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Piezoelectric and ferroelectric properties of $K_{0.5}Na_{0.5}NbO_3$ ceramics synthesized by spray drying method

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ABSTRACT

Potassium–sodium niobate was synthesized at 800 °C for 1 h using dried precursors in a powder form obtained by the spray drying method. Different samples were sintered from 1060 to 1120 °C for 2 h reaching a relative density as high as 96% of the theoretical value. Piezoelectric and ferroelectric properties were studied for these samples and some of the most prominent results are: k_p, d_{31}, $2P_r$, and $2E_C$ of 0.36, 39 pC/N, 29 μC/cm^2 and 16.5 kV/cm, respectively, for the sample sintered at 1080 °C. The methodology presented in this study can be used to synthesize submicrometer powders.

1. Introduction

The lead zirconate–titanate (PZT) composed of about 60 wt.% of lead has dominated the market of piezoelectric devices during the last 50 years. Nevertheless, some countries have legislated to replace this material by lead-free ceramics [1,2] since lead is a toxic element that affects the human health and the environment. During sintering of PZT, lead oxide is a volatile compound due to its high vapor pressure. Consequently, in recent years diverse materials are being investigated, among them, barium titanate [3], bismuth-alkaline metal titanates and niobates [4–9], especially the $K_{0.5}Na_{0.5}NbO_3$ solid solution abbreviated KNN [10–12]. However, it is difficult to achieve dense KNN materials because of the volatility of sodium and potassium oxides at high temperature.

There are some ways to enhance the sinterability of KNN ceramic materials. In order to improve KNN densification some sintering agents as CuO [13], CeO_2, Y_2O_3, WO_3 and other oxides can be added [14], since these compounds form a liquid phase that promotes sintering at lower temperatures. Another approach is to replace the K/Na normal sites in the perovskite structure (ABO_3) with small quantities of lithium, or to introduce tantalum and antimony in the structure at the B site [15–18]. Also the addition of strontium, barium and magnesium titanates have been studied [19,20].

It is well known that processing methods affects the final properties of ceramics powders. Concerning lead-free piezoceramics, it is desirable to reduce the particle size of the precursor powders in order to increase the driving force for sintering. Few methods have been used for synthesizing KNN and similar compositions [21–25]. Most studies are carried out with conventional ceramic fabrication technique [14–20], which involves one or two stages of milling and long calcination time at temperatures ≥800 °C, in order to obtain the perovskite phase. On the other hand, the sol–gel [23–25] route has been used for the synthesis of nanometric particles but it involves the use of alkoxides, which are expensive and they should be handled with special care to avoid the rapid hydrolysis with moisture.

In this work we reported the synthesis of KNN by the spray drying technique, with the aim to reduce calcination time and milling steps before sintering. We also investigated the effect on the ferroelectric and piezoelectric properties as a function of the sintering temperature.

2. Experimental procedure

For the synthesis of lead-free piezoceramics with $K_{0.5}Na_{0.5}NbO_3$ composition the following raw materials were used, Nb_2O_5 (99.99%), K_2CO_3 (99.8%), Na_2CO_3 (99.9%), HF (40%) NH_4OH (40%), citric acid monohydrate (99.9%) and deionized water. First, 15 g of

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niobium oxide were dissolved in 300 ml of hydrofluoric acid at 70 °C under constant stirring for 8 h. A clear solution was produced and ammonium hydroxide was added until reaching complete precipitation of niobic acid. The precipitate was washed three times with deionized water to eliminate residual ions. Then, the niobic acid was dissolved in a 0.3 molar solution of citric acid (CA) (molar ratio of CA:Nb = 4:1), this stage is used to stabilize the niobium ions. Sodium and potassium carbonates were dissolved in deionized water such that a stochimetric KNN composition was achieved. The solution of carbonates was added to the niobic acid/citric acid mixture under constant stirring for 30 min to get a homogeneous composition. The final solution was fed into a spray drying equipment (Mini-spray Drier YAMATO). The obtained dried powders were calcined at 800 °C for 1 h.

The calcined powders were uniaxially pressed into disk shaped pellets of 13 mm in diameter and 1.5 mm in thickness, and sintered at different temperatures between 1060 and 1120 °C for 2 h in air without special processing or sintering aids. The powders and sintered samples were characterized by X-rays powder diffraction at room temperature with Cu Kα radiation using a Bruker Advanced D-8 diffractometer. Scanning electron microscopy (SEM) images were obtained by a Leica Cambridge Stereoscan 440 microscope at 20 kV. Also, the synthesized powders were observed with transmission electron microscopy (TEM) with a Phillips TECNAI at 200 kV. Bulk densities of sintered ceramics were measured by the Archimedes method. With the aim of determining dielectric and piezoelectric properties, the sintered pellets were polished and silver paste was applied in both faces and annealed at 600 °C for 30 min. Dielectric and piezoelectric measurements were carried out using an Agilent 4294A Precision Impedance Analyzer. The dielectric constant (ε) and dielectric losses ($\tan\delta$) at 100 kHz were measured from room temperature up to 500 °C.

For piezoelectric characterization the samples were poled in a silicone oil bath under 3–5 kV mm^{-1} dc field at 130 °C for 30 min. The data were processed through an iterative method described in detail elsewhere [26,27]. Measurements were performed after more than 1 day of the poling process. The polarization versus electric field (P–E) hysteresis loops were acquired with a Radiant Precision Workstation at 100 Hz.

3. Results and discussion

The SEM and TEM images of powders calcined at 800 °C can be seen in Fig. 1(a) and (b), it is possible to observe that powders consist of agglomerates that have particle size smaller than 1 μm (average grain size of 0.281 μm measured on bright field TEM images), which is an important feature for the subsequent compaction and sintering, because the smaller the particle size is, the greater the driving force for sintering. The powders have a cubic-like shape characteristic of KNN perovskite phase. On the other hand, the short calcination time avoids considerable volatilization of potassium that takes place when conventional mixed-oxide route is used [10,11].

The corresponding XRD patterns of the calcined powder at 800 °C (Fig. 2(a)) and sintered samples from 1060 to 1120 °C (Fig. 2(b)–(e)) are shown in Fig. 2. It can be seen that the calcined powder as well as sintered the samples have a pure perovskite phase. An orthorhombic crystalline structure could be assigned to the sintered ceramics, as reported in the literature (JCPDS No. 71-2171) [1,28], and the main Bragg reflections are shown. Recalling the phase diagram of $KNbO_3$–$NaNbO_3$ [12], the KNN composition is close to two orthorhombic phases, both ferroelectric in the rich $NaNbO_3$ and $KNbO_3$ regions.

Fig. 3 shows the morphology of sintered pellets. The presence of some pores is evident in Fig. 3(a), which corresponds to the sample sintered at 1060 °C. This sample has a density of 4.27 g/cm^3,

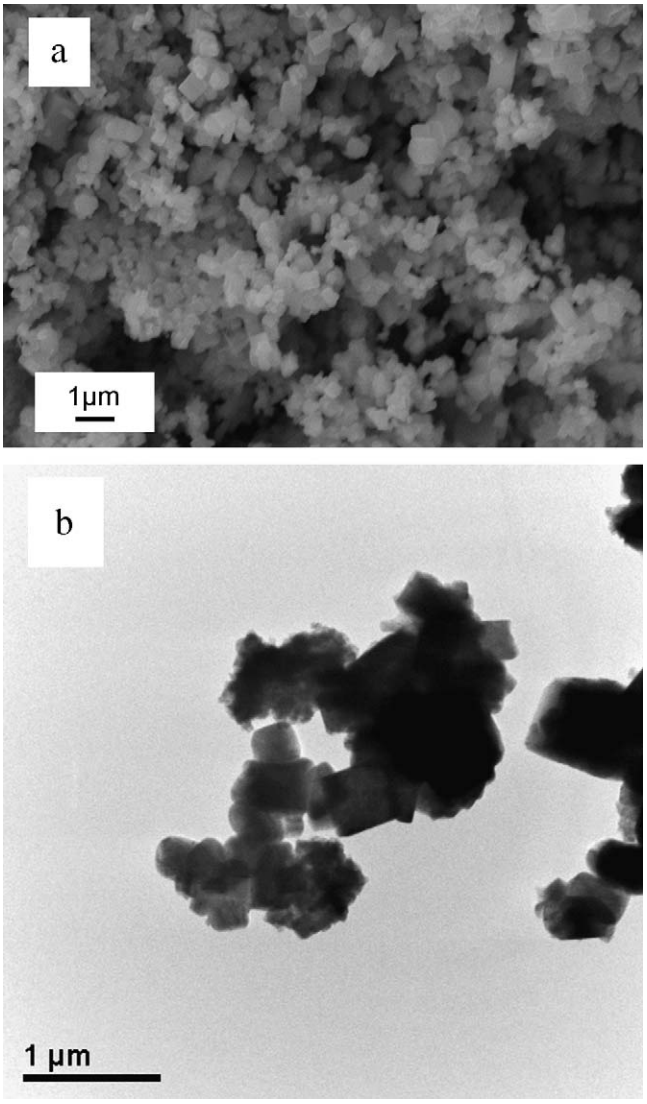

Fig. 1. SEM (a) and bright field TEM (b) images of KNN powder annealed for 1 h at 800 °C.

equivalent to 94.6% of theoretical value (4.51 was taken as reference) [1]. Moreover, the morphology is pseudo-cubic with grain sizes ranging from 0.5 to around 5 μm. In Fig. 3(b) is observed that the grain size increased when the sintering temperature was

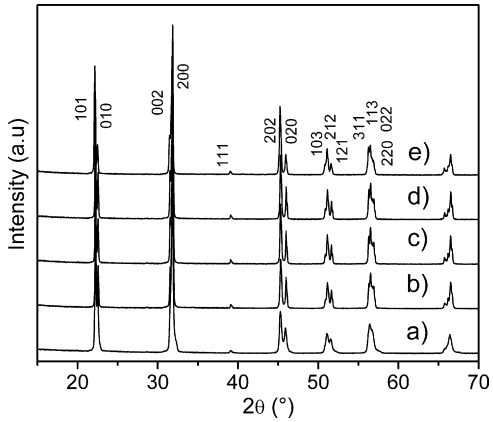

Fig. 2. XRD patterns of: (a) the calcined powder at 800 °C, and sintered samples using (b) 1060 °C, (c) 1080 °C, (d) 1100 °C and (e) 1120 °C for 2 h.