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Compositional inhomogeneity and segregation in $(K_{0.5}Na_{0.5})NbO_3$ ceramics

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ABSTRACT

In this report, the effects of the calcination temperature of $(K_{0.5}Na_{0.5})NbO_3$ (KNN) powder on the sintering and piezoelectric properties of KNN ceramics have been investigated. KNN powders are synthesized via the solid-state approach. Scanning electron microscopy and X-ray diffraction characterizations indicate that the incomplete reaction at 700 °C and 750 °C calcination results in the compositional inhomogeneity of the K-rich and Na-rich phases while the orthorhombic single phase is obtained after calcination at 900 °C. During the sintering, the presence of the liquid K-rich phase due to the lower melting point has a significant impact on the densification, the abnormal grain growth and the deteriorated piezoelectric properties. From the standpoint of piezoelectric properties, the optimal calcination temperature obtained for KNN ceramics calcined at this temperature is determined to be 800 °C, with piezoelectric constant $d_{33}=128.3$ pC/N, planar electromechanical coupling coefficient $k_p=32.2\%$, mechanical quality factor $Q_m=88$, and dielectric loss tan $\delta=2.1\%$.

1. Introduction

(K,Na)NbO_3 (KNN)-based lead-free ceramics have attracted considerable attention due to their excellent piezoelectric properties and high Curie temperature [1–6]. However, it is difficult to obtain dense KNN-based ceramics by a conventional sintering process because of the high volatility of alkaline elements, narrow sintering temperature range, and compositional segregation [4,5]. It is well known that sintering of the ceramic green body can be affected by the characteristics of the powders that depend on the synthesis method and processing [7]. To date, it has been reported that KNN ceramic powders can be synthesized by chemical methods such as solid-state reaction (SSR) [8–12], hydrothermal [13–15], sol–gel [16–18], precipitation [19], and mechanochemical activation [20] et al. Among these synthesis methods, SSR is an accessible and inexpensive approach, and it is thus widely employed for KNN synthesis. Generally, alkaline carbonates, such as K_2CO_3 and Na_2CO_3, have been used as starting materials for the synthesis of KNN ceramic powder by SSR. According to Malic et al., the KNN solid solution forms via the intermediate $(K,Na)_2Nb_4O_{11}$ phase, with the rate of the diffusion-controlled reaction determined by the diffusion of the slower species [21]. The difference between the K^+ and Na^+ diffusion rates likely leads to local inhomogeneity in the KNN solid solution, which can, in principle, be diminished by increasing the calcination temperature [21]. However, the elevated calcination temperature may result in severe evaporation of alkaline elements. To date, most studies report calcination temperatures between 750 °C and 950 °C [8]. To the best of our knowledge, there have been few reports on the effects of the calcination temperature of KNN powders on the sintering and piezoelectric properties of KNN ceramics. In this paper, the effects of calcination temperature on these properties are systematically investigated in detail.

2. Experimental procedure

$(K_{0.5}Na_{0.5})NbO_3$ samples were prepared by the conventional mixed-oxide process using K_2CO_3 (>99%), Na_2CO_3 (>99.8%) and Nb_2O_5 (>99.5%) as starting materials. Prior to use, the carbonates were dried at 120 °C for 12 h, and then all powders were weighed according to the nominal compositions and ball-milled for mixing for 6 h in a nylon jar with zirconia balls. The mixed powders were dried and then calcined in an alumina crucible at 700–900 °C with a step of 50 °C for 2 h. For convenience of description, the calcined powders were labeled as KNN700, KNN750, KNN800, KNN850, and KNN900. For the fabrication of ceramics, the calcined powders were ball-milled for 6 h and dried. The pellets were prepared by pressing the powders in a 15 mm diameter die at 100 MPa, then sintering at 1040 °C to 1080 °C for 4 h and finally furnace-cooling

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to room temperature.

The phases in the calcined powders were identified using X-ray powder diffraction (XRD, D8 ADVANCE A25, Bruker, Germany). The particle size and morphology of the calcined powders and the microstructure of the sintered samples were characterized using scanning electron microscopy (SEM, Hitachi S4800, Ibaraki, Japan). To measure the electrical properties, silver electrodes were coated on both surfaces of each sintered disks by firing at 550 °C for 20 min. The samples were immersed in silicone oil and poled in a 3 kV/mm field at room temperature or 120 °C for 30 min. The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric constant testing meter (ZJ-4AN, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The electromechanical coupling factor k_p and mechanical quality factor Q_m were measured using an impedance analyzer (PV 80, Beijing, China).

3. Results and discussion

The SEM images of calcined KNN powders are shown in Fig. 1. The calcination temperature has a significant effect on the particle size and morphology of KNN powders. In KNN700 and KNN750, irregular nanosized particles can be observed. When calcination temperature reached 800 °C, cuboid particles appear. Further increase of the calcination temperature leads to a larger population and coarsening of the cuboid particles. The sub-micrometer cuboid particle is observed in KNN900. The formation of cuboid particle is considered to be related to the presence of the liquid phase [11].

The XRD patterns of the powders calcined at various temperatures in the 700–900 °C temperature range are shown in Fig. 2 (a). Broad peaks near the expected positions of the desired KNN phase were present in the sample calcined at 700 °C for 2 h. However, as shown in Fig. 2(b), the peaks progressively sharpened and shifted toward lower 2θ values as the calcination temperature was increased, suggesting that the product obtained by calcination at 700–850 °C was not a chemically homogeneous solid solution phase. As stated previously, this compositional inhomogeneity in solid solution resulted from the difference between the diffusion rates of sodium and potassium ions. Spatial variations in the Na and K fractions due to the incomplete reaction would produce a series of KNN solid solution with different K/Na coexisting in the sample. For simplicity, we hypothesize that the KNN sample consists of a K-rich phase and a Na-rich KNN phase. According to the $KNbO_3$–$NaNbO_3$ phase diagram, the melting temperature is elevated in the Na-rich phase and is lowered in the K-rich phase from the 1110 °C melting point of the chemically homogeneous $(K_{0.5}Na_{0.5})NbO_3$ [22]. Therefore, appropriate compositional segregation that produces more of the K-rich phase at low calcination temperature (i.e., 700 °C) should give rise to a lower sintering temperature for KNN, as will be verified in the discussion below.

To study the effect of calcination temperature on the sintering of KNN ceramics, the radical shrinkage of KNN discs sintered at 1040–1080 °C was measured with the results presented in Fig. 3. It can be seen that the calcination temperature has a significant impact on the sintering of KNN ceramics. For KNN ceramics that were sintered at a single temperature, lower calcination temperature corresponded to higher shrinkage, indicating that lower calcination temperature KNN powders could be sintered to high density at lower temperatures. We note that in particular for KNN700 and KNN750, the highest shrinkage is obtained by 1070 °C sintering, whereas for KNN800, KNN850 and KNN900, maximum shrinkage is observed after sintering at 1080 °C. Moreover, the maximum shrinkage and density for all the sintered samples were observed in the KNN700 sample sintered at 1070 °C, which cannot be explained based only on the powder particle size. Microstructure observations discussed below indicate that the K-rich phase in KNN700 and KNN800 powders plays a key role in microstructure evolution.

The powder calcination temperature influences the microstructure of KNN ceramics, as seen from Fig. 4 that shows the comparison of the ceramics sintered from the KNN700 and KNN800 powders. For KNN700 powders, the grain size of the ceramic slightly increased as the sintering temperature increased

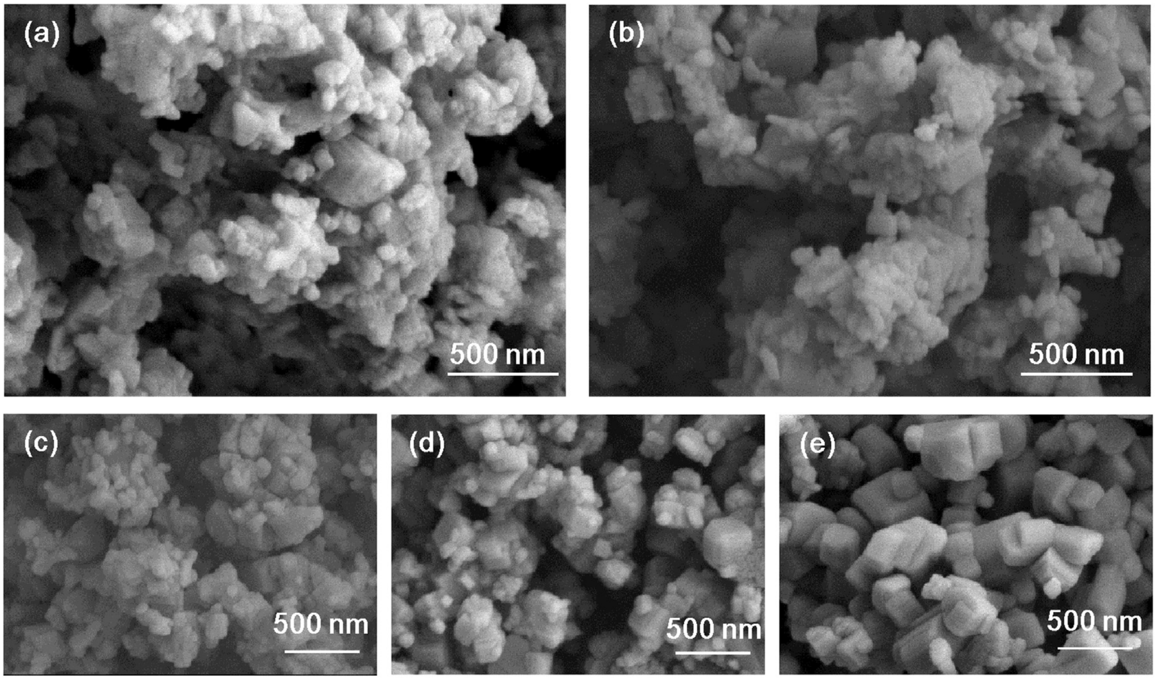

Fig. 1. SEM images of KNN powders calcined at (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C, and (e) 900 °C for 2 h.