INFLUENCE OF THE SINTERING CONDITIONS ON THE MICROSTRUCTURAL, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF La DOPED KNNTa CERAMICS

INFLUENCIA DE LAS CONDICIONES DE SINTERIZACIÓN EN LAS PROPIEDADES MICROESTRUCTURALES, DIELÉCTRICAS Y PIEZOELÉCTRICAS DE CERÁMICAS KNNTa DOPADAS CON La

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Two batches of lead free ceramics of the composition $(K_{0.5}Na_{0.5})_{0.95}La_{0.016}Nb_{0.9}Ta_{0.1}O_3$ (KNNTaLa) were sintered between 1150 and 1180 °C. In the first batch, the samples were prepared in a sealed crucible embedded in powders of the same composition and, in the second, they were sintered in open air. Measurements made by X-ray diffraction, scanning electron microscopy and analysis of the phase transition and electromechanical response show, in general, a better performance for the encapsulated samples where very high values of density are obtained (about 97% of the theoretical density). La doping of KNNTa ceramics shifts its transition temperatures toward lower values, from 361 °C to 317 °C for the tetragonal-cubic (ferroelectric-paraelectric) and from 187 °C to 150 °C for the orthorhombic-tetragonal (ferroelectric-ferroelectric) transitions in this particular composition. The obtained electromechanical parameters are reasonably good and show the potentiality of the KNNTaLa ceramic as a commercial piezoelectric material.

Dos series de cerámicas libres de plomo de composición $(K_{0.5}Na_{0.5})_{0.95}La_{0.016}Nb_{0.9}Ta_{0.1}O_3$, fueron sinterizadas entre 1150 y 1180 °C. En la primera serie las muestras fueron preparadas en un crisol encapsulado embebido en el polvo de la misma composición, mientras que la segunda fue preparada al aire. Los resultados obtenidos por la difracción de rayos X, microscopía electrónica de barrido, análisis de la transición fases y la respuesta electromecánica muestran, en general, un mejor desempeño de las muestras encapsuladas en las que fue obtenido un alto valor de la densidad (cerca del 97% del valor teórico). El dopamiento con La de las cerámicas KNNTa desplaza la temperatura de transición a valores menores, de 361 °C a 317 °C para la transición tetragonal-cúbica (ferroeléctrica-paraeléctrica) y de 187 °C a 150 °C para la ortorrómbica-tetragonal (ferroeléctrica-ferroeléctrica).Los parámetros electromecánicos obtenidos son razonablemente buenos y muestran el potencial del KNNTaLa como material piezoeléctrico comercial.

INTRODUCTION

It is well known that many useful devices, simple or sophisticated such as capacitors, actuators, ultrasound sensors and sources, proximity detectors, SAW filters, among others, are based on the extraordinary properties of the $Pb(Zr_{1-x}Ti_x)O_3$ piezoelectric family, particularly in compositions around its morphotropic zone in the phase diagram [1,2,3]. Despite the excellent properties of PZT based materials, these compounds have the obvious disadvantages associated with the volatility and the toxicity of PbO which can pollute the environment and damage human health. Therefore there is a great demand for alternative lead-free piezoelectric materials with high performance. It is for this reason that in the last years material scientists have tried very hard to find a suitable lead free substitute for PZT [4,5,6,7]. In this line of thought, in 2004, Japanese scientists obtained a compound with properties

comparable to those of PZT based on the complex perovskite $KNbO_3$-$NaNbO_3$ (KNN) doped with Ta, Li and Sb, using a complex and original preparation process. The result was a textured ceramic with good physical properties [8]. In spite of this initial success, great efforts are currently being dedicated to improve on such properties using traditional ceramic preparation methods [4-10, 11]. The problems to be addressed are the high volatilization of potassium (K) and sodium (Na) during the preparation process as well as the obtainment of high density ceramics. The influence of La and Ti doping on the properties of KNN was previously investigated [12]. In this work, ceramic samples of KNN simultaneously doped with La and Ta, were successfully synthetized by two variants of the traditional ceramic method: in the first, the sintering stage was done in a crucible open to the air and in the second in a sealed crucible embedded in powder of the same composition to compensate volatilization losses. Structural, morphologic,

dielectric, and piezoelectric characterization was performed on the resulting samples.

EXPERIMENTAL

La doped $(K_{0.5}Na_{0.5})Nb_{0.9}Ta_{0.1}O_3$ (KNNTa) ceramics with composition $(K_{0.5}Na_{0.5})_{0.95}La_{0.0166}Nb_{0.9}Ta_{0.1}O_3$ (KNNTaLa) were prepared using the solid state synthesis technique. Raw material powders of K_2CO_3 (99.0 %, FagaLab), Na_2CO_3 (99.0 %, FagaLab), La_2O_3 (99.99 %, metal basis, Alfa Aesar), Nb_2O_5 (99.9 %, metal basis, Alfa Aesar) and Ta_2O_5 (99.8 %, metal basis, Alfa Aesar) were used as starting reactants. The powders were ground and mixed by magnetic agitation in alcohol at 400 rpm for 24 h, calcined at 800 °C for 5 h and ground again. This process was carried out twice. Cylindrical pellets, 11 mm diameter and 1 mm thick were then fabricated by uniaxial pressing the powders at 3 Ton/cm² sintering them at temperatures between 1150 °C and 1180 °C looking for the optimum temperature. Half of the samples were sintered in open air (labeled A) and the other half were encapsulated in their own atmosphere (labeled E). The sample density was measured by Archimedes technique. Phase composition was determined by X-ray diffraction (XRD) using a Philips X´pert diffractometer with KαCu radiation. Morphology and microstructural features were determined with a JEOL JSM 5300 Scanning Electron Microscope (SEM).

Silver electrodes were thermally diffused onto the samples flat surfaces for electrical characterization. Relative permittivity and dielectric loss were evaluated in a custom made measuring stage using an HP 4284A LCR bridge. The samples were heated at a 1 °C/min rate under 1 V applied voltage and the measurements were taken in the 100 Hz to 1 MHz frequency range in a 25-450 °C temperature interval controlled within $\pm 1\,^0C$. The electromechanical parameters k_p, d_{31}, s_{11}, in samples poled at 1 kV/mm at 90 ^0C in dielectric oil were determined by the resonance method using a spectrum analyzer built according to IEEE standards for piezoelectric materials and the expressions for k_p, d_{31}, s_{11} from [13].

RESULTS AND DISCUSSION

The optimal sintering temperature for KNNTaLa was found to be 1170-1180 °C using the measured density as the main criterion, among others. The idea was to get as close to the theoretical density as possible.

In Table I the sintering temperatures and corresponding experimental densities, as well as the density percentage with respect to the theoretical density value obtained from the XRD measurements are displayed. Encapsulation in the sintering process of the samples performed at practically the same temperature (a 10 ^0C difference) produces an important change in the density from 92 for A to 97 % for E, for samples of similar composition, obtained by the two sintering methods. In our case, the density of E samples is higher than that reported for the KNNTa$_{0.05}$ La$_{0.015}$ [14]. A density of about 97% of the

theoretical value (the amount of the second phase could not be taken into account in the calculation), as calculated from the lattice parameters of the majority phase obtained from XRD is obtained for the encapsulated samples and it is shown in Table I.

| Table I |
| Values of sintering temperature, density, maximum permittivity, dielectric loss, orthorhombic-tetragonal and Curietransitions temperatures. |

Sample	Ts (°C)	ρ (g/cm³)	ε_{max}/5kHz	Tanδ/5kHz	T_{O-T}(°C)	T_C(°C)
E	1180	4.72 97%	1990	0.070	150	317
A	1170	4.51 92%	1365	0.075	150	314

Fig. 1 shows the XDR pattern taken from a cylindrical-disk-shaped E sample sintered at 1180 °C. The reflections of a majority phase and those of a second phase marked with an asterisk (*) are observed and are identified with a tungsten-bronze structure, belonging to KLi$_3$Nb$_5$O$_{15}$ (PDF 030122 ICDD) and K$_3$Li$_2$Ta$_5$O$_{15}$ (PDF 0400349 ICDD) according to [15, 16]. The lattice parameters of both phases were determined by least square fitting using the FullProf software. From the refinement process, using an orthorhombic structure belonging to *Bmm*2 space group for the majority phase and tungsten-bronze structures belonging to the *P4bm* space group, the lattice parameters $a = 5.629$ Å, $b = 3.945$ Å, and $c = 5.606$ Å were determined for the majority phase and a=12.554 Å y c=5.098 Å for the secondary phase. According to [15], this secondary phase is formed when the K/Nb is modified. The parameters of the majority phase are slightly smaller than those of KNNTa, a result that may be interpreted as evidence of the incorporation of the lanthanum cation into the crystalline structure of KNNTa, given that the La ion is similar in size to the Na ion but considerably smaller than the K ion. The presence of a secondary phase also found by D. Lin et al. [16] and N. Klein et al. [9] is marked in the profile in Fig.1.
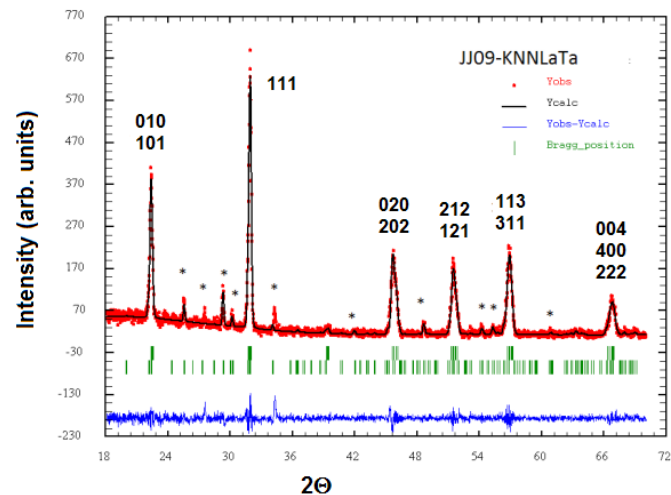
Figure 1: Experimental (points) and calculated (by least squares method, continuous line) XRD patterns of the of the KNNTaLa sample sintered at 1180°C; the difference between patterns is shown at the bottom. Bragg positions are shown with dashed vertical.

The XRD pattern of the A sample is similar in all aspects to the XRD pattern of the E sample showing that the structure of the KNNTaLa does not change with the sintering method, therefore, it is omitted.
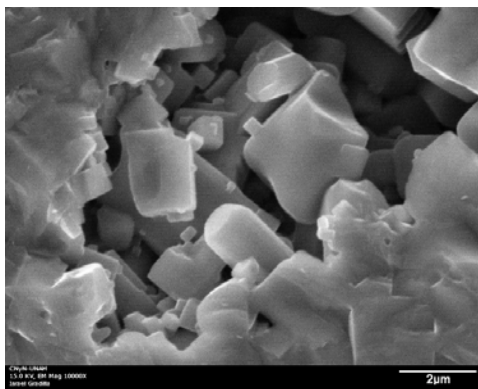

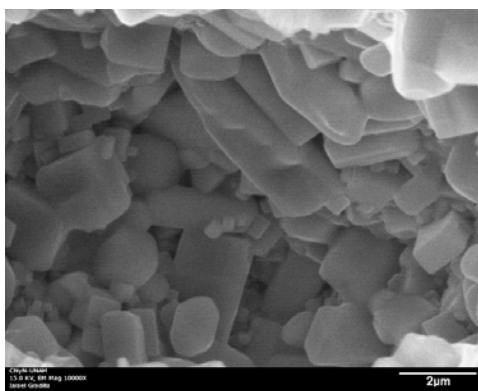Figure 2: SEM micrograph of a KNNTaLa encapsulated sample, sintered at 1180 ºC.

Figure 3: SEM micrograph of KNNTaLa sample sintered at 1170 ºC in air.

Figures 2 and 3 show the scanning electron microscope (SEM) micrographs of A and E KNNTaLa ceramic samples sintered in air at 1170 ºC and 1180 °C, respectively. The micrographs were taken from fractured samples.

The statistically determined average grain size was 0.7 µm for the E and 0.9 µm for the A samples. Even though the grain sizes are somewhat similar, the morphology is slightly different in that the edges in the A samples are not as sharp. Both types of samples look dense with small porosity, consistent with the density measurements.

For KNNTaLa the O-T transition takes place at around 150°C as reported by other authors [14]. The T-C transition for $KNNTa_{0.5}La_{0.015}$ is reported in [14] at 249 °C while for KNNTaLa it occurs at 314 °C for E and 317 °C for A samples. The O-T and T-C transition temperatures shift to lower temperatures with respect those of $KNNTa(T_C = 361$ ⁰C and $T_{O-T}=187$⁰C [16]), making evident the incorporation of the La ions into the structure. A broadening of the transition curves with respect to those of the KNNTa compound is observed [14]; it is due to the La ions sharing the A site with those of K and Na and also to the effect of the above mentioned secondary phase which is ferroelectric with a T_c around 100 ⁰C influencing the permittivity vs. temperature behavior in both E and A samples.
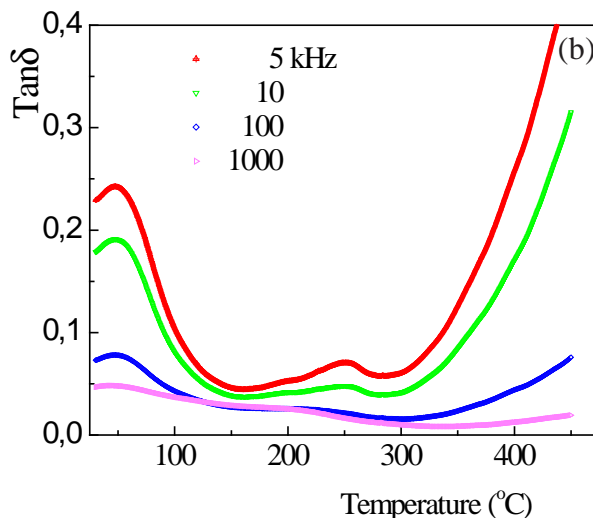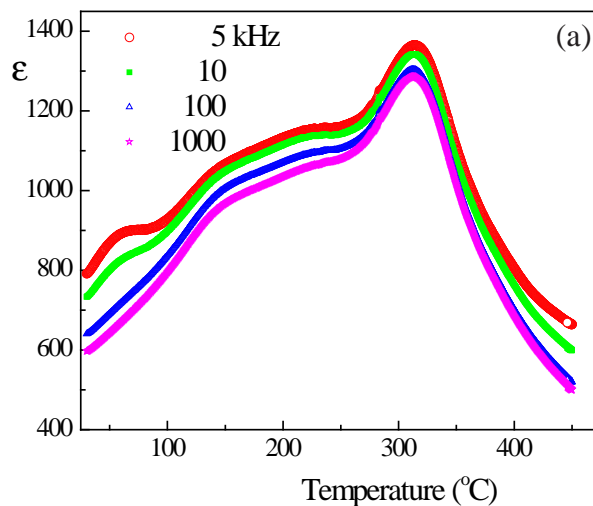

Figure 4: Temperature dependence of (a) the relative permittivity and (b) dielectric loss, at 5,10,100,1000 kHz for KNNTaLa sample sintered at 1170 °C.

The peak values of the relative dielectric permittivity for the encapsulated (E) samples are similar to those reported in [14]. This values decrease when the samples are sintered in open air giving us an indication of the sensitivity of the sample's properties with the sintering conditions. By encapsulating the sample in an atmosphere with the same composition as the sample, a better thermodynamical equilibrium is achieved, the loss of Na and K by volatilization is drastically reduced and the K/Na ratio deviates very little from 1. As a consequence, a reduction of the dielectric loss is observed for the encapsulated samples as compared with those prepared in open air. By comparing Figures 4b and 5b it is clearly shown that the samples sintered in air present higher losses that may be attributed to higher conductivity.

However, a significant feature is the fact that for the T-C transition there is no shift of the permittivity maxima with frequency, showing that the tetragonal to cubic is a normal transition and not a relaxor behavior.

The incorporation of La renders a more disordered material where three ions randomly share the same crystallographic

A site of the perovskite smoothening and broadening the O-T and T-C transitions. As is well known, the addition of lanthanum to the composition of many lead free ferroelectric compounds has the effect of shifting the transition temperature to lower values and also of decreasing the values of the relative permittivity maximum [17]. When we compare the relative permittivity vs. temperature curves for the E and A samples it is clearly observed that higher values of ε and lower of tanδ are obtained for the encapsulated samples suggesting that the prevention of the losses of K and Na due to their volatility produces samples with better dielectric properties. The secondary phase is ferroelectric with Tc around 100 ^{0}C [14] causing the observed anomalies in the permittivity and dielectric losses vs. temperature curves at low temperature.
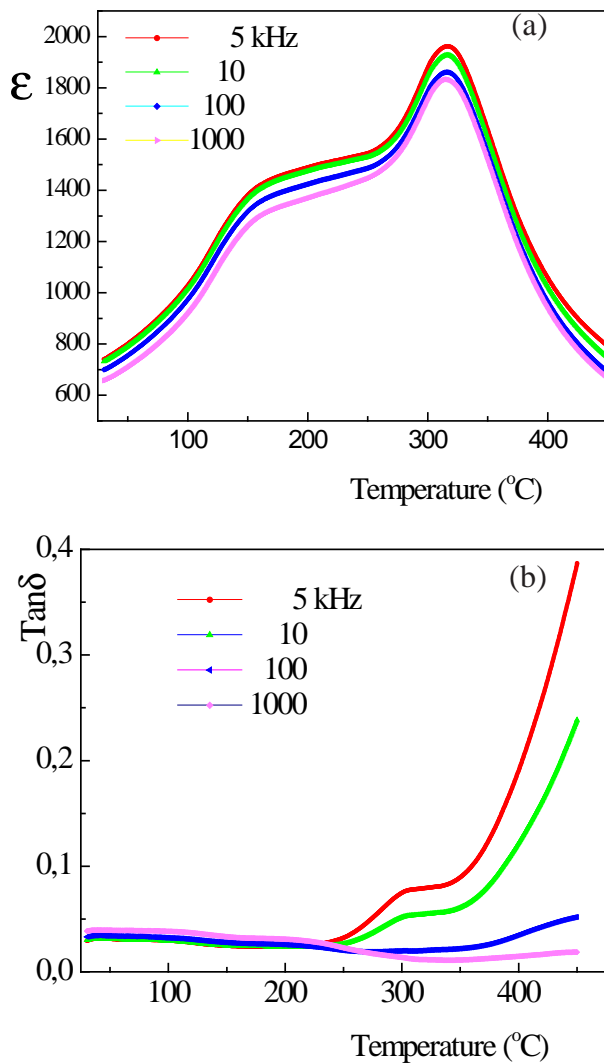
Figure 5: Temperature dependence of (a) the relative permittivity and (b) dielectric loss, at 5,10,100,1000 kHz for KNNTaLa sample sintered at 1180 °C.

Fig. 6 shows the electromechanical response obtained by means of the impedance modulus Z(Ω) vs. frequency measurements for the E and A samples, under the same geometric conditions, poled at 1 kV/mm based on the expressions in [13,18]. It is observed from the graph in Fig. 6 that the value of $\Delta Z = Z_{max} - Z_{min}$, corresponding to the electromechanical resonance region, is larger for the E sample than for the A sample (see

inset in Fig.6). This is a consequence of a higher polarization achieved in the encapsulated samples as compared with the samples sintered in air, for the same poling field.
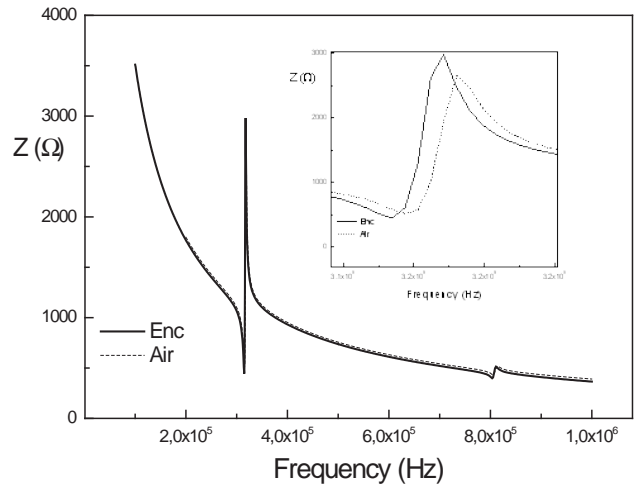
Figure 6: Impedance vs. Frequency of samples KNNTaLa sintered in open air and encapsulated

Table II presents the experimental values of the electromechanical parameters. It can be observed that the difference in the values of k_p for the samples prepared in open air and the encapsulated samples is not significant. Those values, however, are reasonable good taking into account the low poling field (1 kV/mm) used for these samples in contrast to the higher one of 4 kV/mm used by other authors [14]. When comparing the values of the electromechanical parameters obtained in this work with those reported for commercial PZT ceramics [19] it can be concluded that La, Ta doped KNN has good potential for future electromechanical applications.

Table II Comparison of the piezoelectric coefficients of samples sintered in air and encapsulated with the values of commercial samples.					
Sample	k_p	k_{31}	σ	$S_{11} *10^{-12}$ (m^2/N)	d_{31} pC/n
E	0.153	0.10	0.042	10	-6.46
A	0.148	0.10	0.077	7	
PZ45[19]	0.030	-----	0.250	8	-1.70
PZA5[19]	0,080	----	0.200	22	-11.5

CONCLUSIONS

An optimized route for the obtainment of high density (97 % of the theoretical value) La modified KNNTa ceramics is presented. A strong influence of the sintering conditions is acknowledged where the encapsulation of the reactants to prevent K and Na losses by volatilization is a key step in the sintering process. The improvement due to the preparation method is made evident by comparing with the values obtained for samples sintered in open air. However both samples had the same orthorhombic perovskite structure. Traces of a secondary phase were identified and their lattice parameters were determined. It was found that La substitution influences the phase transitions (orthorhombic to tetragonal and tetragonal

to cubic) of KNNTaLa by shifting the critical temperatures toward lower values. An improvement is reported with respect to the results published by other authors [14]. In summary, the studied composition together with the proposed preparation technique provides an alternative to commercial ceramics as piezoelectric materials.

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