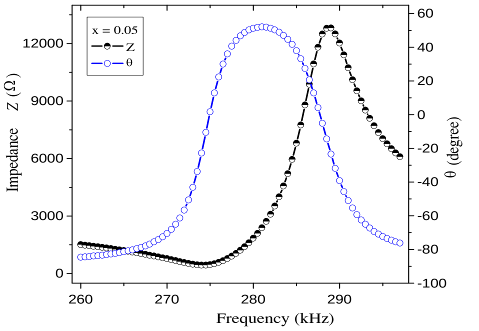

Figure 7. The spectrum of radial resonance of KNLN*x*S ceramic sample with x = 0.05 sintered at 950°C

To determine piezoelectric properties of ceramics, resonant vibration spectra of samples were measured at room temperature, figure 7 shows the spectrum of radial resonance of KNLN*x*S ceramic sample with x = 0.05 sintered at 950°C. As seen, impedance Z reaches the minimum value at 274kHz frequency and maximum value at 289kHz frequency. From these resonant spectra, piezoelectric parameters of ceramics were determined**.** Figure 8 shows the electromechanical coupling factors (k_p, k_t), the piezoelectric constant (d_{33}) change as a function of the Sb content of KNLN*x*S ceramics sintered at 950ºC. When the content of Sb increases from x = 0 to 0.05, the values of k_p, k_t, and d_{33} are rapidly increased and reach largest values for k_p of 0.36, k_t of 0.43, d_{33} of 151pC/N at x = 0.05, then decrease. This may be related to the density of ceramics with changing the content of Sb.

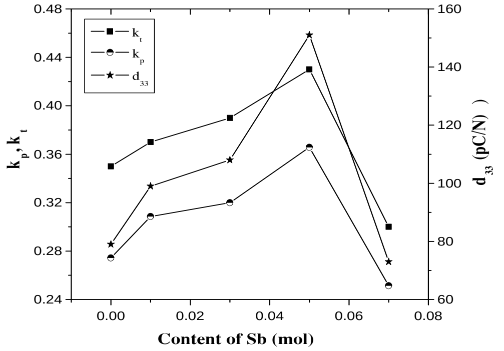

Fig. 8. The Sb content dependence of the values k_p, k_t, and d_{33}, of KNLNxS ceramic system sintered at 950°C

Figure 9 shows the shape of ferroelectric hysteresis loops of the KNLN*xS* ceramic samples measured at room temperature. From the shape of these loops, the remanent polarization (P_r) and the coercive field (E_C) were determined. With increasing of Sb content, a sharp increase in P_r was observed for samples until $x = 0.05$, reaches the highest value (10.14μC/cm^2), and then decreases, while the coercive field E_C decreases from 11,83 to 5,23kV/cm. These results are in good agreement with the studied dielectric and piezoelectric properties of the ceramic samples.

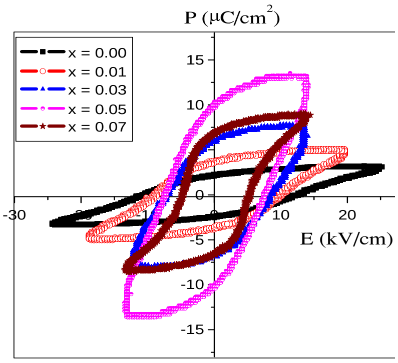

Fig. 9. Hysteresis loops of KNLNxS ceramic samples sintered at 950°C

CONCLUSION

The effect of Sb addition on the electrical properties of the $(K_{0,48}Na_{0,48}Li_{0,04})(Nb_{1-x}Sb_x)O_3$ + 0.25 wt.% CuO ($x = 0.0 \div 0.07$) piezoelectric ceramics was investigated. The addition of Sb improved the density of the ceramics at a low sintering temperature (950°C). All samples have pure perovskite phase with an orthorhombic symmetry, the crystal lattice volume has decreased with Sb substitution.

The ε (T) curves of the ceramic samples has two peaks: a peak corresponding to the orthorhombic-tetragonal ferroelectric phase transition temperature ($T_{O\text{-}T}$) (in the range of 67 - 134ºC), and the other peak corresponding to the ferroelectric-paraelectric phase transition temperature (T_C) (in the range of 238 and 435ºC). When the Sb concentration increases, both T_C temperature and the $T_{O\text{-}T}$ decrease. At the Sb content of 0.05 mol, physical properties of ceramics are best: the density of 4.21g/cm^3; the electromechanical coupling factor, $k_p = 0.36$ and $k_t = 0.43$; the dielectric constant, $\varepsilon = 360$; the dielectric loss (tanδ) of 0.025; the piezoelectric constant (d_{33}) of 151 pC/N; the remanent polarization (P_r) of 10,14μC/cm^2.

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