

Sodium niobate ceramics prepared by mechanical activation assisted methods

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Abstract

Sodium niobate is an interesting material that is nowadays considered to be used as a lead-free piezoelectric ceramic. However, it is very difficult to process fully dense ceramics of this composition starting from crystalline powdered precursors. It seems a priority to develop a new synthesis route for the processing of high quality ceramics. A new synthesis method based on high-energy milling, not yet explored for this type of materials, has been applied to obtain NaNbO_3 . Stoichiometric mixtures of analytical grade Na_2CO_3 and Nb_2O_5 were mechanically activated in a vibrating-type mill. A progressive broadening of the different X-ray diffraction peaks was observed when the milling time was increased. The starting products did not become amorphous. The thermal behaviour of the milled samples was studied by high temperature in situ X-ray powder diffraction and thermal analysis techniques. Ceramic materials were processed by natural sintering and hot-pressing or a combination of both. Ferro-piezoelectric properties were measured to assess their practical use as piezoceramics.

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1. Introduction

Sodium niobate, NaNbO_3 , is of particular interest for the number of its successive transitions between different phases, all of them belonging to the perovskite structural type.¹ Some solid solutions based on this material have ferroelectric and good piezoelectric properties.^{2–4}

Alkali metal niobate powders are usually prepared via conventional ceramic synthesis. The solid-state reaction route is not appropriated because high temperatures and long times are needed, which can lead to the volatilisation of the alkali metal. Moreover, this method provides products with large and inhomogeneous particle sizes.

Many chemistry-based processing routes have been developed to facilitate the reactions in the solid state.⁵ These routes, described in the literature, are

coprecipitation and sol-gel processes,^{4,6} hydrothermal synthesis⁷ and polymeric precursor processes.⁸ However, most of these chemistry based routes require high-purity inorganic or organometallic reactants, which are more expensive than the widely available oxides and carbonates.

Mechanochemical techniques were developed for the synthesis of alloys and intermetallic compounds.⁹ Recently, mechanical activation has been applied to the preparation of amorphous and nanocrystalline materials,^{10,11} as well as in the synthesis of new compounds¹² and in the improvement of their physico-chemical characteristics.^{13,14} High-energy milling makes the activated powder more reactive and capable of faster reactions, because the homogeneity of the mixture is increased, the size of crystallites reduced and the crystal structure damaged.¹⁵ Therefore, the necessary calcination step to synthesize the designed phase is completed at a lower temperature and in a shorter time.¹⁶

The aim of this work is the study of the synthesis of NaNbO_3 and the preparation and characterization of the ferro-piezoelectric properties of NaNbO_3 ceramics from mechanically activated precursors.

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2. Experimental procedure

NaNbO_3 ceramic precursor powders were prepared according to the following procedure: a stoichiometric mixture of analytical-grade Nb_2O_5 and Na_2CO_3 was homogenized by hand in an agate mortar. Then the mixture was mechanically activated using an agate pot and a 5 cm diameter ball of the same material in a vibrating-type mill Fritsch Pulverisette 0.

For the sake of comparison, NaNbO_3 powder was also prepared by a solid-state reaction from Nb_2O_5 and Na_2CO_3 by successive thermal treatments at increasing temperatures from 400 to 800 °C, over 12 h each, and followed by cooling by quenching.

The samples were characterized by X-ray diffraction (XRD), at room and increasing temperatures, thermogravimetric (TG) and differential thermal analysis (DTA) as described elsewhere.¹⁶ Ceramics were prepared from the mechanically activated precursors in a single thermal treatment in which both synthesis and sintering took place. Activated powders during 30 days were shaped by uniaxial pressing at 210 kg cm⁻² as thin disks of approximately 10 mm diameter and 2 mm thickness. Green disks were isostatically pressed at 2000 kg cm⁻². Ceramics were prepared by natural sintering, hot-pressing or a combination of both.

Ceramics were lapped to a ratio thickness/diameter of 1/10, and Pt electrodes were painted on the major faces and sintered at 700 °C for 30 min, so as to prepare the capacitor samples for the electrical measurements. Dielectric measurements on unpoled samples as a function of the temperature were carried out as described

elsewhere,¹⁷ during heating and cooling runs at a rate of 1 °C min⁻¹.

The samples were poled in a silicon oil bath at 50 kV cm⁻¹, for 20 min at 180 °C. The piezoelectric d_{33} coefficient was measured in a Berlincourt-meter at 100 Hz. Dielectric, elastic and piezoelectric constants and electromechanical coupling factors corresponding to the thickness and radial (planar) extensional vibration modes of the thin disk shaped ceramic resonators were calculated by an automatic iterative method described elsewhere.^{18,19} This method was modified so as to perform calculations from the measured files, independently of the complex impedance measurements at resonance taken at increasing temperatures in a dynamic process, using a HP4192A impedance analyzer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $\text{Nb}_2\text{O}_5/\text{Na}_2\text{CO}_3$ mixture treated in the vibrating-type mill for increasing times. The pattern of the initial mixture shows the diffraction peaks of Nb_2O_5 and Na_2CO_3 . After 7 days of milling, the unique phase detectable is Nb_2O_5 , while Na_2CO_3 become amorphous. Even after 30 days of activation the amorphization of Nb_2O_5 does not take place. However, the significant broadening in the peaks shows that a reduction of the crystallite sizes has been produced.

To make a comparative investigation of the thermal behaviour of the samples as a function of the milling time, samples milled for 10, 20 and 30 days were investigated by DTA, TG and XRD at increasing temperatures.

TG tracing acquired from a heating/cooling cycle of powder milled for different times are shown in Fig. 2. All TG curves are very similar, exhibiting two important weight-loss steps: the first one between room temperature and 125 °C, and the second one between 400

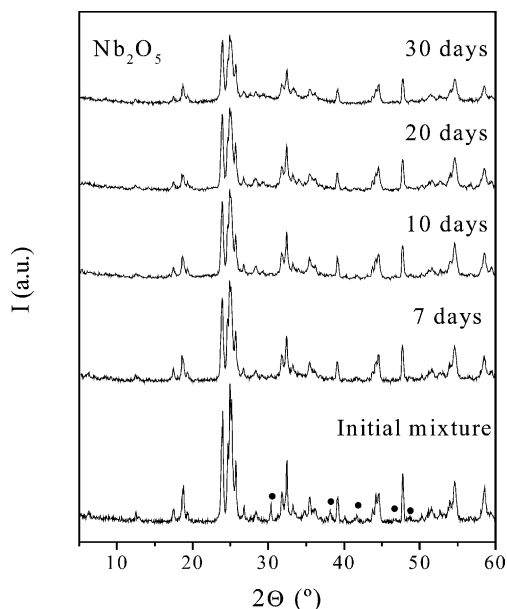


Fig. 1. XRD patterns of $\text{Na}_2\text{CO}_3/\text{Nb}_2\text{O}_5$ mixture after different activation times. (• = Na_2CO_3).

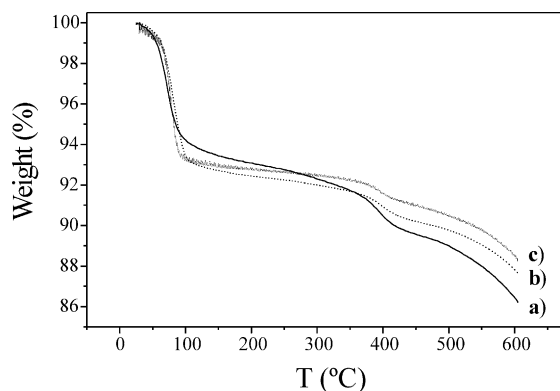


Fig. 2. TG tracing of $\text{Na}_2\text{CO}_3/\text{Nb}_2\text{O}_5$ mixture mechanoactivated for: (a) 30; (b) 20; and (c) 10 days.

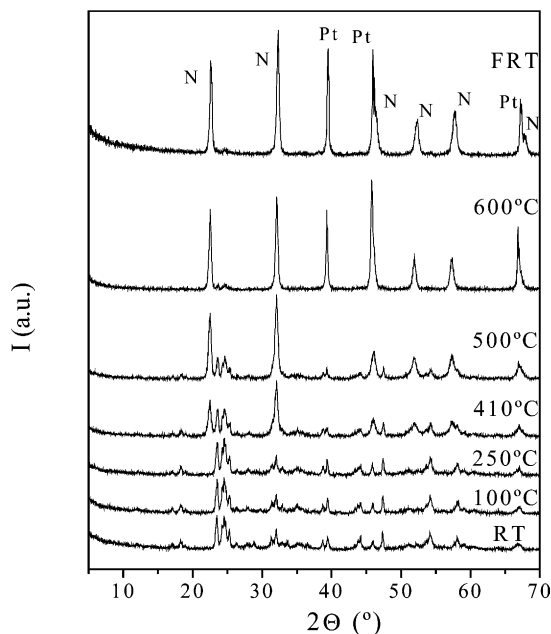


Fig. 3. XRD recordings of 30-day-milled $\text{Na}_2\text{CO}_3/\text{Nb}_2\text{O}_5$ sample at increasing temperatures. (Pt=platinum sheet, N= NaNbO_3 , RT=room temperature, FRT=final room temperature).

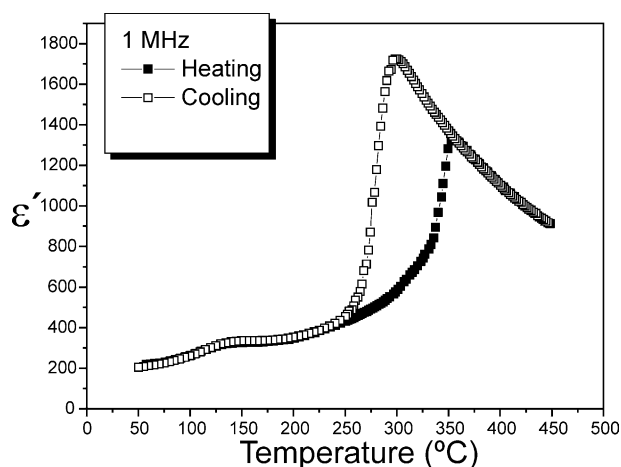


Fig. 4. Temperature dependence of the permittivity for the hot-pressed ceramic from powder activated over 30 days.

and 600 °C. DTA curves displayed only one endothermic peak at 80 °C, corresponding to the first weight-loss step.

The TG and DTA recordings can be understood on the basis of XRD at increasing temperatures. As an example, Fig. 3 shows the evolution with temperature of the X-ray diffraction patterns for the case of the Nb_2O_5 and Na_2CO_3 mixture milled for 30 days. At 250 °C, patterns are similar to those for the as-milled powder, where only Nb_2O_5 broadened peaks are observed. Thus, the first weight-loss step measured by TG at low temperature, as well as the endothermic peak observed in the DTA curve, is probably just due to loss of water coming from hydration of powder during milling. The

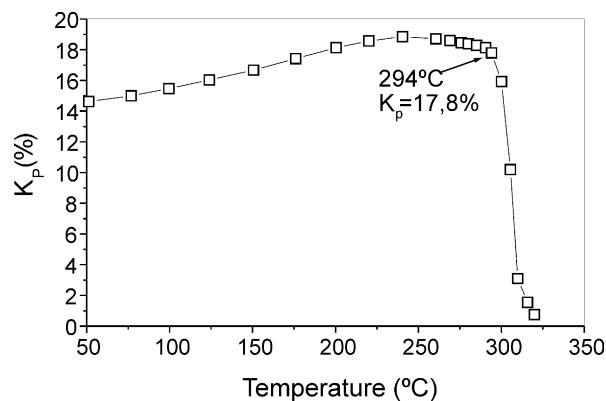


Fig. 5. Temperature dependence of the planar electromechanical coupling factor for the hot-pressed ceramic from powder activated over 30 days.

second weight loss is most probably due to the decomposition of Na_2CO_3 , since the crystallization of NaNbO_3 starts at 410 °C. This process occurs slowly over a very large temperature interval, and consequently, no well defined peaks can be detected by DTA. A pure phase is obtained at 600 °C from powders activated over 30 days, but not for the reactants milled for 10 and 20 days, where some unreacted Nb_2O_5 can be observed. As a contrast, cumulative thermal treatments up to 750 °C for 12 h each are needed to obtain NaNbO_3 by solid-state reaction.

All the sintered ceramics, in conditions ranging from 900 °C for 1 h to 1200 °C for 4 h, show densities that are lower (ranging from 1.90 to 2.34 g cm⁻³, respectively) than the green density (2.89 g cm⁻³). Indeed, an expansion of the green pellets during sintering was observed. The origin of this is the formation of porosity while the weight loss, due to decarboxylation, that extends up to temperatures higher than 600 °C, occurs. As an alternative way to avoid this generation of porosity, and in order to keep the strategy of ceramic processing with a unique thermal treatment, hot-uniaxial-pressing (HP) was successfully tested and denser ceramics were obtained, even at 900 °C for 1 h (3.57 g cm⁻², 78% of the theoretical density). The optimum condition (4.21 g cm⁻², 92% of the theoretical density) was found for HP at 1000 °C for 2 h and ~200 kg cm⁻².

XRD of both the sintered and hot-pressed ceramics show that all of them are single phase and isostructural with NaNbO_3 (JCPDS-ICDD file no. 33-1270).

Figs. 4 and 5 show the temperature dependence of the real part of the dielectric permittivity and of the planar electromechanical coupling factor, respectively.

At the heating run the dielectric anomaly, reported for NaNbO_3 single crystals²⁰ and the antiferroelectric character at ~354 °C is observed. The thermal hysteresis showed by this anomaly has also been previously reported.

Table 1

Room temperature piezocharacterization results of hot-pressed ceramic at 1000 °C for 2 h from powder activated over 30 days

Planar mode	Thickness mode
Fundamental mode measurement $F_s = 323.72 \text{ kHz}$, $F_p = 326.25 \text{ kHz}$ $K_p = 0.139$ $K_{31} = 0.084$ $N_p = 3571 \text{ kHz mm}^{-1}$ coeff. Poison $\sigma = 0.282$ $c_{11}^E = (12.76 + 0.06i) \times 10^{10} \text{ N m}^{-2}$ $s_{11}^E = (8.51 - 0.04i) \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ $s_{12}^E = (-2.40 + 0.01i) \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ $d_{31} = (-8.71 + 0.09i) \times 10^{-12} \text{ C N}^{-1}$ $\epsilon_{33}^T = (144.4 + 1.77i)$	Second overtone measurement $F_s = 14.640 \text{ kHz}$, $F_p = 14.644 \text{ kHz}$ $K_t = 0.176$ $N_t = 3045 \text{ KHz.mm}$ $c_{33}^D = (15.56 + 0.31i) \times 10^{10} \text{ N m}^{-2}$ $h_{33} = (22.73 + 4.20i) \times 10^{-12} \text{ C N}^{-1}$ $\epsilon_{33}^S = (102.32 + 1.40i)$ $d_{33} (\text{Berlincourt}) = 40 \times 10^{-12} \text{ C N}^{-1}$

Poling induces a ferroelectric phase in the antiferroelectric NaNbO_3 that shows piezoelectric activity at room temperature as the data in Table 1, corresponding to the hot pressed ceramic at 1000 °C for 2 h, reveals. This piezoelectric activity extends up to a temperature close to 300 °C (Fig. 5). A relatively small change, an increase, of the planar electromechanical coupling factor up to this temperature was observed.

4. Conclusions

A study concerning the synthesis of NaNbO_3 has been carried out using a mechanical activation route from stoichiometric $\text{Nb}_2\text{O}_5/\text{Na}_2\text{CO}_3$ mixture. The synthesis begins at 410 °C for all milling times. A pure phase is obtained by a single thermal treatment at 600 °C from the 30-day activated mixture.

Dense ceramics were obtained by hot-uniaxial-pressing at 1000 °C for 2 h from powder activated over 30 days. A dielectric anomaly of antiferroelectric character was measured at 354 °C. Poling induces ferroelectricity and a piezoelectric activity that extends up to ~ 300 °C.

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