



# 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  $\mu\text{C}/\text{cm}^2$  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.

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## 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<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub> 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<sub>3</sub>) 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  $\geq 800$  °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<sub>2</sub>O<sub>5</sub> (99.99%), K<sub>2</sub>CO<sub>3</sub> (99.8%), Na<sub>2</sub>CO<sub>3</sub> (99.9%), HF (40%) NH<sub>4</sub>OH (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 stoichiometric 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 K $\alpha$  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 ( $\epsilon$ ) 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<sup>-1</sup> 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  $\mu$ m (average grain size of 0.281  $\mu$ m 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<sub>3</sub>–NaNbO<sub>3</sub> [12], the KNN composition is close to two orthorhombic phases, both ferroelectric in the rich NaNbO<sub>3</sub> and KNbO<sub>3</sub> 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<sup>3</sup>,

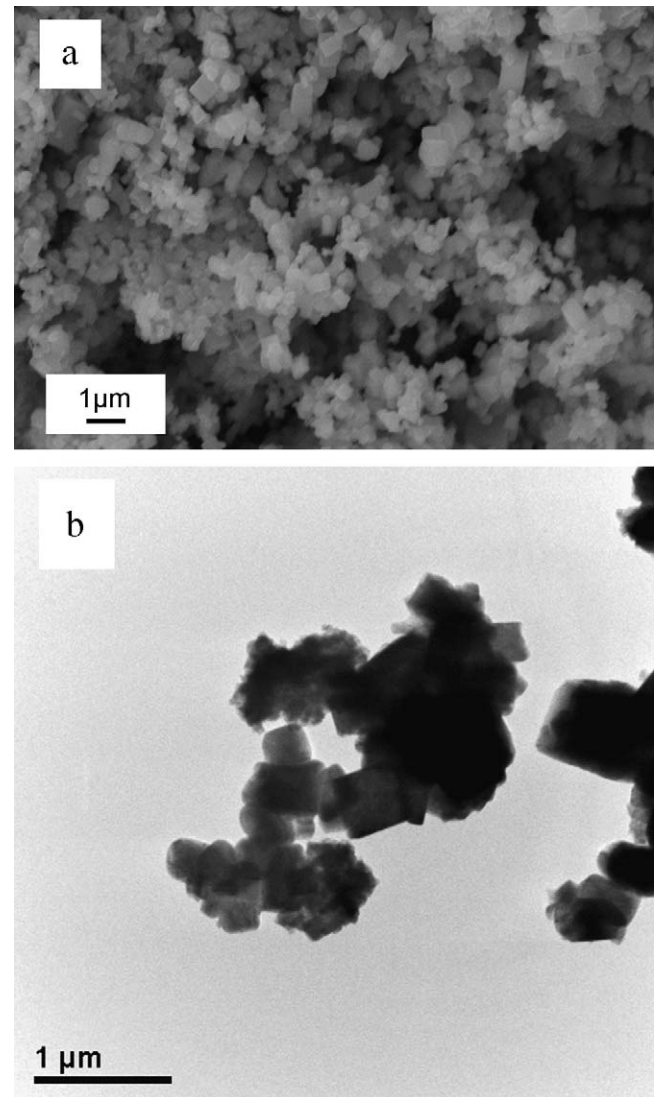


Fig. 1. SEM (a) and bright field TEM (b) images of KNN powder annealed for 1 h at 800 °C.

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  $\mu$ m. In Fig. 3(b) is observed that the grain size increased when the sintering temperature was

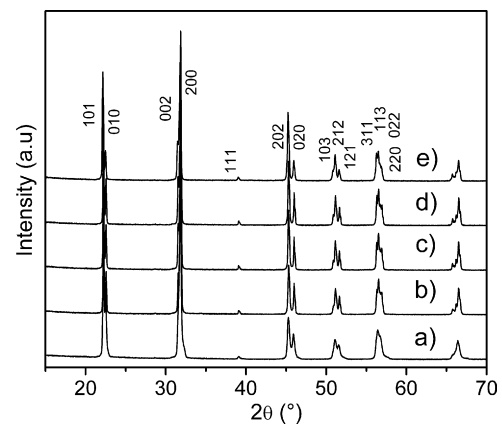


Fig. 2. XRD patterns of: (a) the calcined powder at 800 °C, and sintered samples using (b) 1060 °C, (c) 1080 °C, (d) 1100 °C and (e) 1120 °C for 2 h.

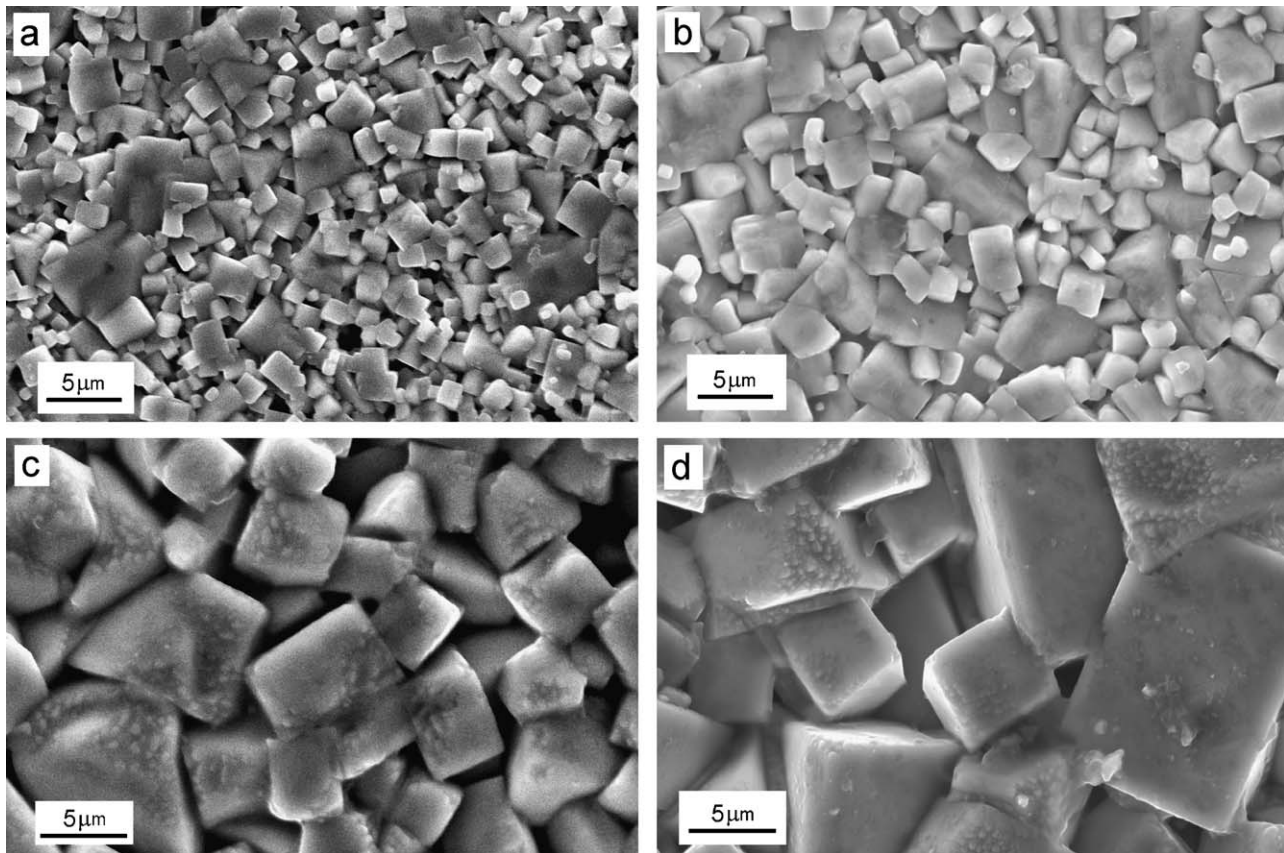


Fig. 3. SEM pictures of KNN sintered samples for 2 h at: (a) 1060 °C, (b) 1080 °C, (c) 1100 °C and (d) 1120 °C.

raised to 1080 °C and a higher density was achieved, 4.33 g/cm<sup>3</sup> (96%). Fig. 3(c) and (d) show that, when the sintering temperature increases further, the grain size also increases. For the sample sintered at 1120 °C, grains grow at a maximum size of ~10 μm. But, in contrast to the grain size, the density diminishes from 4.33 at 1080 °C to 4.17 g/cm<sup>3</sup> (92%) at 1120 °C. The decrease in density would be the consequence of a liquid phase formation at 1120 °C, because it is close to the melting point of the KNN, which is considered to be 1140 °C, and the volatilization of alkaline elements as well [29].

The dielectric constant ( $\epsilon$ ) and dielectric losses ( $\tan \delta$ ) measured at 100 kHz for the sintered samples, are shown in Fig. 4. Two transitions are observed in the dielectric constant curves (Fig. 4(a)):  $T_{O-T}$  around 195 °C and  $T_C$  at 420 °C, as is reported in several works for bulk ceramics [1,15], in contrast to the single crystals [30–33], where a wide range exists in both  $T_{O-T}$  (160–205 °C) and  $T_C$  (390–410), depending upon composition and lattice defects. It is clearly seen that the sample sintered at 1080 °C has a higher dielectric constant in the transition ( $T_C$ ), and at room temperature KNN ceramics have dielectric constant near 300. In the literature, for polycrystalline KNN ceramics dielectric constant around 450 are reported [1,14], while for single crystals Chen et al. [30] measured 185 in KNN-LN composition. Lin et al. [32] found 240 for KNN, and Uršič [31] reported 1015 in KNN, also. The  $\tan \delta$  shifts from 1.6 to 2.7% at room temperature, as it can be seen in Fig. 4(b). Most investigations report values of around 4% for polycrystalline KNN ceramics [1,18,29,34], and it is important to underline the low losses found for the ceramics sintered at 1060 and 1080 °C. Comparing with single crystal reports whose losses are near 1% [30–32] our results are a little higher, except for Kizaki and coworkers [33] whose reported near 4% (less than 10%). Concerning the two phase transitions observed in the dielectric constant versus temperature,

these are also identified in the  $\tan \delta$  graph. From room temperature and even beyond the first transition ( $T_{O-T}$ ), dielectric losses do not exceed 2.5% for 1060 and 1080 °C. In contrast, for 1100 and 1120 °C, they are close to 3% at room temperature. The increase in dielectric losses that occurs in both samples sintered at 1100 and 1120 °C could be related to the presence of vacancies due to the considerable loss of alkali compounds [30,33] generating also oxygen vacancies. This increment in conductivity is revealed when temperature surpasses 250 °C (Fig. 4(b)).

The ferroelectric loops acquired are shown in Fig. 5. The average  $2P_r$  increases from 23.2 to 51  $\mu\text{C}/\text{cm}^2$ , as is observed in Fig. 5(a)–(d) for samples sintered from 1060 to 1120 °C. At first glance, it seems that the sample sintered at 1120 °C has the best ferroelectric and piezoelectric properties, nevertheless  $2E_C$  has a different behavior, it starts at 19.1 kV/cm, reaches a minimum of 16.5 kV/cm at 1080 °C and increases again until 18.1 kV/cm at 1120 °C. Samples with good piezoelectric and ferroelectric properties should have high  $P_r$  and low  $E_C$ . Zuo et al. [14] investigated ferroelectric properties in KNN and doped KNN, finding a remnant polarization of 15  $\mu\text{C}/\text{cm}^2$  ( $2P_r \sim 30 \mu\text{C}/\text{cm}^2$ ), for KNN. On the other hand, Chen et al. [13] determined 17  $\mu\text{C}/\text{cm}^2$ , and Guo et al. [16] measured 10  $\mu\text{C}/\text{cm}^2$  in KNN-LT. All samples have well-saturated ferroelectric loops, except for the sample sintered at 1120 °C that has a rounded-like shape, attributable to some degree of conductance. This conductance at room temperature results from the oxygen vacancies generated at high sintering temperature and, since 1120 °C is close to the KNN melting point (1140 °C), these vacancies are considerable, which induce some conductivity at room temperature when a high electric field is applied, as discussed for dielectric losses. This phenomenon is mainly encountered in single crystals [30,33], where it was not possible to polarize the samples, and only Mn-doped KNN [33] gave a high

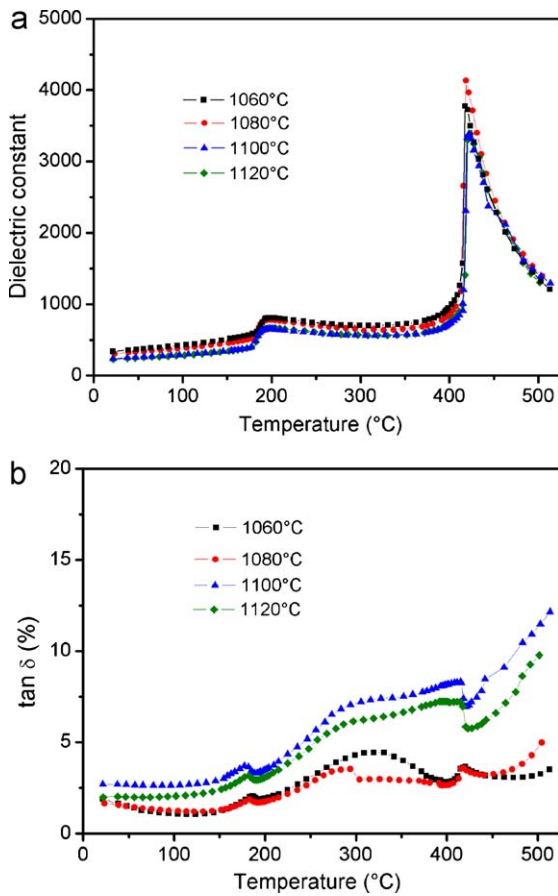


Fig. 4. Dielectric constant (a) and  $\tan \delta$  (b) measured at 100 kHz for KNN sintered pellets between 1060 and 1120 °C.

remnant polarization ( $40 \mu\text{C}/\text{cm}^2$ ). Uršič et al. [31] also measured  $17 \mu\text{C}/\text{cm}^2$  in their crystals.

Piezoelectric properties are closely related to densification in lead-free ceramics. When density increases, the  $k_p$  and  $d_{31}$  also

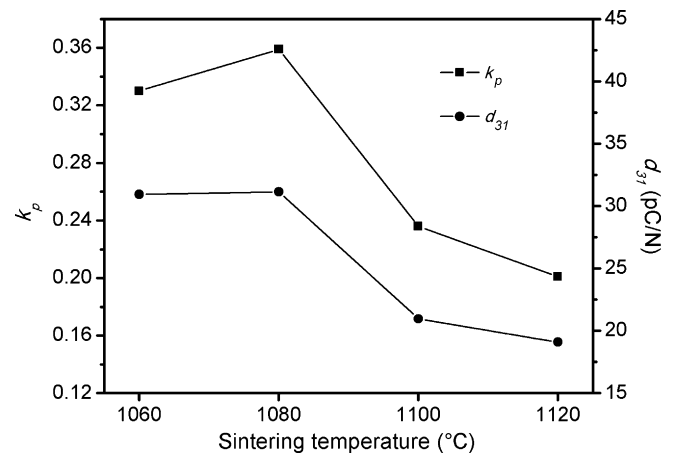


Fig. 6.  $k_p$  and  $d_{31}$  as function of the sintering temperature for KNN sintered ceramics.

increase.  $k_p$  and  $d_{31}$  have similar trends as it is shown in Fig. 6.  $k_p$  first increases from 0.33 at 1060 °C to 0.36 at 1080 °C, and then decreases. The lowest  $k_p$  of 0.20 was found at 1120 °C. The extreme values for  $d_{31}$  are 31.1 and 19.1 pC/N for 1080 and 1120 °C, respectively. Also, the piezoelectric properties are closely related to ferroelectric properties. As mentioned above, the highest density and best ferroelectric properties were found in the sample sintered at 1080 °C, which corresponds to the enhanced piezoelectric properties for this sample. At higher sintering temperature, the detrimental effect on properties is caused by the volatilization of potassium and the formation of the liquid phase. Several studies had pointed out the narrow sintering temperature range to achieve samples with acceptable properties [1,14,19,35]. For comparison, Ringgaard and colleagues [1] achieved a  $k_p$  of 0.39 in KNN, while Guo and co-workers [16] found 0.37 for Li-Ta co-doped KNN. Zuo et al. [14] reported 0.31–0.4 in KNN depending on milling conditions. To our knowledge, the best  $k_p$  reported for pure KNN is that of Jaeger and Egerton [36] who employed hot pressing. For the piezoelectric constant  $d_{31}$ , Ringgaard [12] reported 40 pC/N for un-doped KNN and 30 pC/N for doped samples. Jaeger and Egerton

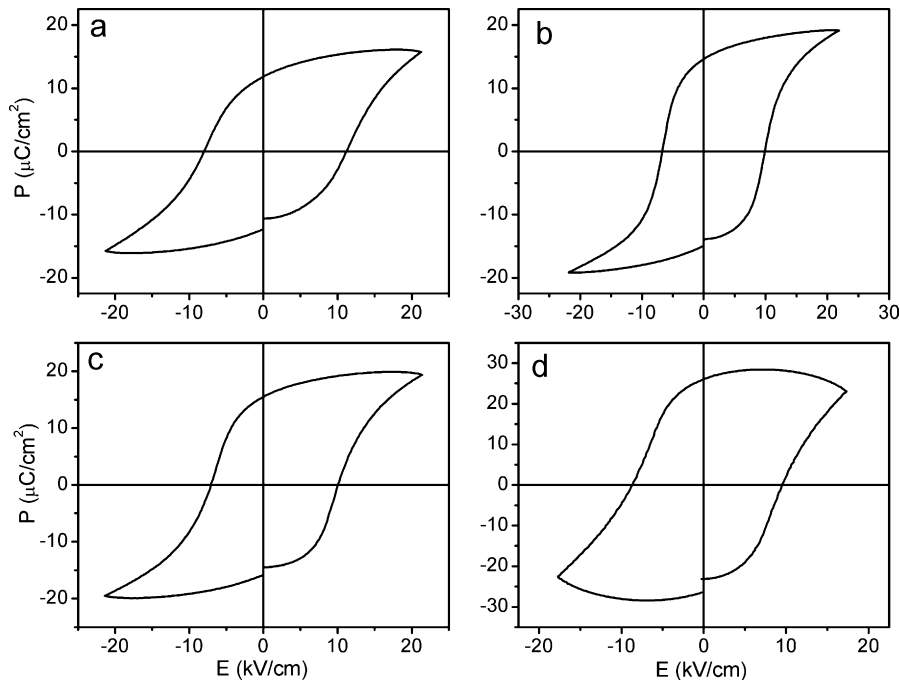


Fig. 5.  $P$ - $E$  hysteresis loops of KNN ceramics: (a) 1060 °C, (b) 1080 °C, (c) 1100 °C and (d) 1120 °C.

found 32 and 49 pC/N for air sintered and hot-pressed samples, respectively.

The ferroelectric and piezoelectric properties measured in this work are comparable with those reported in other studies.

#### 4. Conclusions

It was possible to synthesize a  $K_{0.5}Na_{0.5}NbO_3$  (KNN) solid solution using the spray drying technique at low temperature (800 °C), with an average particle size of 0.281  $\mu\text{m}$ . Several sintered samples were prepared. The sample sintered at 1080 °C had the highest properties with  $k_p$ ,  $d_{31}$ ,  $2P_r$ , and  $2E_C$  of 0.36, 30 pC/N, 29  $\mu\text{C}/\text{cm}^2$ , and 8.2 kV/cm, respectively. These values are comparable with those reported in the literature, and the  $\tan \delta$  is even lower than the reported for pure KNN. Then, spray drying method could be used for synthesizing submicrometer powders at low temperature. The calcination time reduction at crystallization stage reduces volatilization of alkali compounds. Also, the grain growth was reduced, avoiding additional grinding steps as in conventional solid-state method.

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