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Lanthanum and niobium doping on PZT ceramic synthesis

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INTRODUCTION

By using doping agents in PZT ceramics it has been possible to considerably change their properties.15 Different concentrations of those doping agents cause alterations, not only on the process for obtaining the ceramics,5 but also on their final properties. It is observed that the structural parameters are changed, the grain size of the sintered 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 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 (ABO3), 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 (rPb = 1.20, rLa = 1.14., rZr = 0.79, rTi = 0.86, rNb = 0.68, rBa = 0.90)8 and the electronegativities (Pb2+:1.55, La3+:1.08, Zr4+:1.22, Ti4+:1.32, Nb5+:1.23) of cations are similar.8 Each substitution causes an electrical unbalance of the structure given by the difference in valence ([Pb2+, La3+], (Zr4+, Ti4+, Nb5+))9 and that unbalance is equalized by the appearance of vacancies located at the grain border10 by preventing the border movement, by limiting the grain growth, and by facilitating the material sinterization. In this condition, the stoicho-

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(Zr0.54 Ti0.46)O3 + x % p B, in the equation (B = Nb2O5 or La2O3, x = 0; 0; 8, 1.0, (%w, p,p)). The analysis by X Ray Diffraction and Optical Microscopy tests were carried out. As a result, the presintered 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 fibre 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 permittivity increases as the doping concentration increases. The Curie point is 30 degrees below the reported value for a pure undoped PZT ceramic system.

RESUMEN. Se estudió el efecto que produce el dopaje sobre la estructura y las propiedades de cerámicas piezoeléctricas tipo plomo-circonio-titánio (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(Zr0.54 Ti0.46)O3 + x % p B, en el que (B = Nb2O5 o La2O3, x = 0; 0; 8, 1.0, (%w, p,p)). El análisis por Difracción de Rayos X y Microscopía Óptica condujo a los resultados siguientes: los polvos presinterizados presentan una distribución 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 nióbio que con lantano. Las mejores características piezoeléctricas fueron obtenidas para 0.8 % en peso de nióbio 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 permittividad eléctrica. La temperatura de Curie es 30 grados menor que la reportada para una PZT sin dopar.

Key words: piezoelectric ceramics, PZT, sintering, La and Nb doping.

Palabras clave: cerámicas piezoeléctricas, PZT, sinterización, dopantes La y Nb.

metric relationships \( \rho_0 = \frac{3C_l}{\pi R^2} \) 

\( \rho \) is the density reached by the com-

pact during the sinterization (g/cm\(^3\)).

The purpose of this work was to study the ceramic system ZPTZ/46 [Pb/Zr\(_{0.54}\)Ti\(_{0.46}\)O\(_3\)] doped at different lanthanum and niobium concentra-
tions, by focusing attention on the sinterization process, by analyzing the process behavior at different times, and looking for the best con-

ditions in the shorter time possible. Section 2 shows the exhibition of the experiments performed and the measured and calculated param-

eters 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 com-

positions (Pb\(_{1-3x/2}\)La\(_x\)V\(_{Pb\_x/2}\) (Zr\(_{0.54}\)Ti\(_{0.46}\)O\(_3\)) y Pb(Zr\(_{0.54}\)Ti\(_{0.46}\))_1-5y/4 NbyV\(_{2/3}\)O\(_{5/2}\)) are valid, where Vz ap-

proximated by X Ray Diffraction.

\[ \rho = \frac{\Delta L}{L_0} \] 

where: \( \Delta L \) is the height for the starting 

material and \( L_0 \) is the height for the starting 

basis.

The electrical measurements of ca-

pacities (C) and electrical losses (tg \( \delta \)) were obtained in a Philips RLC PM 

6303 bridge, the real \( \varepsilon' \) and imagi-
nary \( \varepsilon'' \) dielectric constants were cal-

culated through the following ex-

pressions: \( \varepsilon' = \frac{2C_l}{\pi R^2} \) \( \varepsilon'' = \varepsilon' \cdot \tan \delta \) \( \varepsilon = \varepsilon' + j\varepsilon'' \) \( \varepsilon'' = \varepsilon' \cdot \tan \delta \) \( \varepsilon = \varepsilon' + j\varepsilon'' \)

The Curie\(^{13}\) point (\( T_C \)) was deter-

mined from the C variation (mea-

sured at the RLC bridge) with the 

temperature.

RESULTS AND DISCUSSION

Sinterization study

In the sinterization process, the greatest changes appear at the ini-

tial moments when a fast growth of the relative density occurs. For Lan-

thanum, 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 \( \rho/\rho_T \) is 0.6 % for Lanthanum and 1.3 % for 

Niobium.

An important parameter during the sinterization study is the densifi-

cation ratio \( \varepsilon' \), it informs about the 

condition attained by the material 

during the heating process. The densifi-

cation ratio \( \varepsilon' \) generally, for all 

the doping concentrations, shows an 

expected behavior,\(^{13}\) in the first mo-

ments 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 \( \theta \) it is observed that the 

more important contractions of the 

ceramics occur until 30 min, from 

this time the niobium contrac-

tions are small if compared to those 

occurring at the initial moments, in 

the case of lanthanum, dilations 

occur for the three concentration 

studied (Fig. 3).

Microstructural study

The pre-sintered powder (green 

material) shows a distribution of narrow particle sizes, from 1 to 3 \( \mu \)m.

Optical microscopy reveals a strong influence of the doping con-

centration on the grain size of the sintered 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 ac-

companied by smaller grain sizes 

(Table 1), so it can be deduced that the inhibition of the grain growth has as consequence, higher densifi-
cations during sinterizing. This result agrees with those by Tin et al., 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 authors9,17,18); 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) over (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. 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 reflection 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 1.** Dependence of the grain sizes of the sinterized material at 1523 K, 100 min according to the Nb concentration.

<table>
<thead>
<tr>
<th>Nb (%)</th>
<th>Grain size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>14 - 36</td>
</tr>
<tr>
<td>0.4</td>
<td>7 - 20</td>
</tr>
<tr>
<td>0.6</td>
<td>4 - 14</td>
</tr>
<tr>
<td>0.8</td>
<td>2 - 5</td>
</tr>
<tr>
<td>1.0</td>
<td>1 - 2.5</td>
</tr>
</tbody>
</table>

**Fig. 1.** Relative density ($\rho_0/\rho_t$) against the sintering time to different lanthanum and niobium concentrations for a sintering temperature = 1523 K.

**Fig. 2.** Densification ratio ($\varepsilon_\rho^*$) during sintering time to different lanthanum and niobium concentrations for a sintering temperature = 1523 K. Notice how after 100 min the densification is identical for both dopants.

**Fig. 3.** Compact volumetric contraction regarding the material in green ($\theta$) with the sintering time for the three lanthanum and niobium concentrations for a sintering temperature = 1523 K.
Table 2. Comparative results of the experimental data obtained for both doping agents in the different concentrations. Error of equipment ± 0.001 nm.

<table>
<thead>
<tr>
<th>Concentration (% p/p)</th>
<th>Experimental parameters</th>
<th>For lanthanum</th>
<th>For niobium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>c (nm)</td>
<td>a/c</td>
<td>c (nm)</td>
</tr>
<tr>
<td>0.6</td>
<td>0.407 74</td>
<td>0.980 33</td>
<td>0.416 9</td>
</tr>
<tr>
<td>0.8</td>
<td>0.407 66</td>
<td>0.984 59</td>
<td>0.415 6</td>
</tr>
<tr>
<td>1.0</td>
<td>0.408 52</td>
<td>0.993 82</td>
<td>0.413 8</td>
</tr>
</tbody>
</table>

Dielectric Study

In all cases, a decrease of the losses with the increase of the doping agent concentration is obtained. Permittivity 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, 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 shown 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 authors for this kind of ceramics.

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.

BIBLIOGRAPHY


