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THE STUDY OF ANOMALIES IN THE PZT MATERIAL

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ABSTRACT

Lead zirconate titanate $PbZr_{0.52}Ti_{0.48}O_3$ (PZT52) sample was prepared using the conventional solid state reaction. The nanosized PZT52 sample shows a mixture of phases tetragonal and rhombohedral, and a grain size of about 31 nm calculated from the Scherrer equation. The sample sintered at 900 °C for 4 hours showed a diffuse maximum of the permittivity of about 5354 located at the temperature of 412 °C. XPS analysis of the sample reveals the presence of contaminants, and a composition, after sintering, similar to the nominal one.

INTRODUCTION

Lead titanate (PT) is known as ferroelectric perovskite structure ABO_3, with piezoelectric properties, electro-optical and pyroelectric. from M. Kellati, It is known by its first order of Curie transition and a Curie temperature equal to Weiss 490 °C, much higher than the ambient temperature, by its very modest relative dielectric constant of 200, as well as spontaneous polarization $80.10^{-5}cm^{-2}$. It is also known by its tetragonal structure at room temperature. The existence of a structural disorder in compounds with a perovskite structure induces drastic changes in the physical properties of the materials. Substitutions at both A- and B- sites have been used to modify the properties of PT in different research works (for example: Fares Kahoul, Louanes Hamzioui, I.V. Ciuchi, Firas Fouad Abdullah, A. Molak, P. Amonpattaratkit). Which makes it very useful in industry. Especially in electronics, such as ferroelectric nonvolatile memories, piezoelectric transducers, and pyroelectric detectors. The materials like PZT have been the subject of intense investigations. In fact, the PZT appeared in 1954 and is the first major source of ferroelectric perovskite structure. But according to the more or less of titanium or zirconium, mechanical properties, coupling, and dielectric loss of PZT change.

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Thus compositions of PZT near the morphotropic phase boundary MPB has been involved in the manufacture of transducers and constitute their main application. T. Lamcharfi say the appearance of this phase depends mainly on the preparation procedure and the grain size. In this article we are interested in the structural, micro structural and dielectric studies of PZT ceramic which composition is close to that of the MPB phase.

Experimental

Lead zirconate titanate $PbZr_{0.52}Ti_{0.48}O_3$ (PZT52) sample was prepared using the conventional solid state reaction. The first step is to mix the basic oxides by grinding manual and to add pure acetone and to sit for 15 min. After drying and grinding the mixture to another, the second step in the development was the calcination step or the heat treatment of the PZT powder. Finally to get the ceramic sintering step is a necessary step after the forming. The preparation steps were diagrammed in Fig. 1.

RESULTS AND DISCUSSION

XRD pattern of the PZT sample annealed for 6 h at 1000 °C is shown in Fig. 2. Existence of a mixture of phases (that is to say the tetragonal phase and rhombohedral phase) is confirmed, according to T. Lamcharfi, Hongliang Du and A. Bouzid, by the presence of three peaks between position angles 43 ° and 46 °.

The IR spectroscopy (in the range of 4000-400 cm^{-1}) of the PZT52 heat treated at 1000 °C for 6h are presented in Fig.3. In the case of ABO_3 type perovskite compounds, a broad band is observed for each spectrum of about 750 to 400 cm^{-1}, and another band of 400 to 300 cm^{-1}. According to A. Khorsand Zak these bands are related to vibrations of B-O (BO_6 and B-O for ABO_3 structure). The spectrum also shows the presence of a single absorption band centered around 600 cm^{-1}; from K. Bouayad this band shows the vibration of metal-oxygen octahedra ZrO_6 and TiO_6, and from A. Elmesbahi is the signature of establishment of the crystalline phase of PZT. Pure lead titanate has ten active modes between 100 and 800 cm^{-1} (Fig.4), but the addition of zirconium in the titanium site produced a reduction and an expansion of active modes present as well as the disappearance of some other modes in comparison with the pure PT (Fig.5).

found to be about 31 nm for the sample heat treated at 1000 °C. After sintering at 900 °C for 4 h, the PZT powder grain size increased to 2 μm (Fig.6). In addition to the phase transition anomaly produced at 412 °C, spectra of Fig. 7 reveal the presence of a second anomaly at 275 °C. Also, a maximum value of the dielectric constant, equal to 5354, was obtained from this sample and a glass transition temperature of the ferroelectric phase to the paraelectric phase of the order of 412 °C. A bibliographic given on this sample was grouped in Table 1. We can see that, regardless of the preparation method, dielectric constant is intimately linked to the sintering temperature. Over this temperature is high, over the grain size is large, the material is then denser and the dielectric constant is greater. A comparison of our results with the literature also helps to show a link between the sintering temperature and the transition temperature.

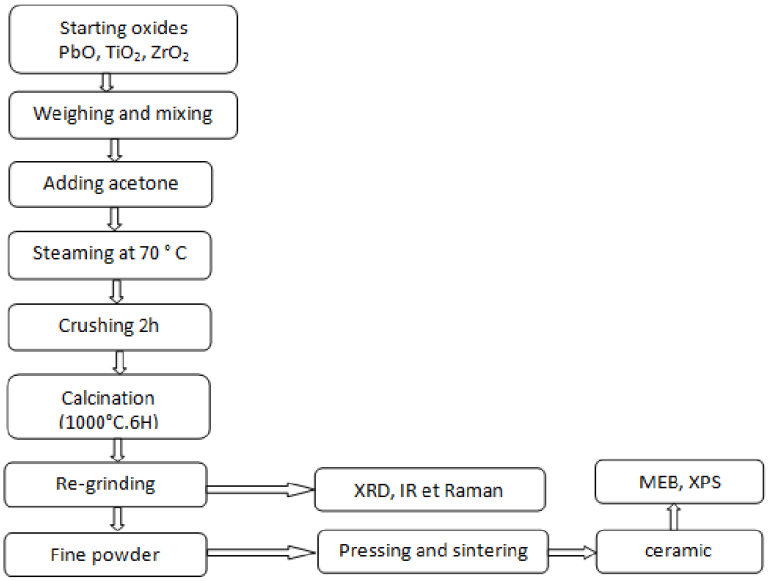

Figure 1. Flowchart of procedure used in the preparation of PZT sample

Table 1. Bibliographic data on the PZT material in the vicinity of the morphotropic phase (□ our samples)

Composition	Synthetic Procedure	Sintering conditions	Tm (°C)	Grain size of the powders (μm)	$\varepsilon_{r\,max}$	Reference
PbZr0.52Ti0.48O3	Voie solide	900 °C/4H	412	~ 0.031	5354	■
PbZr0.53Ti0.47O3	Voie solide	1250 °C/4H	380	---	6500	[S.M. Gupta]
PbZr0.52Ti0.48O3	Voie solide	---	375	---	40000	[E. M. Bourim]
PbZr0.52Ti0.48O3	Hydrothermale	850 °C/2H	362	---	3168	
		1100 °C/2H	352	----	31890	[T. Lamcharfi]
		1200 °C/2H	351		41495	
PbZr0.52Ti0.48O3	Sol gel	1100 °C/4H	~ 378	~ 1μm	23842	[K. Bouayad]
		1200 °C/4H	380	~ 1μm	28532	
		1230 °C/4H	358	~ 1μm	32514	

Table 2. Atomic percentages of the elements present in the sample surface PZT52

Element	Al 2s	C 1s	Ca 3s	O 1s	Pb 4f	Ti 2p	Zn 2p	Zr 3d	Si 2p
Pourcentage atomique	0.86	22.92	0.17	49.43	12.75	3.35	0.26	4.70	5.56

The average particle size of PZT52 is determined by means of the X-ray line broadening method using the Scherrer equation: $D = \frac{K\lambda}{B_{hkl}\cos\theta}$ [A. Khorsand Zak], where D is the particle size in nanometer, λ is the wavelength of the radiation, k is a constant equal to 0.94, B_{hkl} is the peak width at half-maximum intensity and θ is the peak position. The average particle size is

The high temperature sintering made lowers the transition temperature; result corroborated by a study on Nb-doped PZT52 [K. Bouayad]. Low temperature dielectric measurements have revealed the presence to two anomalies in the real part of the dielectric constant of PZT materials near the MPB. The occurrence of the anomaly corresponding to the lowest temperature was imputed to a tetragonal to monoclinic

phase transition which was supported by XRD studies of Noheda *et al*. The presence of such anomaly has also been reported in dielectric studies of PZT materials near the MPB.

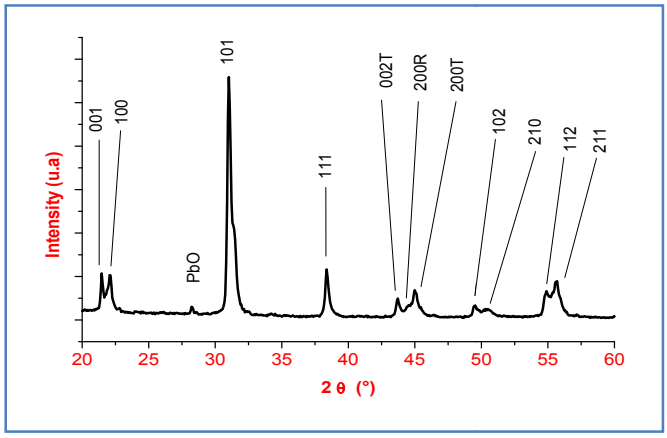

Figure 2. Spectrum of X-ray diffraction of the sample PZT52

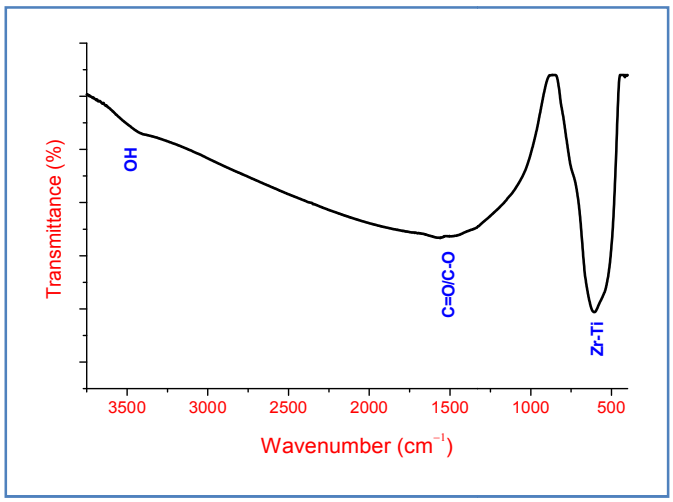

Figure 3. IR spectrum of the sample PZT52

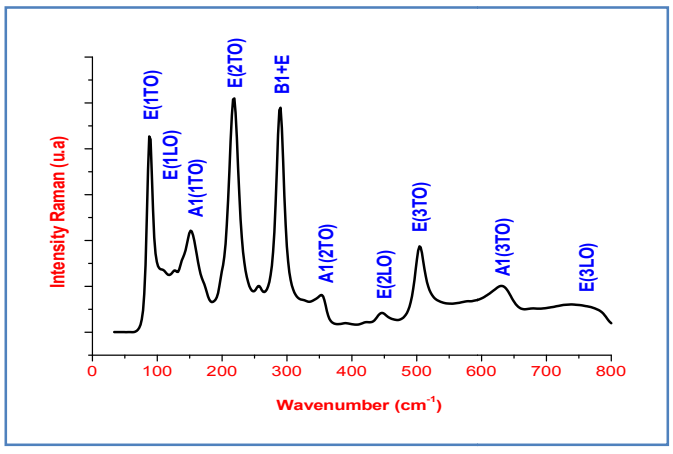

Figure 4. Raman spectrum of the sample PT

Lamcharfi *et al*. (2008) have observed the same anomaly at 262.5 ° C in the hydrothermally prepared PZT52 sample, and have interpreted it as due to intrinsic mechanisms, Bouzid *et al*. (2005) have imputed the presence of two such anomalies in PZT54 prepared by solid state reaction, located at 180 °C and 370 °C, to the transition of the rhombohedral phase to tetragonal phase and to the transition to the tetragonal phase to cubic phase, respectively. Bouayad and all. Its share in allocated the second anomaly observed at 180 °C in the sample PZT52 prepared by the sol-gel method with phase transitions.

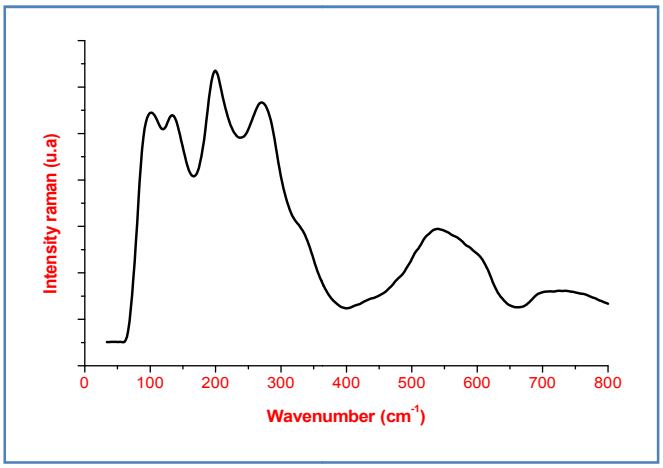

Figure 5. Raman spectrum of the sample PZT52

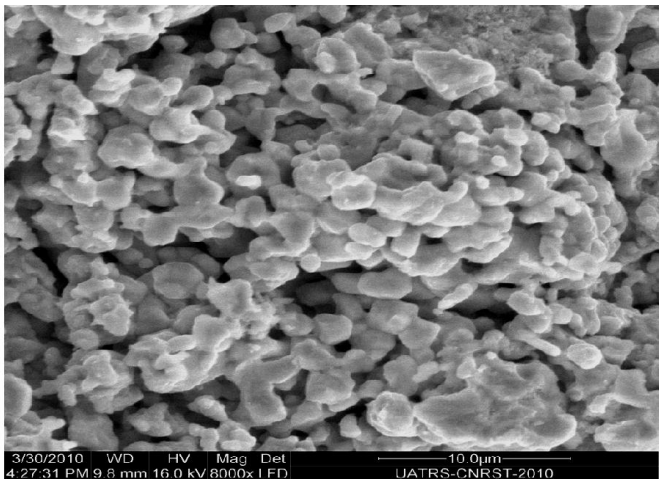

Figure 6. SEM image of a pellet sintered at 900 °C for 4 hours of sample PZT52

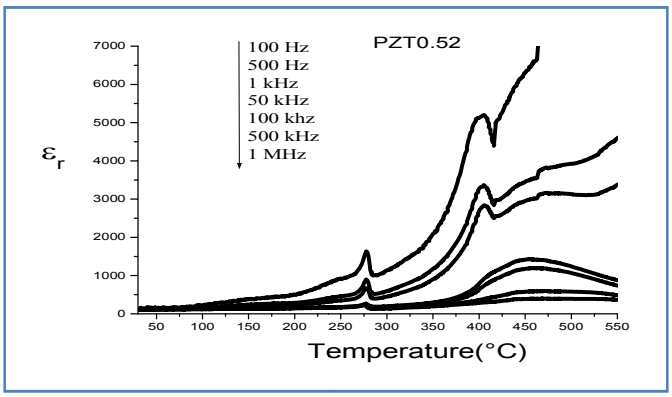

Figure 7. Spectrum of the dielectric constant of the sample PZT52 depending on the temperature

The study by Bouzid and all. on the PZT material, prepared by solid route, on the border of the stage morphotropic, revealed the presence of two phases (tetragonal and rhombohedral) in

the XRD spectrum of the sample PZT54/46 sintered at 1250 °C for 4 hours, and the tetragonal phase in the XRD spectrum of PZT50/50 sample sintered 1250 °C ; The evolution according to the temperature XRD spectra of the sample PZT54 shows a transition stage of the morphotropic (at room temperature) in the tetragonal phase (at temperature 200 °C and 300 °C) and the tetragonal phase (at 300 °C) to the cubic phase (at 371 °C).

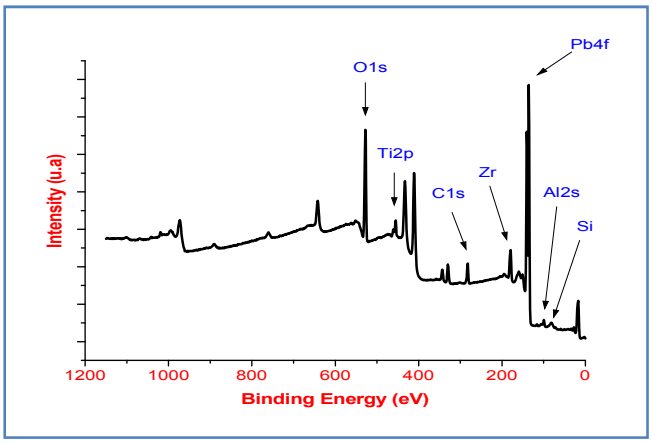

Figure 8. XPS spectrum analysis of the sample PZT52

These results lead us to attribute the anomaly of the dielectric constant observed at 275 °C the transition of the morphotropic phase toward the tetragonal phase. This could be confirmed from the characterization by XRD high temperature by scanning the entire area of 200 °C to 300 °C. The result of XPS characterization, presented in Fig. 8. Consists in a spectrum with several peaks corresponding to the presence of chemical elements on the surface. In addition de-convolution of each peak indicates its chemical affiliations. The atomic concentrations of the various elements on the surface are determined by calculating the area under the peaks corresponding. They are summarized in Table 2.

We observe the presence of elements. We find there: Al, C, Ca, O, Pb, Si, Zn, Ti et Zr. Elements present, except carbon, for their low concentrations, beings are considered contaminants of surfaces. For carbon, the de-convolution of the peak C1s shows the presence of three peaks with very similar energies which are of the order of 285 eV, 286.5 eV and 289 eV, associated according to Lin and Zhu, (2000) with links respectively C-C/C-H, C-O and C=O. Carbon is not linked the carbon matrix of the PZT material be deduced it is essentially present as hydrocarbons adsorbed on the surface. The derived composition from XPS analysis is $PbZr_{0.59}Ti_{0.41}O_3$. The good agreement between the nominal composition different elements PZT constituting the matrix and that deduced shows that the compositions are not affected by the high sintering temperatures.

Conclusion

Pure nanosized PZT52 sample was synthesized using the conventional solid state reaction and characterized by XRD, IR and Raman. The XRD patterns indicated that the perovskite were free of the pyrochlore phase. The grain size was about 31nm calculated from the Scherrer equation. In addition to the anomaly that corresponds to the transition from ferroelectric phase to paraelectric phase, dielectric measurements showed the presence of a second anomaly at position 275 °C. This anomaly may be due to a transition from morphotropic to tetragonal structure, followed, at 412 °C, by the phase transition from ferroelectric to paraelectric. After 4 hours of heat treatment at 900 ° C the derived composition from XPS analysis is $PbZr_{0.59}Ti_{0.41}O_3$.

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