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Effect of Bi^{3+} ion on piezoelectric properties of $K_xNa_{1-x}NbO_3$

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Abstract This paper describes the material preparation and characteristics of potassium sodium niobate, $K_xNa_{1-x}NbO_3$ (KNN), with Bi^{3+} doping. Some physical properties including density, dielectric constant, loss tangent and ferroelectric hysteresis, were examined. The samples were characterized by using X-ray diffraction method and the grain size was measured by using SEM micrographs. Dielectric constant, loss tangent, and electromechanical coupling coefficient of samples were measured at different frequencies. The changes in physical properties are remarkable when KNN is doped with Bi^{3+} ions.

Keywords Potassium sodium niobate · Bismuth · Doping · Lead-free · Piezoelectric

1 Introduction

As a promising candidate for a lead-free piezoelectric system, potassium sodium niobate, $K_xNa_{1-x}NbO_3$ (KNN) with perovskite type structure has been given attention due to its relatively low dielectric constant and high electromechanical coupling coefficients, especially near the equimolar composition ($K_{0.5}Na_{0.5}NbO_3$) [1]. The 1:1 ratio of K and Na has been the preferred choice for most of the works on the system [2]. The system was reported to be very difficult to synthesize using the conventional solid-state reaction method. Several methods such as hot pressing, hot iso-static pressing (HIP), cold iso-static pressing (CIP), and sinter-forging process were investigated for the development of KNN with high densities [2–5]. In addition, studies with experiments on dopants such as Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} etc. have also been reported [2, 6, 7].

In this paper, bismuth trioxide was used for doping the base material. The hot-pressed method is used in the synthesis process. Electromechanical coupling coefficient, density, dielectric constant, loss tangent and ferroelectric hysteresis, were measured. The samples were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

2 Experimental

The specimens in this study were prepared by the conventional solid-state reaction. The starting materials were K_2CO_3, Na_2CO_3, Nb_2O_5, and Bi_2O_3, of 99.94, 99.56, 99.5 and 99% purities, respectively. 1.0 wt% extra Bi_2O_3 was added in the mixture. The final composition of Bi^{3+}-doped KNN was $(K_{0.47}\square_{0.02}Na_{0.5}Bi_{0.01})NbO_3$, where □ represents cation vacancy. It is believed that Bi_2O_3 as a fluxing agent decreases the sintering temperature of the ceramics. The starting materials were milled in a polyethylene jar with ZrO_2 balls for 3~6 h using ethanol as the medium. After being dried, the powders were calcined at 900 °C for 2 h. The calcined powders was ground and

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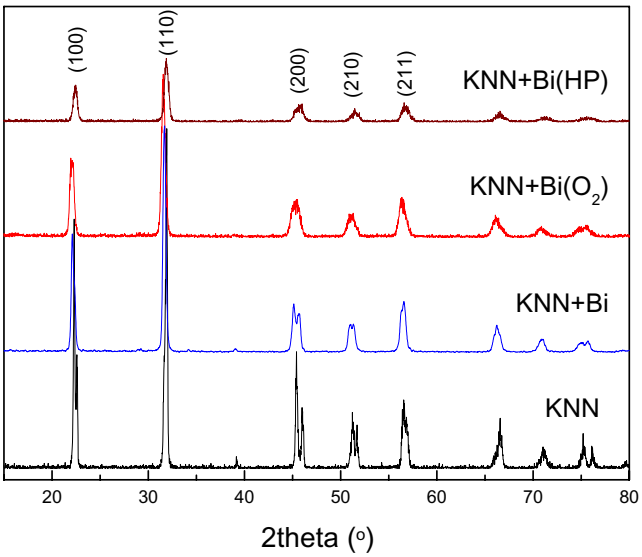

Fig. 1 XRD patterns of undoped KNN calcined at 900 °C (*KNN*), Bi^{3+}-doped KNN sintered at 1155 °C in air (*KNN+Bi*), Bi^{3+}-doped KNN sintered at 1155 °C in O_2 [*KNN+Bi(O2)*], and hot-pressed Bi^{3+}-doped KNN sintered at 1130°C [*KNN+Bi(HP)*]. All of them sintered for 2 h

pressed into discs of 15 mm in diameter with a thickness of approximately 1 mm. A number of discs were sintered at a temperature of 1155 °C for 2 h in a sealed alumina crucible in air. The rest were sintered at 1155 °C for 2 h in oxygen. Some of the samples were hot-pressed at 1130 °C for 2 h. The densities of the discs were measured using the Archimedes method [5]. The crystal structures were determined by XRD (Rigaku D/Max 2550V) using Cu-K_α radiation.

For electrical characterizations, samples were polished and painted with silver paste on two sides, and finally poled in a silicon oil bath at 120 °C for 30 min. Dielectric constants were obtained using an HP4192A LF (5 Hz~13 MHz) and an HP4991A RF (1 MHz~3 GHz) impedance analyzers. Piezoelectric constants d_{33} were measured by a quasi-static d_{33} meter (Model ZJ-3A, Institute of Acoustics, Beijing). Ferroelectric hysteresis loop was obtained by a TF Analyzer 2000 FE-Module ferroelectric tester.

Table 1 Comparison of the properties of different KNN ceramics.

Samples	Tc (°C)	(ε_r^T) (1 kHz)	Pr ($\mu C/cm^2$)	K_p	d_{33} (pC/N)	tan δ	P (g/cm^3)
$Na_{0.5}K_{0.5}NbO_3$ (air-sintered) [3]	420	290 (100 kHz)	18	0.36	80	/	4.25
Bi^{3+}-doped KNN (air-sintered)	/	1,259	23.6	0.24	106	0.069	4.59
Bi^{3+}-doped KNN (O_2-sintered)	373	1,309	/	0.283	127	0.058	4.66

3 Results and discussion

Figure 1 shows the XRD patterns of undoped KNN calcined at 900 °C for 2 h and Bi^{3+}-doped KNN sintered under different conditions. The XRD analysis indicated that Bi^{3+} dopant did not change the perovskite type structure of KNN.

The radius of Bi^{3+} (r_{Bi}^{3+}=1.03Å) is smaller than that of K^+ (r_K^+=1.38 Å), and approximately equals to that of Na^+ (r_{Na}^+=1.02Å). As a result, it is easy for Bi^{3+} to substitute K^+

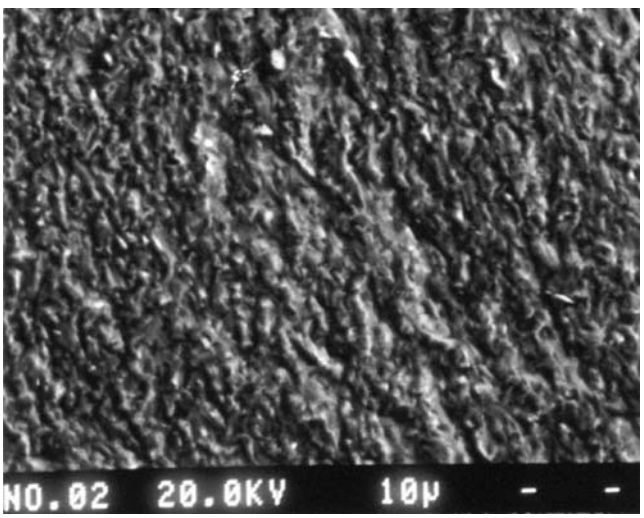

Fig. 2 SEM micrograph (1,000×) of the fracture surface of Bi^{3+}-doped KNN sintered at 1155 °C

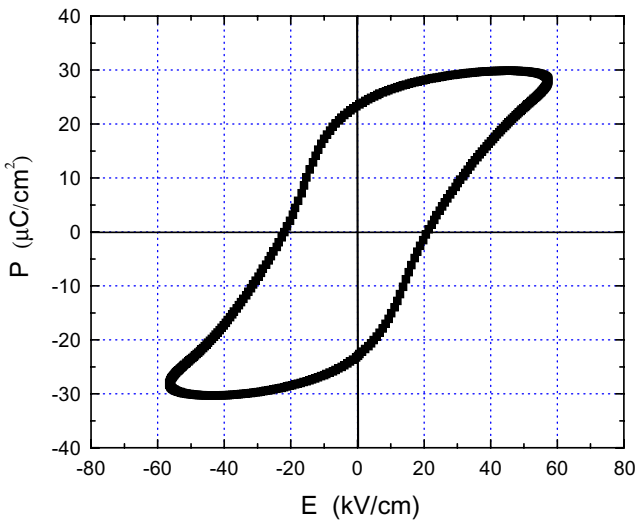

Fig. 3 P–E hysteresis loop of O_2-sintered Bi^{3+}-doped KNN at 18 °C at 10 Hz

cations, which can increase the stability of perovskite structure determined by the tolerance factor $t\left(t=(r_A+r_O)/\sqrt{2}(r_B+r_O)\right)$ [8].

The fracture surface of Bi^{3+}-doped KNN ceramic shown in Fig. 2 exhibits a predominantly intergranular type of fracture. The sample consists of randomly distributed grains. The size of grains is 1~3 μm estimated from the SEM micrograph.

Using the Archimedes method, the densities of the ceramics were obtained, as shown in Table 1. It's assumed that the substitution of element Bi^{3+} in place of K^+ increased the density. The atomic weight of the Bi (208.98 g/mol) is approximately five times that of K (39.098 g/mol).

Figure 3 shows the P–E hysteresis loop of O_2-sintered Bi^{3+}-doped KNN at 18 °C at 10 Hz. The measurement was carried out at a maximum electric field of 20 kV/cm. The loop was still not saturated which probably caused by a leakage current. Bi^{3+}-doped KNN shows the typical ferroelectric hysteresis loop. The remanent polarization Pr is 23.6 μC/cm^2 and coercive electric field Ec is 21.0 kV/cm. According to Table 2, these Pr and Ec values are larger than those of KNNs with other dopants.

Figure 4 shows the dielectric properties of air-sintered Bi^{3+} -doped KNN. From Fig. 4(a) we can observe that the Curie temperature is around 370 °C and the permittivity peak, which is flat from 100 to 200 °C, shows a ferroelectric-ferroelectric transition. The positions of the dielectric maxima are slightly shifted to the left (lower temperatures) with the increase of frequency. The frequency dispersion is almost absent. Figure 4(b) shows the dielectric loss versus temperature. The loss factor plots at 0.1 and 1 kHz have peak temperatures lower than that of the dielectric constant maxima, while the plots at 100 kHz and 1 MHz nearly have same peak temperatures as that of the dielectric constant maxima. The abrupt increase in the loss is apparently due to the increase in conductivity at high temperatures [10]. The plot for 10 kHz is found to be almost flat, which is quite different from the data for other frequencies. It implies that this material has some dielectric relaxation in the lower frequency regions. However, the exact explanation for the phenomenon is still under investigation.

From Table 1 we can see that the values for ρ, d_{33}, Pr and ε_r^T of Bi^{3+}-doped KNN are much larger than those of other KNN ceramics. These values for $Na_{0.5}K_{0.5}NbO_3$ are from Jaeger and Egerton [3].

Table 2 Comparison of coercive electric field Ec and remanent polarization Pr of different KNN ceramics.

Material	Ec (kV/cm)	Pr (μC/cm^2)
Bi^{3+}-doped KNN	21.0	23.6
NKN+5 mol% LT [9]	12.5	9
Sr-KNN [6]	12	6
KNN [5]	9.0	8.9

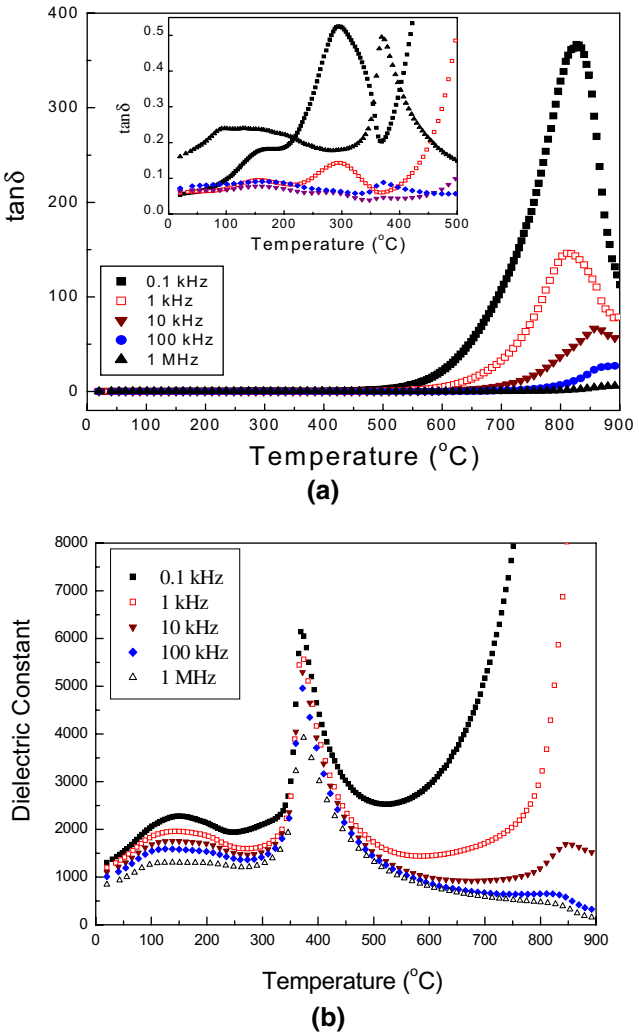

Fig. 4 Temperature dependence of (**a**) dielectric constant and (**b**) loss tangent of air-sintered Bi^{3+}-doped KNN for different frequencies

4 Conclusion

The Bi^{3+}-doped KNN ceramics synthesized in this work have a higher ρ, d_{33}, Pr and ε_r^T than that of undoped KNN with air-sintering process [density ρ (4.59 g/cm^3), piezoelectric coefficient d_{33} (106 pC/N), dielectric constant, ε_r^T (1259), remanent polarization Pr (23.6 μC/cm^2) for air sintered Bi^{3+}-doped KNN]. The doping of Bi^{3+} did not change the crystal structure of KNN. The Bi^{3+} ions are located in the K^+ sites of KNN ceramics. The piezoelectric properties of Bi^{3+}-doped KNN are to be improved through further investigations. The piezoelectric and dielectric properties indicate that this material can be an applicable lead-free piezoceramic.

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