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Preparation and Characterization of PbTi0_3 Ceramics Modified by a Natural Mixture of Rare Earth Oxides of Xenotime

***Jair Baltazar-Rodrigues*[a]*, *Pedro Rodrigues Jr*[a], *Gerson K. da Cruz*[a],**

***Manuel H. Lente*[b], *José A. Eiras*[b]**

[a]*Departamento de Física, Universidade Estadual de Ponta Grossa – UEPG,*
Campus de Uvaranas, Av. Carlos Cavalcanti, CEP 84030-900, Ponta Grossa, PR, Brasil
[b]*Departamento de Física, Universidade Federal de São Carlos – UFSCar,*
Rod. Washington Luis, Km 235, CEP 13565-905, São Carlos, SP, Brasil

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Lead titanate ceramics modified by xenotime (Xm) with nominal composition (Pb, Xm)TiO_3, Xm 10 or 15 mol %, were prepared by the conventional oxide mixture technique. Xenotime is a natural mineral consisting of a mixture of rare earth oxides. Thermal, structural and electric properties were investigated through differential and gravimetric thermal analysis, X-ray diffraction and dielectric measurements as a function of temperature. The results of both compositions revealed a higher density and free of cracks ceramic body, compared to pure $PbTiO_3$ prepared by the same procedure. On the other hand, the structural characteristics and Curie temperature are nearly the same as those of pure $PbTiO_3$. The hysteresis loop measured at room temperature revealed a hard ferroelectric material with coercive field of 10.7 kV/cm and a remanent polarization of 0.2 μC/cm^2. These finding reveal a material with properties that highlight potential to be used as electronic devices that operate at high temperature and high frequencies.

Keywords: *ferroelectric ceramics, xenotime, modified lead titanate*

1. Introduction

Lead titanate $PbTiO_3$ - PT has a perovskite crystal structure (ABO_3) with relatively high Curie temperature (490 °C) and dielectric constant around one order of magnitude lower than those of $BaTiO_3$ – BT (120 °C) or Pb(Zr,Ti)O_3 – PZT (~360 °C). Bulk polycrystalline PT is difficult to be prepared through conventional sintering due to its large spontaneous polarization, which is established when it is cooled below the Curie temperature (T_C). At T_C a cubic to tetragonal phase transition occurs, with large anisotropic thermal expansion (expansion of the unit cell parameters along tetragonal *c* axis and contraction along *a* axis), with tetragonality ratio of *c/a* = 1.064[1]. Due to this high tetragonality ratio the samples tend to crack, breaking the ceramic body.

Substitution of cations in A or B sites in PT composition has been widely studied in order to improve the sintering process, ceramic density and consequently the mechanical strength. Lead zirconate titanate (PZT) solid solutions are an example of high density ceramics, obtained by B-site substitution, in which improved piezoelectric properties and high Curie temperature can be achieved, when compared to BT solid solutions[2,3]. On the other hand, substitution of Pb in A-site of the $PbTiO_3$ perovskite, has yielded ceramics characterized by large electromechanical anisotropy, i.e., a large piezoelectric response in the direction of the poling field compared to the piezoelectric effect in the perpendicular directions[4-9].

Ito et al.[7] and Takeuchi et al.[9] carried out investigations on rare earths modified $PbTiO_3$ ceramics, looking for dielectric, piezoelectric and surface acoustic wave (SAW) properties of (Pb,Ln) (Ti,Mn)0_3 ceramics, with Ln = 0.08 mol% and Mn = 0.02 mol%, where Ln = La, Ce, Pr, Nd, Sm and Gd. All compositions presented complete solid solutions, in which the increase of the rare earth ionic radii promoted reduction in the Curie temperature accompanied by increase in the dielectric constant, in the surface acoustic wave (SAW) velocities, in the electromechanical coupling factors and frequency constants.

Garcia and Eiras[10] studying the addition of La and Mn into $PbTiO_3$ ((Pb_{1-x},La_x) (Ti_{1-y},Mn_y)0_3 ceramics with x = 0.025; 0.05;.0.10; 0.15; 0.20 and y = 0.00; 0.01), showed that as the La content increases the relative dielectric constant increases, while Curie temperature decreases. Otherwise, the addition of the Mn improves the sample densification without substantial effects on these properties.

However, the addition of isolated rare earth to PT composition can be expensive due to the high costs of the separation process of each element from the minerals. Some experiences using rare earth oxides of xenotime were successful to prepare superconductors ceramics[11,12]. Xenotime is a phosphate that contains the oxides of heavy rare earth elements (from Gd to Lu), where Y, Yb, Er, and Dy oxides are the elements with higher concentration, as shown in Table 1[13,14]. These elements show ionic radii close to 18% smaller than the Pb ionic radii. It is well known that significant solubility takes place for differences up to 15% between ionic radii of the exchanged ions and

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*e-mail: jbr@uepg.br

Table 1. Rare earth oxides content in xenotime.

Element oxide	mol %	Element oxide	mol %
CeO_2	0.07	Lu_2O_3	2.59
Pr_6O_{11}	0.01	Y_2O_3	44.71
Dy_2O_3	10.20	Nd_2O_3	0.03
Ho_2O_3	3.13	Sm_2O_3	0.24
Er_2O_3	13.64	Eu_2O_3	0.03
Tm_2O_3	2.84	Gd_2O_3	1.14
Yb_2O_3	19.98	Tb_4O_7	1.39

decreases for greater differences[3,15]. This suggests the that the rare earth ions can only substitutes the only A-sites in the ABO_3 perovskite. As some of these elements may not completely substitute Pb atoms in the PT composition, due to the ionic radii difference, some small additional phases may be segregated.

This work purposes is to investigate the synthesis of Xm modified $PbTiO_3$ – PXT ceramics using the conventional oxide mixture method. Thermal differential and thermal gravimetric analyses have been used to identify phase formation and to determine the appropriated calcination temperature for the PXT powders. Furthermore, structural and dielectric properties of the ceramic bodies were investigated through X-ray analysis and capacitance measurements. Experimental results are compared to some of those reported for pure and modified PT.

2. Experimental Procedure

Xm modified $PbTiO_3$ – PXT ceramics were prepared through the conventional oxide mixture method, starting with Xm, and high purity PbO and TiO_2 oxides as precursors. The amount of each oxide was calculated considering the nominal formula $(Pb_{1-x.}Xm_x)TiO_3$. In this procedure it is assumed that each rare earth element of the mixture replaces lead atoms. However, to maintain the structure neutrality, for each two Xm^{+3} atoms incorporated one Pb^{+2} vacancy is created. Therefore, according the nominal formula, an excess of lead oxide (equal to x/2) will be present in the compositions, taking into account only substitution of Pb by Xm atoms. Therefore, the increase in Xm contents in the composition increases PbO excess in the compositions.

Samples were prepared using 10 or 15 mol% Xm contents to investigate the influence of the rare earth oxide concentration (REO) in dielectric and ferroelectric properties of the ceramics.

The REO (Xm), extracted from mineral xenotime originated from Pitinga mine, in Brazil, consists of a mixture of heavy rare earth oxides, with the concentrations shown in Table 1.

The mixed oxides were submitted to wet ball milling for 3 h. Some amount of these powders was separated for differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). Following the data extracted from DTA - TGA analysis, the powders were calcined at 550 ºC for different times in order to obtain intermediary phases formation before a complete solid state reaction of the oxides. After milled, dried and grounded the powders were calcined for 3 h at 1000 ºC in air atmosphere. The calcined powders were reground in wet ball milling for 3 h. After drying the calcined powders were mixed with 1.5 mass% of polyvinyl alcohol (PVA) binder. Pellets of approximately 15 mm in diameter and 1.4-2.0 mm in thickness were pressed uniaxially at 200 MPa and isostatically at 400 MPa. The pressed pellets were sintered at 1050 °C, 1100 °C and 1150 °C for 3 h, inside a closed alumina crucible, under rich lead oxide atmosphere to prevent lead oxide loss of the green ceramics. The sintered pellets were lapped to make their surfaces flat and parallel with thickness of approximately 1mm. For electric measurements, silver electrodes were painted on both faces of the pellets and fired at 400 °C.

The X-ray analysis using CuK_α radiation was performed on calcined powder and on a PXT15 powder, obtained from a pellet sintered at 1150 °C that was fractured, ground and stress relaxed by thermal treatment at 400 °C for 30 min. The relative dielectric permittivity k was determined through capacitance measurements performed at 1.0 kHz, and calculated by equation

$$k = C.d/\varepsilon_o.A, \tag{1}$$

where C is the capacitance, d is the sample thickness, A is the sample area and ε_o is the vacuum permittivity. Additionally, dissipation factors (tgδ) were measured too. These measurements were performed using a LCR meter, Minipa model MXB - 820.

The $(Pb,Xm)TiO_3$ phase transition temperatures were determined through measurements of capacitance versus temperature, in a homemade system. The variation of polarization and coercive field of the PXT samples was recorded at 10 Hz with modified Sawer Tower circuit at room temperature.

3. Results and Discussion

Figures 1 and 2 shows the DTA - TGA curves of the mixture of PbO, TiO_2 and Xm powders, where Xm concentrations are 10 or 15 mol%, respectively. The DTA curve in Figure 1, of $Pb_{0.9}Xm_{0.1}TiO_3$ – PXT10 composition shows exothermic peaks at 265 °C, 355 °C, 650 °C and 855 °C, and an endothermic peak at 860 °C. The first exothermic peak and corresponding weight loss, shown by the TGA curve, at 265 °C, is related to oxidative decomposition of the organic material present in the composition. The second exothermic peak and corresponding weight loss, at 355 °C, is associated to solid state reaction of PXT powders, as well as the beginning of crystallization and release of oxygen excess. This reaction was confirmed by X-ray analysis, as will be discussed below. The third one is an exothermic peak around 650 °C, without weight loss, associated to a minor phase formation of $Y_2Ti_2O_7$, confirmed by X-ray analysis on this composition, shown in Figure 3b. The fourth is an exothermic peak at 850 °C, without weight loss, associated to a complete formation of the PXT phase, and the fifth one is an endothermic peak at 860 °C related to the start of the volatilization of PbO excess present in the composition[16], as shown by TGA curve in Figure 1.

The DTA curve in Figure 2, for $(Pb_{0.85}Xm_{0.15})TiO_3$ – PXT15 composition, shows the same exothermic and endothermic peaks, at the same temperatures, as shown in Figure 1 for PXT10. The weight loss of PXT15 shown by TGA curve is the same as PXT10. The difference between the two measurements is the amount of weight loss. For PXT10 the weight loss is near 3% at 400 °C and near 3.5% at 1000 °C, as shown in Figure 1, while for PXT15 it is around 4% at 400 °C and close to 4.5% at 1000 °C (Figure 2). The weight loss is greater for composition with larger concentration of Xm because xenotime components are trivalent and lead is divalent, so when two atoms of xenotime components are introduced into PXT composition, three atoms of lead are released due to ionic nature of the composition.

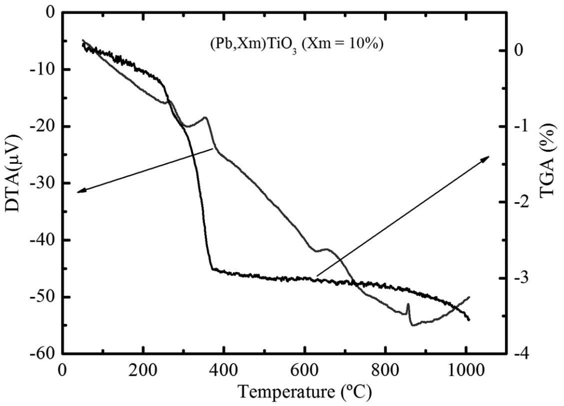

Figure 1. Differential (DTA) and thermogravimetric (TGA) analysis of the PXT10 powders mixture.

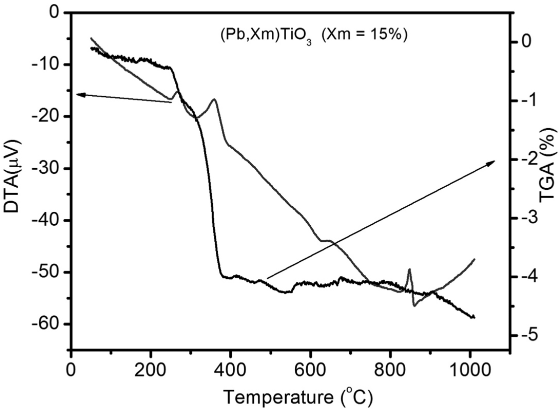

Figure 2. Differential (DTA) and thermogravimetric (TGA) analysis of the PXT15 powders mixture.

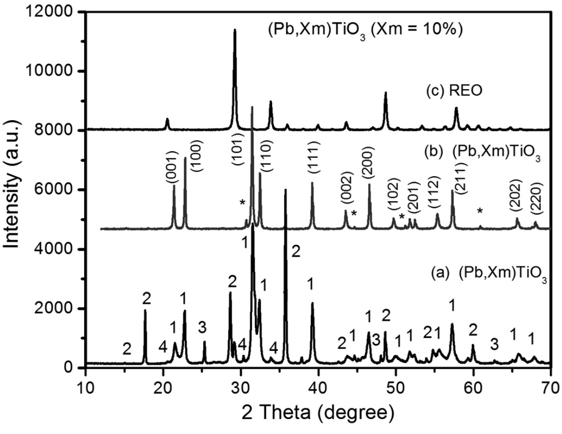

Figure 3. X-ray diffraction pattern of the powders: (a) PXT10 calcined at 550 °C, where (1) identifies PXT phase; (2) PbO; (3) TiO_3; (4) Y_2O_3; (*) pyroclore phase; (b) PXT10 calcined at 1150 °C and (c) Rare Earth Elements of Xenotime (REO).

Figure 3 shows the XRD patterns for the PXT10 powder calcined at different temperatures and of the REO powders. Figure 3a shows the X-ray pattern of the PXT10 powder calcined at 550 °C, where it is possible to recognize the presence of the PXT phase, PbO phases (litharge and massicot, TiO_2 and a small amount of Y_2O_3 phase. Figure 3b shows the X-ray pattern of PXT10 powder calcined at 1000 °C. At this temperature of calcination takes place a complete solid state reaction of all elements of the composition, including the incorporation of PbO and TiO2 phases, which were not completely incorporated during calcinations at 550 °C. Figure 3c shows the X-ray pattern of xenotime powder, which is dominated by diffraction peaks of elements with major concentrations in the mixture of REO. These elements show a cubic unit cell, and they are: Y_2O_3 showing lattice parameters **a** = 10.598 Å (PDF card # 86 – 1326), Yb_2O_3 showing lattice parameters **a** = 10.434 Å (PDF card # 41 – 1106), Er_2O_3 showing lattice parameters **a** = 10.582 Å (PDF card # 43 – 1018) and Dy_2O_3 showing lattice parameters **a** = 10.667 Å (PDF card # 9 – 197). The X-ray pattern of xenotime obtained in this work is consistent with that of Vernilli et al.[17].

The PXT15 powder calcined at 550 °C present a similar X-ray pattern as the PXT10. Figure 4 shows the X-ray patterns for the PXT10 and PXT15 powders calcined at 1000 °C. Also, in this case the two patterns are similar, including the occurrence of a small amount of the pyroclore phase $Y_2Ti_2O_7$. This pyroclore phase was attributed to a small amount of Y_2O_3 not incorporated in the composition during calcinations at 550 °C, and that crystallize at 650 °C, as shown by DTA – TGA analysis of the two PXT compositions. Additionally, a residual PbO phase (peaks at $2\theta = 28.89°$ and 35.5°) remains unreacted.

The occurrence of PXT10 and PXT15 phases from mixed PbO, TiO_2 and Xm powders, calcined at 550 °C, demonstrated by X-ray analysis in Figure 3a corroborates the DTA-TGA analysis shown in Figures 1 and 2, where it is possible to observe between 300 and 400 °C a reaction correlated by mass loss and exothermic peak, demonstrating solid state reaction of PXT. A comparison between diffraction patterns for PXT powders calcined at 550 °C and 1000 °C, Figure 3a, b, confirms that PXT is the phase already formed at 550 ºC. This confirms the assumption about the PXT phase crystallization in the DTA – TGA analysis. Furthermore, the X-ray peaks of REO in Figure 3c do not appear in the X-ray pattern of PXT calcined at 550 °C. This indicates that REO was fully incorporated in the composition during the calcination process at 1000 °C, except for the small amount of Y_2O_3, indicated in Figure 3b.

The PXT10 powder calcined at 1000 °C show a tetragonal symmetry with lattice parameters = 3.899 Å

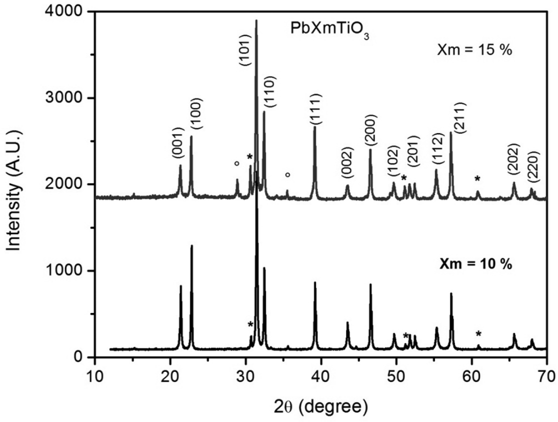

Figure 4. X-ray diffraction patterns of PXT10 and PXT15 powders calcinated at 1000 °C, where (*) represents pyroclore phase and (°) PbO phase.

and = 4.157 Å and tetragonality ratio (/) = 1.066. For PXT15 powder calcined at 1000 °C also a tetragonal symmetry was determined, with lattice parameters = 3.902 Å and = 4.160 Å and tetragonality ratio (c/) = 1.066. The tetragonality ratios were calculated using peaks associated to the Miller indices (100), (001), (200) and (002). These results revealed a typical tetragonal phase, like that of pure PT composition[1], for which the *c*/*a* is equal 1.064. Surprisingly, even increasing the amount of the REO content in the composition the tetragonality factor does not change for the PXT samples.

As observed by Ito et al.[7], decreasing the ionic radii of rare earths atoms introduced in PT compositions, there is an increase in the lattice parameter and a slight decrease in the parameter. In the xenotime composition, elements with major concentration (Y, Yb, Er and Dy) are the ones that have smaller ionic radii when compared to Pb. This could explain why PXT composition showed lattice parameters , and tetragonality ratio (/) close to those of pure PT powders. Conversely, the other elements of xenotime showing larger ionic radii and lower concentration in the mixture should cause contrary effects in the PXT lattice parameters. However, as the concentration of these elements can be considered negligible their effect in the PXT lattice parameters seems to be irrelevant.

The PXT10 and PXT15 powders were uniaxially pressed in pellet samples with diameters of 15.0 mm. Next, these pellets were isostatically pressed and the sample diameters reduced to 14.2 mm. These pellets were sintered at three different temperatures: 1050, 1100 and 1150 °C. The sample densifications after sintering were monitored through samples density, calculated by geometrical method (Table 2). For PXT10 powder a unit cell volume of 63.196 Å^3 was obtained and a theoretical density of 7.576 g/cm^3, whereas for PXT15 was 63.335 Å^3 and 7.295 g/cm^3, respectively.

The geometrical densities for PXT10 sintered at 1050, 1100 and 1150 °C were 79.6%, 85.5% and 90.9% of the theoretical density, respectively. While for PXT15 sintered at 1050, 1100 and 1150 °C the geometrical density were of 85.8%, 91.4% and 95.3% of the theoretical density, respectively.

Table 2. Sintering temperature, density, relative dielectric permittivity and dissipation factor of (PbXm)TiO$_3$ ceramic compositions.

Sample	Sintering Temperature (°C)	Density (g/cm^3)	*K*	*Tg*δ
PXT10	1050	6.04	-----	-------
PXT10	1100	6.48	156	0.036
PXT10	1150	6.89	157	0.031
PXT15	1050	6.26	-----	-------
PXT15	1100	6.67	156	0.040
PXT15	1150	6.95	163	0.030

The PXT10 and PXT15 compositions show the highest densification for sintering temperature of 1150 °C, being the PXT15 densification greater than that of PXT10. This is due to a higher lead substitution in PXT15 than in PXT10, which generates more defects in PXT15 and affects the kinetics of crystallization during sintering[16,18]. The X-ray pattern of PXT15 sample obtained for a sample sintered at 1150 °C is similar to that of the powder calcined at 1000 °C, except for the small amount of PbO remaining in the calcination procedure. This is an indication that at this sintering temperature the PbO phase was incorporated in the composition or volatilized.

The dielectric characterizations were not performed in the samples of PXT10 and PXT15 sintered at 1050 °C, because phase segregation was detected. Conversely, for PXT10 and PXT15 pellets sintered at 1100 °C and 1150 °C, the capacitances and dissipation factors were measured simultaneously at room temperature. The relative dielectric permittivity was calculated with equation 1. The relative dielectric permittivity and dissipation factor values for PXT10 are 157 and 0.031, while for PXT15 they are 163 and 0.030, respectively (Table 2). The values of relative dielectric permittivity for PXT are lower than those of the pure PbTiO$_3$, estimated in ≈ 200, or solid solutions based in PT[3], as PLT and PZT, whose values in general lie between 200 and 1000.

The dissipation factor values are reduced when sintering temperature increases from 1100 to 1150° C. The reduction of the dissipation factor indicates that these samples reached an improvement in homogeneity, just because a high dissipation factor is an indication of defects in the structure, composition deficiency or spatial charges[15].

The Curie temperature was determined in PXT samples sintered at 1150 °C through dielectric measurements as a function of the temperature. These samples were selected because of their higher densities and lower dissipation factors, compared to the samples sintered at 1100 °C. In Figures 5 and 6 were shows relative dielectric permittivity as a function of the temperature for PXT10 and PXT15, respectively. For both compositions the Curie temperature, corresponding to a ferroelectric to paraelectric phase transition (tetragonal to cubic), is around 480 °C. The PXT10 sample shows a strong influence of conductive contributions in the dielectric permittivity values, mainly at temperatures beyond the phase transition point, as shown in Figure 5.

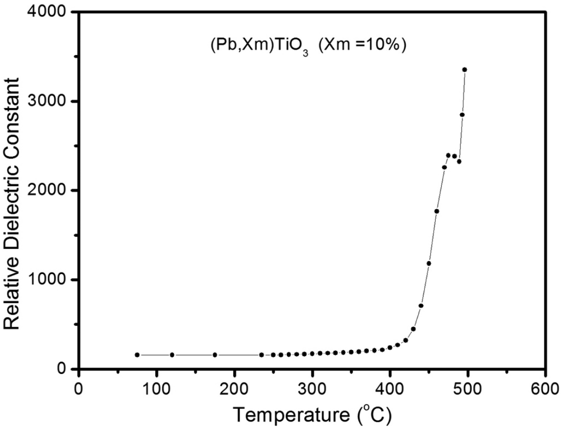

Figure 5. Relative dielectric permittivity as a function of temperature for PXT10 sample sintered at 1150 °C.

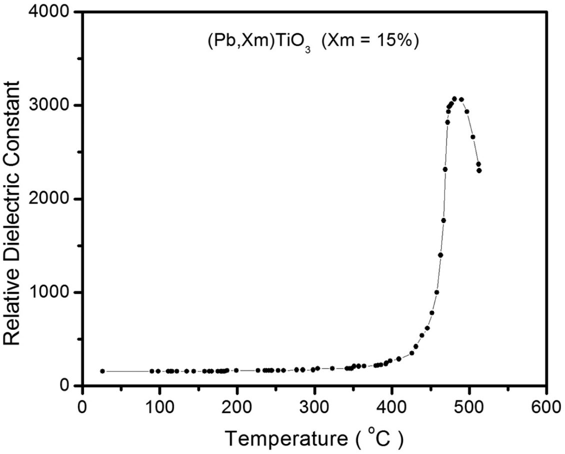

Figure 6. Relative dielectric permittivity as a function of temperature for PXT15 sample sintered at 1150 °C.

The occurrence of higher conductive contribution in the PXT10 samples is not yet clear, since processing, structure, densification and dissipation factors are practically the same for both samples.

The PXT phase transition temperatures are close to that of the pure PbTiO$_3$ composition (490 °C), while for the majority of compositions based on PT[3], this temperature is below 400 °C. That means, even with the addition of 10 to 15 mol% REO to the PT, the Curie temperature did not decrease as it commonly occurs with other dopants. This is an indication that PXT ceramics are a potential candidate to be used in high temperature and high frequency applications.

The hysteresis loop measured at room temperature in the PXT15 sample, sintered at 1150 °C, is presented in Figure 7.

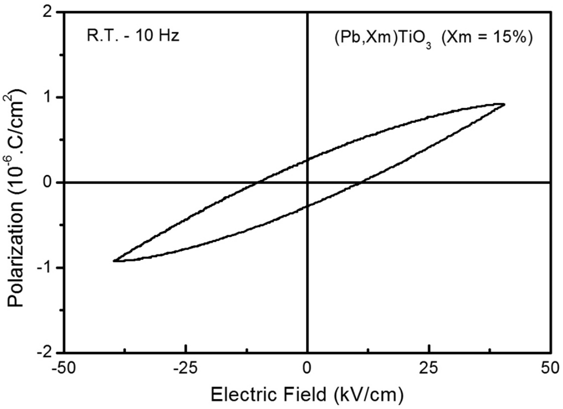

Figure 7. Hysteresis loop measurements performed at room temperature in the PXT15 sample sintered at 1150 °C.

The results revealed a coercive field of 10.7 kV/cm and a remanent polarization of 0.2 μC/cm^2. The hysteresis loop points out to a hard ferroelectric material, requiring high DC electric fields and high temperature to be poled.

Due to its large tetragonality ratio (*c*/*a*) it may impose an increase in the electromechanical anisotropy, as observed by Ravender Tickoo[19] for (Pb,La)TiO$_3$ compositions. Further studies are in progress focused on the poling of PXT samples. Also, new studies are being carried out to determine the specific mechanism that reduces the dielectric permittivity and increases the Curie temperature of these compositions.

4. Conclusions

Lead titanate ceramics modified with 10 and 15 mol% of a natural mixture of rare earth oxide of xenotime were prepared by conventional technique and the samples obtained were dense and free of cracks ceramic bodies. PXT compositions show low relative dielectric permittivity and high Curie temperatures, compared to others based PbTiO$_3$ ceramics compositions, features that are important to produce piezoelectric devices for operate at high frequencies and high temperatures.

The dielectric permittivity and Curie temperature values of PXT ceramics pointed out a very low sensibility of these compositions to different xenotime contents, confirmed by similar properties of PXT10 and PXT15 compositions.

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