

Investigation of Multiferroic Properties of Fe<sup>3+</sup> and (La<sup>3+</sup>, Fe<sup>3+</sup>) doped PbZr<sub>0.53</sub>Ti<sub>0.47</sub>O<sub>3</sub> Ceramics

*Original*

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*Availability:*

This version is available at: 11583/2862178 since: 2021-01-19T09:53:41Z

*Publisher:*

Institute of Electrical and Electronics Engineers Inc.

*Published*

DOI:10.1109/EExPolytech50912.2020.9243856

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# Investigation of Multiferroic Properties of Fe<sup>3+</sup> and (La<sup>3+</sup>, Fe<sup>3+</sup>) doped PbZr<sub>0.53</sub>Ti<sub>0.47</sub>O<sub>3</sub> Ceramics

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**Abstract**—In the present paper, the effects of (Fe<sup>3+</sup> and La<sup>3+</sup>) and of Fe<sup>3+</sup> on the properties of Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub> (PZT) ceramic materials have been studied. Conventional solid reaction method has been used for the sintering of the ceramic materials and their multiferroic properties have been investigated. The structure, the electric and magnetic properties of the ceramic materials have been explored. In case of iron ions or lanthanum and iron ions doping, the PZT ceramic materials show simultaneous effects of both ferromagnetism and ferroelectricity at room temperature with magnetic and dielectric properties suggestive of multiferroic behaviour in these systems. Introduction of the addition of La<sup>3+</sup> together with Fe<sup>3+</sup> has determined a major improvement of the electric properties. The magnetic properties decrease with the introduction of La<sup>3+</sup> along with Fe<sup>3+</sup>.

**Keywords**—*multiferroics, PZT ceramics, dielectric, ferroelectric*

## I. INTRODUCTION

Multiferroics are a class of so-called intelligent materials in which at least two of the following three properties coexist simultaneously: ferroelectricity, ferromagnetism and ferroelasticity [1-4]. Thus, these materials have (i) a spontaneous polarization that can be reoriented when we apply an electric field, (ii) a spontaneous deformation that can be reoriented when we apply a stress, and (iii) a spontaneous magnetization that can be reoriented when we apply a magnetic field [5]. For “multiferroic” materials, multiplestate memory elements, magnetically modulated piezoelectric transducers and electric field-controlled ferromagnetic resonance devices have been suggested as applications [6,7]. The magnetoelectric effect (ME) is defined by the appearance of an electric polarization when applying a magnetic field or conversely the appearance of an induced magnetization under an applied electric field [8].

In recent years, researchers' studies have focused on composites with functional properties [9 - 11]. Multiferroic composites (e.g., combination of piezoelectric and ferrite materials) occupy an important place in this research. In multiferroic materials, the applied magnetic field can

modify/change the spontaneous electric polarization and conversely the applied electric field can modify/change the spontaneous magnetization. In multiferroics materials, the internal effects are dependent on the elastic coupling between the piezoelectric and magnetostrictive components. Thus, the mechanism of achieve the ME coupling is not well defined [12]. However, recently dynamic studies and relevant electronic models have been proposed [13]. The research has been directed to obtain multiferroic materials based on solid solutions with perovskite structure. Of particular interest are the compositions with the general formula Pb(B'B'')O<sub>3</sub>, where the position B' is occupied by Fe<sup>3+</sup>. The piezoelectric commercial compositions Pb(Zr,Ti)O<sub>3</sub> (PZT) have been used for high performance actuators and transducers in arrears to their superior dielectric and piezoelectric properties. The most studied and used piezoelectric materials with perovskite structures are those described by the general formula PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> [14-19].

A composition of interest is that in which Fe<sup>3+</sup> is used as a dopant below the solubility limit in PZT. Defective dipole formation occurs and partial load is compensated by oxygen vacancies [20]. It is known that doping the A position with La<sup>3+</sup> together with Pb<sup>2+</sup> favors the electrical order in PZT compositions [21,22]. Doping with Fe<sup>3+</sup> in position B generates the magnetic order by forming a magnetic moment. The appearance of the two phenomena that coexist in these modified PZT compositions is the basis of potential new applications [22]. In modified PZT compositions undesirable phases (pyrochlor) can occur which leads to a decrease in electrical properties [23], but very high values of piezoelectric coefficients can also be obtained together with relatively high ME coupling (e.g Fe<sup>3+</sup> doped PLZT 9/65/35 ceramics) [24]. Fe<sup>3+</sup> has an important role in obtaining new perovskite structures with properties that change in the magnetic field, similar to PFN ceramics [20,25]. Multiferroic materials (in which, as mentioned above, electric polarization and magnetization can coexist) are the new candidates for spintronic compounds but so far only a

few materials that are multiferroic have been reported [26,27].

On this background, in the present paper a systematically investigations of the structural, electrical, ferroelectric and magnetic properties of PZT modified ceramic system is descibed.

## II. EXPERIMENTAL PROCEDURE

High purity powders (> 99.5%) of PbO (Aldrich), TiO<sub>2</sub> (Aldrich), ZrO<sub>2</sub> (Alfa Aesar), La<sub>2</sub>O<sub>3</sub> (Merck) and Fe<sub>2</sub>O<sub>3</sub> (Loba), were used to prepare the desired compositions of PFZT and PLFZT ceramics by the conventional solid reaction method. The oxide constituents were weighed in accordance with the molecular formula: Pb<sub>(1-3x/2)</sub>(Fe<sub>0.5</sub>)<sub>x</sub>(Zr<sub>0.57</sub>Ti<sub>0.43</sub>)<sub>(1-x/4)</sub>O<sub>3</sub> - named PFZT and Pb<sub>(1-3x/2)</sub>(Fe<sub>0.5</sub>La<sub>0.5</sub>)<sub>x</sub>(Zr<sub>0.57</sub>Ti<sub>0.43</sub>)<sub>(1-x/4)</sub>O<sub>3</sub> - named PLFZT, where x = 0.09.

The milling process was carried out in a Retsch planetary ball mill for 10 h at room temperature using distilled water. Once dried, the mixtures were calcinated at 870 °C for 5 h. The heating/cooling rate was 5 °C/min. Then the calcination compositions were milled again for 16 hours in distilled water, dried and mixed with 5% polyvinyl alcohol (PVA) solution as a binder and uniaxially pressed as discs using hydraulic pressing at a pressure of 110 MPa.

The green ceramic discs, each measuring 12 mm in diameter and 1.5 mm in thickness, were sintered for 2 h at 1200 °C and 1230 °C in a closed alumina crucibles which contained PbZrO<sub>3</sub> to inhibit PbO evaporation from the ceramic samples. The heating and cooling rates being fixed at 5°C/min. After sintering, all the samples were lapping at 1 mm height and then silver electroded on both plan parallel surfaces and fired at 650 °C for 30 min. The density of each sintered sample was determined by Archimede's method. X-ray diffraction (XRD) was performed in  $\theta$  - 2 $\theta$  configuration using a Bruker D8Discover diffractometer with CuK $\alpha$  (1.5406 Å) radiation with a 1D LynxEye detector. The XRD measurements were performed at room temperature in continuous scan mode at 2 $\theta$  angle from 10° to 70°, with an increment of 0.004°. The experimental patterns were indexed by ICDD PDF2 database. Then the structure was studied using Rietveld refinements [28]. The morphology and grain size of the sintered samples has been studied by Scanning Electron Microscopy (SEM) with FEG-SEM-FIB Auriga Workstation produced by Carl Zeiss, Germany. The capacitance and the dielectric loss (tan  $\delta$ ) were measured using LCR meter HM 8018 (HAMEG type), at 1kHz. The P-E hysteresis loops of unpoled samples were measured using the TF analyzer 2000 (Aixact System). Magnetic measurements of the samples were carried out using a laboratory-fabricated vibrating sample magnetometer (VSM Lake Shore model 7300).

## III. RESULTS AND DISCUSSION

### A. Structural analysis

By X-ray diffraction analysis, it is found that all the compositions have main perovskite tetragonal phase. The addition of Fe<sup>3+</sup> and La<sup>3+</sup> did not significantly modify the ferroelectric phase at MPB, but leads to a slightly lower tetragonality (i.e., c/a ratio) and lattice shrinkage on c axis noticeable also on unit cell volume. Mass differences,

electron structure and radius among Pb<sup>2+</sup>, Zr<sup>4+</sup>, Ti<sup>4+</sup> and dopants ions which relieve the tetragonal lattice distortion lead to the reduced lattice parameter values (Tab. 1).

TABLE 1. LATTICE PARAMETERS A, C, TETRAGONALITY AND CRYSTALLITE SIZE RESULTED BY RIETVELD REFINEMENT

Samples	Temperature T [°C]	Cell parameter a [Å]	Cell parameter c [Å]	Tetragonality c/a	Crystallite size [nm]/ Space group
PZT (PDF 01-072-7166)	-	4.0174	4.1420	1.03	-/ Tetragonal P4mm(99)
PFZT	1200	4.0248	4.1191	1.02	57/ Tetragonal P4mm(99)
	1230	4.0249	4.1226	1.02	51/ Tetragonal P4mm(99)
PLFZT	1200	4.0213	4.1145	1.02	74/ Tetragonal P4mm(99)
	1230	4.0187	4.1181	1.02	75/ Tetragonal P4mm(99)

All the sintered compositions reveal a perovskite structure meaning that the dopants (La<sup>3+</sup> and Fe<sup>3+</sup>) diffuse into the PZT lattice and form a solid-solution.

### B. Microstructural analysis

The SEM images (x50000) reveal for all sintered samples a dense microstructure with a grain distribution, which is influenced by the nature of the dopant and by the sintering temperature. Figure 1 shows that the samples (PFZT and PLFZT) sintered at 1200 °C have a homogeneous microstructure. There are two types of tetragonal grains, some of which are of small size and placed at the intergranular boundary of large granules. The addition of the La<sup>3+</sup> leads to increase the homogeneity of the microstructure.

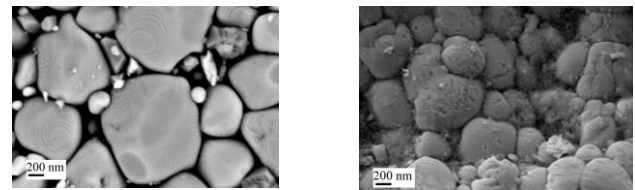


Fig. 1. SEM images of samples sintered for 2 h at 1200°C, (a) PFZT and (b) PLFZT

Similarly to the previous images, the samples sintered at 1230 °C appear with a homogeneous microstructure (Fig. 2)

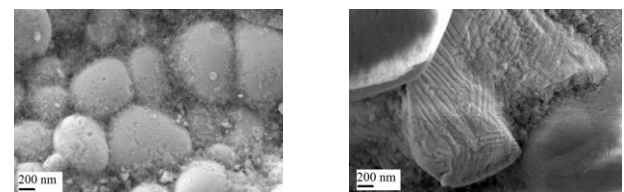


Fig. 2. SEM images of samples sintered for 2 h at 1230 °C, (a) PFZT and (b) PLFZT

and show a morphology with rounded polyhedral particles.

For the donor (La) and acceptor (Fe) doped composition PLFZT, the effect of grain growth inhibition was lowered as shown in Fig. 2(b); this is because of the lowered vacancy density resulting from charge compensation by substitution of lower valency cation  $Fe^{3+}$  on B site.

### C. Electrical properties

For all sintered samples the values of the dielectric parameters (dielectric constant -  $\epsilon_r$  and dielectric losses -  $\tan \delta$ ) have been collected in Tab. 2.

TABLE 2. THE DIELECTRIC PROPERTIES FOR THE SAMPLES PFZT AND PLFZT SINTERED AT 1200 °C AND AT 1230 °C

Temperature T [°C]	Samples	dielectric constant $\epsilon_r$	loss factor $\tan \delta * 10^{-3}$
1200	PFZT	848	2.89
	PLFZT	1143	1.82
1230	PFZT	1028	2.36
	PLFZT	1050	3.26

The increase of the crystallites and the size of the granules leads to the increase of the value of  $\epsilon_r$  with the development of the ordered regions inside the disordered matrix. This dielectric behavior is consistent with the structural results obtained [29]. The increase in  $\tan \delta$  observed in PFZT samples sintered at 1200 °C and in PLFZT samples sintered at 1230 °C can be attributed to structural defects, existing pores or can be attributed to the development of nanoregions due to the complex composition [30].

### D. Ferroelectric properties

Ferroelectric hysteresis loops of the unpoled samples measured at room temperature are presented in Fig. 3. All the sintered samples are ferroelectrics. As it can be observed, typical hysteresis loops were obtained for all the sintered compositions, showing a remnant polarization ( $P_r$ ) and coercive field ( $E_c$ ) of 2.48 ( $\mu C/cm^2$ ) and 1586.49 (V/cm), respectively, for the PLFZT sample sintered at 1230 °C.

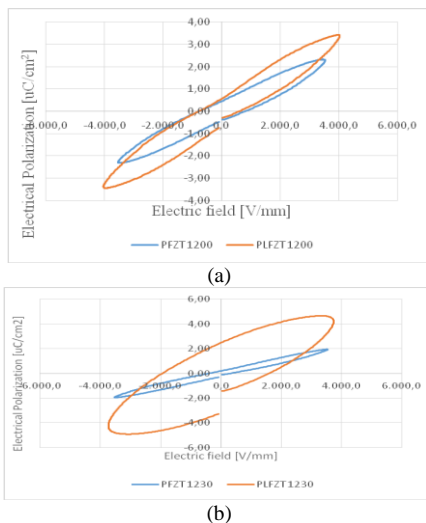


Fig. 3. Room temperature hysteresis loops for the samples PFZT and PLFZT sintered at (a)1200 °C and at (b) 1230 °C

TABLE 3. FERROELECTRIC PARAMETERS OBTAINED FROM THE HYSTERESIS LOOPS OF THE FIG. 3.

Temperature T [°C]	Samples	Polarization $P_r$ ( $\mu C/cm^2$ )	Polarization $P_s$ ( $\mu C/cm^2$ )	Coercive field $E_c$ (V/mm)
1200	PFZT	0.4541	2.2805	802.623
	PLFZT	0.5638	3.3803	600.023
1230	PFZT	0.200	1.9393	296.473
	PLFZT	2.4859	4.2164	1586.49

### E. Ferromagnetic properties

The obtained values of the ferromagnetic parameters, e.g remnant magnetization ( $M_r$ ) and coercive field ( $H_c$ ), are shown in the Tab. 4. The PLFZT samples are not ferromagnetic which can be explained by the fact that  $La^{3+}$  has an influence on exchange interaction between  $Fe^{3+}$  ions.

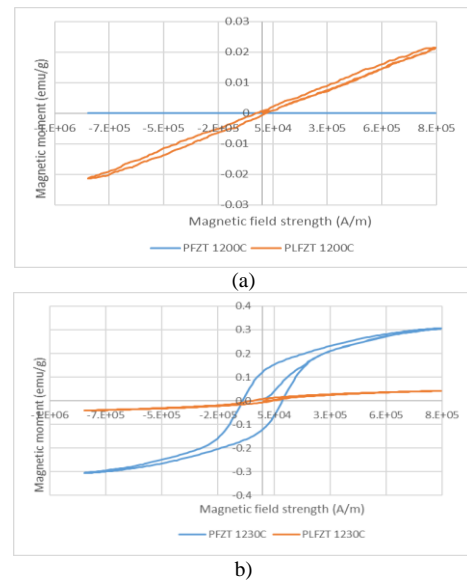


Fig. 4. Room temperature ferromagnetic hysteresis loops for the samples PFZT and PLFZT sintered at (a)1200 °C and at (b) 1230 °C

TABLE 4. FERROMAGNETIC PARAMETERS OBTAINED FROM THE FERROMAGNETIC HYSTERESIS LOOPS OF THE FIG. 4.

Temperature T [°C]	Samples	Magnetization $M_r$ (emu/g)	Magnetization $M_s$ (emu/g)	Coercive field $H_c$ (Oe)
1200	PFZT	0.12	0.3	1109
	PLFZT	0	0.02	285
1230	PFZT	0.13	0.31	1252
	PLFZT	0.007	0.04	578.1

The remnant magnetization ( $M_r$ ) and coercive field ( $H_c$ ) values of the samples sintered at 1200 °C and at 1230 °C decrease with the addition of La ions (Fig. 4 and Tab. 4). The compositional dependence may be attributed also to the presence of the small amount secondary phase, undetected by XRD, in the PLFZT compositions, in good agreement with the previous report by Raevski et al. [33] in the PFT–PT solid solution ceramics.

#### IV. CONCLUSIONS

PZT (Zr/Ti=57/43) ceramics, modified with Fe<sup>3+</sup> and La<sup>3+</sup> and Fe<sup>3+</sup>dopants, have been synthesized by a solid-state reaction process. When the La ion content is adding in the Fe doped PZT, the electrical properties have the tendency showing the increased values ( $\epsilon_r$ ).

#### ACKNOWLEDGMENT

The authors acknowledge the financial support of the Ministry of Research and Innovation, through PN 19310103/ 2019 for making possible the dissemination of these results. The authors are especially grateful to their colleagues Marinescu Virgil and Manta Eugen for their help for SEM micrographs and magnetic measurements.

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