Sodium-lithium niobate piezoceramics prepared by mechanochemical activation assisted methods

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The environmental protection issues are driving forces nowadays in the scientific research on materials. From this point of view, it is a need to find alternatives to the present commercial piezoceramics, based on lead titanates-zirconates. The production of these materials requires handling of big amounts of lead oxide, which is highly toxic. Alkaline niobate piezoceramics are considered a good alternative for the future substitution of commercial piezoceramics by lead-free materials. However, the processing of these ceramics is difficult by conventional ceramic routes. There is a need to search for new routes of processing.

The mechanochemical activation was used in this work for the first time to get $Na_{1-x}Li_xNbO_3$ ceramics in the Na rich region. Stoichiometric mixtures of Na_2CO_3 or Na_2O, Li_2CO_3 and Nb_2O_5 were activated in a vibrating mill. A progressive broadening of the X-ray diffraction peaks of the mixtures was observed as the milling time increased. Nevertheless, the precursors did not became fully amorphous. The thermal evolution of the activated precursors was also tested. Ceramics were obtained by sintering or hot pressing and their piezoelectric properties were studied.

Keywords: sodium-lithium niobate, piezoceramics, ferroelectrics, mechanical activation

Piezoceramicas de niobato de sodio y litio preparadas por métodos asistidos de activación mecanoquímica

La protección medioambiental es uno de los factores que impulsan diversas áreas de la investigación en materiales. Existe la necesidad de la búsqueda de alternativas a las cerámicas ferro-piezoeléctricas comerciales basadas en los titanatos-circonatos de plomo, que requieren el manejo de grandes cantidades de óxido de plomo, muy tóxico, en su procesado. Los niobatos alcalinos se consideran buenos candidatos para esta sustitución. Sin embargo, es difícil conseguir cerámicas con altas densificaciones. De aquí la necesidad de investigar nuevas rutas de procesado.

La activación mecanoquímica se ha utilizado por primera vez en este trabajo para obtener cerámicas de $Na_{1-x}Li_xNbO_3$, en la región rica en Na. Se han activado mecanoquímicamente mezclas estequiométricas de Na_2CO_3 o Na_2O, Li_2CO_3 y Nb_2O_5 en un molino vibratorio. Se ha observado el progresivo ensanchamiento de los picos de difracción de rayos X de las mezclas a medida que se aumentaba el tiempo de molienda, pero los precursores no llegan a ser amorfos para la difracción de rayos X. A partir de estos precursores se han obtenido cerámicas mediante sinterización o prensado en caliente y estudiado sus propiedades piezoeléctricas.

Palabras clave: mobato de litio y sodio, piezocerámicas, ferroeléctricos, activación mecanoquímica

1. INTRODUCCION

Alkaline niobate ceramics (1, 2) are consider a good alternative for the future substitution of commercial piezoceramics by lead-free materials. However, the processing of these ceramics is difficult by conventional ceramic routes. There is a need to search for new routes of processing.

The method of mechanical alloying has been already used to obtain nanocrystals, intermetallic compounds, such as ferromagnetic alloys, amorphous materials and non-oxide ceramics, such as carbides and nitrides. It consists of a prolonged milling of powder reactants that causes an intense mechanical action on the particles, which can be subjected to shock pressures of the order of 5-15Gpa (3). In a first stage of the process, a reduction of the particle size takes place, which is followed by the occurrence of local changes of pressure and temperature in each of the continuous contacts between particles. These give place to shock-assisted and shock-induced chemical changes, that lead to mechanosynthesis, and to the creation of non-equilibrium point defects and new paths for motion of defects, that lead to the amorphization of the powder. The energy storage in the activated particles leads to the reduction of the energy barrier for occurrence of solid state reactions, which results in reduction of

the synthesis temperature and the appearance of new phases that cannot be obtained by conventional solid state reactions (4). The use of this route to obtain ferro-piezoelectric ceramics is scarce and very recent (5-8). Results are very encouraging for the processing of dense ceramics by natural sintering when synthesis or sintering presents difficulties. Such is the case of lead zirconate titanate PZT(52/48) ceramics from perovskite nanocrystals, obtained from mechanosynthesis, that could be sintered at temperatures as low as 950ºC without previous calcination (6). Unfortunately, piezoelectric properties were not reported.

The processing of other ferroelectric ceramics from mechanochemically activated precursors, the bismuth-layered perovskites such as Bi_3TiNbO_9 (BTN) (7) and its solid solutions with $SrBi_2Nb_2O_9$ (SBN) (8), was also successfully tested by the authors. Improvement of the synthesis and sintering conditions, as well as the piezoelectric properties, was achieved.

The aim of this work is to evaluate the effect of the mechanochemical activation on precursor powder mixtures for the preparation of ceramics of $(Na,Li)NbO_3$ and the characterization of the piezoelectric properties of these ceramics.

2. EXPERIMENTAL

NaNbO$_3$ (NN) and Na$_{0.95}$Li$_{0.5}$NbO$_3$ (LNN) ceramic precursor powders were prepared from stoichiometric mixtures of analytical-grade Nb$_2$O$_5$ and Na$_2$CO$_3$, Li$_2$CO$_3$ or Na$_2$O, which were initially homogenized by hand in an agate mortar. Then, the mixture was placed in an agate pot with a 5 cm diameter ball of the same material and mechanically activated using a vibrating-type mill Fritsch Pulverisette 0. In all cases, the mechanochemical treatments were carried out in air, for times ranging from 1 h to 30 days.

X-ray diffraction patterns of the powders after the activation were measured at room temperature with a Siemens Kristalloflex 810 computer controlled diffractometer, and a D501 goniometer provided with a 2θ compensating slit and a graphite monochromator. Patterns were collected between 5-60º (2θ) with increments of 0.05 º(2θ), counting time of 4 seconds per step; the goniometer was controlled by a DACO-MPV2 computer. TG curves were recorded up to 600 ºC on a Seiko 320 instrument at a heating rate of 10ºC. min^{-1}. About 10 mg of sample was used for each run. Al$_2$O$_3$ was used as the reference material.

Powders were shaped by uniaxial pressing at 210 kg.cm^{-2} as thin disks of ~10mm diameter and 2 mm thickness. Disks were isostatically pressed at 2000 kg.cm^{-2} and then natural sintering was carried out on a Pt foil. Also, disks were hot-pressed in alumina dies and surrounded by alumina powder at temperatures of 900 and 1000ºC and ~200kg. cm^{-2}.

Sintered disks were lapped to a ratio thickness/diameter of 1/10, typically 8 mm diameter and 0.8mm thickness, and electrodes were painted on the major faces, so as to prepare the capacitor samples for the electrical measurements. The samples were poled in a silicon oil bath at 50 kV.cm^{-1}, for 20 minutes at 180ºC. Complex impedance measurements as a function of the temperature were carried out in a HP4192A impedance analyzer on samples with Pt electrodes, as described in (9), during heating and cooling runs at a rate of 2ºC.min^{-1}. The piezoelectric d$_{33}$ coefficient was measured in a Berlincourt-meter by the direct piezoelectric effect at 100Hz. 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. An automatic iterative method, described elsewhere (10,11), of calculation of these parameters was applied, starting from complex impedance measurements at the appropriated frequencies.

3. RESULTS AND DISCUSION

3.1. Ceramic Precursor powder of NaNbO$_3$

The effect of the mechanochemical activation on the mixture of Nb$_2$O$_5$ / Na$_2$CO$_3$ (C-NN) has recently been reported (12). Figure 1 shows the XRD patterns of the Nb$_2$O$_5$ / Na$_2$O mixture (O-NN) treated in the vibrating-type mill for increasing times. For comparative purpose the Nb$_2$O$_5$ pattern is also shown. After 7 days of milling, the unique detected phase is Nb$_2$O$_5$, while Na$_2$O become amorphous. Even after 30 days of mechanical treatment amorphization of Nb$_2$O$_5$ does not take place. However, two important facts can be observed: the significant broadening in the peaks meaning that a reduction of the crystallite sizes took place; and the presence of new diffraction peaks, mainly at about 8.9 and 7.8 Å, due to the mechanosynthesis of the mixed niobium-sodium compound Na$_7$(H$_3$O)Nb$_6$O$_{19}$(H$_2$O)$_{14}$ after 7 days of milling (JCPDS -ICDD file no. 77-0059).

In Figure 2, the TG curve exhibits two weight-loss steps: the first one, very important, between room temperature and 125ºC, and the

second one between 200 and 500ºC. The first weight-loss step at low temperature is probably just due to loss of the hydration water coming from the decomposition of the mechanosynthesized powder during milling. The second weight loss, much less important, can be due to the total elimination of water from the H$_3$O$^+$ groups that are more strongly bonded in the Na$_7$(H$_3$O)Nb$_6$O$_{19}$(H$_2$O)$_{14}$ compound. Finally, from 520 to 600 ºC on heating and from 600 ºC to room temperature on cooling, no weight evolution is observed, indicating that the formation reaction has finished at 520 ºC and its stability on heating/cooling processes.
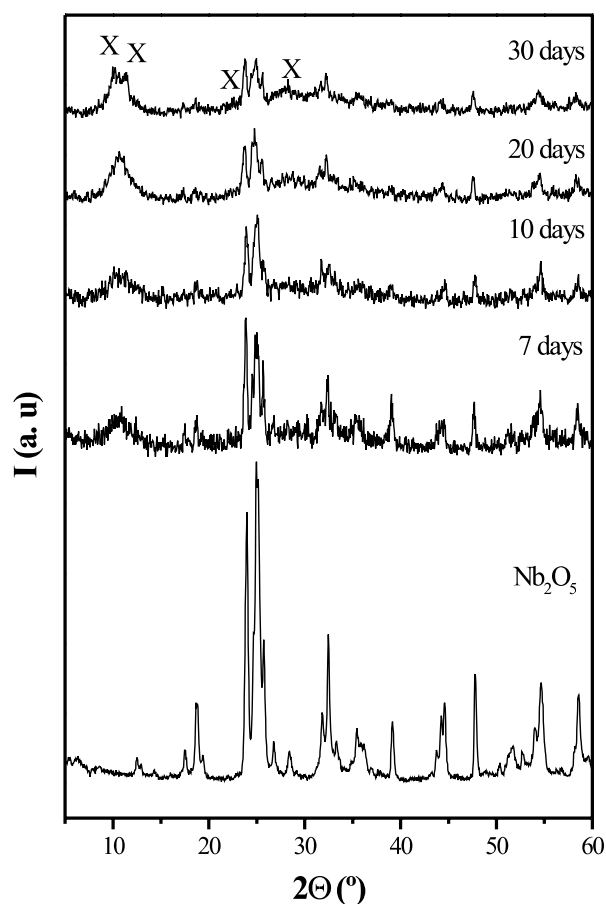

Figure 1. XRD patterns of the Na$_2$O/ Nb$_2$O$_5$ mixture as a function of the milling time. (X = Na$_7$(H$_3$O)Nb$_6$O$_{19}$(H$_2$O)$_{14}$, JCPDS-ICDD file no. 77-0059)
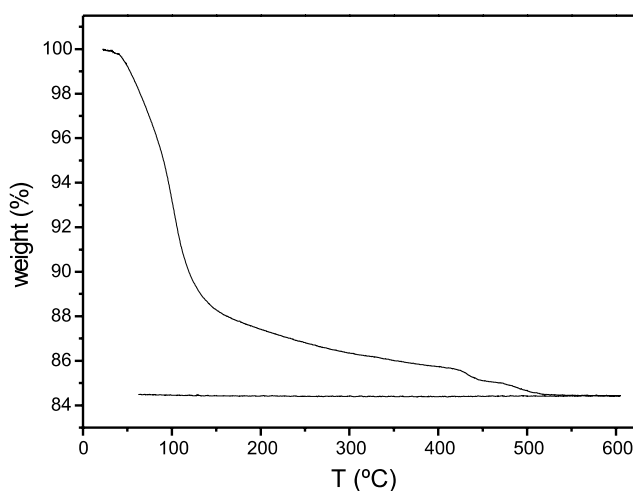

Figure 2. TG analysis curve of the Na$_2$O/ Nb$_2$O$_5$ mixture after 30 days of activation.

3.2. Ceramic Precursor powder of (Li,Na)NbO$_3$

The evolution with the milling time of the mixture 0.95 Na$_2$CO$_3$ + 0.05 Li$_2$CO$_3$ + Nb$_2$O$_5$ (C-LNN), Figure 3, is very similar to that previously reported for C-NN mixture (12). The XRD pattern of the initial mixture shows the diffraction peaks of Nb$_2$O$_5$, Na$_2$CO$_3$ and Li$_2$CO$_3$. When the milling time increases from 7 to 30 days, neither an amorphization process nor mechanosynthesis of new compounds take place, however the significant broadening in the diffraction peaks of the starting products shows that a significant reduction of the crystallite sizes has been produced.

TG tracing acquired from a heating/cooling cycle of powder milled for 30 days is shown in Figure 4. The TG curve exhibits two important weight-loss steps: the first one between room temperature and 125°C, and the second one between 350 and 600°C. The first step can be attributed to loss of water coming from hydration of powder during milling. The second weight loss is more likely due to decomposition of Na$_2$CO$_3$. This weight loss process does not finish at 600 °C, but it continues in the cooling process, indicating that the perovskite formation was not completed at 600°C.

3.3. Ceramic Processing

XRD of the ceramics show that all of them are single phase and isostructural with NaNbO$_3$ (JCPDS-ICDD file no. 33-1270). Table I shows all the sintering and hot pressing conditions tested to obtain ceramics in a single thermal treatment from C-NN, O-NN and C-LNN activated precursors, hereinafter called as the corresponding precursor. All the sintered C-NN ceramics show densities, which are lower than the green density. An expansion of the green pellets during sintering was observed. The origin of this is the formation of porosity while a weight loss step takes place, like in the thermal evolution just described for C-LNN (Figure 4), and extends up to temperatures higher than 600°C (12). 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 dense ceramics obtained (Table I).

A relevant enhancement of the ceramic density is reached starting from O-NN and C-LNN when comparison with C-NN is considered. Table I shows the densities of the three types of ceramics sintered at 1200°C-2h. The reason for the better sintering of O-NN ceramics can be found in the thermal stabilization of the precursor at 520°C (Figure 2). The substitution of the lighter and smaller Li$^+$ ion for Na$^+$, which promotes the mass transport during sintering, is most probably the reason for the higher density obtained in the C-LNN ceramic.

TABLE I. DENSITY OF CERAMICS FOR THE TESTED SINTERING AND HOT-PRESSING CONDITIONS

Processing Temperature-time	Activated C-NN for 30 days	Activated C-LNN for 30 days	Activated O-NN for 30 days
Sintering	DENSITY (g.cm^{-3}) and D/ D$_{th}$ (%)		
900°C-1h	1,90 (42%)	---	---
1000°C-1h	2,07 (45%)	---	---
1050°C-1h	2,24 (49%)	---	---
1100°C-2h	2,05 (45%)	---	---
1200°C-2h	2,06 (45%)	3,89 (85%)	3,97 (87%)
Hot-pressing			
900°C-1h	3,57 (78%)	---	---
1000°C-1h	4,01 (88%)	---	---
1000°C-2h	4,21 (92%)	4,01 (88%)	---
NaNbO3 theoretical density Dx = 4.575 g.cm^{-3}. Green density after isostatic pressing = 2.89 +/- .04g.cm^{-3}			
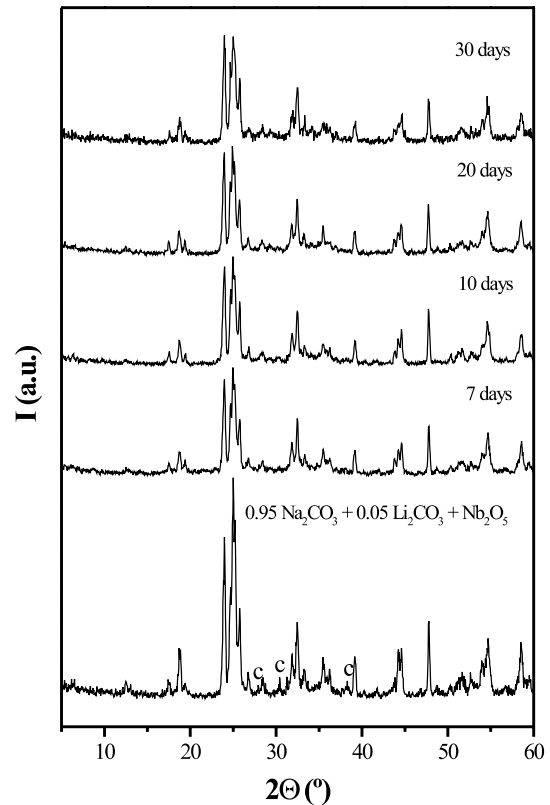
Figure 3. XRD patterns of the 0.95 Na$_2$CO$_3$ + 0.05 Li$_2$CO$_3$ + Nb$_2$O$_5$ mixture as a function of the milling time. (c = Na$_2$CO$_3$. Li$_2$CO$_3$ diffraction peaks are not observed in those patterns)
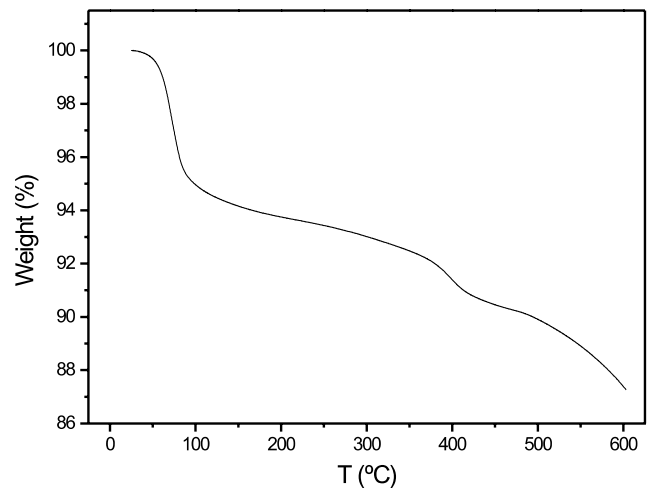

Figure 4. TG analysis curve of the 0.95 Na$_2$CO$_3$ + 0.05 Li$_2$CO$_3$ + Nb$_2$O$_5$ mixture after 30 days of activation.

3.4. Piezoelectric Characterization

Poling induces a ferroelectric (FE) phase in the antiferroelectric (AFE) NaNbO$_3$. The hot-pressed C-NN ceramic shows piezoelectric activity from room temperature (Table II) up to a temperature close to 300°C (Figure 5). A relatively small change of the planar electromechanical coupling factor, k$_p$, of thin C-NN ceramic disks up to this temperature was observed (Figure 5). Note the jump in Figure 5 for the elastic constants, c$_{11}^E$ and s$_{11}^E$, near 150°C. This jump states where a dielectric anomaly has been observed, for both single crystals and ceramics of NaNbO$_3$, and a second order phase transition between two orthorhombic AFE phases has been found by X-ray and Raman scattering studies (2).
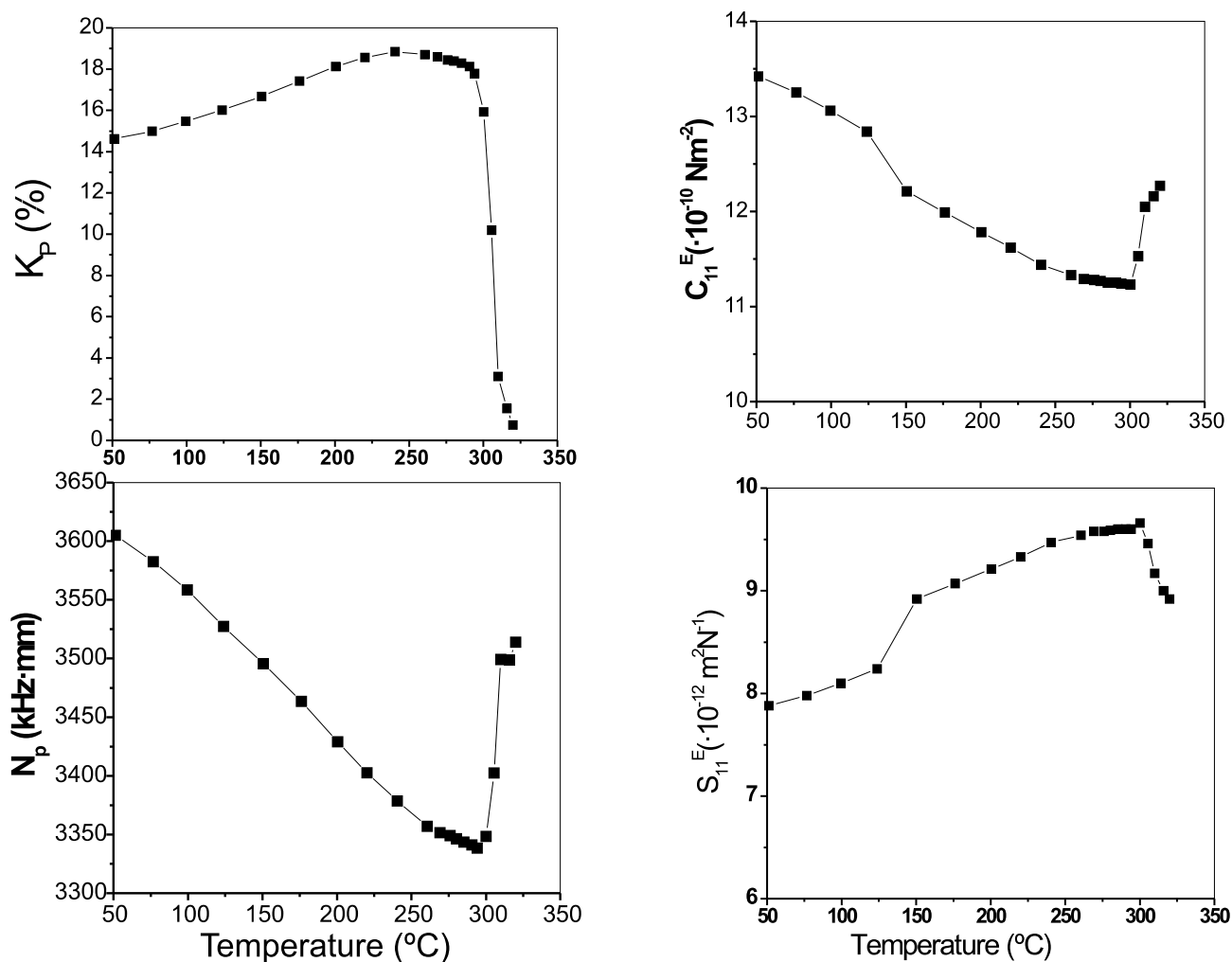
Figure 5. Evolution with the temperature of the parameters obtained from the planar resonance of a thin C-NN ceramic disk obtained by hot-pressing: (a) electromechanical coupling factor, kp, (b) frequency number, Np, and elastic constants (c) c_{11}^E and (d) s_{11}^E.

TABLE II. PIEZOELECTRIC CHARACTERIZATION AT ROOM TEMPERATURE FROM THE PLANAR AND THICKNESS RESONANCE MODES OF THIN C-NN AND C-LNN CERAMIC DISKS.

PLANAR MODE Fundamental mode measurement			THICKNESS MODE Second overtone measurement		
parameter	C-NN ceramic	C-LNN ceramic	parameter	C-NN ceramic	C-LNN ceramic
f_s (kHz)	323.72	351.5	f_s (kHz)	14640	14080
f_p (kHz)	326.25	353.1	f_p (kHz)	14644	14090
k_p (%)	13.9	10.6	k_t (%)	17.6	23.2
k_t (%)	8.4	6.5			
N_p^{31} (kHz.mm)	3571	3480	N_t (kHz.mm)	3045	2844
coeff. Poison (σ^p)	0.282	0.236			
c_{11}^E (10^{10} N.m^{-2})	12.76 + 0.06i	11.52 + 0.01	c_{33}^D (10^{10} N.m^{-2})	15.56 + 0.31i	12.61+0.36i
s_{11}^{11E} (10^{-12} m^2.N^{-1})	8.51 - 0.04i	9.20 – 0.009i			
s_{12}^{11E} (10^{-12} m^2.N^{-1})	-2.40 + 0.01i	-2.18 + 0.002i	h_{33} (10^{12} C.N^{-1})	22.73 + 4.20i	26.82 + 0.79i
			ε_{33}^S	102.32 + 1.40i	106.67+0.93i
d_{31} (10^{-12} C.N^{-1})	-8.71 + 0.09i	-6.48 + 0.03i	Berlincourt d (10^{-12} C.N^{-1}) $_{33}$	40	30
ε_{33}	144.4 + 1.77i	120.0 + 0.62i			

Table II also shows the result of the piezoelectric characterization of the C-LNN ceramic. It is remarkable the higher piezoelectric anisotropy, ratio k_t /k_p, of the C-LNN ceramic with respect to the C-NN one. The differences in the elastic constants are mainly attributable to the highest density and, consequently, lower remanent porosity of the hot-pressed C-NN ceramic.

4. CONCLUSIONS

The effect of the mechanochemical activation in a vibrating mill on stoichiometric mixtures of Na_2CO_3 or Na_2O, Li_2CO_3 and Nb_2O_5 was determined and compared. A progressive broadening of the X-ray diffraction peaks of the mixtures was observed as the milling time increased. Nevertheless, the precursors did not become fully amorphous. For the mixture of Na_2O/ Nb_2O_5 the mechanosynthesis of a transient phase was observed. The thermal evolution of the activated Na_2O/ Nb_2O_5 mixture, that shows full weight stabilization at 520ºC, explain the best results of the ceramic processing from this precursor.

Ceramics of NN and LNN were obtained in a single treatment of sintering or hot pressing in which synthesis, grain growth and sintering takes place. Their piezoelectric, dielectric and elastic properties were determined from resonances of thin poled disks. C-NN ceramics showed a value of k_p of 18% at 295ºC.

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