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Synthesis of PZT Ceramics by Sol-Gel Method and Mixed Oxides with Mechanical Activation Using Different Oxides as a Source of Pb

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1. Introduction

Lead titanate zirconate is a ferroelectric material that presents excellent piezoelectric and pyroelectric properties, applied to actuators transductors and generators. Despite of the study of new lead-free ferroelectric materials that are being studied nowadays, few of these can compete with the properties of PZT (Aman et al., 2010; Ky et al., 2010; Sawawuchi,1952; Shrout & Zhang, 2007; Wei et al., 2010; Zhang et al., 2010; Zhou et al.,2004.

It is well known that within the different compositions of PZT (Zr/Ti) the compositions closer to the morphotropic line (composition 53/47) show the best ferroelectric, piezoelectric and pyroelectric properties (Jaffe et al., 1954). Which has been attributed to the coexistence of a mixture of rhombohedral and tetragonal phases, as well as to the existence of a monoclinic phase (Noheda et al., 2000). The width of the morphotropic phase boundary varies and depends on the homogeneity of the composition, the synthesis method and the conditions of the mixture processing (Shirane & Takeda,1952a; 1952b; Sooksaen et al., 2008).

Despite the existence of different well established methods for the preparation of ferroelectric ceramics, the necessity of controlling stoichiometry, doping, grain size, porosity, the homogeneity of the obtained phases, the control of the particle size in submicrometric powders, the obtention of thin films through different techniques, as well as lowering costs of processing and utilization of low-toxicity reactives, make important the exploration of variants in synthesis methods (Charles et al., 1992, Gringber & Rappe, 2007, Hammer & Hoffman, 1998, Heywang etal., 2008; Pontes et al., 2004).

There are several routes reported in the literature for synthesis of ferroelectric PZT ceramics (Guarany et al., 2007, Legrand et al., 2007) with the subsequent densification by pressureless sintering in oxygen rich atmosphere. The mechanochemical process is based on mechanical

energy (associated e.g. to high energy ball milling) instead of thermal energy to provide the activation energy for solid-state reaction and has several advantages over both conventional solid-state reaction and wet-chemical processes, including the use of low-cost raw materials, simplicity of the process, and the ability to obtain fine particles (Hurtado-Macias et al.,2008). For instance, some reports show that PZT powders were successfully prepared by mechanochemical synthesis in a significantly shorter time in comparison with literature data, using a planetary ball mill (Brankoviĉ et al., 2003a; Brankoviĉ et al., 2003b; Legrand et al, 2007; Schwartz et al., 2004). However, the mechanosynthesis process, using different kind of high energy ball milling, is a complex process and hence involves optimization of a number of variables that are sensitive to the type of milling process to achieve product phases with Perovskite structures.

In the case of the mixed oxides and posterior calcination and sintering, in this work a mechanoactivation stage is added in the oxides stoichiometric mixture without introducing excess of Pb, through high energy milling, exploring milling times in rough conditions during 4, 8 and 12 hrs in a spex-8000.D mill. Additionally, in this work, despite the traditional method where PbO (litharge) is utilized as source of Pb, the process of obtention of PZT with two additional Pb oxides, that in general are not so frequently used in the literature, PbO_2 (plattnerite) and Pb_3O_4 (minium) are studied. Kinetic studies are performed by means of x-ray diffraction, Rietveld analysis during milling stages (Kong et al., 2008), and thermal treatments at 300ºC (at this temperature the changes obtained in the milling time are manifested), 500, 700, and 900ºC, in compositions near the morphotropic line, 55/45, 53/47, and 52/49 for the three different sources of lead.   According with the phase diagram of PZT, these compositions show rhombohedral phases, a mixture of tetragonal/rhombohedral and tetragonal phases respectively. In this case it t is important to find the best combination of processing parameters to synthesize pure PZT, and compare the results of the mechanochemical synthesis of $Pb(Zr_{53}Ti_{47})O_3$, using different Pb oxides as precursors by carrying out a quantification of the phase contents.

In the case of sol-gel processing and with the purpose of comparing the materials obtained, the same compositions of the oxides mixture combined with mechanicoactivation were sintered. The 2-metoxyethanol route (Zhang et al.,2001) was utilized again without the introduction of lead excess in the stoichiometry of the initial solution. The sol-gel process has been used since it has the advantages of low temperature processing, high purity and very good composition control (Coffman et al., 1994). Sol-gel precursors can be used for the preparation of PZT thin films by spin or dip coating and also for the synthesis of PZT powders, that can be used also for the preparation of bulk samples [11-13]. In this work the 2-metoxyethanol polymeric sol-gel route was used following the method described by Coffman et al (Coffman & Dey, 1994, Coffman et al., 1996) to prepare solutions of PZT precursor, inducing thereafter a gelation stage by adding ethylenglycol and water. Using these precursors it was possible to synthesize crystalline PZT powders at low calcination temperatures. The chosen compositions of PZT were those of Zr/Ti ratios close to the morphotropic phase boundary in both sides of the MPB the tetragonal and romboedric phases (55/45, 53/47, 51/49).

Morphological, structural, dielectric permittivity, hysteresis cycles and Pyroelectric response were conducted, which then are compared with the corresponding results obtained by the oxide mixture and mechanicoactivation for the three different sources of Pb.
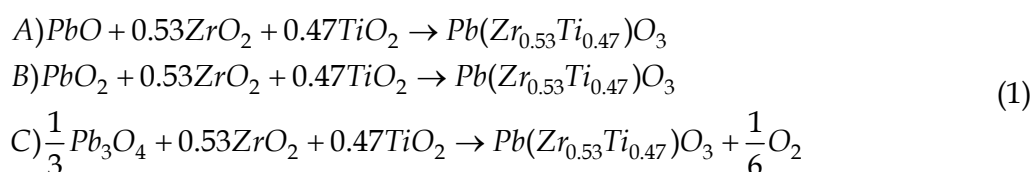
Comparing both routes of synthesis regarding costs, security and speed, the mechanicoactivation route is the most favored, nevertheless because of the purity of the

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powders obtained and the control of the Phases. The sol-gel method is also appropriate, with the problem of the use of the toxic reactive 2-metoxiethanol, which must be handled very carefully, additionally the cost of the precursors utilized is high. However, in this work ceramics with similar characteristics and ferroelectric behaviors in both synthesis routes were obtained.

2. Synthesis of materials

2.1 Mixture of powders oxides with mechanical activation

PZT powders were synthesized by a combination of mechanosynthesis and calcination treatments. Commercial powders of lead oxide (PbO, Fisher Sigma Aldrich 99.9%), lead oxide IV (PbO_2 Sigma Aldrich 97%), lead oxide II-IV (Pb_3O_4, Fermont 99.8%) were used as Pb sources, zirconium dioxide (ZrO_2, Sigma Aldrich 99.9%) and titanium dioxide (TiO_2, Fermont 99.99%) were mixed with the corresponding Pb oxide following stoichiometric ratios to obtain PZT samples with a composition of Zr/Ti=53/47, that corresponds to a tetragonal phase close to the morphotropic phase boundary (MPB). The stoichiometric balance for each lead oxide was done according to Eq. 1.

$$
\begin{aligned}
&A) PbO + 0.53 ZrO_2 + 0.47 TiO_2 \rightarrow Pb(Zr_{0.53}Ti_{0.47})O_3 \\
&B) PbO_2 + 0.53 ZrO_2 + 0.47 TiO_2 \rightarrow Pb(Zr_{0.53}Ti_{0.47})O_3 \\
&C) \frac{1}{3} Pb_3O_4 + 0.53 ZrO_2 + 0.47 TiO_2 \rightarrow Pb(Zr_{0.53}Ti_{0.47})O_3 + \frac{1}{6}O_2
\end{aligned}
\tag{1}
$$

The samples and mixture powders will be identified with the corresponding source of lead oxide A(PbO), B(PbO_2) and C(Pb_3O_4). Powder mixtures in stoichiometric ratio (53/47 composition) were milled at 4, 8 and 12 h with zirconia balls of 1.27×10^{-2} m in diameter in a nylamid cylindrical vial (60×10^{-6} m^3) at room temperature in air atmosphere using a high energy mixer/mill. The charge ratio (CR) was 10:1. Thereafter, the milled powders were uniaxially pressed at 588 MPa to obtain green samples with a diameter of 1.27×10^{-2} m. Calcination treatments were done during 4 h at 300, 500, 700 and 900 °C with a heating and cooling rates of 2 and 5 °C/min, in air atmosphere, respectively.

2.2 Sol-gel method

The synthesis of PZT powders was carried out starting with the precursor solution of PZT prepared by the sol-gel process using the 2-metoxyethanol route following the method described by Coffman et al., (Coffman & Dey, 1994, Corrman et al., 1996). Precursors were prepared using lead acetate, Ti-isopropoxide and Zr-n-propoxide (99.9, 97 and 70% purity, respectively, Sigma-Aldrich), as starting materials. Precursors reaction was activated with 2-metoxyethanol leading to the corresponding metal-methoxyethoxides (lead acetate previously dehydrated) and thereafter the three metal-methoxyethoxides (Pb, Zr and Ti) were mixed and kept in the gelation process adding ethylenglycol and the required amount of water. The gel was dried at 100ºC and heat treated in two stages. The first heat treatment was carried out at 400ºC for two hours with a heating rate of 9°C/min. The obtained powder agglomerates were manually milled in a mortar and then calcined at 850°C for 4h with a scan rate of 9°K/min to promote the formation of the Perovskite structure of PZT. After this second heat treatment, the carbon compounds were eliminated leading to nanometric PZT powders with high purity.

3. Experimental results

3.1 Kinetics aspects in the PZT formation during mechanical milling and thermal treatment

For comparison purposes, the structure of commercial powders used as precursors was characterized by XRD and is shown in Figure 1. Previous to the milling, a mixture of orthorhombic and tetragonal phases was identified in the PbO powder, whereas in PbO_2 and Pb_3O_4, platnerite and minium were identified, both having tetragonal phase. Further on, TiO_2 and ZrO_2 powders showed anatase (tetragonal) and monoclinic phases, respectively. These results are important to identify phase transformations after milling and heat treatments. Figure 1 also shows the structural evolution due to milling at times from 4 to 12 h of all powder mixtures. Increasing the milling time leads to a clear diminution of peaks intensity, which causes difficulties in the quantification of phases. Nevertheless, few comments of clear effects regarding phase transformations are given in this section.
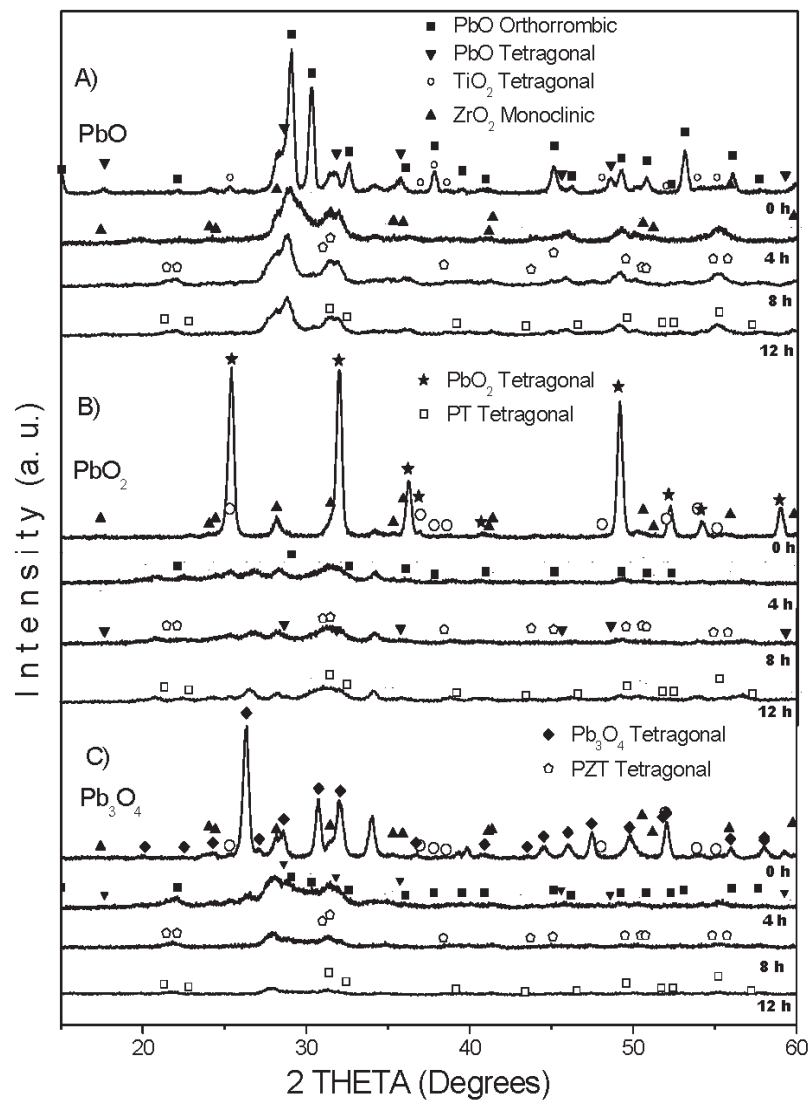
Fig. 1. Evolution of the XRD patterns with milling time of the mixture starting oxides, of three studied set of samples, A) (ZrO_2, TiO_2, PbO), B) (ZrO_2, TiO_2, PbO_2) and C) (ZrO_2, TiO_2, Pb_3O_4)
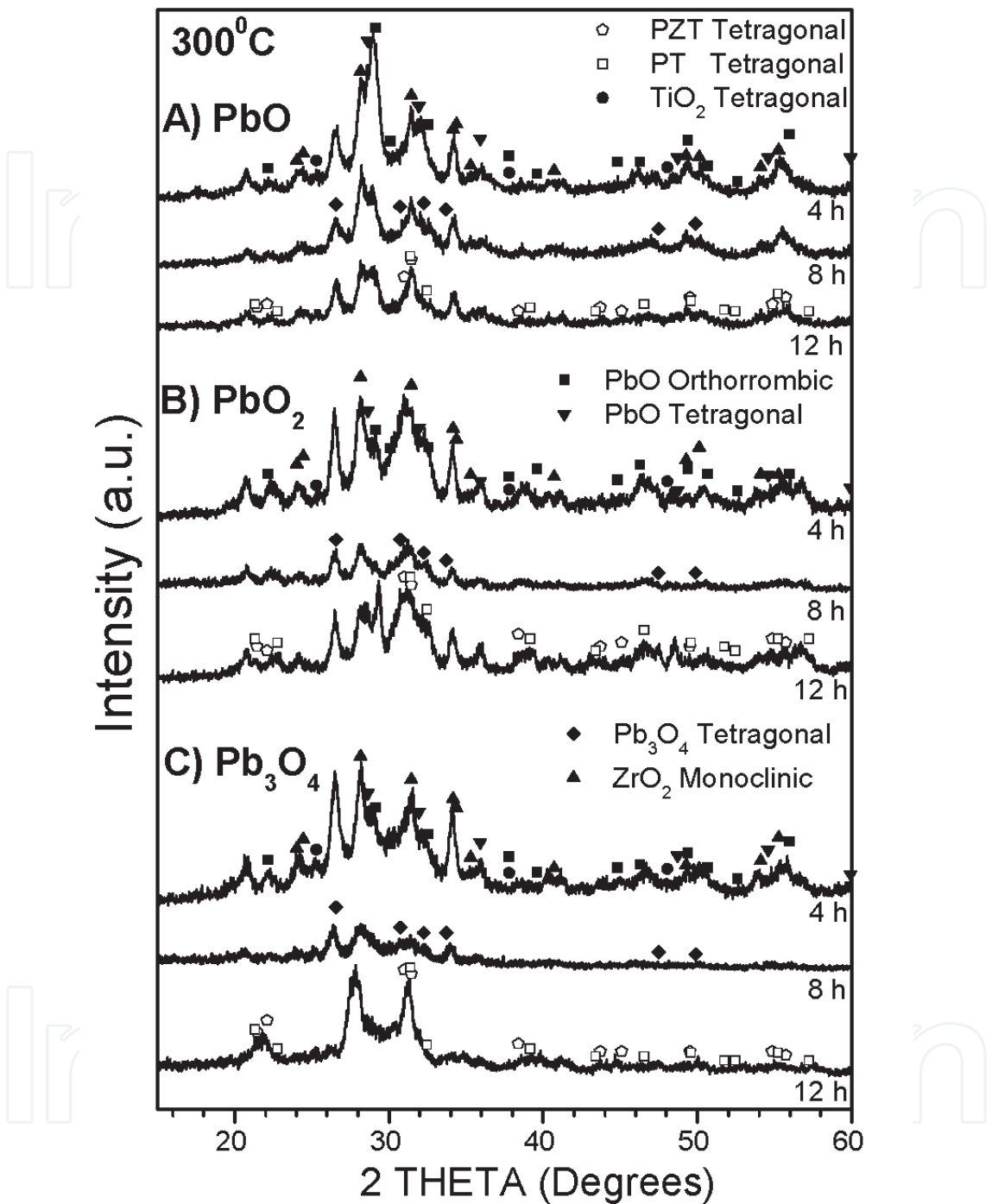
Fig. 2. XRD-patterns evolution of set samples: A (PbO), B (PbO2) and C (Pb3O4). Thermal treatment at 300°C after milling   time at 4, 8 and 12 h

In the case of mixtures with PbO, 4 h of milling are enough to cause almost a full phase transformation from orthorhombic to tetragonal of the PbO powder (PbO-t), which originally showed two phases. For this particular case, at 4h of milling the ZrO_2 powder kept the monoclinic phase and additional peaks can be found around 20, 22, 31-32, 46 and 55-56°

in 2 theta scale. The new peaks are identified with a mixture of PZT and $PbTiO_3$ (PT), both having tetragonal phase. Increasing the milling time causes further transformations, where the correspondent XRD patterns are constituted principally by PbO, ZrO_2 PZT and PT. The powder mixtures prepared with $B(PbO_2)$ before milling show the Platnerite phase (tetragonal phase). After 4 h of milling, the intensity of PbO_2 diffraction peaks are drastically reduced. The XRD pattern has the PbO_2 and ZrO_2 visible as well as additional peaks appearing around 21, 22, 27, 38.8, and 56.5° of 2-theta, which were identified as PZT and PT both in tetragonal phases. Increasing the milling time to 8 and 12 h doesn´t cause further changes in the phase constitution. For the mixture prepared with Pb_3O_4, the XRD peaks show the expected phases corresponding to the starting oxides, Pb_3O_4 (minium, tetragonal phase), ZrO_2 (monoclinic) and TiO_2 (tetragonal). After 4 h of milling the XRD pattern also shows a dramatic phase transformation observed with the diminution intensity of the Pb_3O_4 tetragonal peaks. This effect was completed increasing the milling time to 8 and 12 h. Additional peaks at 22 and 55°, which correspond to the tetragonal phase of PZT already, appear at 4h of milling. At 8 and 12 h of milling the powder mixture is conformed by the PZT, PT and ZrO_2 phases.

Summarizing, in all mixtures, varying the Pb source (PbO, PbO_2 and Pb_3O_4), the mechanochemical activation produces an effect of particle size diminution of the original oxides that causes diminution in intensity of the diffraction peaks, and gives place to small quantities of $PbTiO_3$ and PZT. Heat treatments carried out at low temperatures (300 °C) will be used to further analysis of the influence of milling time on the phase contents in the different powder mixtures, which will be discussed in the next paragraphs.

Figures 2 to 4 show the structural evolution due to thermal annealing (T_a = 300, 500, 700°C and 900°C) for each set of samples after they were milled at (t_m= 4, 8 and 12 hours). As mentioned before, heat treatments at the lowest temperature helps to quantify the effect of milling time, since no dramatic phase transformations are expected at 300°C (Babushkin et al., 1996). For instance, the phase transformation from orthorhombic to tetragonal phases of PbO, which happens by increasing the milling time from 4 to 12 h, already discussed in Figure 1 is herewith confirmed.

Fig. 2 shows the XRD patterns of the samples annealed at 300°C, some peaks are well defined and permit us to identify the phase transformation due to milling effect. For example the Pb_3O_4, ZrO_2, and PbO (orthorhombic) phases are observed in the three set of samples, additionally to PZT and PT presents in the samples without thermal annealing. In the C samples the peaks (100), (110) and (112) at 22, 32 and 56° respectively are best resolved corresponding to the perovskite PZT phase. For t_m=12 h the XRD patterns of samples A and B are constituted by PT, PZT, PbO, Pb_3O_4 and ZrO_2, at difference the C samples show the PT, PZT, ZrO_2 and PbO phases, the Pb_3O_4 phase is not observed.The Rietveld refinement analysis of these patterns clearly revealed the formation of PZT and PT, where the former increases from 7 to 12 wt.% as a function of milling time. The PT content remains constant around 12 wt.% irrespective of milling time. Further on, the PbO-t content diminished (from 15 to 10 wt.%) increasing the milling time, giving place to PT and PZT

Fig.3 shows the XRD patterns for the set of samples annealed at 500°C. At this temperature the formation of PZT phase independently of the previous milling time is clearly observed. Although significant differences among these set of samples are observed. The A samples, besides the PZT phase, show ZrO_2 and PbO phases. The B sample also shows the ZrO_2 and PT phases as well. And the C samples also show the PbO phase, but their peaks show lower intensity than samples A and B at 8 and 12 h.
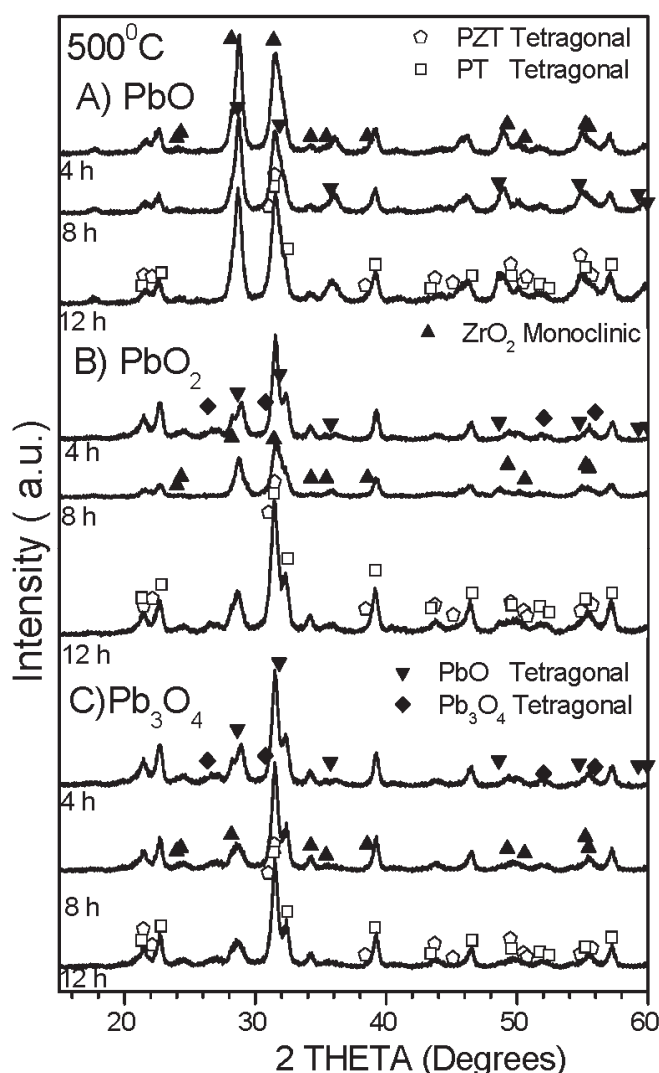
Fig. 3. XRD-patterns evolution of set samples A(PbO), B(PbO$_2$) and C(Pb$_3$O$_4$). Thermal treatment at 500°C after milling time at 4, 8 and 12 h.

Fig. 4a shows the effect of thermal annealing at T_a=700°C. The A samples at 4 and 8 h of milling show the PZT phase (91 and 90 %wt respectively) and a small peak associated with PbO (around 10% wt). At 12 h of milling aside from the PZT phase, the pyrochlore phase (10%wt) is also present, in these sense, long periods of milling in the PbO case give place to the undesirable pyrochlore phase. In the B samples with 4 h of milling, the PZT (97%wt) phase and pyrochlore (3%wt) phase are shown. Nevertheless, in this case there is a reversed effect because at 8 and 12 h of milling only the PZT (94% wt) and PbO (6%wt) phases are present. In the C samples the PZT phase (around 97%wt) at all milling times in its tetragonal phase and a small peak associated with PbO (around 3%wt) are observed. Fig. 4b shows the XRD patterns of the samples annealed at 900°C during 4 hrs. In the A samples at 4 h of milling, only the PZT phase is observed. Additionally At 8 h of milling, the PbO (4%wt) and pyrochlore phases (3%wt) are present. Finally at 12 h of milling, besides the PZT, the PbO phase is also observed. For the set of samples B and C at all milling times the perovskite in its tetragonal phase was obtained.
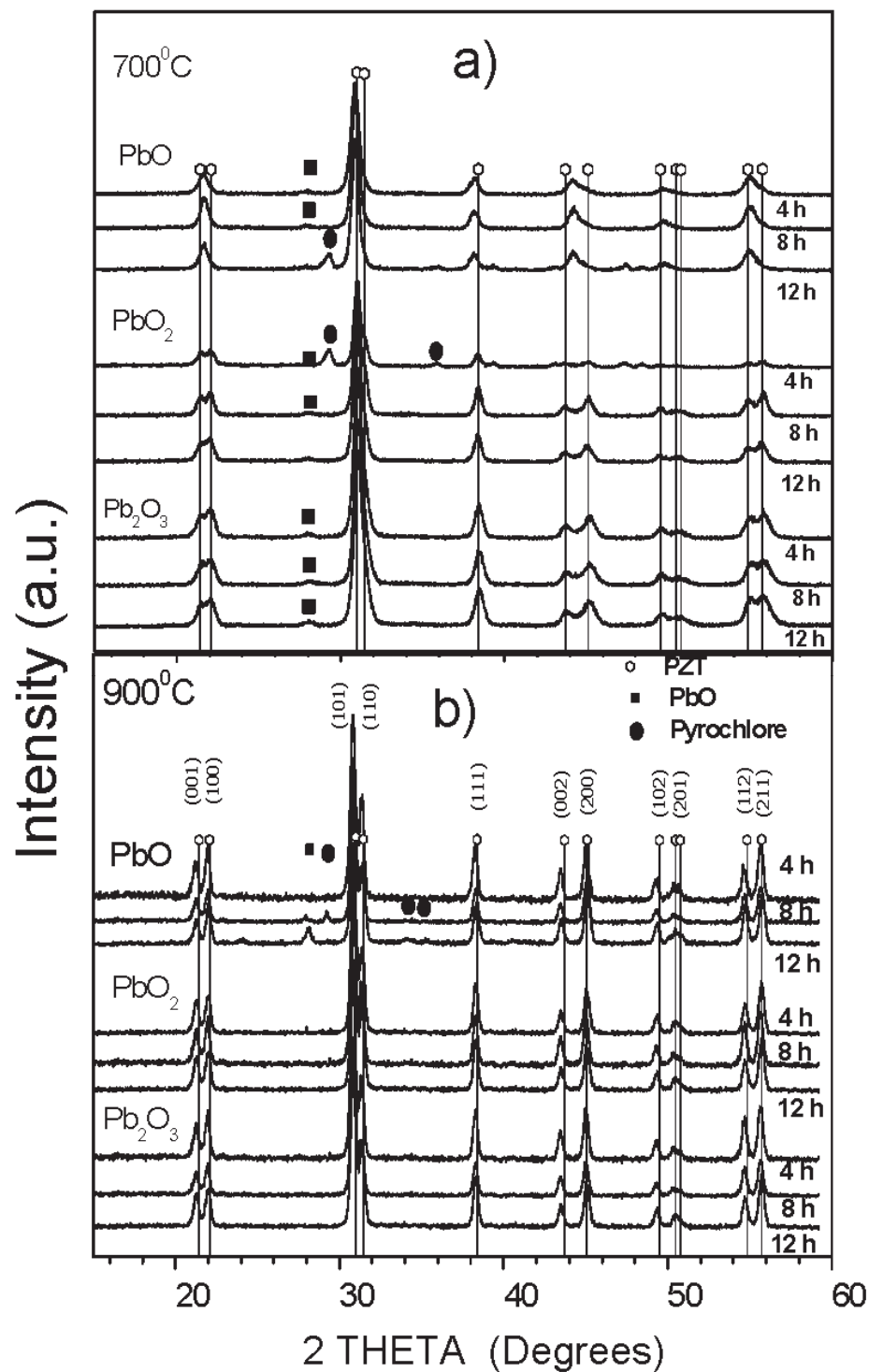
Fig. 4. Evolution of XRD-patterns from the set of samples A(PbO), B(PbO$_2$) and C(Pb$_3$O$_4$). Thermal treatment at a) 700°C and b) 900°C, after milling time at 4, 8 and 12 h.

Fig. 5 shows the representative results of quantitative analysis (obtained by Rietveld analysis) of the evolution of crystalline phases observed during the mechanical milling (4,8 and 12 h) with a corresponding heat treatment at 300 , 500, 700 and 900 °C, for the sample A (PbO), similar results were obtained in samples B and C. On the other hand Figure 6

shows the comparative analysis of the concentrations evolution of ZrO_2 and PZT for the three sets of samples prepared with different lead oxides as a function of thermal treatment after they were submitted to a milling process during 4h.
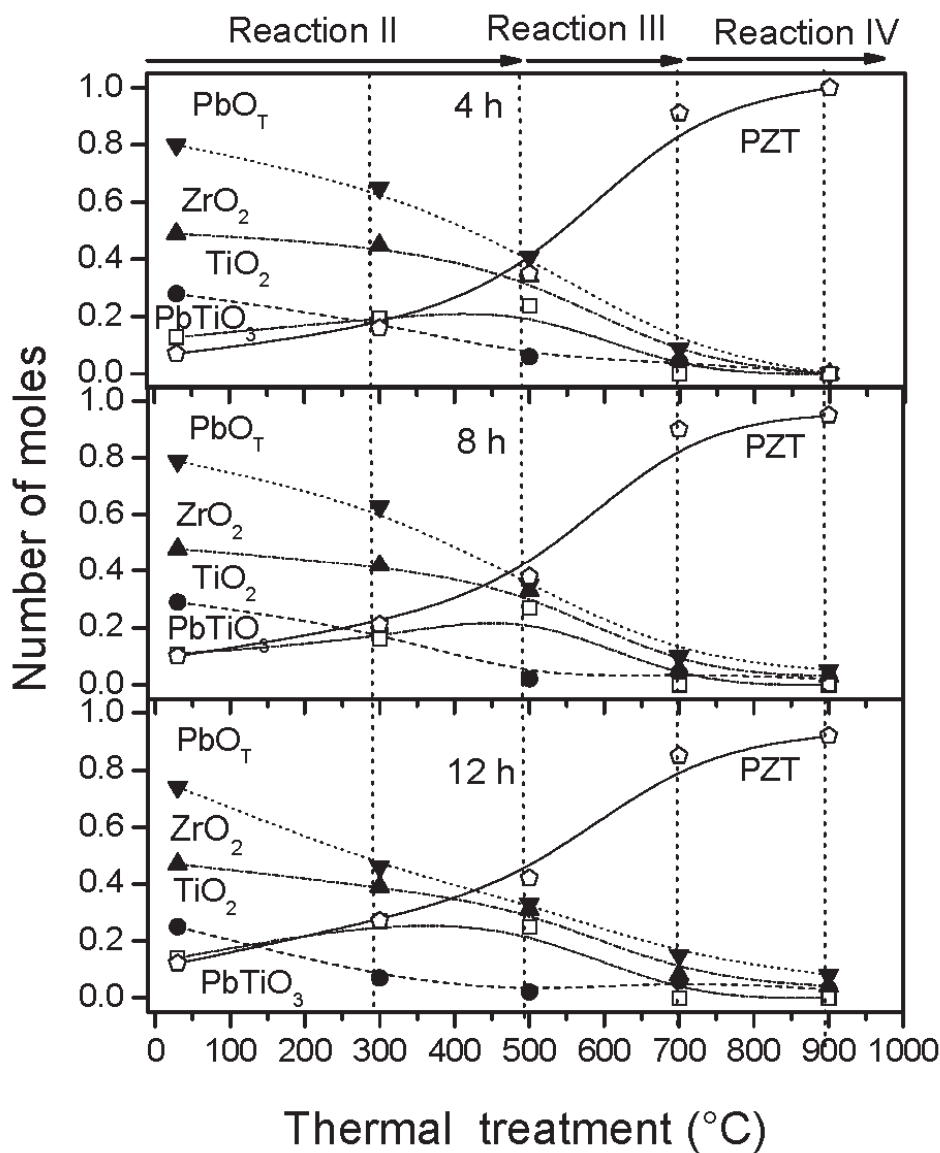
Fig. 5. Evolution concentration of the mixture oxides after 4 h of milling as a function of the thermal treatment in the obtention of PZT using PbO precursor.

The concentration of oxides shown in Figures 5 and 6 at 30 ° C, correspond to the molar amount quantified by the Rietveld method of powder mixture subjected to a grinding 4, 8 and 12 hours without heat treatment, which started from a stoichiometric ratio, depending on the type of oxide used for the composition 53/47 of PZT.

In the work of (Babushkin & Lindbach, 1996) related to the kinetics of formation of PZT obtained by the traditional method of mixing oxides, four regions of transformation are established, which may be susceptible to particle size, impurities and morphology of the starting powders. These regions are defined by the temperatures of treatment as follows:
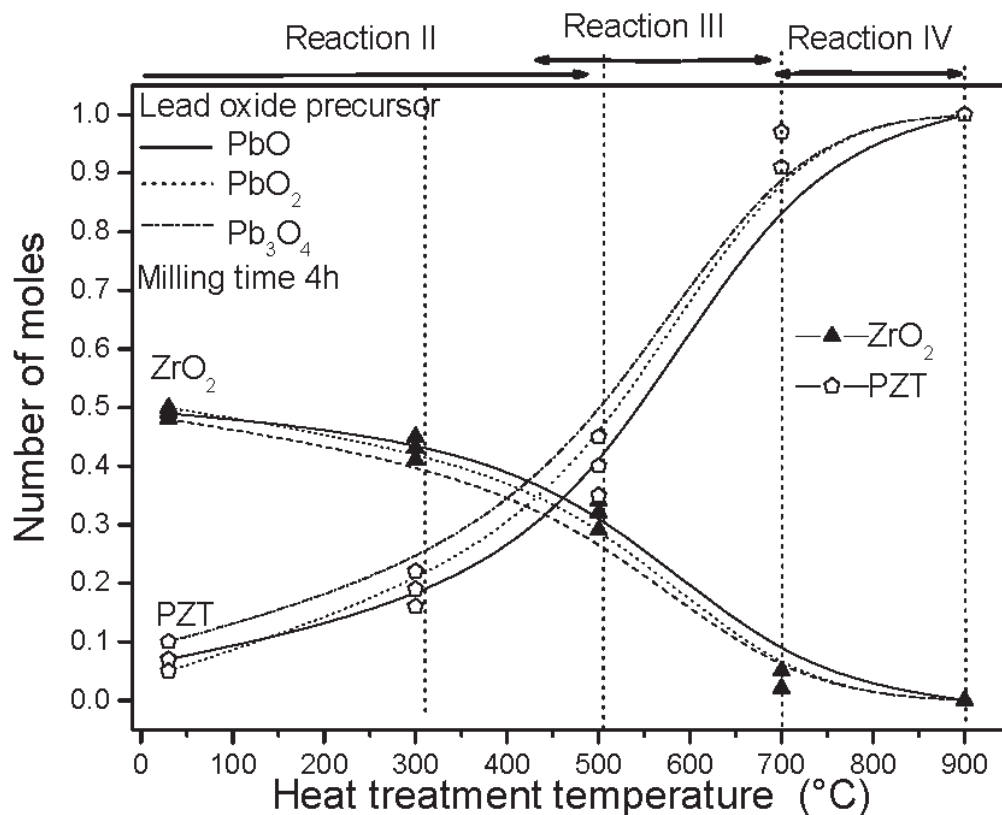
Fig. 6. Evolution concentration of ZrO_2 and PZT as a function of thermal treatment after a milling time of 4 h, for mixture powders with A (PbO), B(PbO$_2$) and (Pb$_3$O$_4$) as source of Pb.

i. (T<350ºC) no reaction is present.

ii. $PbO + TiO_2 \rightarrow PbTiO_3$, from 350 to approx. 630ºC, formation of PT.

iii. $PbTiO_3 + PbO + ZrO_2 \rightarrow Pb(Zr_xTi_{1-x})O_3$ from 650 to approx. 950 ºC, reaction of ZrO_2 and formation of PZT.

iv. $Pb(Zr_xTi_{1-x})O_3 + PbTiO_3 \rightarrow Pb(Zr_xTi_{1-x})O_3$; among 700 and 950 ºC, complete reaction of PZT.

The synthesis of $Pb(Zr_xTi_{1-x})O_3$ by solid state reaction has been reported to be mainly attributed to Pb^{2+} ion diffusion, which is necessarily enhanced by the starting powders ranging from submicrometric to nanometric sizes. The mechanism of reaction starts with the formation of tetragonal $PbTiO_3$, which reaches a maximum at temperatures close to 680ºC, with a subsequent reaction of the remaining ZrO_2 and TiO_2 leading to the complete solid state reaction of mixtures of $PbTiO_3$ and PZT at temperatures above 800ºC.

In the case of oxide mixtures with mechanical activation, the reactions that occur with the milling and heat treatments can be summarized into four stages, following the scheme of (Babushkin & Lindbach) . The first stage is developed during the milling process, and the rest of the reactions of the stage are shown in Figure 5 and 6. The effect of the high energy milling is to lower the temperatures of the reaction in the formation of PZT. The reaction regions observed are the following:

i. Mechanical activation by high energy milling, which leads to phase transformations in the oxide precursors and the formation of PT and PZT with concentrations between 7 and 12% (30 º C).

ii. Increased concentration of PT (17 to 33%) and PZT (16 to 42%), with the reduction of ZrO2 (48 to 35%) in a temperature range from 300 to 500 º C.

iii. $PbTiO_3 + PbO + ZrO_2 \rightarrow Pb (Zr_xTi_{1-x}) O_3$ (increase of the molar concentration of PZT up to 83%) in a temperature range from 400 to 700 º C.

iv. $Pb (Zr_xTi_{1-x}) O_3$ $PbTiO_3 + \rightarrow Pb (Zr_x'Ti_{1-x}) O_3$ PZT complete transformation. (between 700 and 900 º C)

Now, we attempt to compare our obtained results with the the mechanochemical activation by high energy ball milling of the powders respect to the known kinetic process.

After 4 h of milling, a mixture of phases of the starting powders with partially reacted PT and PZT can already be observed. Thus, such milling conditions allow us to have a premature mixture of reactions II and III, which increases with the milling time and happens before any heat treatment. After heat treatments at 700ºC, high PZT concentrations are obtained between 85 to 97% and the full reaction of PZT is already completed at 900ºC. Again compared with the typical kinetic reaction kinetic of PZT, which is typically completed at temperatures higher than 900ºC, the mechanochemical activation allows to lower the calcination temperatures and high concentration of PZT is obtained at 700ºC.

One of the main differences of the results obtained in this study with those reported by (Babushkin, & Lindbach), is that the activation by mechanical milling allows the transformation of phases at temperatures below 350 ° C, including the formation of PT and PZT which appear during milling (at concentrations of 7-12%) and are increased with heat treatments. Typically, the reaction process of ZrO_2 initiates at 650ºC, but the milling step allow (Figures 5 and 6) that in this case starts his reaction from 300 ° C. The formation of PZT and consumption of ZrO_2 with heat treatment is very similar for all three types of samples studied obtained with different types of oxides. From the beginning, the PbO starts to decrease, contributing as zirconia to the formation of PZT. At temperatures between 300 and 500 ° C   the highest concentration of PT is shown, which like the PbO and ZrO_2, after 500 ° C contribute to the formation of PZT, at this temperature there is an appreciable increase in PZT concentration.

3.2 Electrical properties
3.2.1 Hysteresis cycles

Figure 7 shows the curves of hysteresis loops of PZT samples with 53/47 composition obtained by sol-gel method and mixed oxide (PbO and Pb_3O_4 as sources of Pb). Fig 7A) shows that the samples obtained by mixing oxides have a higher remanent polarization than that obtained by sol-gel, and within those obtained by mixture oxides, the sample obtained using Pb_3O_4 has a remanent polarization higher than the sample prepared with PbO.

The coercive fields have very similar values for the samples obtained by sol-gel and that obtained with Pb_3O_4, however the sample with PbO has a higher coercive field. In fig. 7B) it can be seen that the variation of the ratio of the remanent polarization to maximum polarization (Pr / Pm) as a function of applied bias field, has values very similar to the sol-gel samples, and to that obtained with PbO (about 88% for bias fields of 45 kV / cm) . On the other hand the sample with Pb_3O_4 presents values close to 98%, indicating that it virtually retains its polarization value after removing the bias field.
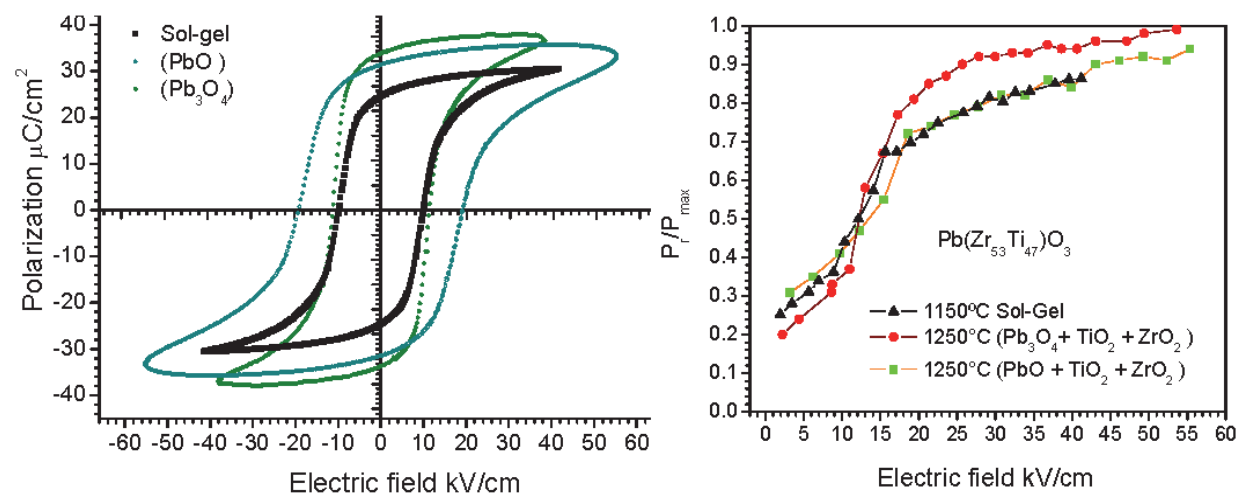
Fig. 7. A) Histeresys cycles for PZT (53/47) samples obtained by sol-gel and mixture oxides using PbO, and Pb_3O_4. B) Evolution of the ratio (Pr/Ps) as a function of the maximum electric field applied in the same samples as in the case of A) .

Table 1 shows the comparative parameters among the PZT samples obtained with oxide mixtures and by the sol-gel method, like the density, remnant polarization, coercive field, Curie temperature. In general, it can be observed that the values of the densification are higher than 93% of the theoretical value; the samples obtained with Pb_3O_4 show higher remnant polarization and lower values of coercive fields and their Curie temperature values are between 388 and 400ºC. From this comparative values it is possible to establish that those samples obtained with Pb_3O_4 showed the best ferroelectric values.

Zr/Ti	Precursor	$T_{sint.}$ (°C)	E_{max} (kV/cm)	P_r ($\mu C/cm^2$)	E_c (kV/cm)	P_r/P_{max}	$\rho(g/cm^3$	T_c (°C))
55/45	Pb_3O_4	1250	27.08	25.55	10.814	0.90	7.52	392
	PbO	1250	27.23	19.13	11.765	0.80	7.48	388
	Sol-gel	1150	34.99	13.18	8.77	0.77	7.83	393
53/47	Pb_3O_4	1250	53.62	34.02	11.301	0.99	7.47	396
	PbO	1250	55.34	31.35	18.045	0.94	7.54	394
	Sol-gel	1150	41.18	34.65	9.89	.87	7.87	396
51/49	Pb_3O_4	1200	33	29.73	10.874	0.89	7.88	400
	PbO	1200	42.11	23.45	10.181	0.82	7.7	397
	Sol-gel	1150	45.4	33.38	11.54	0.86	7.78	400

Table 1. Comparative ferroelectric values of PZT samples obtained with mixture oxides and by the sol-gel method.

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3.2.2 Dielectric function

Figure 8 shows the dielectric permittivity and dielectric loss as a function of temperature for the composition 53/47, obtained atA) 10 kHz and B) 1 MHz. The maximum of the dielectric permittivity is used to estimate the Curie temperature (data showed in Table1), where the samples suffer a phase transition from ferroelectric to paraelectric state. In general, the dielectric permittivity shows a strong dependence on temperature and varies from 1000 at 200ºC to 20000 close to the Curie temperature. The samples obtained by sol-gel and Pb_3O_4 show similar values for 10 khz and 1 Mhz, nevertheless, the sample obtained with PbO shows minor values at 1 Mhz.
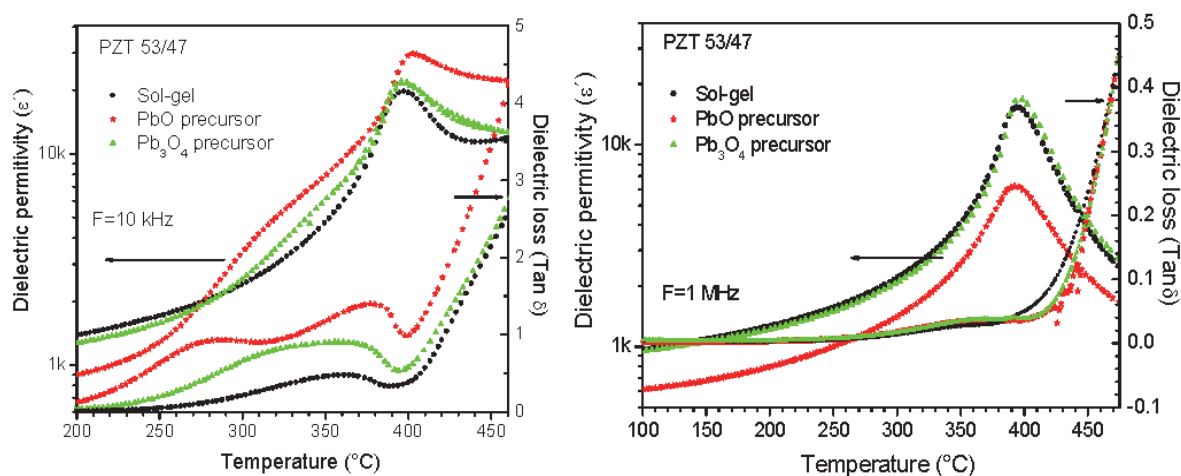
Fig. 8. Dielectric permittivity and dielectric loss of the samples obtained by mixture oxides and sol-gel, composition 53/47 as a function of temperature. A) Curves obtained at 10 khz and B) Curves obtained at 1 Mhz.

It is important to point out here that the samples obtained with PbO_2 although the corresponding structural phase of all compositions of PZT reported here were obtained, the corresponding electrical characterization was not measured, because it shows a high conductivity, due to the high vacancies concentration.

3.2.3 Photopyroelectric response

Figure 9 shows the photopyroelectric signal as a function of the modulation frequency, using a pohotopyroelectric system, (Mandelis & Zver, 1985, Marinelli et al., 1990, Balderas-López etal., 2007) of samples obtained by the sol-gel method and by mixture oxides with mechanical activation. For both set of samples the composition 53/47 shows the higher signal, and the samples obtained by the sol-gel method show a slightly higher signal than the samples obtained by the mixture oxides. For purpose of using these samples as photopyroelectric detectors they have a similar behaviour, nevertheless, the samples obtained by the sol-gel method show best response and it is inferred that they have a higher pyroelectric coefficient.
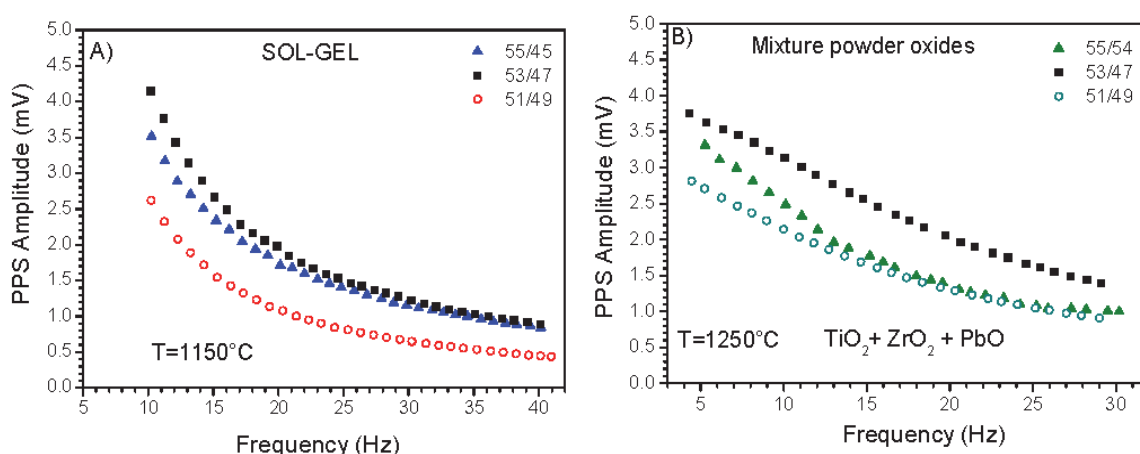
Fig. 9. Pyroelectric response in PZT samples with compositions 55/45, 53/47 and 51/49 obtained by A) Sol-gel method and B) mixture oxides with mechanical activation using PbO as Pb source

4. Conclusion

The mechanical activation stage in the oxide mixtures process is a critical step, since it allowed to obtain PZT ceramics using the common Pb oxides (PbO, PbO_2 and Pb_3O_4) combined with a further thermal treatment. The mechanical activation process produces particle size reduction, promotes the transformation of PbO to its tetragonal phase and the formation of $PbTiO_3$ and PZT, thus decreasing the synthesis temperature of PZT powders. These ceramic powders are homogeneous and with submicrometric size, and therefore highly reactive, this favours the reactivity of ZrO_2, leading to the early formation of PZT (350°C) compared to synthesis temperature of traditional methods. This result is important, since it allows to avoid lead oxide evaporation during the heat treatment for the reaction to form the Perovsquite phases at 900°C.

The mechanism of phase transformation of the mixtures by milling seems to be the compatible with the crystalline structure of the raw materials to the perovsquite structure. PbO in its orthorhombic phase transforms to tetragonal phase during milling, and then the perovskite phase of $PbTiO_3$ and PZT is formed. Increasing its concentration for the thermal treatment from 300°C, 500°C and 700°C. The samples A, B and C at 4h of milling and 700°C of thermal treatment reach concentrations around 91, 97 and 97 % of PZT respectively. A milling time of four hours is the best condition to promote the early formation of PZT in the three set of samples with different Pb oxides.

Comparing both routes of synthesis regarding costs, security and speed, the mechanicoactivation route is the most favoured. Nevertheless because of the purity of the powders obtained, and the control of the phases, the sol-gel method is also appropriate, with the problem of the use of the toxic reactive 2-metoxiethanol, which must be handled very carefully. Additionally the cost of the precursors utilized is high. In this work however ceramics with similar characteristics and ferroelectric behaviours from both synthesis routes were obtained.

5. Acknowledgment

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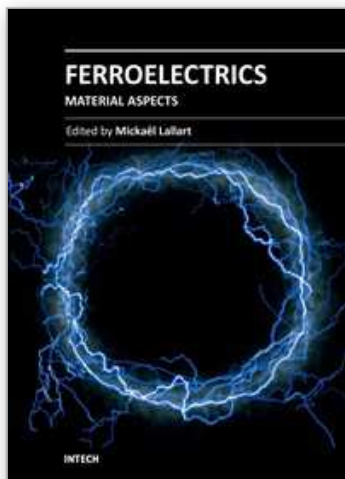
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Edited by Dr. Mickaël Lallart

Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on ways to obtain high-quality materials exhibiting large ferroelectric activity. The book covers the aspect of material synthesis and growth, doping and composites, lead-free devices, and thin film synthesis. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric materials, allowing a deep understanding of the material aspects of ferroelectricity.

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