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Effect of ZnO on the microstructures and piezoelectric properties of $K_{0.5}Na_{0.5}NbO_3$ ceramics

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Lead-free ZnO added $K_{0.5}Na_{0.5}NbO_3$ piezoelectric ceramics have been prepared by a conventional solid state process. The XRD results show that all the $K_{0.5}Na_{0.5}NbO_3$ ceramics with various ZnO contents are single phase with an orthorhombic perovskite structure. The bulk density obtained by the Archimedes method indicates that the addition of ZnO improves the density of $K_{0.5}Na_{0.5}NbO_3$ ceramics under the same sintering conditions. Especially, at a level of 1 mol% ZnO, the sample sintered at 1100 °C for 1h exhibits the highest bulk density (ρ = 4.28 g/cm^3) and shows optimal piezoelectric properties, d_{33} = 135 pC/N and k_p = 0.40.

Key words: Lead-free piezoelectric, $K_{0.5}Na_{0.5}NbO_3$, ZnO, Microstructure.

Introduction

Lead zirconate titanate (PZT)-based ceramics show excellent electrical properties. They are widely used in actuators and sensors as well as in microelectronic devices [1-2]. However, the toxicity of lead oxide and its high vapor pressure during processing have led to a demand for alternative lead-free piezoelectric materials. Among the lead-free materials, $K_{0.5}Na_{0.5}NbO_3$ (KNN) exhibits optimal piezoelectric properties, (piezoelectric constant d_{33} = 70 pC/N, electromechanical coupling coefficient k_p = 0.25) [3]. As a result, KNN-based ceramics recently have attracted a considerable attention as one of the most promising candidates for lead-free piezoelectric ceramics [4-11].

However, it is difficult to obtain dense KNN ceramics with a homogenous microstructure by conventional ceramic processing, because of the volatilization of alkaline elements at high temperatures. Thus, many researchers focused on the producing dense KNN ceramics without volatilization of K and Na using special preparation techniques, such as hot pressing [12], spark plasma sintering [13] and hot forging [14]. However, these processing techniques are expensive and complex for electronic ceramics. In general, low melting-temperature additions such as glass, CuO, V_2O_5, $K_{5.4}CuTa_{10}O_{29}$ have been widely used as sintering aids to improve the sintering ability as well as the microstructures, and further to enhance the electric properties [15-17].

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In this study, the effect of ZnO as a sintering aid on the density, microstructure, and piezoelectric properties of KNN ceramics was investigated.

Experimental Procedure

ZnO added $K_{0.5}Na_{0.5}NbO_3$ ceramics were prepared by a conventional ceramic fabrication technique. Highly-pure Na_2CO_3(99.8%), K_2CO_3(99.9%), and Nb_2O_5(99.9%) were used as raw materials and mixed thoroughly in ethanol using a zirconia ball mill for 24h according to the stoichiometric ratio of KNN which was dried, and then calcined at 800 °C for 10 h. The phase composition of this calcined powder is pure KNN as confirmed by XRD. Then the KNN powders with x mol% ZnO additions where x was 0, 0.5, 1.0, and 2.0 respectively were ground and mixed thoroughly with a polyvinyl alcohol (PVA) solution as a binder, and then pressed into disk samples with diameter of 12 mm and thickness of about 1.5 mm. These pellets were heated slowly to 650 °C and soaked for 2 h to remove the binder, and then sintered at 1060-1140 °C for 1 h in air, followed by furnace cooling. Silver electrodes were printed on the top and bottom surfaces of the samples for subsequent poling and measurements.

The phase compositions and the crystal structures of the samples were confirmed by an X-ray diffractmeter (PW3050/60, MPSS using Cu $K_{\alpha 1}$ radiation). The bulk density was measured by the Archimedes method. A field emission scanning electron microscope (FE-SEM, Hitachi S-4800) was used to observe the microstructures. The samples were polarized along the thickness direction under a poling electric field of 2-3 kV/mm at 120 °C for 30 minutes in a bath of silicon oil. After the samples were aged for 24 h after poling, the piezoelectric coefficient

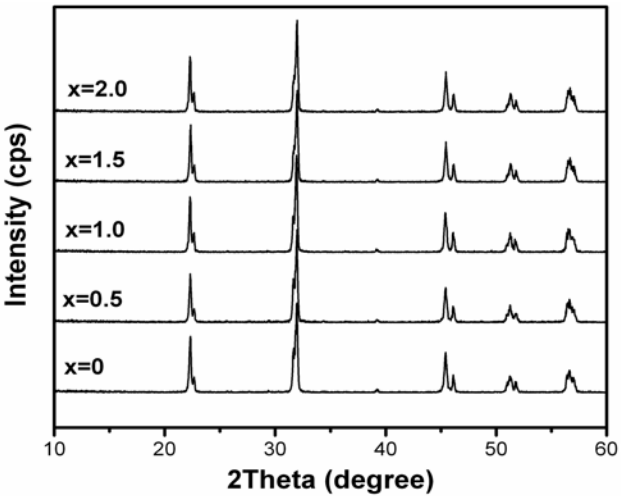

Fig. 1. XRD patterns of the $K_{0.5}Na_{0.5}NbO_3$ ceramics as a function of xmol% ZnO sintered at 1100 °C for 1 h.

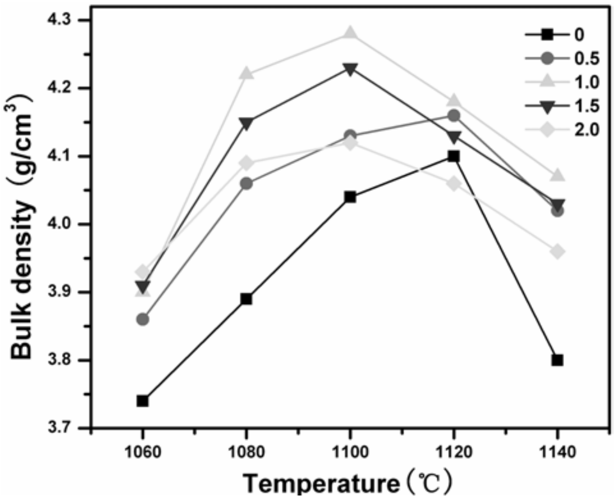

Fig. 2. Bulk densities of the $K_{0.5}Na_{0.5}NbO_3$ ceramics as a function of xmol% ZnO.

d_{33} values were measured by a quasistatic d_{33} meter (Model ZJ-3D, Institute of Acoustics Academic, China) and an impedance analyzer HP4294A using resonance and antiresonance techniques on the basis of IEEE standards, respectively. The polarization hysteresis loops were measured using a Radiant Technologies RT66A test system in silicon oil at room temperature with 3 kV/mm.

Results and Discussion

Fig. 1 shows the XRD patterns of the ZnO added KNN ceramics sintered at 1100 °C for 1h. All samples exhibit a single phase of orthorhombic perovskite, due to the low concentration of ZnO. This means Zn^{2+} ions might have entered the KNN ceramic matrix. Because the radius of the Zn^{2+} ion (0.74Å) is similar to that of the Nb^{5+} ion (0.64Å), the Zn^{2+} ions are considered to have entered the B sites of the perovskite unit cell and replaced the Nb^{5+} ions. A similar result was also observed in CuO added 0.95NKN-0.05BT ceramics [18]. In addition, it is known that an unstable secondary phase $K_4Nb_6O_{17}$ may result from slight changes in the stoichiometric ratio because of the highly volatile nature of K_2O during sintering [19]. $K_4Nb_6O_{17}$ shows deliquescence when exposed to humidity. However, all our samples showed no deliquescence, when they were exposed to water for 30 days.

Fig. 2 shows the bulk densities as a function of sintering temperature in the KNN ceramics with various ZnO concentrations. One can note that the density changes significantly in this narrow range of sintering temperature. The densities increase when the sintering temperature increases, and then decreases at higher sintering temperatures (1120 or 1140 °C) for all samples. With the same sintering temperature, the density of the ceramics with ZnO is higher than that of the pure KNN. With an increase of the content of ZnO, the optimum sintering temperature shifts to the lower temperature. After it is sintered at 1100 °C for 1h, the $K_{0.5}Na_{0.5}NbO_3$ ceramic sample with 1 mol% ZnO had the highest density value of 4.28 (g/cm^3) (near 95% of the theoretical density).

Fig. 3 shows the scanning electron microscope (SEM) images of the KNN ceramics with different ZnO contents sintered at 1100 °C for 1h. For the pure KNN ceramic (i.e. , x = 0), a small amount of pores was observed as shown in Fig. 3(a). As the x value increases from 0 to 1.0%, the grains grow slightly larger, and the pores gradually become fewer in Fig. 3(b) and (c). When x increases to 2.0%, as observed in Fig. 3(d), the grains become larger, accompanied by a few abnormally large grains that may lead to the small reduction in bulk density. These variations in the microstructures with the content of ZnO are in agreement with the results in Fig. 2.

Fig. 4 and 5 show the change in the piezoelectric coefficient (d_{33}) and electromechanical coupling coefficient (k_p) of the different ZnO added KNN ceramics as a function of the sintering temperature. Fig. 4 illustrates that the d_{33} increases and then decreases with an increase in the temperature, which is in accordance with the changes in the bulk density. A more attractive point is that with an increase in the ZnO content, the d_{33} firstly increases and then drops a little at the x level of 2.0%, under the same sintering conditions. This result implies that the piezoelectric properties are closely correlated with the microstructures. In particular, when sintered at 1100 °C for 1 h, the 1.0 mol%-ZnO added KNN ceramic exhibits the highest d_{33} of 135 pC/N. Similar to the d_{33}, the k_p of these KNN-based ceramics has a strong dependence on the ZnO concentration and sintering temperature as shown in Fig. 5. A maximum k_p of 0.40 has been obtained in the 1.0 mol%-ZnO-doped KNN ceramic sintered at 1100 °C for 1 h. This should be attributed to the increase of the density. This sample has a relatively homogenous microstructure with less pores and other physical flaws, and thus it is easy to avoid electrical breakdown and

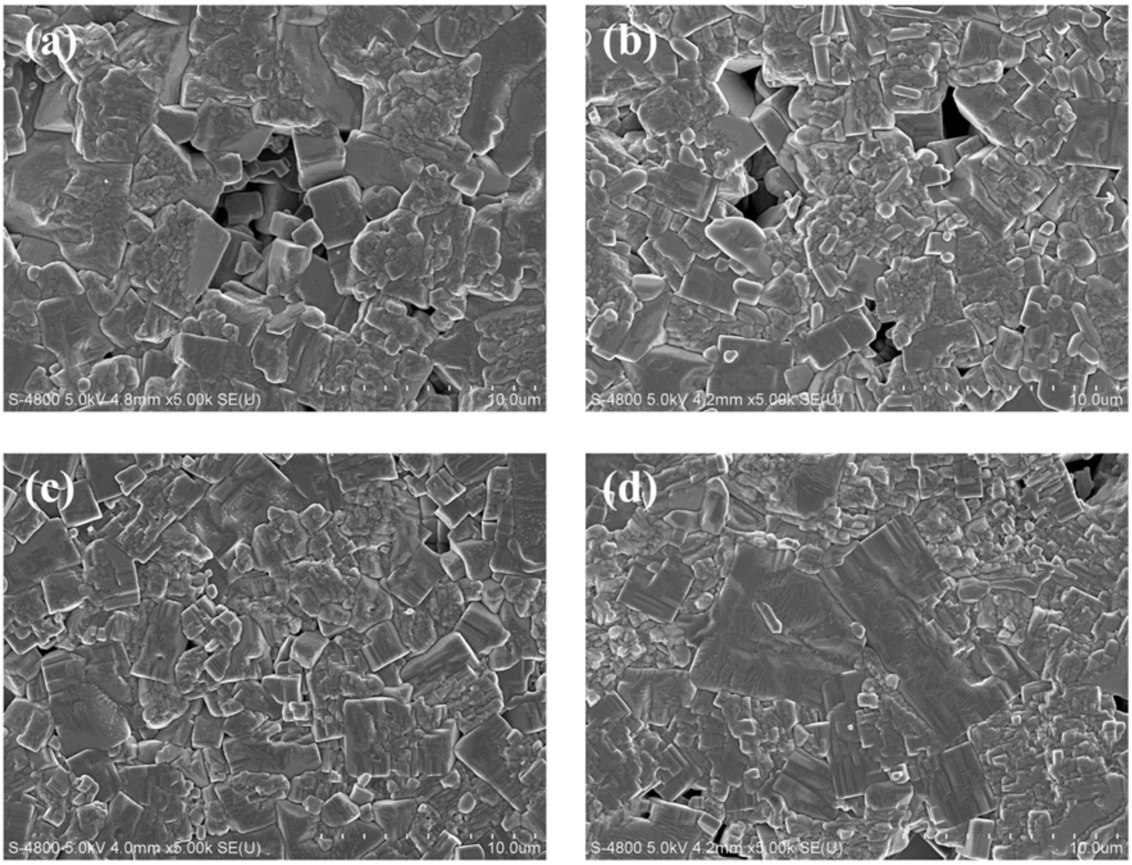

Fig. 3. SEM images of the $K_{0.5}Na_{0.5}NbO_3$ ceramics with xmol% ZnO sintered at 1100 °C for 1h (a) x = 0; (b) x = 0.5; (c) x = 1.0; (c) x = 2.0.

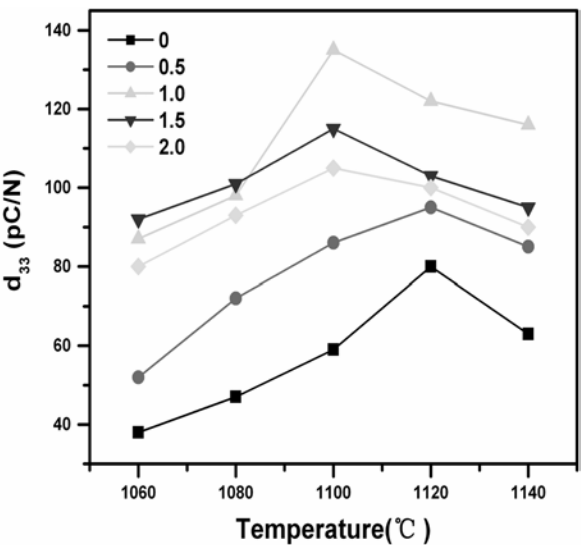

Fig. 4. d_{33} of the $K_{0.5}Na_{0.5}NbO_3$ ceramics as a function of xmol% ZnO.

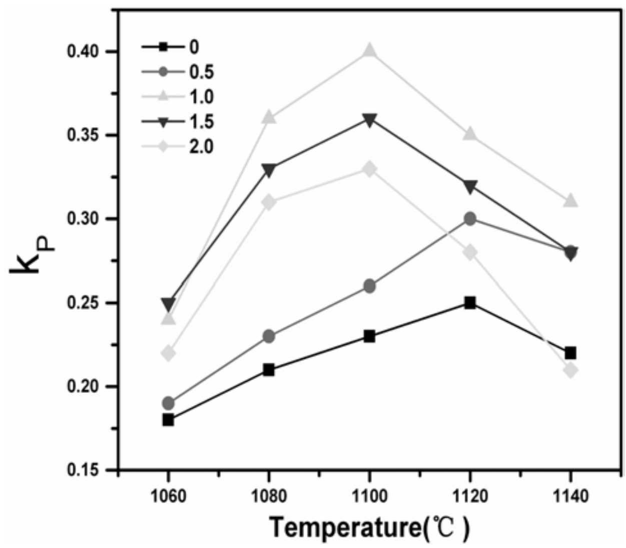

Fig. 5. k_p of the $K_{0.5}Na_{0.5}NbO_3$ ceramics as a function of xmol% ZnO.

obtain a better poling effect.

Fig. 6 shows the P-E hysteresis loops of the different ZnO added KNN ceramics. The coercive field (E_c) of the KNN ceramic was approximately 1.06 kV/mm and increased slightly with an increase in the ZnO content to 1.24 kV/mm for the 2.0 mol% ZnO-added KNN ceramic. The remnant polarization (P_r) of the pure KNN ceramic was approximately 14.85 μC/cm^2, with an increase in the ZnO content, the P_r firstly increases and then drops a little at the x level of 2.0%. Therefore, it is considered that the KNN ceramic is transformed into a hard piezoelectric material with the addition of ZnO.

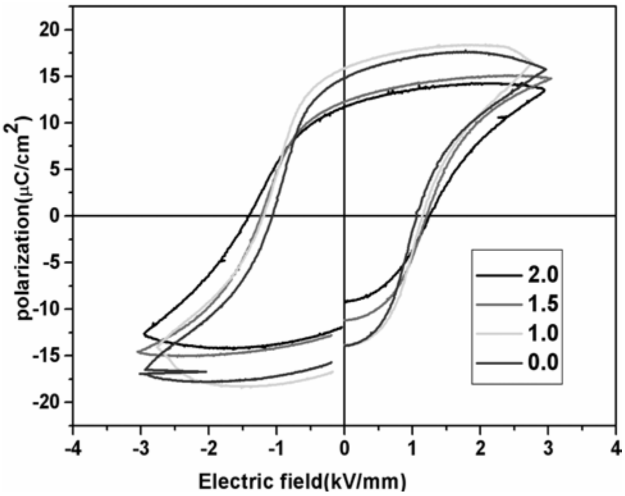

Fig. 6. The P-E hysteresis loops of the $K_{0.5}Na_{0.5}NbO_3$ ceramics as a function of xmol% ZnO.

Conclusions

Lead-free $K_{0.5}Na_{0.5}NbO_3$ ceramics with various ZnO additions have been prepared by conventional ceramics processing. The single orthorhombic perovskite phase of KNN was found in all ZnO added ceramics. The density and piezoelectric properties of KNN ceramics were enhanced effectively by adding ZnO. The KNN ceramics with 1.0 mol% ZnO showed optimal density and piezoelectric properties ($\rho = 4.28$ g/cm^3, $d_{33} = 135$ pC/N, $k_p = 0.40$, $P_r = 16$ μC/cm^2).

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