Suitability of the PLZTN 54/46 ceramic system for designing pulse-echo sensors

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The present work aims at analyzing the influence of both Lanthanum (La) and Niobium (Nb) when simultaneously doping the PZT ceramic system with the same doping level (x). XRD, SEM, dielectric and piezoelectric measurements were carried out in order to characterize and analyze the suitability of these soft materials as pulse-echo sensors. An optimum doping level is found with best piezoelectric performance and merit figure $d_h g_h$ for hydrophones.

Keywords: PZT; ferroelectricity; piezoelectricity; soft ceramics; sensors.

En el presente trabajo se analiza la influencia del dopaje simultáneo con Lantano (La) y Niobio (Nb) en el sistema cerámico PZT para iguales concentraciones de los dopantes (x). Difracción de Rayos X (DRX), Microscopía Electrónica de Barrido (MEB) y mediciones dieléctricas y piezoeléctricas fueron efectuadas para caracterizar el material y analizar la posible utilidad de estos cerámicos blandos como sensores pulso-eco. Se encontró un nivel óptimo de dopaje con la mejor respuesta piezoeléctrica y mejor figura de mérito $d_h g_h$ para hidrófonos.

Descriptores: PZT; ferroelectricidad; piezoelectricidad; ceramicos blandos; sensores.

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1. Introduction

Weak hydrostatic pressure wave sensor (hydrophones) are one of the oldest applications for which modified PZT ceramics were used. Besides, there exists a figure of merit for hydrophones ($d_h g_h$) which is a parameter that takes into account the change in polarization and the voltage generated in the active element working into a very high impedance load. This figure of merit is not usually high in pure PZT ceramics [1], and modifications are needed in order to make them suitable for hydrophone applications. The wide variety of modifications that have been explored are very well explained elsewhere [2]. In this work we shall introduce a novel soft double-doping modification to the PZT 54/46 ceramic system, with La and Nb at the same doping level (x), that shows good piezoelectric performance and high figures of merit $d_h g_h$ for hydrophones. In addition, a characterization study of the material is also shown and discussed.

2. Synthesis

The conventional oxides/carbonates route was used starting from very pure powder reagents that were stoichiometrically weighted in order to obtain the desired composition, $Pb_{1-3x/2}La_x\Delta^A_{x/2}(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nb_x\Delta^B_{x/4}O_3$, x being the doping level of both La and Nb (mole%), and taking into account the generation of vacancies (Δ) on the A and B sites of the perovskite structure. Three different doping levels were used, x = 0.4, 1.0 and 1.4 mole%; from now on,

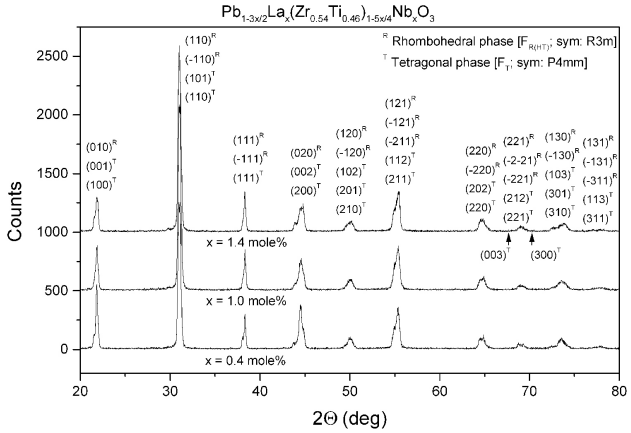

FIGURE 1. Indexed X-Ray diffraction patterns for the PLZTN x/54/46 ceramic system studied. The mixture of F_T and $F_{R(HT)}$ phases can be easily seen, as well as the predominance of the rombohedral phase.

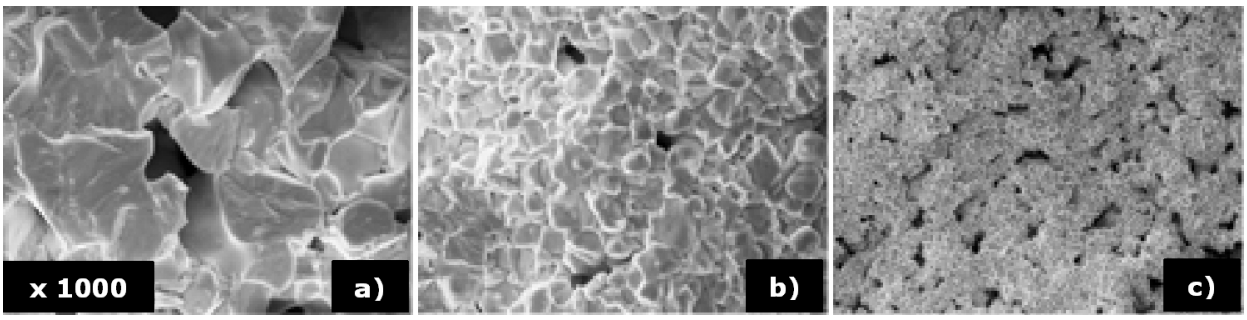

FIGURE 2. SEM micrographs of the PLZTN x/54/46 ceramic system with; a) x = 0.4; b) 1.0 and c) x = 1.4 mole%. It can be seen how grains become smoother and smaller when the doping level increases. The presence of pores is also detected for every sample studied.

we shall refer to this compound as PLZTN x/54/46. Calcination was carried out at 950°C for 90 min. and sintering was achieved at 1250°C for 120 min. A detailed description of the synthesis process can be found in [3]. The cylindrical samples were then cut into thin disks, plated and poled near saturation at 4 kV/mm.

3. XRD and phase formation

The X-rays diffraction patterns for each composition are shown in Fig. 1. A mixture of tetragonal (F_T) and rombohedral ($F_{R(HT)}$) perovskite phases was detected, as reported for near MPB Zr/Ti ratios [2], the latter being the predominant phase with no significant variation in the lattice parameter in the $F_{R(HT)}$ phase ($\sim$ 4.07 Å), the tetragonality for the F_T phase ($\sim$ 1.02) nor the $F_{R(HT)}/F_T$ ratio ($\sim$ 85%/15%).

4. Scanning electron microscopy

SEM analysis (Fig. 2) showed the strong influence of both La and Nb on the grain size and morphology. Grains were smoother and smaller as dopant concentration was increased. This inhibitor behavior on grain growth has been previously reported for each of our dopants in the PZT ceramic system [4,5], but not for both acting simultaneously. Porosity also decreased with higher doping levels.

5. Dielectric study

As both atoms enter A and B sites, and Pb vacancies are created, long range interactions are affected and so the thermal energy needed for the ferroelectric/paraelectric phase transition decreases. Hence, the Curie temperature (T_C) decreases when x is increased, as seen in Fig. 3a. Besides, detected phase transitions were all normal as exemplified in Fig. 3b. On the other hand, while at room temperature, permittivity increased with dopant concentration, mainly because of the lower values of porosity. This fact can be explained by using the Bruggeman model for inhomogeneous media [3,5].

6. Piezoelectric performance

Near saturation poled samples (at 4 kV/mm) were characterized according to the IEEE Standards on Piezoelectricity [6].

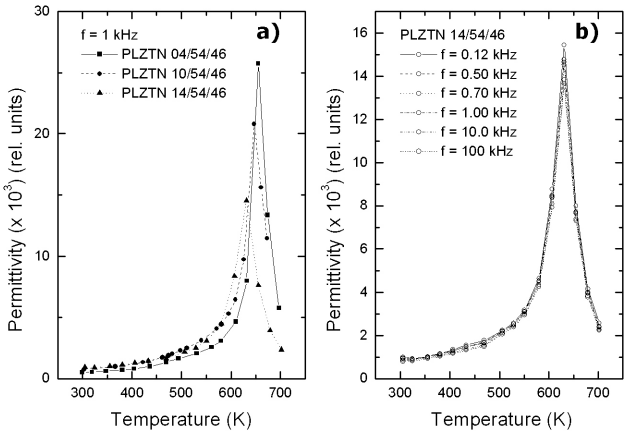

FIGURE 3. Dielectric behavior of the PLZTN x/54/46 ceramic system. a) Samples measured at all frequencies shown lower T_C as doping level raised. Only the 1 kHz curves are shown. b) Normal transitions where detected for every composition studied. PLZTN 14/54/46 is shown as an example.

TABLE I. Calculated values of some important parameters for the studied samples. The calculation procedure followed the IEEE Standards on Piezoelectricity. Poling field was $\sim$ 4 kV/mm.

	PLZTN 4/54/46	PLZTN 10/54/46	PLZTN 14/54/46
$N_p - N_t$ (m/s)	1729 - 1543	2020 - 1843	1715 - 1353
$K_p - K_t$	0.418 - 0.571	0.496 - 0.500	0.373 - 0.523
ε_{33}	5.03	7.72	9.51
$d_{31} - d_{33}$ (10^{-12} C/N)	-89.34 - 390	-112.58 - 320	-106.59 - 305
$d_h g_h$ (10^{-15} m^2/N)	8878	1173	894

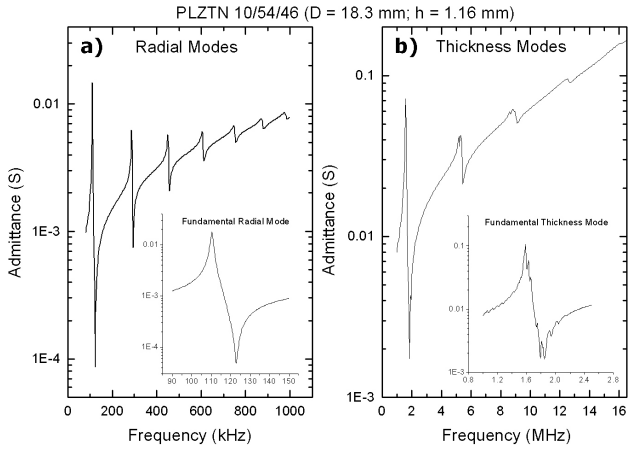

FIGURE 4. Radial (4-a) and thickness (4-b) modes for the PLZTN 10/54/46. The fundamental modes are shown in each case, as well as the dimensions of the cylindrical plate.

Fig. 4 shows typical resonance curves measured for radial and thickness modes. The figure of merit for hydrophones $d_h g_h = (d_{33} + 2d_{31})^2/\varepsilon_{33}$ was calculated and these results, plus some other important operation parameters, are shown in Table I. The respectable value of $d_h g_h$ reached for the 4/54/46 composition should be noted but, as a practical handicap, its low dielectric constant makes any impedance matching with capacitance loads difficult. Besides, it has the lowest coupling factor $k^2 \propto d_{31}^2/\varepsilon_{33}$ and we do not consider it useful for practical "generator" applications. Credit must be given, however, to the other two compositions, especially the 10/54/46 with good overall features, better coupling factor and highest K_p values. In the 14/54/46 sample, mechanical losses were high and, in spite of its high dielectric constant, the effects of reduced grain size and, therefore, domain size, were predominant.

7. Conclusions

The PLZTN x/54/46 has shown a pure perovskite phase with coexisting tetragonal (F_T) and rombohedral ($F_{R(HT)}$) phases, and the grain size was dramatically reduced with further doping as well as porosity. The Curie temperature was reduced as the long range interactions were weakened due to the simultaneous A and B sites substitutions with La and Nb, respectively. The PLZTN 10/54/46 showed, in our opinion, the best overall piezoelectric performance and hydrophone-like behavior, while the other two compositions were affected by their structural features discussed above.

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