

# Piezoelectric properties of pure and (Nb<sup>5+</sup> + Fe<sup>3+</sup>) doped PZT ceramics

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## Abstract

This work evaluates the effect caused by the addition of Fe<sup>3+</sup> and Nb<sup>5+</sup> ions on the piezoelectric properties of lead zirconate titanate. Three compounds were obtained using the conventional method of mixture of oxides. The oxides were calcined at 850 °C and after that submitted to a uniaxial pressure of 70 MPa and an isostatic pressure of 200 MPa. Subsequently, the samples were sintered at 1200 and 1250 °C for 3.5 h. The surfaces were metalized and polarized in order to determine the piezoelectric properties. High concentration of dopants in lead zirconate titanate yielded high values of dielectric constant ( $K_{33}^T$ ) and specific mass. Moreover, there was an increase of the factor of electromechanical coupling ( $K_p$ ) when compared to the pure PZT ceramics, associated with a decrease in the mechanic quality factor.

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## 1. Introduction

Ceramics based on lead zirconate titanate are largely used in electronic industry because of the useful piezoelectric properties. Several devices, such as transducers and integrated circuits for microelectronic applications, use this type of ceramics [1–3].

The piezoelectric properties of PZT (Lead zirconate titanate) ceramics are influenced by the type and content of dopants. The dopant can improve the sintering process, producing ceramics with high specific mass, reducing the lead oxide evaporation and avoiding the formation of second phases [4–6]. Besides, dopants also engender the substitution of A or B cations of ABO<sub>3</sub> perovskite structure. Ions of higher valence, such as Nb<sup>5+</sup>, cause vacancies in the A cation, called lead vacancies; and the lower valence ions, as Fe<sup>3+</sup>, result in oxygen vacancies [7].

The lead vacancies provide a mechanism of internal stress relief because of reduction of cell parameter ratio,  $c/a$ , at a given dopant concentration. Moreover, these vacancies cause small distortion of the unit cell and increase the mobility of the domain walls. The additives that produce equivalent effects

are named donor atoms. Thus, doping the lead zirconate titanate ceramics with Nb atom reduces the coercitive field, lowers aging kinetic and elasticity modulus and increases dielectric constant ( $K_{33}^T$ ). If compared with pure PZT, the addition of Nb atom can additionally increase the piezoelectric coupling factor ( $k_p$ ) and decrease the mechanic quality factor ( $Q_m$ ) [8–10].

The additives that increase the amount of oxygen vacancies cause a small reduction of the unit cell dimensions, increase the internal stress and, consequently, increase the coercitive field. Therefore, the additives that accept electrons are called hardener additives. The material doped with iron presents lower dielectric constant and loss constant, with an increase of mechanic quality factor [8,11,12]. Therefore, according to Takahashi [13], the vacancies of oxygen generated by the addition of iron are suppressed when there are equimolar compositions of niobium and iron.

Piezoelectric ceramics, PZT, are indicated for application in hydro-acoustic transducers of types I, II or III depending on dopant used. Type I, II and III transducers use doped piezoelectric ceramics with Sr, Nb and Fe atoms, respectively [14,15].

Based on the influences of each dopant on piezoelectric ceramic properties, this work analyses the simultaneous addition of dopants. Two dopants (niobium and iron) were used, focusing on the improvement of the dielectric and

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piezoelectric properties. Doing so, the doping can promote intermediary properties in II and III PZT types, since the PZT ceramic doped with iron has low dielectric constant.

## 2. Materials and methods

PZT ceramics were obtained by using the conventional method of mixture of oxides.  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$ , with 99.99 and 99.98% purity, respectively, were used in PZT ceramic production of different compositions. Lead, titanium and zirconium oxides used in the experiments had 99.00%, 99.23% and 95.76% purity, respectively.

The powders were obtained in Zr/Ti stoichiometry equals to 53/47, which is near the morphologic phase boundary. Additionally, an excess of 3% of lead oxide related to the stoichiometry amount was used for all samples. The dopants were added at 1.5 and 1.5 mol% of  $\text{Fe}^{2+}$  and  $\text{Nb}^{5+}$  ions, or equivalently, 0.5 and 0.5 mol% of  $\text{Fe}^{2+}$  and  $\text{Nb}^{5+}$  ions.

The oxides were ground during 48 h in ball mill in presence of isopropyl alcohol. Subsequently, the powder was dried, sieved and calcined during 3.5 h at 850 °C. After that, the polyvinyl alcohol (PVA – 15%, w/v) was added at a ratio of 2% of total powder weight. For each processing condition a pure powder was also sintered.

Samples with diameter of 20 mm were obtained after being submitted to uniaxial and isostatic pressures of 70 and 200 MPa, respectively. Finally, the samples were sintered at 1200 and 1250 °C for 3.5 h in sealed alumina crucibles. The material of PZT sacrifice substrate was a commercial composition EC-69. The powder used around the samples was a mixture of 95 wt%  $\text{PbZrO}_3$  and 5 wt%  $\text{ZrO}_2$ . During the sintering, this powder was employed in 10% of sample weight in the crucible. Five samples were produced for each data physical properties presented.

During the preparation process, the piezoelectric ceramic samples were ground with emery paper of silicon carbide with 380, 400 and 600 mesh, until the thickness reached a range from 1.5 to 1.8 mm. After that, the samples were coated with silver ink and placed into an oven at 590 °C for 3 h.

At last, the metal-coated samples were polarized in bath of silicone oil at 80 °C. Samples with high amount of dopants were polarized with electric field of 8 kV/mm and less doped ones with 5 kV/mm intensity. On the other hand, pure ceramics were performed with 3 kV/mm electric field intensity. Two samples were produced for determining each data piezoelectric properties presented at different electric field intensity (8, 5 and 3 kV/mm). Additional sample was prepared for each condition and performed at 3 kV/mm electric field intensity to qualitatively compare the electric field effects.

The piezoelectric properties, such as capacitance ( $C_p$ ), dielectric loss ( $\tan \gamma$ ), resonance impedance ( $Z_r$ ), resonance frequency ( $F_r$ ), anti-resonance frequency ( $F_a$ ) and dielectric constant ( $K_{33}^T$ ) were obtained by using an impedance analyzer (HP 4294A LP, Gain Phase Impedance Analyzer), in the frequency range from 100 to 200 kHz.

## 3. Results and discussions

Fig. 1 shows the distribution of particle sizes of powders calcinated at 850 °C for 3.5 h. For all compositions, the values of equivalent spherical diameter corresponding to 50% of accumulated mass were below 0.70, 0.45 and 0.51  $\mu\text{m}$ , respectively, for the compositions  $\text{Pb}_{1.03}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ ,  $\text{Pb}_{1.03}(\text{Zr}_{0.525}\text{Nb}_{0.005}\text{Ti}_{0.465}\text{Fe}_{0.005})\text{O}_3$  and  $\text{Pb}_{1.03}(\text{Zr}_{0.515}\text{Nb}_{0.015}\text{Ti}_{0.455}\text{Fe}_{0.015})\text{O}_3$ . These distributions of particle sizes were satisfactory for PZT ceramics because they favor the formation of dense materials as depicted in the results of Tables 2–4.

Fig. 2 presents the morphology of fracture surface of pure and doped materials, sintered at 1200 and 1250 °C for 3.5 h. The fracture propagation of samples sintered at 1250 and 1200 °C was transgranular and intergranular, respectively. In this sense, high temperature promotes grain growth and iron dopant engenders transgranular fracture. In pure material sintered at 1250 °C was observed a grain growth related to transgranular fracture. As to the doped material, also sintered at 1250 °C, was observed a grain growth besides the possible oxygen vacancies. Thus, the observed fracture morphology can be ascribed to both phenomena [16].

Few pores are present in samples prepared with three compositions and prepared in two temperatures. These results are expected, considering that the specific mass, for all of processing conditions, were above 95% of theoretical values.

Table 1 shows high mass loss for both samples, pure PZT and for those with low dopants concentration under elevated sintering temperatures. However, for all tested concentrations, these high values of mass loss do not significantly reduce the specific mass of materials. Indeed, the final specific mass remained above 95% of theoretical value, being 7.76  $\text{g}/\text{cm}^3$  the lowest result. Therefore, the specific mass values of doped and pure samples were similar.

A great problem of PZT preparation is to keep the desired composition, since the lead oxide evaporation tends to modify the

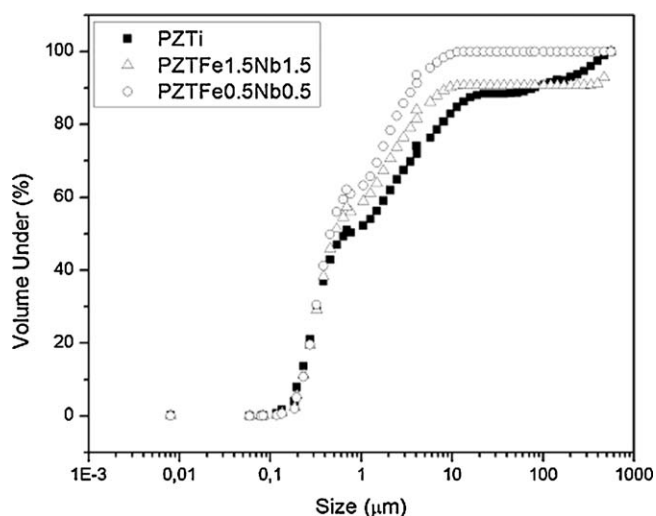


Fig. 1. Distribution of particle sizes of pure PZT,  $\text{PZTFe}_{0.5}\text{Nb}_{0.5}$  and  $\text{PZTFe}_{1.5}\text{Nb}_{1.5}$  powders.

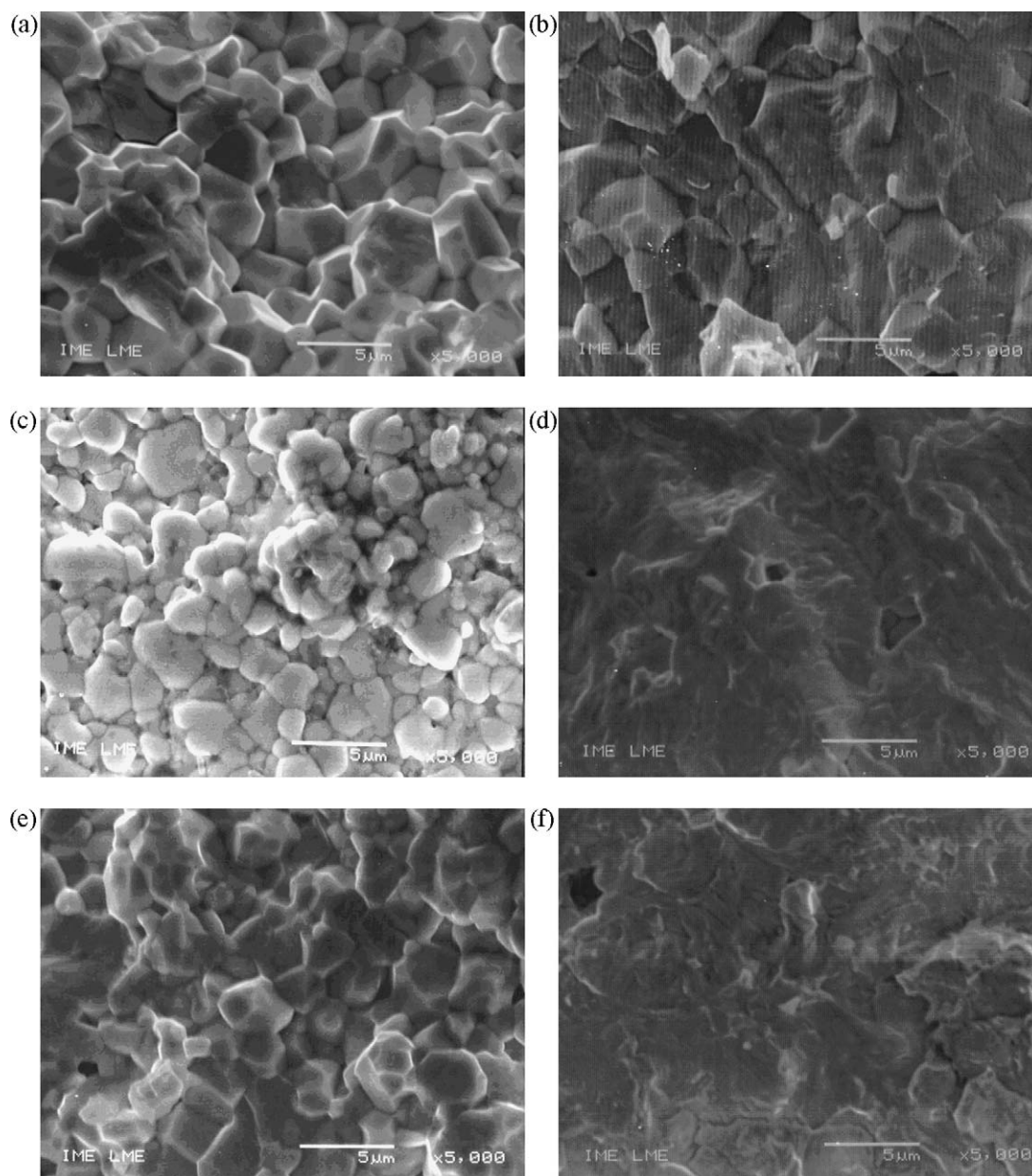


Fig. 2. Photomicrograph fracture surfaces of sintered samples. (a) Pure PZT 1200 °C/3.5 h; (b) Pure PZT 1250 °C/3.5 h; (c) PZTFe<sub>0.5</sub>Nb<sub>0.5</sub> 1200 °C/3.5 h; (d) PZTFe<sub>0.5</sub>Nb<sub>0.5</sub> 1250 °C/3.5 h; (e) PZTFe<sub>1.5</sub>Nb<sub>1.5</sub> 1200 °C/3.5 h; (f) PZTFe<sub>1.5</sub>Nb<sub>1.5</sub> 1250 °C/3.5 h.

stoichiometry, with concomitant decrease of density. In the present case, the mass loss of pure sample can be related to the volatilization of lead oxides and PVA during the sintering step. Besides the loss of lead oxide, other factor that controls the PZT formation is the penetration of dopant in the crystalline structure of perovskite [12]. These processes can explain the small mass losses of samples with high amount of dopants; and high loss for

pure ceramic, mainly due to the evaporation of lead oxides. The dopants hinder the evaporation of the lead oxides.

The retraction of ceramic samples was not significantly influenced by the presence of high amount of dopants, remaining around 13.90% for radial retraction. However, in pure ceramics, the radial retraction was less than, or equal to 12.38%, when sintered in the high temperature (Table 1).

Table 1  
Loss of mass and retraction percentage of PZT ceramics.

	PZT (Pure)		Fe <sub>0.5</sub> Nb <sub>0.5</sub>		Fe <sub>1.5</sub> Nb <sub>1.5</sub>	
	1200 °C	1250 °C	1200 °C	1250 °C	1200 °C	1250 °C
Mass loss (%)	5.68	6.60	4.97	5.29	3.43	4.42
Retraction (%)	12.45	12.38	13.93	13.84	13.86	13.95

Table 2  
Piezoelectric properties of pure PZT ceramics.

$T$ (°C)	Density <sup>a</sup>	<sup>b</sup>	$k_p$	$C_p$ (pF)	$Q_m$	$N_p$ (Hz m)	$K_{33}^T$	$\tan \delta$
1200	7.80	97.50	0.44	904.78	532.16	2305	777	0.007
1250	7.71	96.38	0.43	872.99	648.77	2298	749	0.006

<sup>a</sup> Density obtained by the Archimedes method.

<sup>b</sup> Percentage of density related to the theoretical value.

Table 3  
Piezoelectric properties of PZT ceramics doped with Fe<sub>0.5</sub>/Nb<sub>0.5</sub>.

$T$ (°C)	Density <sup>a</sup>	<sup>b</sup>	$k_p$	$C_p$ (pF)	$Q_m$	$N_p$ (Hz m)	$K_{33}^T$	$\tan \delta$
1200	7.78	97.25	0.56	942.35	450.3	2239	859	0.008
1250	7.76	97.00	0.56	883.15	516.5	2248	802	0.007

<sup>a</sup> Density obtained by the Archimedes method.

<sup>b</sup> Percentage of density related to the theoretical value.

Table 4  
Piezoelectric properties of PZT ceramics doped with Fe<sub>1.5</sub>/Nb<sub>1.5</sub>.

$T$ (°C)	Density <sup>a</sup>	<sup>b</sup>	$k_p$	$C_p$ (pF)	$Q_m$	$N_p$ (Hz m)	$K_{33}^T$	$\tan \delta$
1200	7.85	98.13	0.56	1141.55	383.99	2204	1012	0.007
1250	7.80	97.50	0.56	1143.34	353.47	2221	1002	0.006

<sup>a</sup> Density obtained by the Archimedes method.

<sup>b</sup> Percentage of density related to the theoretical value.

The values of dielectric loss constant were small for pure (Table 2) and doped ceramics, performed with different electric field intensities (Tables 3 and 4) and at a fixed 3 kV/mm. The doping did not cause important changes at high concentration of dopants in the dielectric loss constant presented at 3 kV/mm electric field intensity of polarization, 0.008 at 1200 °C and 0.005 at 1250 °C. Therefore, the low concentration of dopants for two temperatures decreases dielectric loss constant to 0.004 when compared with pure ceramics (Table 2).

For ceramics polarized at 3 kV/mm electric field intensity, the findings result that the dielectric constants are in the range 864–1085, and electromechanical coupling factors ( $k_p$ ) vary from 0.53 to 0.57. However, the mechanic quality factors range from 229 to 322, and the constant frequencies from 2178 to 2244. Similar results were obtained from polarized samples at different intensities of electric fields (Tables 3 and 4). Pure ceramics produced the lowest values of dielectric constant and electromechanical coupling factor ( $k_p$ ) as well as the highest values of mechanic quality factor ( $Q_m$ ), and constant frequency ( $N_p$ ), as observed in Table 2.

The following results refer to polarization performed under the same electric field intensity. The pure ceramics showed lowest dielectric constant (see Table 2, 777 at 1200 °C and 749 at 1250 °C) and the less doped ceramics yield an increase of dielectric constant (915 at 1200 °C and 864 at 1250 °C). The more doped samples produced high dielectric constant values, regardless the sintering temperature (1085 at 1200 °C and 1054 at 1250 °C). Thus, the oxygen vacancies (Fe<sup>3+</sup> ions) were suppressed with an equimolar doping [13], which did not tend to reduce the dielectric constant. The niobium ions affect

several characteristics of ceramics: cause lead vacancies that reduce the stress level in the crystalline lattice and allow internal movements. Therefore, these effects increase the dielectric constant value [4].

The increase of dopant concentration gives high dielectric constants (1085 at 1200 °C, 1054 at 1250 °C) and a reduction of the mechanic quality factor (205 at 1200 °C, 229 at 1250 °C), for the samples polarized under 3 kV/mm. These results were similar to those obtained at different electric field intensities as observed in Table 3. So, it suggested that, for the same concentration, the effect caused by the donor atoms electrons on piezoelectric properties is predominantly ascribed to accepting electron atoms [7]. Thus, donor dopant, as niobium, would simultaneously increase the dielectric constant and decrease the mechanic quality factor [13]. The lead vacancies related to the presence of niobium atom facilitate the material diffusion, resulting in an easy sintering process and also resulting in ceramics with higher dielectric constants. These characteristics of ceramics allow them to be used as PZT of type III, applied in hydro-acoustic transducers due to their high electromechanical transduction capability. The used doping process has produced PZT ceramics with high dielectric constant values and reasonable mechanic quality factor.

#### 4. Conclusions

The employed doping process produced lead zirconate titanate ceramics of type III with high electromechanical transduction capability, proper to be used in hydro-acoustic



equipments. The obtained piezoelectric properties were superior to that found in current ceramics, *i.e.*, high dielectric constants and a slightly decrease of mechanical quality factor.

The highest concentration of dopant ions results in ceramics with high dielectric constants, low mass losses and low mechanical quality factors in comparison to those produced from less dopant ceramics. The results suggest that the dopants hinder the evaporation of lead oxides.

Oxygen vacancies ( $\text{Fe}^{3+}$  ions) were suppressed by an equimolar doping [13], which did not tend to reduce the dielectric constant. The  $\text{Nb}^{5+}$  ions cause lead vacancies and decrease the stress in the crystalline lattice. Moreover, they also allow internal movements and increase the dielectric constant [4]. Therefore, both effects increase the dielectric constant values. So, it suggested that, for the same concentration, the effect caused by the donor atom on piezoelectric properties is predominantly ascribed to acceptor atom [7]. Thus, donor dopant, as niobium, would simultaneously increase the dielectric constant and decrease the mechanical quality factor. In conclusion, the produced ceramics have suitable properties to be employed in electronic devices.

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