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Effect of Sintering Temperature on Microstructure and Physical Properties of CuO-Doped $0.96(K_{0.5}Na_{0.5})NbO_3$–$0.04LiNbO_3$ Lead-Free Piezoelectric Ceramics

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The $0.96(K_{0.5}Na_{0.5})NbO_3$–$0.04LiNbO_3$ (KNLN) doped with 0.25 wt.% CuO (KNLN-CuO) piezoelectric ceramics have been fabricated successfully by the conventional solid-state reaction method at different sintering temperatures from 900 to 1050 °C. The introduction of CuO significantly improved the sinterability of ceramics, the KNLN-CuO ceramics could be well sintered at a low temperature and exhibited a dense microstructure. The effect of sintering temprature on the structure, microstructure and electrical properties of KNLN-CuO ceramics was studied. Experimental results showed that at the sintering temperature of 950 °C, the KNLN-CuO ceramics exhibit the good electrical properties: the density of 4.14 g/cm^3; the electromechanical coupling factor, $k_p = 0.33$ and $k_t = 0.43$; the dielectric constant, $\varepsilon = 349$; the dielectric loss, $tg\delta = 0.008$; the piezoelectric constant, $d_{33} = 130$ pC/N, the remanent polarization, $P_r = 8.43$ μC/cm^2.

Keywords: Lead-Free, Structure, Microstructure, Sintering Temperature, Ferroelectric.

1. INTRODUCTION

In the last decades, many scientists are interested in research and application of PZT-based piezoceramics due to their excellent piezoelectric properties [1]. However, lead is a toxic element, the development of lead-free piezoelectric ceramics with excellent electrical properties to replace Pb-based ceramics in a variety of devices is necessary [2–6].

During recent years, intensive efforts have been made to develop lead-free piezoelectric ceramics with perovskite structure, among them, piezoelectric ceramics on the basis of (Na, K)NbO_3 (KNN) have attracted much attention due to their strong ferroelectric properties, high Curie temperature (about 420 °C) and environmentally friendly, capable of replacing lead-based ceramics [4, 7–10]. On the other hands, because of the high volatility and hygroscopic of the alkaline elements at high sintering temperatures, it is very difficult to obtain KNN ceramics with high density, good electrical properties by conventional sintering technique [11]. Therefore, the problem of controlling the volatility of the alkaline elements by lowering the sintered temperature of the ceramics or modified KNN ceramics by the appropriate impurity components to form new KNN-based ceramics are expected to improve the density and electrical properties of KNN based ceramics. The studies usually focus on (Na, K)NbO_3–$LiNbO_3$ (KNLN) solid solutions [3, 12].

The method to reduce the sintering temperature of KNN based ceramics is to add sintering agents such as ZnO [13], CuO [14–16], MnO_2 [17], $K_4CuNb_8O_{23}$ (KCN) [8]. Among them, copper oxide (CuO) has been shown to be effective in reducing the sintering temperature for Pb-based and free-lead ceramics [15, 16]. The increased sinterability and enhanced density of KNN based ceramics with CuO addition was explained by the formation of a liquid phase during the sintering due to the reaction of CuO and Nb_2O_5 [14, 16]. In addition, many studies have shown that the sintering temperature of the ceramics plays an important role in physical properties of the KNN based ceramics [17, 18]. However, until now

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these problems have not been studied in detail for the CuO doped $0.96(Na_{0.5}K_{0.5})NbO_3$–$0.04LiNbO_3$ ceramics. In this paper, we present some results on the effect of the sintering temperature on the physical properties of the $0.96(Na_{0.5}K_{0.5})NbO_3$–$0.04LiNbO_3$ doped with 0.25 wt.% CuO ceramics.

2. EXPERIMENTAL PROCEDURE

The $0.96(K_{0.5}Na_{0.5})NbO_3$–$0.04LiNbO_3 + 0.25$ wt.% CuO (KNLN-CuO) piezoelectric ceramics were synthesized by a conventional mixed-oxide method. K_2CO_3, Na_2CO_3, Li_2CO_3, and oxide CuO, Nb_2O_5 (purity $\geq$ 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 hours to minimize the effect of moisture. Mixed powder was milled for 20 hours with the ZrO_2 balls in ethanol. The dried powder was calcined at 850 °C for 2 hours twice. The powder was re-milled between two calcinations in order to improve chemical homogeneity. Thereafter the calcined powders were ball milled again for 16 hours. The ground materials were pressed into disk 12 mm in diameter and 1.5 mm in thick under 1.5 T/cm^2. To limit the evaporation of alkaline elements, these pellets were covered by the powders with the same composition and then were sintered at different temperatures of 900, 950, 1000, and 1050 °C for 2 hours.

The crystal structure of the ceramic samples was examined by X-ray diffraction (XRD, D8 ADVANCE). 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 24 hours 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.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns in the range of 2θ from 20° to 80° of the KNLN-CuO ceramics sintered at different temperatures of 900, 950, 1000, and 1050 °C for 2 hours.

It can be seen that all the ceramic samples have typical perovskite structure with orthorhombic symmetry, this has shown that the phase transition does not occur as the sintering temperature increases. In addition, with different sintering temperatures, there is no change on the peak position and peak shape of the KNLN-CuO ceramics.

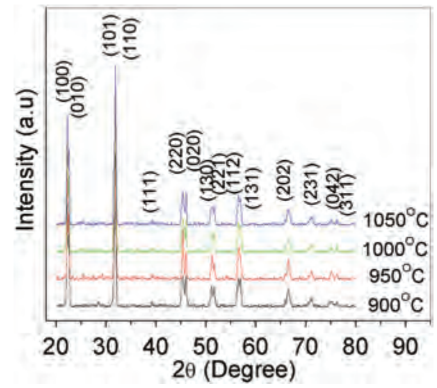

Figure 1. X-ray diffraction patterns of the KNLN-CuO ceramics sintered at 900 °C, 950 °C, 1000 °C and 1050 °C for 2 hours.

These results are consistent with the work of Bahanurddin et al. [17]. From the XRD patterns also show that no secondary phase was detected, it is suggested that Li^+ and Cu^{2+} ions have been diffused into the KNN crystal lattice to form a homogeneous solid solution, with Li^+ entering the Na^+, K^+ sites and Cu^{2+} occupying the Nb^{5+} sites due to the radius of the Cu^{2+} ion (0.73 Å) is similar to that of the Nb^{5+} ion (0.64 Å) [16, 19].

Figure 2 shows the measured density of KNLN-CuO ceramics as a function of sintering temperature. As seen, with the sintering temperature increases from 900 °C to 1050 °C, the density of the KNLN-CuO ceramic samples increases from 4.09 g/cm^3 to 4.14 g/cm^3, reaches the highest values of 4.14g/cm^3 at 950 °C sintering temperature, then decreases as the temperature exceeds 950 °C. According to our research result, with the undoped KNLN samples, to obtain average density of 4.09 g/cm^3, the ceramics must be sintered at a relatively high temperature (1050 °C). Thus, the addition of CuO remarkably improved the sinterability of KNLN ceramics and the relative high density value could be achieved at low sintering temperature. This result can be explained by the formation of a liquid phase during the sintering [14].

Figure 3 shows ceramic sample sintered at low temperature of 900 °C had a porous microstructure with small

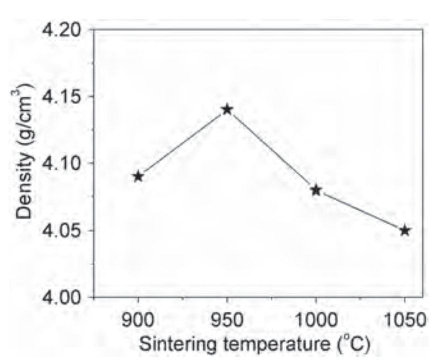

Figure 2. The density of KNLN-CuO ceramics as a function of the sintering temperatures.

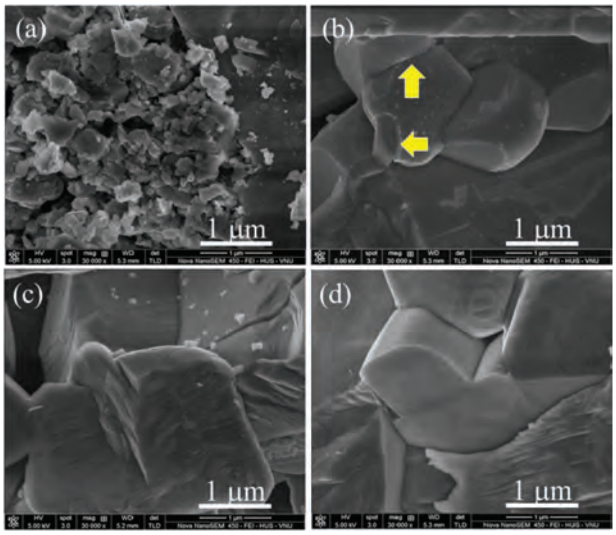

Figure 3. The SEM micrographs of KNLN-CuO ceramics with different sintering temperatures.

grains and discrete distributions, corresponding to low density, indicating that not sintered materials at 900 °C temperature. However, when the sintering temperature increased to 950 °C, the dense and uniform microstructure with enlarged grains was developed (Fig. 3(b)). From Figure 3(b) also show that at grain boundaries exist an amorphous phase, as indicated by the yellow arrows. Therefore, it was considered that densification and grain growth of the KNLN ceramics doped with CuO might be explained by the liquid-phase sintering [20]. Figures 3(c)–(d) shows the KNLN-CuO ceramics sintered at temperature of 1000 °C and 1050 °C, enlarged grains can be observed showing an abnormal grain growth, however, the microstructure of samples becomes more porous may be due to the evaporation of alkali metal at high sintering temperature [21], their density was found to be smaller than as compared to the ceramics sintered at 950 °C.

Figure 4 shows the room temperature dielectric constant ε and dielectric loss $tg\delta$ were measured at 1 kHz frequency of KNLN-CuO ceramics as function of the

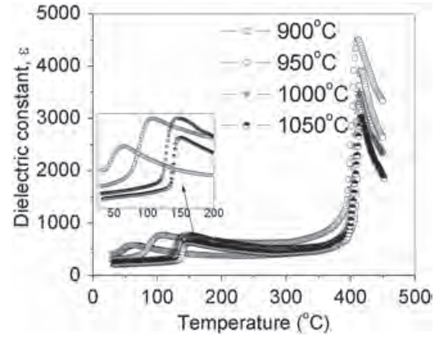

Figure 5. Temperature dependence of dielectric constant ε of the KNLN-CuO ceramics sintered at different temperatures.

sintering temperatures. The dielectric constant ε increases with the sintering temperature increases and reaches highest value (349) at 950 °C sintering temperature. However, when the sintering temperature is higher than 950 °C, the dielectric constant ε decreased. Meanwhile, dielectric loss $tg\delta$ reveals an opposite trend to dielectric constant ε as indicated in the Figure 4. The lowest value of $tg\delta$ (0.008) appears at 950 °C corresponding to the highest value of ε. These are may be related to density and microstructure of ceramics.

Figure 5 shows the temperature dependence of the dielectric constant was measured at 10 kHz frequency of KNLN-CuO ceramics sintered at different sintering temperatures. As seen, the dielectric peaks of ceramic samples at different sintering temperatures are still sharp, indicating that the ceramics are a normal ferroelectric [12]. In addition, two transitional points corresponding to the orthorhombic-tetragonal ferroelectric phase transition temperature ($T_{\text{O-T}}$) and ferroelectric-paraelectric phase transition temperature (T_C) are observed during the measured temperature range. With increasing of sintering temperature, T_C Curie temperature is almost constant (412°), this is consistent with the structure of the ceramics does not change as the sintering temperature increases as shown above. Meanwhile the $T_{\text{O-T}}$ transition temperature increases from 64 °C to 149 °C as the sintering temperature increases from 900 °C to 1050 °C. Reason for the shift

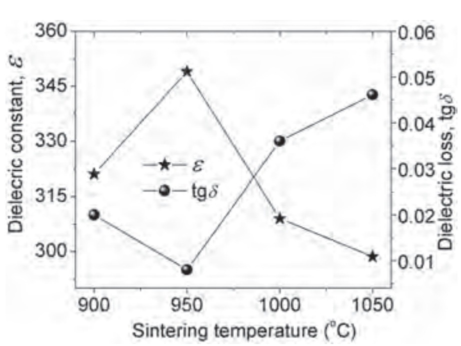

Figure 4. Room-temperature dielectric constant ε and dielectric loss $tg\delta$ of KNLN-CuO ceramics with different sintering temperatures.

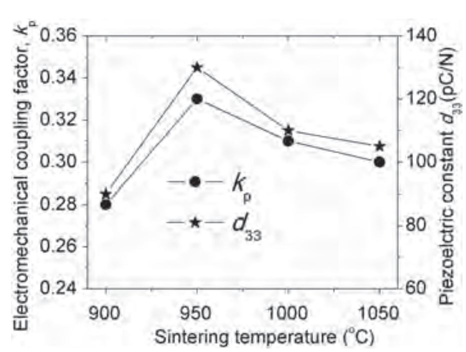

Figure 6. The CuO content dependence of the values k_p, k_t and d_{33}, of KNLN-xCuO ceramic system sintered at 950 °C.

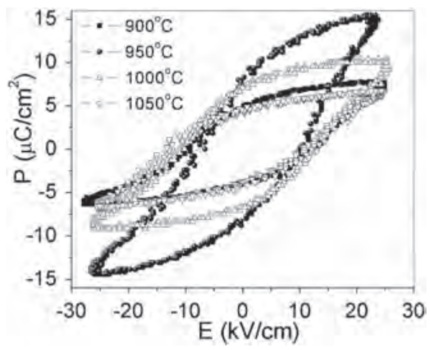

Figure 7. Hysteresis loops of KNLN-*x*CuO ceramic samples sintered at 950 °C.

of $T_{\text{O-T}}$ value in this work is unclear but should be linked with K and/or Na loss during the processing. Many authors have suggested that the shift of $T_{\text{O-T}}$ for many lead free ceramics can be related with Bi and/or Na loss [22, 23].

Figure 6 shows the electromechanical coupling factor (k_p) and the piezoelectric constant (d_{33}) of KNLN-CuO ceramics change as a function of the sintering temperature. It shows that the influence of sintering temperature on k_p and d_{33} is similar to ε, increasing with increasing sintering temperature, reaching the highest value of 0.33 and 130 pC/N, respectively at 950 °C and then decreases.

Figure 7 shows the *P–E* hysteresis loops of the KNLN-CuO ceramics as functions of the sintering temperature 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 the sintering temperature from 900 °C to 1050 °C, the remanent polarization (P_r) increases, reaches the highest value (8.43 μC/cm^2) at 950 °C, and then decreases, while the coercive field E_C fluctuates with the increase of the sintering temperature, reaches the lowest value (10.76) at 950 °C. These results are in good agreement with the studied dielectric and piezoelectric properties of the ceramic samples.

4. CONCLUSION

The effect of sintering temperature on the structure, microstructure and physical properties of the $0.96(K_{0.5}Na_{0.5})NbO_3$–$0.04LiNbO_3$ + 0.25 wt.% CuO ceramics was investigated. All samples have pure perovskite phase with orthorhombic symmetry, the phase transition does not occur as the sintering temperature varies. The addition of CuO improved the sinterability and increasing the density, grain size of the ceramics at low sintering temperature. Experimental results showed that at the sintering temperature of 950 °C, the KNLN-CuO ceramics exhibited the good electrical properties: the density of 4.14 g/cm^3; the electromechanical coupling factor, $k_p = 0.33$ and $k_t = 0.43$; the dielectric constant, $\varepsilon = 349$; the dielectric loss ($tg\delta$) of 0.008; the mechanical quality factor (Q_m) of 133; the piezoelectric constant (d_{33}) of 130 pC/N, the remanent polarization (P_r) of 8.43 μC/cm^2.

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