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 diffrac- tion 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.

1. Introduction

Sodium niobate, NaNbO3, 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 highpurity 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.

2. Experimental procedure

NaNbO3 ceramic precursor powders were prepared according to the following procedure: a stoichiometric mixture of analytical-grade Nb2O5 and Na2CO3 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, NaNbO3 powder was also prepared by a solid-state reaction from Nb2O5 and Na2CO3 by successive thermal treatments at increasing temperatures from 400 to 800 ºC, 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 ºC 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 ºC min^{-1}. The samples were poled in a silicon oil bath at 50 kV cm^{-1}, for 20 min at 180 ºC. The piezoelectric d33 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 Nb2O5/Na2CO3 mixture treated in the vibrating-type mill for increasing times. The pattern of the initial mixture shows the diffraction peaks of Nb2O5 and Na2CO3. After 7 days of milling, the unique phase detectable is Nb2O5, while Na2CO3 become amorphous. Even after 30 days of activation the amorphization of Nb2O5 does not take place. However, the significant broadening in the peaks shows that a reduction of the crystallite sizes has been produced.

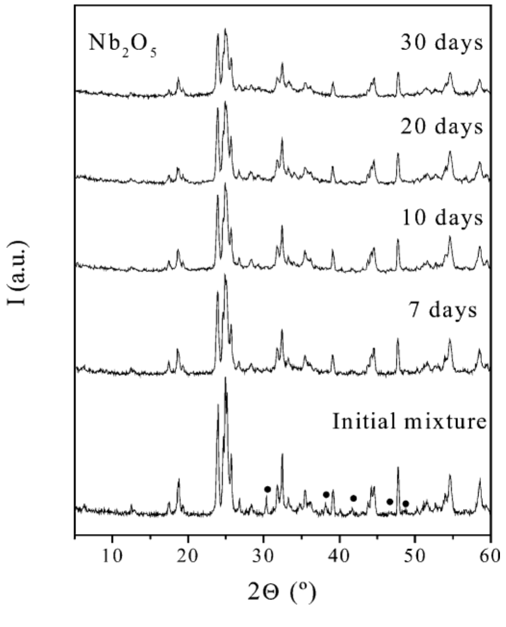


Fig. 1. XRD patterns of Na_2CO_3/Nb_2O_5 mixture after different activation times. (●=Na_2CO_3).

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.

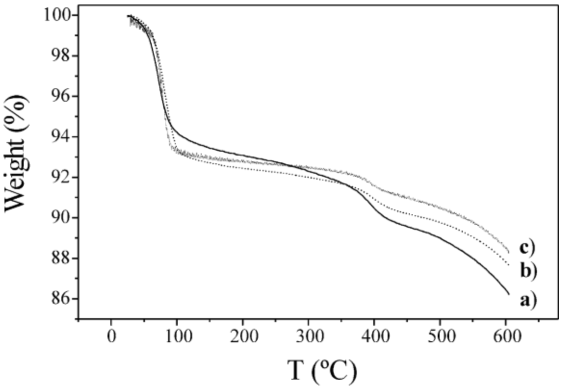


Fig. 2. TG tracing of Na_2CO_3/Nb_2O_5 mixture mechanoactivated for: (a) 30; (b) 20; and (c) 10 days.

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 ºC, and the second one between 400 and 600 ºC. DTA curves displayed only one endothermic peak at 80 ºC, 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 Nb2O5 and Na2CO3 mixture milled for 30 days. At 250 ºC, patterns are similar to those for the as-milled powder, where only Nb2O5 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 second weight loss is most probably due to the decomposition of Na2CO3, since the crystallization of NaNbO3 starts at 410 ºC. 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 ºC from powders activated over 30 days, but not for the reactants milled for 10 and 20 days, where some unreacted Nb2O5 can be observed. As a contrast, cumulative thermal treatments up to 750 ºC for 12 h each are needed to obtain NaNbO3 by solid-state reaction.

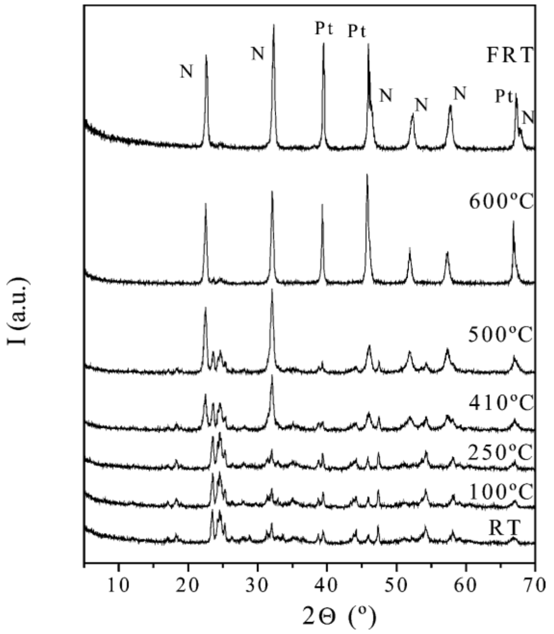


Fig. 3. XRD recordings of 30-day-milled Na2CO3/Nb2O5 sample at increasing temperatures. (Pt=platinum sheet, N=NaNbO3, RT=room temperature, FRT=final room temperature).

All the sintered ceramics, in conditions ranging from 900 ºC for 1 h to 1200 ºC 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 ºC, 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 ºC for 1 h (3.57g 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 ºC 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 NaNbO3 (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 NaNbO3 single crystals20 and the antiferroelectric character at 354 ºC is observed. The thermal hysteresis showed by this anomaly has also been previously reported.

Poling induces a ferroelectric phase in the antiferroelectric NaNbO3 that shows piezoelectric activity at room temperature as the data in Table 1, corresponding to the hot pressed ceramic at 1000 ºC for 2 h, reveals. This piezoelectric activity extends up to a temperature close to 300 ºC (Fig. 5). A relatively small change, an increase, of the planar electromechanical coupling factor up to this temperature was observed. 4.

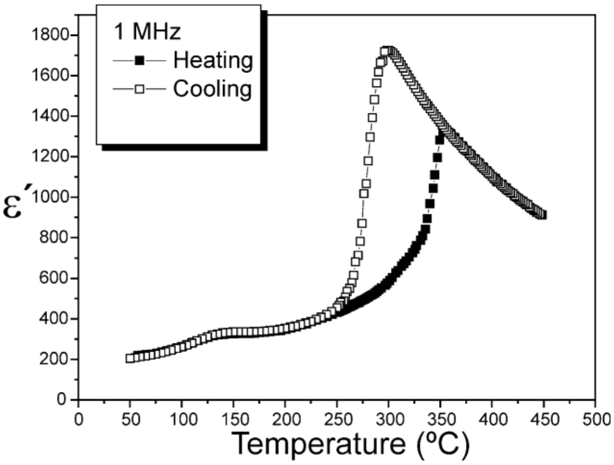


Fig. 4. Temperature dependence of the permittivity for the hot-pressed ceramic from powder activated over 30 days

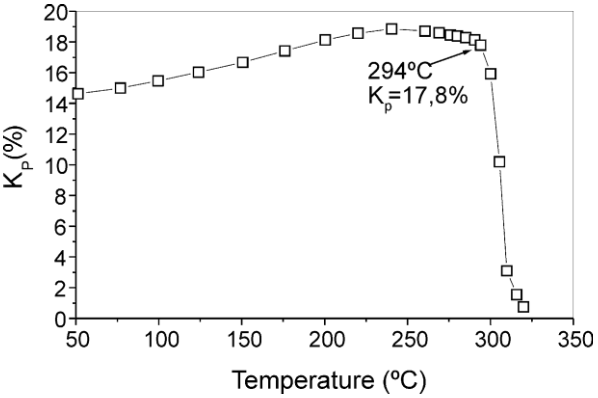
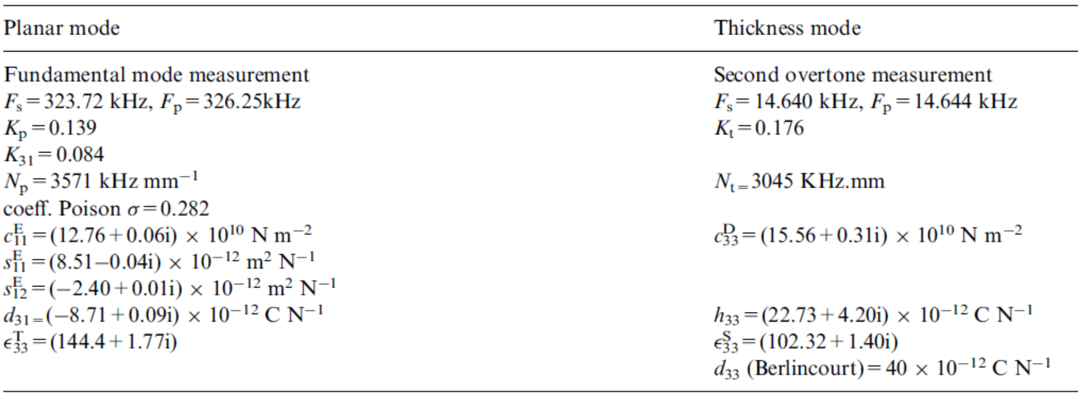


Fig. 5. Temperature dependence of the planar electromechanical coupling factor for the hot-pressed ceramic from powder activated over 30 days.

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

Conclusions

A study concerning the synthesis of NaNbO3 has been carried out using a mechanical activation route from stoichiometric Nb2O5/Na2CO3 mixture. The synthesis begins at 410 ºC for all milling times. A pure phase is obtained by a single thermal treatment at 600 ºC from the 30-day activated mixture. Dense ceramics were obtained by hot-uniaxial-pressing at 1000 ºC for 2 h from powder activated over 30 days. A dielectric anomaly of antiferroelectric character was measured at 354 ºC. Poling induces ferroelectricity and a piezoelectric activity that extends up to 300 ºC.

Acknowledgements

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