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Influence of calcination temperature on the piezoelectric properties of Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics

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Abstract

The effects of calcination temperature on the bulk density, piezoelectric, and ferroelectric properties were investigated for the Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics. The calcination temperatures were varied from 750 to 950 °C by 50 °C differences. An tetragonal XRD pattern, consistent with single-phase $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ was obtained after calcination at 850 °C for 2 h. And the experimental results showed that Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics calcined at 850 °C had a remnant polarization $P_r = 24.5\ \mu C/cm^2$, bulk density $= 4.32\ g/cm^3$, piezoelectric constant $d_{33} = 282$ pC/N and electromechanical coefficient $k_p = 37.8\%$.

Keywords: Ag_2O; Lead-free; Calcination temperature

1. Introduction

Until now, piezoelectric ceramics could probably be represented by $Pb(Zr,Ti)O_3$ (PZT) based ceramics; such as $Pb(Ni,Nb)O_3$–$Pb(Zr,Ti)O_3$ (PNN–PZT) [1], $Pb(Mg,Nb)O_3$–$Pb(Zr,Ti)O_3$ (PMN–PZT) [2], $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$ (PNN–PZN) [3], and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) [4]. However, lead based piezoelectric materials pose serious problems of toxicity and volatilization. Therefore, there have been strong demands for the development of lead-free piezoelectric ceramics to reduce the environmental problems.

In the past few years, many papers have reported the use of bismuth–titanate ($Bi_4Ti_3O_{12}$) [5] and potassium sodium niobate ($(K_{0.5}Na_{0.5})NbO_3$ (KNN) [6] families to replace lead-based piezoelectric ceramics. Among the candidates for lead-free piezoelectric ceramics, KNN ceramic has been recently considered as a promising material for lead-free piezoelectric systems due to its high piezoelectric coefficient of 416 pC/N and high Curie temperature of 253 °C [7]. Pure KNN ceramics are very difficult to densify by ordinary sintering process. It is generally believed that high sintering temperature can improve the density and piezoelectric properties. However, in pure KNN ceramics fabricated by the conventional sintering methods, densification is known to be difficult because the phase stability is limited to 1140 °C according to the phase diagram for $KNbO_3$–$NaNbO_3$ [8]. Therefore, in order to improve density and piezoelectric properties, various techniques of synthesis have been utilized, such as hot pressing and spark plasma sintering process, to obtain KNN ceramics with high densities [9,10]. Recently, normal sintering processes have been successfully applied to the fabrication of dense KNN-based ceramics [11,12]. Some dopants can be added to the KNN ceramics to improve the piezoelectric properties as well. Dopants, such as CuO, ZnO, MnO_2, and $LiTaO_3$ can increase the density by lowering the sintering temperature of ceramics [13–15]. Guo et al. reported that $(K_{0.5}Na_{0.5})NbO_3$–$LiNbO_3$ ceramics have a high piezoelectric constant ($d_{33} = 235$ pC/N) and electromechanical coefficient ($k_p = 44\%$) by employing the conventional ceramics process [16].

In this study, we propose a compatible niobate component to improve the piezoelectric properties of $(K,Na)NbO_3$ based piezoelectric systems. $Ag(Ta,Nb)O_3$ ceramics, which has ferroelectric–antiferroelectric phase transition near 182 K, has perovskite structure at room temperature with lattice parameter $a = b = 3.92$ Å and $c = 3.93$ Å [17]. Both $(K_{0.5}Na_{0.5})$

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NbO_3–$LiNbO_3$ and $Ag(Ta,Nb)O_3$ have perovskite structures with similar lattice parameters. Moreover, Ag dopant plays the role of a sintering aid for low temperature co-fired ceramics. Ag_2O was employed as an additional dopant to improve the piezoelectric properties. From our previous study, we found that 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ lead-free piezoelectric ceramics have a high piezoelectric coefficient of 274 pC/N [18]. Therefore, we focused on the preparation of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ lead-free piezoelectric ceramics at different calcination temperatures, and systemically investigate their dielectric and piezoelectric properties.

2. Experiment

The 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics were prepared by the conventional sintering process. Analytical-grade metal oxides and carbonate powders, $NaCO_3$, K_2CO_3, Li_2CO_3, Nb_2O_5, and Ag_2O were employed in this process. They were milled for 24 h with zirconia balls and ethyl alcohol and then dried for 24 h. They were calcined at 850 °C for 5 h. After the calcinations, Ag_2O powders were added to $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ powders. They were ball milled again, dried for 24 h, and calcined for 2 h. The dried mixture was sieved through a 100-mesh sieve. These powders were mixed with a binder of 3 wt% PVA, and pressed into disks of 12 mm diameter and 1 mm thickness under 98 MPa. These disks were sintered in air at 1080 °C for 2 h. The sintered samples were polished to 0.7 mm and then thermal etched at 1000 °C for 20 min. The bulk density was calculated from mass and dimensions of ceramic pellets. The crystalline structures were investigated by X-ray diffraction analysis employing Cu Ka radiation (Rigaku, D/MAX-2500 V/PC). The microstructure was observed using SEM (Hitachi, S-4300). The frequency

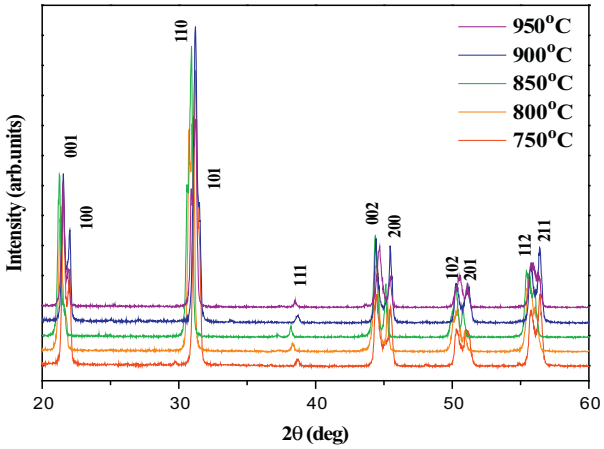

Fig. 1. XRD patterns of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics calcined at different temperatures.

Table 1
Lattice parameters c and a of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics calcined at different temperatures.

Calcination temperature (°C)	Lattice parameters (Å)	
	c	a
750	4.024	3.968
800	4.026	3.971
850	4.029	3.973
900	4.025	3.967
950	4.020	3.966

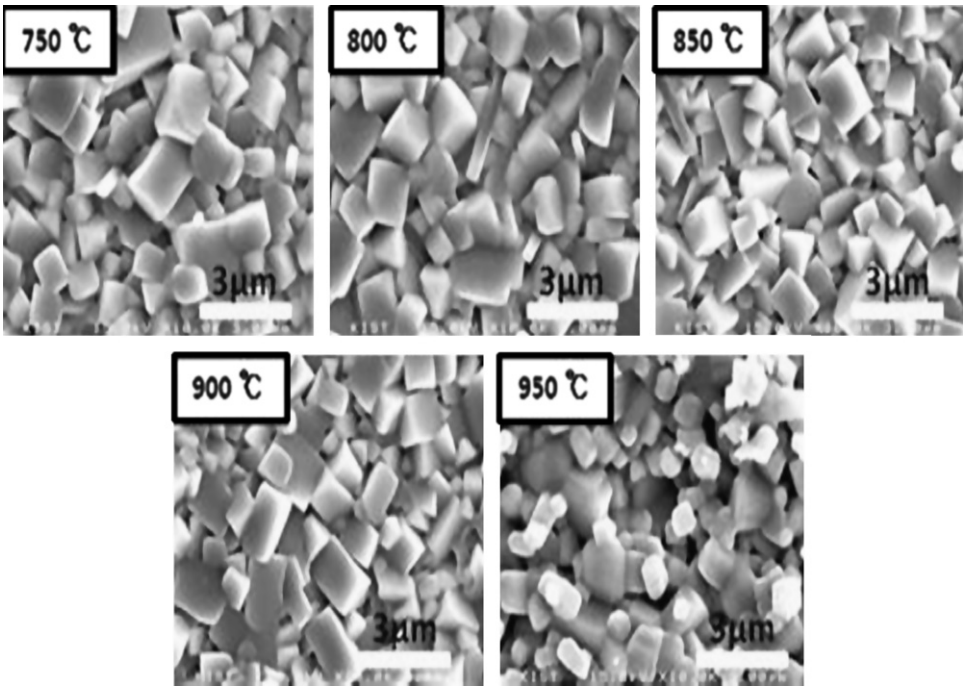

Fig. 2. SEM images of the 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics calcined at various temperatures.

dependence of the dielectric permittivity and loss tangent of the samples were measured employing a precision LCR Agilent 4284 A meter from 1 kHz to 1 MHz. The samples were polled under 3.5 kV/mm in a silicone oil bath at temperature of 120 °C for 30 min, and then the ceramics were cooled to room temperature under the electric field. The piezoelectric constant d_{33} was measured using d_{33} meter (YE 2730A). The temperature dependence of the dielectric constant was obtained using a programmable automatic LCR meter (FLUKE PM 6304).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics calcined at different temperatures in the range of 750–950 °C for 2 h. When the calcination temperature is lower than 850 °C, Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics possess a single perovskite structure suggesting that Ag^+ has diffused into the $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ lattices to form a homogeneous solid solution without any detectable secondary phase. However, increasing the calcination temperature upto 900 °C, it seems that the ceramics begin to lose their tetragonal structures. The lattice parameters of c and a were calculated from Bragg reflection position employing the Bragg law, and fitted by the Nelson–Riley extrapolation function [19] with the least mean square method.

$$\frac{C_{\cos\theta}-C0}{C0} = A\cos^2\theta\left(\frac{1}{\sin\theta}+\frac{1}{\theta}\right) \quad (1)$$

where, $C_{cos\theta}$ interplane distance calculated from the apparent Bragg peak position at 2θ and A is a fitting coefficient. The calculated lattice parameters c and a of ceramics are 4.029–4.020 and 3.973–3.966 Å, respectively. The variation of lattice parameters as a function of the calcination temperature is shown in Table 1.

Fig. 2 shows the SEM images of the specimens. The grain size became smaller gradually with the increase of temperature upto 800 °C. At 850 °C, the specimens have a uniform and dense structure compared with other specimens. However, increasing the calcination temperature further to 900 °C, they have irregular particle sizes with decreased grain sizes. Due to this decreased and irregular grain size, 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics have lower piezoelectric properties than those calcined at 850 °C.

The bulk density and relationship between piezoelectric constant d_{33}, electromechanical coefficient k_p of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics are shown in Fig. 3. It was found that the bulk density, d_{33} and k_p increases with increasing calcination temperature, reaches a maximum value of 282 pC/N and k_p=37.8% at 850 °C, then decreases with increasing calcination temperature. The promotion may be attributed to the increased density and enhancing the poling process. These results indicate that the ceramics calcined at 850 °C possess optimized piezoelectric property. From Figs. 1 and 3, we believe that higher calcination temperatures more than 850 °C makes the Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics lose their uniform structure, and this worsens the piezoelectric properties.

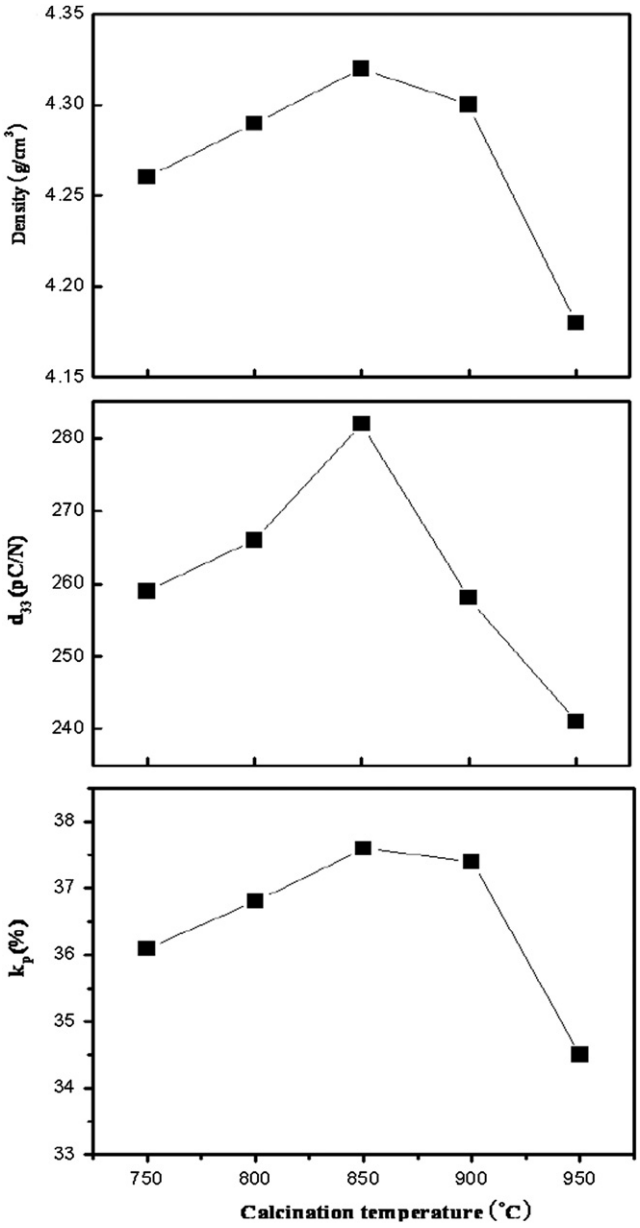

Fig. 3. Bulk density, piezoelectric constant d_{33} and electromechanical coefficient k_p of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics.

Fig. 4 shows the frequency dependence of impedance magnitude and phase angle for Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramic calcined at 850 °C. It has been known that under the ideal poling state, the phase angle will have a value of 90° in the frequency range between the anti-resonance and resonance frequencies. The observed phase angle for Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramic is 75.5°, and exhibits a very sqarelike resonance peak. This is in agreement with the observations for other hard piezoelectric ceramics [20].

Fig. 5 displays the polarization–electric field (P–E) hysteresis loops of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})$

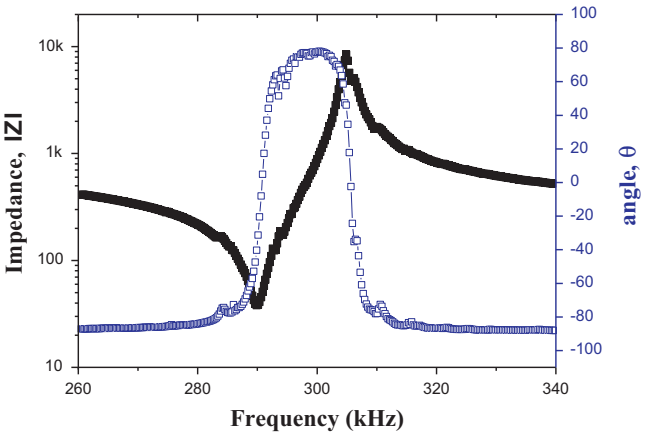

Fig. 4. Frequency dependence of impedance (Ω) and phase angle (deg.) for Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramic calcined at 850 °C.

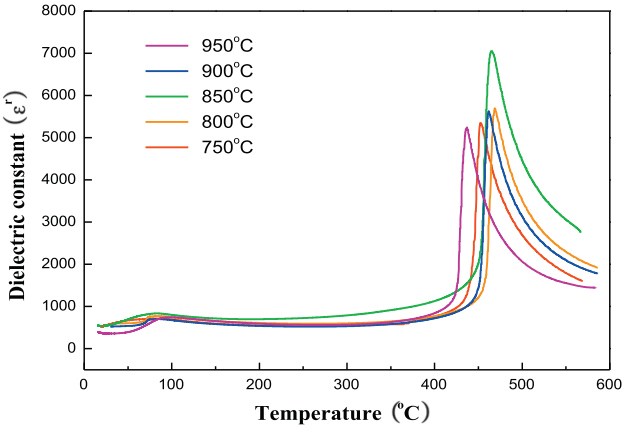

Fig. 6. Temperature-dependent relative dielectric permittivity of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics calcined at different temperatures.

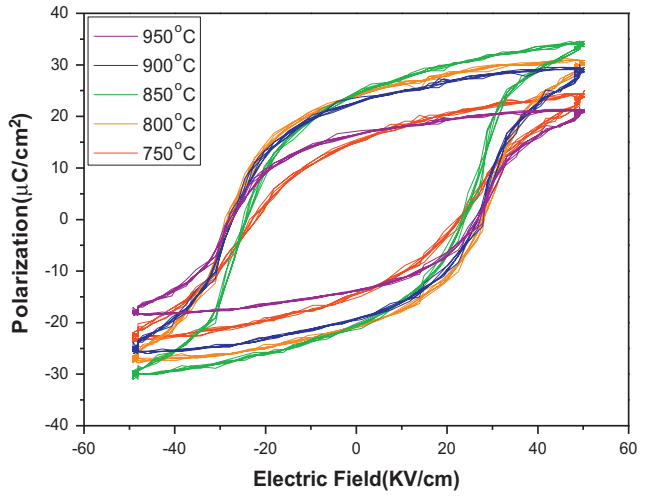

Fig. 5. *P–E* hysteresis loops of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics calcined at different temperatures.

NbO_3–$0.06LiNbO_3$ ceramics. Maximum electric field of 50 kV/cm was applied to the specimens. *P–E* hysteresis loops for the specimen, which was calcined at 850 °C, has the highest remnant polarization of 24.5 μC/cm^2 compared with other specimens. As shown in the Fig. 5 with increasing calcination temperatures, remnant polarization increased upto 24.5 μC/cm^2 for the specimen, which calcined at 850 °C. And then the remnant polarization began to decrease with further increasing calcination temperature. This decreased ferroelectric property was closely related with the leakage current and density of the calcined specimens.

Fig. 6 shows the dielectric constant ε′ as function of the temperature for 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics. The 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics showed tetragonal–cubic transition temperature (T_C) of 437–469 °C, which increased by decreasing the calcination temperature. As you can see in the figure, we found a weak phase transition near 50–100 °C. We believe this phase transition temperature is related with the orthorhombic–tetragonal phase transition. Due to this orthorhombic–tetragonal phase transition near the room temperature, we believe that the piezoelectric properties of 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics increased near room temperature.

4. Conclusion

The 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics were prepared by a mixed-oxide method under various calcinations temperatures. Increasing calcination temperatures indicated that the ceramics have crystallized and possess tetragonal properties. The calcination temperature of 850 °C was an optimized temperature for densification, piezoelectric, and dielectric properties. The density ρ, piezoelectric constant, electromechanical coefficient k_p and dielectric permittivity obtained were 4.32 g/cm^3, 282 pC/N, 37.8% and 652, respectively. This means that 7 mol% Ag_2O doped $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics can be used as an alternative for lead-free piezoelectric applications.

Acknowledgments

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