Lanthanum and niobium doping on PZT ceramic synthesis

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Palabras clave: cerámicas piezoeléctricas, PZT, sinterización, dopantes La y Nb.
Key words: piezoelectric ceramics, PZT, sintering, La and Nb doping.

RESUMEN. Se estudió el efecto que produce el dopaje sobre la estructura y las propiedades de cerámicas piezoeléctricas tipo plomo-circonio-titanio (PZT). Estas cerámicas fueron preparadas por calcinación (presinterización) de mezcla de óxidos y carbonatos metálicos a 1 233 K durante 90 min y su posterior sinterización a 1 523 K durante 30, 60, 100, 150 y 300 min . Las condiciones fueron creadas para obtener el sistema estequiométrico $Pb(Zr_{0,54}Ti_{0,46})O_3$ + x % p B, en el que [B = Nb_2O_5 o La_2O_3 , x = 0,6; 0,8; 1,0, (%, p/p)]. El análisis por Difracción de Rayos X y Microscopia Óptica condujo a los resultados siguientes: los polvos presinterizados presentan una distribuición estrecha de tamaño de partícula (1 a 3 µm); todas las composiciones dieron lugar a muestras de una sola fase, tetragonal. Como tendencia general, el tamaño de grano y la porosidad disminuyen con el aumento de la concentración del dopante. Por Difracción de Rayos X se observa la presencia de una importante textura de fibra en todas las muestras analizadas, con la dirección [001] de las cristalitas paralelas al eje de simetría de las muestras. La intensidad de la textura aumentó con el contenido del dopante, siendo mayor para las muestras dopadas con niobio que con lantano. Las mejores características piezoeléctricas fueron obtenidas para 0,8 % en peso de niobio y 1,0 % en peso de lantano sinterizadas a 100 min . En todos los casos, al aumentar la concentración del dopante disminuyen las pérdidas eléctricas del material y aumenta la permitividad eléctrica. La temperatura de Curie es 30 grados menor que la reportada para una PZT sin dopar.

ABSTRACT. The effect of lanthanum and niobium doping on PZT piezoelectric ceramics was studied. Samples were prepared by burning (presintering) mixed metal oxides and carbonates at 1 233 K for 90 min and subsequent sintering at 1 523 K for 30, 60, 100, 150 and 300 min . The stoichiometric system $Pb(Zr_{0.54}Ti_{0.46})O_3$ + x B [B = Nb_2O_5 or La_2O_3 , x = 0.6, 0.8, 1.0 (%wt)] was finally obtained. X Ray Diffraction and Optical Microscopy tests were carried out. As a result, the presinterized powder shows a distribution of narrow particle sizes (1 - 3 µm);all the compositions produce single-phase tetragonal samples. Grain size and porosity decrease as doping concentration increases. X Ray Diffraction shows important fiber textures appear in all the samples with [001] crystallite direction parallel to sample symmetry axes. Texture becomes more intense as the doping concentration increases and on niobium-doped samples it is more intense than on the lanthanum-doped ones. The most suitable piezoelectric characteristics were obtained for 0.8 (%wt) [Nb] and 1.0 (%wt) [La] sintering during 100 min . It can be observed that electric losses decrease and electric permitivity increases as the doping concentration increases. The Curie point is 30 degrees below the reported value for a pure undoped PZT ceramic system.

INTRODUCTION

By using doping agents in PZT ceramics it has been possible to considerably change their properties.[1-5] Different concentrations of those doping agents cause alterations, not only on the process for obtaining the ceramics,[6] but also on their final properties. It is observed that the structural parameters are changed, the grain size of the sinterized compact, the densification, the electric and piezoelectric properties of the ceramics obtained among others.[7-9]

Lanthanum and niobium are some of the so-called soft doping agents[9] when used in type-PZT piezoelectric ceramics. Lanthanum is introduced in the crystalline network by substituting Lead in the A sites of the perovskite structure (ABO_3), instead, the introduction of Niobium in the crystallographic network is because of the substitution of zirconium and Titanium of the B positions. Those substitutions are allowed because the ionic radii (r_{Pb} = 1.20, rLa = 1.14., r_{Zr} = 0.79, rTi = 0.68, r_{Nb} = 0.69)[10] and the electronegativities (Pb^{2+}:1.55, La^{3+}:1.08, Zr^{4+}:1.22, Ti^{4+}:1.32, Nb^{5+}:1.23) of cations are similar.[10] Each substitution causes an electrical unbalance of the structure given by the difference in valence [(Pb^{2+}, La^{3+}), (Zr^{4+}, Ti^{4+}, Nb^{5+})][10] and that unbalance is equalized by the appearance of vacancies located at the grain border[11] by preventing the border movement, by limiting the grain growth, and by facilitating the material sinterization. In this condition, the stoichiometric relationships $Pb_{1-3x/2}\,Dp_x\,V_{Pb1/2}(Zr_{0.54}Ti_{0.46})O_3$ y $Pb(Zr_{0.54}Ti_{0.46})_{1-3y/2}NbyV_{(ZrTi)1/2}O_3$ are valid, where Vz appointed the vacancies created from the Z cation substitution.

The purpose of this work was to study the ceramic system PZT 54/46 $[Pb(Zr_{0.54}Ti_{0.46})O_3]$ doped at difference lanthanum and niobium concentrations, by focusing attention on the sinterization process, by analyzing the process behavior at different times, and looking for the best conditions in the shorter time possible. Section 2 shows the exhibition of the experiments performed and the measured and calculated parameters are defined. The interpretation of the results is shown in Section 3, that has been divided in three parts. In the first section, the results of the microstructure study are reported, in the second section, sinterization is studied and in the last section, the electrical properties are analyzed.

MATERIALS AND METHODS

The starting reagents were weighed to obtain the desired compositions $(Pb_{1-3x/2}La_x\,VPb_{x/2}(Zr_{0.54}Ti_{0.46})O_3$ y $PTb(Zr_{0.54}\,Ti_{0.46})_{1-5y/4}Nb_y\,V_{(ZrTi)y/4}O_3)$. For preparing the powders, oxides and carbonates of the following metals were used: $PbCO_3$ (98 %, Merck), ZrO_2 (99 %, Merck), TiO_2 (99 %, Merck), Nb_2O_5 and La_2O_3 (Merck spectrally pure).

A homogenization milled of the material was performed in a Resch mill with an Agatha mortar for 120 min . The pre-sinterization was performed in a Nabertherm L08/14 furnace at a temperature of 1 233 K for 90 min . A solution of 10 % polyvinyl alcohol was used as agglutinant. The 13,1 diameter cylinders were shaped at 150 MPa in a Pay Unicam hydraulic press. The sinterizations were performed in the same furnace at 1 523 K for 30, 60, 100, 150 and 300 min . The green and final densities were calculated from the measurement of the dimensions and masses of the cylinders, performed with a micrometer (± 0,01 mm) and a Sartorius scale (± 10^{-4} g).

For the sinterization study three fundamental parameters were analyzed:

1) The relative density ρ/ρ_T, where ρ is the density reached by the compact during the sinterization (g/cm^3) and ρ_T is the theoretical density calculated by X Ray Diffraction.

2) The densification ratio $\varepsilon_{\rho}\cdot$,[11] that can be evaluated by the following ratio:

$$\varepsilon_{\rho}\cdot = \rho^*/\rho \qquad (1)$$

where:

ρ reached density.

ρ* its derivate regarding the sinterization time.

3) The θ,[11] parameter that characterizes the contractions regarding the green compact and is given by:

$$\theta = 1 - \left[\left(1-\frac{\Delta L}{L_0}\right)\left(1-\frac{\Delta R}{R_0}\right)^2\right] \qquad (2)$$

where:

$\Delta L/L_0$ and $\Delta R/R_0$ characterize the longitudinal and radial contractions, respectively and they are given by:

$$\Delta L = L_0 - L \text{ and } \Delta R = R_0 - R \qquad (3)$$

being:

L_0 and L height for the starting moment and for the time *t*, respectively.

R_0 and R radius at the starting moment and at the time *t*.

The study of the θ parameter makes possible to identify three extreme cases in the sinterization process:

1. $\theta = 0 \Rightarrow Vf = Vi$ (does not change the volume of the sample, there is no contraction).
2. $\theta = 1 \Rightarrow Vf <<< Vi$ (very big contractions).
3. $\theta < 0 \Rightarrow Vf > Vi$ (expansions).

Values of $0 < \theta < 1$ must be expected to produce contractions. If the mass is constant, then those contractions imply densification.

The sinterized materials were cut in 1 mm thickness disks; the electrical contact was performed with silver paste. The polarization regime was 2 kV/mm for 15 min at 423 K .

The samples were analyzed by DRX, to verify the appropriate formation of the phase and to observe the possibility of existence of any texture. The diffractograms were performed in a Philips PW 1710 diffractometer with filtered Cu Kα radiation. The optical microscopy was performed in a NEOPHOT-32, the surfaces of the samples were prepared by using, first, a chemical attack and after, a thermal attack.

The piezoelectric characterization was performed by using the standardized resonance method.[12] The electrical measurements of capacity (C) and electrical losses (tg δ) were obtained in a Philips RLC PM 6303 bridge, the real ε' and imaginary ε'' dielectric constants were calculated through the following expressions:[12]

$$\varepsilon' = \frac{4\,C\,L}{\pi\,r^2} \qquad (4)$$

$$\varepsilon'' = \varepsilon' \cdot \mathrm{tg}\,\delta \qquad (5)$$

The Curie[13] point (T_C) was determined from the C variation (measured at the RLC bridge) with the temperature.

RESULTS AND DISCUSSION

Sinterization study

In the sinterization process, the greatest changes appear at the initial moments when a fast growth of the relative density occurs. For Lanthanum, the best results are obtained after 30 min, at 1,0 % in weight 92.8 % theoretical density is reached; for Niobium the stabilization of the relative density occurs after 60 min, for 0.8 % in weight 93.9 % is obtained (Fig. 1). The calculation error of ρ/ρ_T is 0.6 % for Lanthanum and 1.3 % for Niobium.

An important parameter during the sinterization study is the densification ratio $\varepsilon_{\rho}\cdot$, it informs about the condition attained by the material during the heating process. The densification ratio $\varepsilon_{\rho}\cdot$ generally, for all the doping concentrations, shows an expected behavior,[8] in the first moments it is high and the course of time it decreases (Fig. 2). For times longer than 100 min, the samples densify practically in the same way.

Of parameter θ it is observed that the more important contractions of the ceramics occur until 30 min, from this time the niobium contractions are small if compared to those occurring at the initial moments, in the case of lanthanum, dilatations occur for the three concentration studied (Fig. 3).

Microstructural study

The pre-sinterized powder (green material) shows a distribution of narrow particle sizes, from 1 to 3 µm

Optical microscopy reveals a strong influence of the doping concentration on the grain size of the sinterized material (Table 1), with the increase of the doping concentration, reduces the grain size. These results show that the presence of the doping inhibits the grain growth; similar results were found by Atkin *et al.*[14] and other authors.[15] The effect is even more remarkable with the increase of concentration.

The greatest contractions are accompanied by smaller grain sizes (Table 1), so it can be deduced that the inhibition of the grain growth has as consequence, higher densifi-

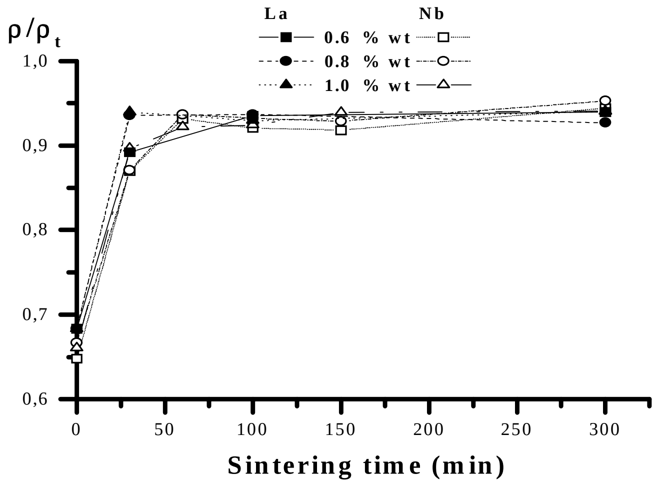

Fig. 1. *Relative density (ρ/ρ_T) against the sintering time to different lanthanum and niobium concentrations for a sintering temperature = 1 523 K*.

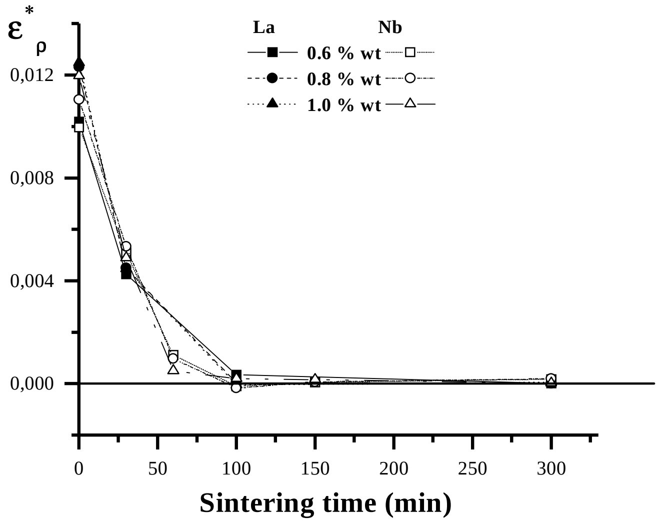

Fig. 2. *Densification ratio (ε_{ρ}^{*}) during sintering time to different lanthanum and niobium concentrations for a sintering temperature = 1 523 K. Notice how after 100 min the densification is identical for both dopants.*

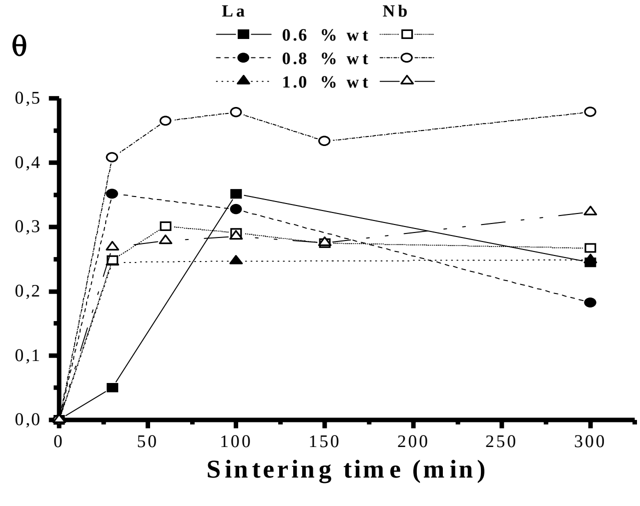

Fig. 3. *Compact volumetric contraction regarding the material in green (θ) with the sintering time for the three lanthanum and niobium concentrations for a sintering temperature = 1 523 K*.

Table 1. Dependence of the grain sizes of the sinterized material at 1 523 K, 100 min according to the Nb concentration.

Nb (%)	Grain size (mm)
0.2	14 - 36
0.4	7 - 20
0.6	4 - 14
0.8	2 - 5
1.0	1 - 2.5

cations during sinterizing. This result agrees with those by Tin *et al.*,[16] and it shows that in presence of the grain growth, the densification ratio are much lower. This way, it can be stated that when Nb and La concentration increases, the system tends to favor the decrease of the specific surface without a grain growth.

The reticular parameters are calculated from the analysis of the diffractograms (Table 2), and it is observed that as the Lanthanum concentration increases, the tetragonal distortion decreases (similar results have been reported in studies on other materials by different authors[9,17,18]); however, for the Niobium-doped ceramics, the observed variations of the relationship among the reticular parameters (c/a) with the doping concentration are of the uncertainty rank, so a considerable influence of the concentration cannot be stated in those parameters.

The results from the diffractograms for different concentrations of doping agents showed only one tetragonal phase in all the cases. An effect of texture was found which favor the peaks (001) on (100) and it is more remarkable in these peaks than in (002)/(200) (Fig. 4). The fact that the texture is increased with the doping agent concentration was also found. This effect was related to the increase of the number of crystallites oriented in the field direction when the doping agent concentration is increased. Law *et. al.*[19] found that the increase of the peak intensities (001) over the (100) and (002)/(200) in ceramics is an evidence of the number of domains oriented to polarization. By comparing the results between both doping agents we found that the effect is not as remarkable for Lanthanum as for niobium.

By considering the X-ray absorption parameters in the samples, it was calculated that the 001/100 reflections characterize a depth of the 4-5 μm kind from the surface, while the 002/200 reflections offer an information related to an approximately double depth.[20]

Table 2. Comparative results of the experimental data obtained for both doping agents in the different concentrations. Error of equipment ± 0.001 nm .

Concentration	Experimental parameters					
	For lanthanum			For niobium		
(%, p/p)	a (nm)	c (nm)	a/c	a (nm)	c (nm)	a/c
0.6	0.407 74	0.415 92	0.980 33	0.408 0	0.416 9	0.978 65
0.8	0.407 66	0.414 04	0.984 59	0.406 2	0.415 6	0.977 38
1.0	0.408 52	0.411 06	0.993 82	0.404 6	0.413 8	0.977 76

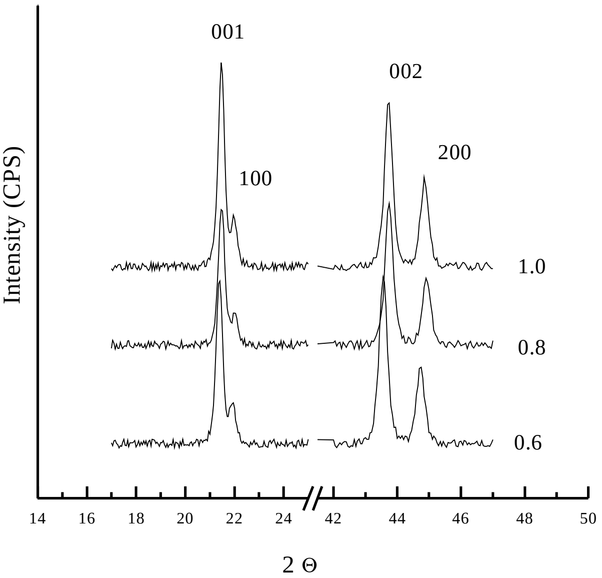

***Fig. 4**. Difractograms for the three niobium concentrations in 2Θ between 14-24 and 44-50. It can be observed the texture effect and how it is increased with the dopant concentration. This effect is more remarkable in the peaks 100/001 than in the 200/002. The intensity increase of the peaks 001 is more remarkable.*

Dielectric Study

In all cases, a decrease of the losses with the increase of the doping agent concentration is obtained. Permitivity behaves as usual, increasing with the concentration of the doping agent (reference). Moreover, (ea) > (ed) is obtained (ea before, (ed) after polarization); this effect has been observed by other authors,[21,22] and we must make clear that for our case, the difference is not really significant for no studied case.

From the measurements of dielectric constant-temperature it is showed that there is only one ferroelectric phase in the samples. The Curie point (Tc) is in the 603 K < Tc < 608 K range, 30 o lower than the reported by other authors8 for PZT of not doped similar concentrations. The electromechanical characteristics show optimal values in the environment of 0.8 % in weight of Niobium Kt = 0,48, Kp = 0,38, Qm = 105 and 1.0 % (p/p) of Lanthanum Kt,= 0,40, Kp = 0,26, Qm = 55 within the interval of values found by other authors for this kind of ceramics.[23,24]

CONCLUSIONS

An increase of density with the increase of the doping agents concentration was found. The fastest densifications correspond to the highest doping agents. A higher densification takes place for a small-size grain. For both doping agents a single tetragonal phase is obtained and there are texture effects increasing the concentration. The Curie point is decreased in 30 degrees regarding a pure PZT. The best electrical properties are obtained for 0,8 % (p/p) Niobium and 1,0 % (p/p) Lanthanum.

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