$K_{0.5}Na_{0.5}NbO_3$ piezoelectric ceramics and its composites fabricated from hydrothermal powders

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Abstract. $NaNbO_3$ and $KNbO_3$ powders were prepared respectively by the hydrothermal synthesis method. The obtained powders were mixed with the molar ratio of 1:1 and dry–pressed, the $(K_{0.5}Na_{0.5})NbO_3$ (KNN) lead–free piezoelectric ceramics were obtained by sintering at 1060–1100 °C at normal atmosphere. The effect of sintering temperature on phase, microstructures, bulk density and electrical properties of KNN ceramics were investigated. The XRD patterns showed that the single solid solution of $(Na, K) NbO_3$ ceramics was acquired. The SEM micrographs exhibited that increasing sintering temperature appropriately would improve grain growth and decrease porosity. K/Na, shrinkage, density, piezoelectric constant d_{33} and dielectric constant increased with the increased sintering temperature. When the sintering temperature was 1100 °C, the d_{33} reached a maximum (110.8 PC/n). Meanwhile, through freeze casting and infiltrating with a polymeric lubricant phase, a layered KNN–epoxy composite was produced using the hydrothermally synthesized $NaNbO_3$ and $KNbO_3$ powders as raw powders. Its microstructures and properties were analyzed.

Introduction

To replace lead–containing piezoelectric materials such as lead zirconate titanate (PZT), Lead–free piezoelectric ceramics have received considerable attentions recently from the viewpoint of environmental protection [1,2,3,4]. The alkaline niobate–based piezoelectric ceramics are considered as good candidates for lead–free piezoelectric ceramics due to their good piezoelectric properties and high curie temperature [5,6]. Among alkaline niobate ceramics, $KNbO_3$ (KN) is ferroelectric and $NaNbO_3$ (NN) is antiferroelectric [7]. $K_{0.5}Na_{0.5}NbO_3$ (KNN), near the morphotropic phase boundary (MPB), possesses much better the piezoelectric and ferroelectric properties than that of pure $KNbO_3$.

Usually, it is very difficult to obtain a dense $K_{0.5}Na_{0.5}NbO_3$ ceramic using powders prepared from traditional solid state reaction, because of the decomposition of KNN beyond 1140 °C and the change in K/Na molar ratio caused by the evaporation of potassium and sodium during the sintering process. This disadvantage limits its wide application seriously. One of the methods to overcome the problem is to use refined powders with high sintering activity.

Various chemical methods have been developed for producing ultrafine ceramic powders such as homogeneous precipitation method [8], polymerized complex method[9],and hydrothermal synthesis method [10,11,12]. Compared with other methods, the hydrothermal method not only provides a low–temperature and environmental friendly process, but also can control more efficiently the morphology and chemical composition of powders [13,14].

In this study, $KNbO_3$ and $NaNbO_3$ powders were synthesized using the hydrothermal method. Using the mixture of $KNbO_3$ and $NaNbO_3$ with molar ratio of 1:1, dense $K_{0.5}Na_{0.5}NbO_3$ ceramics were obtained by ordinary sintering method, and a layered KNN–epoxy composite was prepared by freeze casting and liquid infiltration methods. Their microstructures and the piezoelectric properties were characterized.

Experimental methods

Hydrothermal synthesis

The hydrothermal synthesis of $KNbO_3$ powder was carried out in a 120 cm^3 stainless Teflon autoclave. 0.02 mol niobate oxide was put into 7.5 N KOH solution in an autoclave with a filling factor of about 50 vol%, and then stirred for 30 min. Furthermore, the autoclave was put in an oven and heated to 210 °C for 24 h. For $NaNbO_3$ powder, 7.5 N NaOH was used instead of KOH. Other reaction conditions were the same as for $KNbO_3$. After the hydrothermal reaction, two kinds of powders were filtered with filter papers and washed by deionized water for several times until the pH value was equal to 7. Finally, they were dried at 130 °C for 5 h.

Piezoelectric ceramic preparation

To synthesize $K_{0.5}Na_{0.5}NbO_3$ ceramics, $KNbO_3$ and $NaNbO_3$ powders with molar ratio of 1 were mixed in distilled water. The amounts were 1.500 g and 1.366 g, in order to obtain a molar ratio between potassium and sodium of 1 in the ceramics. The mixed powder was filtered and dried for 120 min at 120 °C. After drying, this powder was ground with alumina mortar and alumina pestle, and filtered with sieve (mesh size 425 μm). The as–prepared powders were pressed into pellets of Φ12 mm×1 mm by a cold–isostatic pressing under 200 MPa for 5 min. The pellets were then sintered at 1060–1100 °C for 130 min in an air environment. The heating rate was 300 °C/h and the cooling rate was 200 °C/h.

Piezoelectric composite preparation

$KNbO_3$ and $NaNbO_3$ powders with molar ratio of 1 were mixed in distilled water to prepare the ceramic slurries with 18 wt% ceramic content. The resulting ceramic slurries were poured into a Teflon mold (Φ12 mm × 20 mm) sitting on a copper rod which was cooled using liquid nitrogen. The solidification rate in the axial direction of the cylindrical samples was estimated to be 6 µm s−1 by observing the time for the slurry at the top of the mould to freeze. The frozen samples were then freeze–dried and subsequently sintered at 1100 °C for 130 min to prepare a porous KNN ceramic. The porous KNN were backfilled with epoxy resin in a vacuum container. The cylindrical composites were then cut along the direction perpendicular to the solidification direction to obtain pellets. The resulting samples were well polished into Φ12 mm×1 mm pellets.

Test and characterization

The linear shrinkages were obtained using measurements of sample dimensions before and after sintering. The density of the samples and the open–porosity of the porous KNN ceramic were measured by Archimedes's method. The phase analyses of powders and the sintered samples were performed using an X–ray diffractometer (BRUKER/AXS) with monochromatic CuKα radiation. The microstructures were analyzed by a scanning electron microscopy (SEM, JSM–6700F).

Before piezoelectric properties measurement, the pellets were polarized. Firstly, gold electrodes were applied on both sides of them by a sputter coater (Sanyu Electron: Quick Coater SG–701) for 3 min. Then, they were immersed in silicon oil and polarized at 175 °C for 20 min under 2.5 kV/mm electric field, and the specimens were cooled to room temperature within the electric field. All the polarized pellets were aged for 24 h. The piezoelectric constant d_{33} was measured using a quasi–static d_{33} meter (YE2730A). The dielectric constant was determined by an impedance analyzer (WK–6500B).

Results and discussion

Fig. 1a and b show the XRD patterns of the $KNbO_3$ and $NaNbO_3$ powders synthesized at 210 °C for 24 h, respectively. The main diffraction peaks of the two powders were assigned to the pure orthorhombic $NaNbO_3$ phase (JCPDS 77–0873) and pure orthorhombic $NaNbO_3$ phase (JCPDS 77– 1098), with good crystallization.

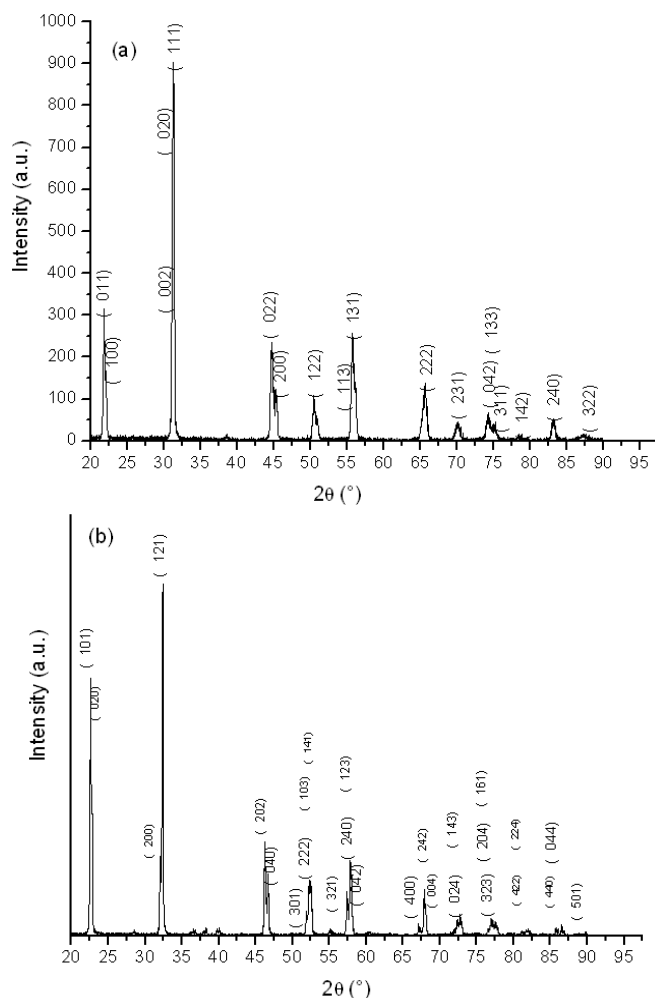Fig. 1. XRD patterns of hydrothermally produced powders: (a) $KNbO_3$ and (b) $NaNbO_3$.

The SEM images of the $KNbO_3$ and $NaNbO_3$ powders obtained from the hydrothermal reactions are shown in Fig. 2a and b, respectively. Well–crystallized cubic $KNbO_3$ and $NaNbO_3$ crystals were be observed and their sizes were less than 1µm.
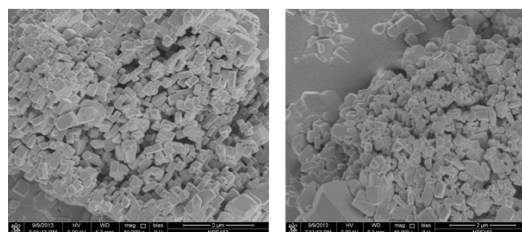

Fig. 2. SEM of hydrothermally produced powder (a) $KNbO_3$ and (b) $NaNbO_3$.

Fig. 3 shows the XRD patterns of the (K, Na)NbO_3 (KNN) ceramic sintered at the range of 1060–1100 °C from mixed $KNbO_3$ and $NaNbO_3$ powders with molar ratio of 1. The KNN ceramic exhibited orthorhombic symmetry with no secondary phase. This indicated that in the sintering process, $KNbO_3$ and $NaNbO_3$ powders resulted in a pure solid solution of $(K_{0.5}Na_{0.5})NbO_3$.

It was also seen that the 2θ of KNN patterns shifted from the right to the left with an increase of sintering temperature. The shift became very prominent when sintering temperature increased from 1080 °C to 1100 °C, which indicated that the ratio of K/Na in the crystal lattice increased evidently. During sintering process of KNN ceramic, Na is more easily evaporated than K. Because the radius of K^+ (0.133 nm) is larger than that of Na^+ (0.097 nm), the larger number of K^+ leads to the larger distance

of the crystal face, and as a result, the 2θ of KNN patterns decreases, according to the Bragg formulary d=λ/(2 sinθ).
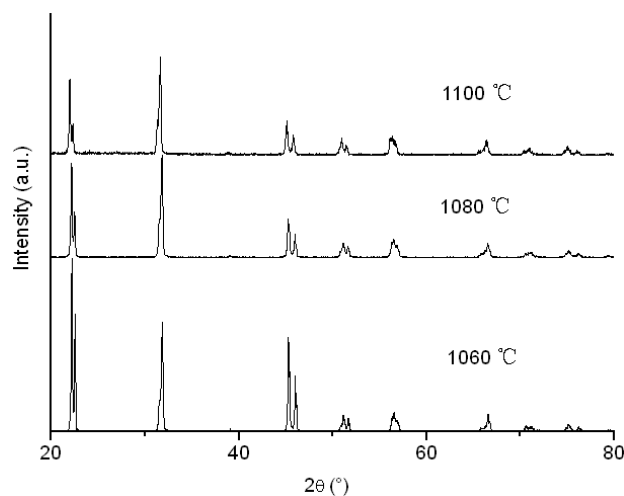

Fig. 3. XRD patterns of KNN ceramics sintered at different temperature.

Fig. 4 shows the SEM photographs of the KNN ceramics sintered at different temperatures. When the sintering temperatures were 1060 °C and 1080 °C, the grain sizes were relatively small (< 3 μm). However, the average grain size was larger in the KNN ceramic sintered at 1080 °C than that of the KNN ceramic sintered at 1060 °C. When the sintering temperature increased to 1100 °C, the grain size increased evidently (more than 10 μm), which was beneficial to improve piezoelectric constants.
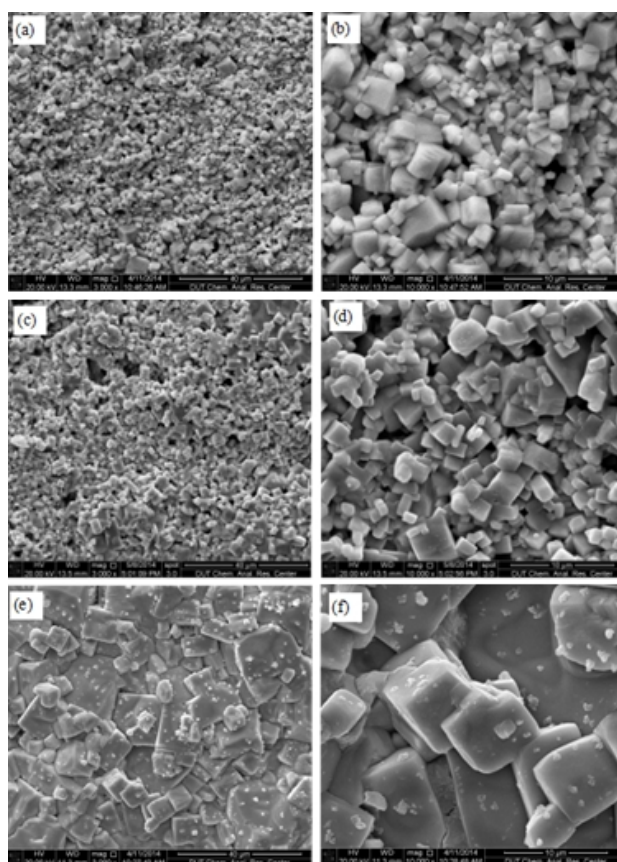

Fig. 4. SEM micrographs of KNN ceramics sintered at different temperature: a, b 1060 °C; c, d 1080 °C; e, f 1100°C.

Fig. 5 and 6 show the curve of shrinkage rate and density versus sintering temperature for the KNN ceramics, respectively. With increase of sintering temperature from 1040 °C to 1080 °C, shrinkage rate

and density increased at a relatively great rate. However, their increasing rates declined sharply when temperature exceeded 1080 °C. The density of the KNN ceramic sintered at 1100 °C was measured to be 4.39 g/cm3, which corresponds to a relative density of 97.4% based on the theoretical density of $(K_{0.5}Na_{0.5})NbO_3$ of 4.506 g/cm^3 [5]. As a result, its closed–porosity was presumed to be 2.6%.
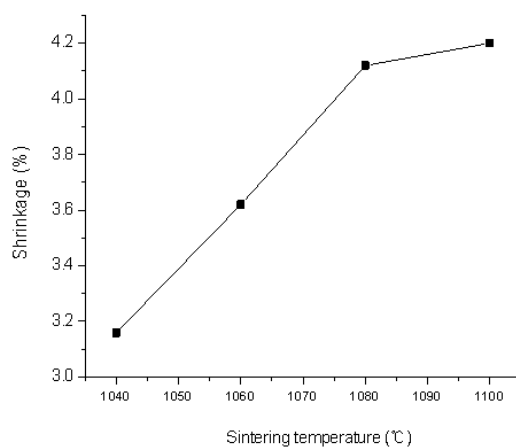

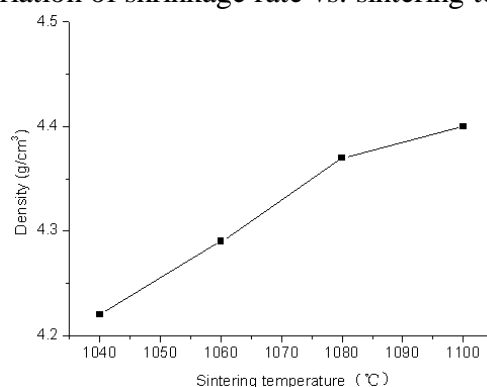Fig. 5. Variation of shrinkage rate vs. sintering temperature.

Fig. 6. Variation of density vs. sintering temperature.

Table 1. Piezoelectric constant, d_{33} and dielectric constant, ε of the KNN ceramics sintered at different temperature.

sintering temperature (°C)	1060	1080	1100
d_{33} (pc/n)	94.6	102.6	110.8
ε (1MHz)	352	410	420

The piezoelectric constant, d_{33} and dielectric constant, ε of the KNN ceramics sintered at different temperature are listed in Table 1. With the increase of sintering temperature, both of d_{33} and ε increased. It was noticeable that K/Na deviated more from 1:1, but d_{33} reached the maximum at 1100 °C. This was likely related to the larger grain and density.

Fig. 7 shows the cross–sectional microstructures of the porous KNN ceramic obtained from the slurry of mixed $KNbO_3$ and $NaNbO_3$ powders with molar ratio of 1. The porous sample exhibited a typical lamellar microstructure, which were formed during the directional freezing.

The density and open–porosity of the porous KNN ceramic sintered at 1100 °C were measured by Archimedes's method. The open–porosity was about 85%, which was mostly determined by the water content in the slurry. The density of the porous KNN ceramic was 3.17 g/cm3, much lower than that of the KNN ceramic disks above mentioned. The closed porosity of the porous KNN ceramic was

calculated and was about 28%, based on the ratio of its density and the theoretical density of $(K_{0.5}Na_{0.5})NbO_3$.
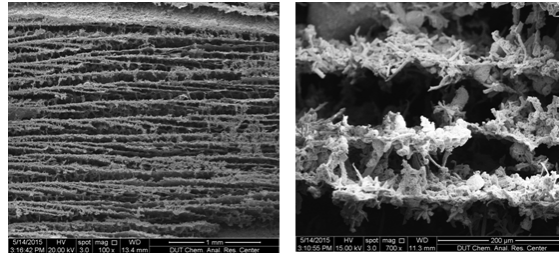

Fig. 7. SEM photographs of the porous KNN ceramic obtained from the slurry of mixed $KNbO_3$ and $NaNbO_3$ powders with molar ratio of 1. Solidification direction is perpendicular to the page.

The dielectric constant at 1MHz and piezoelectric constant d_{33} of the KNN–epoxy aligned (2–2) composite were 22.8 and 15.2 pC/N, respectively. The d_{33} value was much lower compared with the pure KNN ceramics, which may be due to the high–content epoxy phase (nearly equal to open–porosity) of the composite and the high closed porosity of the porous KNN ceramic.

Usually the dielectric constant of ceramic–epoxy composite can be calculated by the following equation [15]:

$$\varepsilon_{com} = v_r \cdot \varepsilon_r + v_c \cdot \varepsilon_c \qquad (1)$$

Where ε_x and v_x are the dielectric constant and the volume fraction of constituent x, respectively; com, r, and c stand for composite, resin and ceramic, respectively. The dielectric constant, ε_{app} of the KNN phase in the composite was also influenced by closed–porosity and can be calculated by the following equation [16]:

$$\varepsilon_{app} = (1-p)(\varepsilon_{s1}-1)/[1+N_i(\varepsilon_{s1}-1)] \qquad (2)$$

where ε_{sl} is the dielectric constant of the dense KNN ceramic; p is the closed–porosity and $N_i = 0.002 \times p$. Based on the test data of the porous KNN ceramic and the dense KNN ceramic sintered at 1100 °C, ε_{app} was calculated to be 243 using Eq. (2). It was reported that the dielectric constant of epoxy resinis is around 4 [17].The expected dielectric constants of the composites were calculated using Eq. (1) to be 28. The calculated value was slightly higher than the measured dielectric constant of the composite, which was maybe attributed to some ignored factors, such as the pores in epoxy and on the interface between epoxy and ceramic.

Conclusion

In this study, potassium niobate and sodium niobate powders were synthesized using a hydrothermal method. These two powders were used to prepare $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramics and a $K_{0.5}Na_{0.5}NbO_3$–epoxy composite. The sintering temperature from 1060 °C to 1100 °C was used. The single solid solution of KNN ceramics was acquired under all sintering temperatures. With the increase of sintering temperature, grain size, shrinkage, density, piezoelectric constant d_{33} and dielectric constant increased, but porosity decreased for the dense KNN ceramics. The KNN–epoxy composite showed a lamellar structure with 90 vol.% epoxy. Its dielectric constant at 1MHz and piezoelectric constant d_{33} were 22.8 and 15.2 pC/N, respectively.

Acknowledgments

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