THE INFLUENCE OF   -PBO$_2$ ON PZT PHASE FORMATION

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ABSTRACT

The reactional mechanism of the formation of solid solution lead-zircono-titanate PZT has been studied using   -PbO$_2$, TiO$_2$ and ZrO$_2$ as starting materials. PZT ceramics were prepared by solid state reaction between oxides at different temperatures. After calcination samples are characterized by thermogravimetry (TGA), differential thermal analysis (DTA), differential scanning, Infrared spectroscopy and x-ray diffraction (XRD). Using lead dioxide (-PbO$_2$) allows PZT powder to be sintered at a temperature as low as 700°C.

Key words: Ceramic; PZT; synthesis; calcinations; thermal analysis; X-ray; IR.

1. INTRODUCTION

Lead Zircono-Titanates of the general formula Pb (Zr$_x$, Ti$_{1-x}$) O$_3$ have been extensively developed for their good dielectric, ferroelectric and piezoelectric properties [1]. At room temperature, the complete solid solution between PbTiO$_3$ and PbZrO$_3$ contains two ferroelectric phases, a tetragonal phase on the titanium-rich side of the phase diagram, and a rhombohedral phase on the zirconium-rich side [2]. The boundary between these two phases is called morpho tropic, and corresponding materials exhibit improved electrical characteristics [3].

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One of the important aims of the technological development of the piezoelectric PZT-type ceramic is the reduction of the formation temperature in order to reduce the energy supplied and processing time. The reaction sequences for the formation of PZT solid solution through solid state reaction are now well known [4-8]. However, several intermediate phases have been reported and different temperatures of formation. This diversity as a function of processing temperature depends on several parameters. As an example, S. VANKATARAMANI et al [7] have shown the significant influence of the particle size of zirconium oxide on the formation of $PbZrO_3$ as an intermediate stage. Previous work of Kumar [9] reported the formation of PZT by Sol-Gel method, leading to smaller particle size with lower temperature of formation. By comparison, solid state processing appears easier to implement. However, liquid processing also allows the control of the stoichiometric coefficients, and provides precursors finely divided and more reactive than the starting materials used in solid route. This paper reports the improvement of the solid state synthesis using $-PbO_2$ as a starting material in place of commercial PbO. It was expected that this oxide could be more reactive.

2. EXPERIMENTAL

The Pb $(Zr_{0.485}, Ti_{0, 515}) O_3$ PZT was synthesized by solid state reaction, near the morphotropic phase boundary (FMP) which separates phases of tetragonal and trigonal symmetry. Reagent grade chemicals (minimum 99%) were used: lead oxide $-PbO_2$, zirconium oxide ZrO_2 and titanium oxide TiO_2. Corresponding JCPDS files are 85-1222, 07-0343 and 04-0477 respectively. Two other compounds, $PbZrO_3$ and $PbTiO_3$, were synthesized in the laboratory using the same starting materials $(ZrO_2, -PbO_2, TiO_2)$ and the same method. These two compounds are the most likely intermediates in the formation of PZT by the procedures described in the literature, as shown schematically in Figure1.
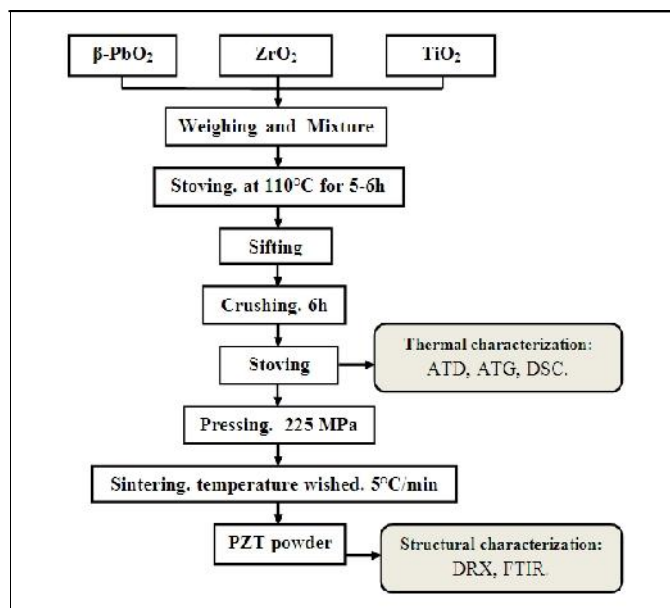
Fig.1. Flow chart used for PZT powder preparation.

A small part of powder mixture (5% of the powder synthesized) was kept for thermal analysis including thermogravimetry (TGA) coupled to differential thermal analysis (DTA). The rest of the powder obtained (95%) was dried and pressed (solid axial 225 MPa) and then calcined at the temperature deduced from thermal analysis. Calcination was implemented for 2 h in a small crucible of alumina, with a heating rate of 5 K/min. Samples obtained at different temperatures were later examined by x-ray diffraction (XRD) and infrared spectroscopy (IR).

The phase formation of PZT and intermediate reactions. Phases resulting from the decomposition of the precursors were analyzed by x-ray diffraction (XRD) (D8-Advanced, Bruker-Siemens, Cu K radiation). Sample composition was assessed by reference to JCPDS files (-PbO$_2$, ZrO$_2$, TiO$_2$, PbTiO$_3$, PbZrO$_3$) or deduced from experimental values of diffraction angles 2 in the case of the different solid solutions.

Thermal analysis (DTA/TGA) was conducted with pure Al$_2$O$_3$ as reference material. The data curves for the composition 0.485 PbZrO$_3$-0.515PbTiO$_3$ were obtained from 25 to 1100°C with a heating rate of 5 K/min. The Infrared absorption spectrum was recorded on a FTIR spectrometer (SHIMADZU FTIR 8000) using KBr pellets.

3. RESULTS AND DISCUSSION

PZT formation and intermediate reactions (decomposition, oxidation, transformation) were followed by TG/DTA thermal analysis (Fig. 2.).
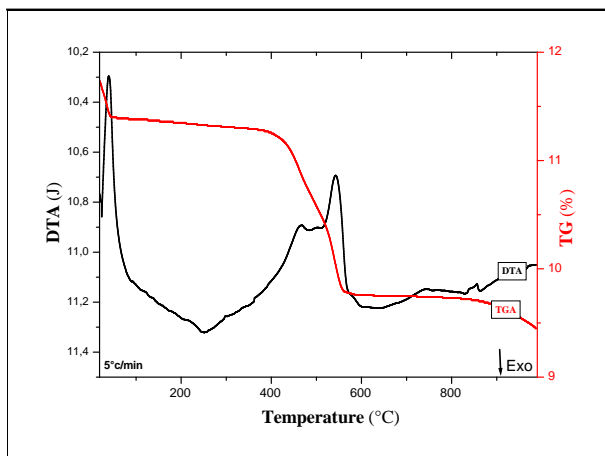
Fig.2. DTA and TG curves of Pb ($Zr_{0,485}$-$Ti_{0,515}$) O_3 samples, at room atmosphere (heating rate: 5 K/min).

There are six steps:

- The first step corresponds to a loss of 3% in mass accompanied by an endothermic peak around 59 °C, that is characteristic of the sample dehydration (release of bound water and adsorbed on the surface).

- The second step between 80 °C and 400 °C presented by a broad exothermic peak associated with low mass loss is an allotropic transformation (phase change) of lead dioxide by the following reaction:

$$\text{-PbO}_2 \longrightarrow \text{PbO}_2 \text{ (HP)}$$
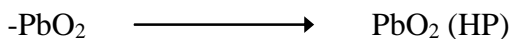
This was verified by XRD of the -PbO_2 calcined at 350°C, following the same thermal processing used for the powder mixture (Fig. 3.).
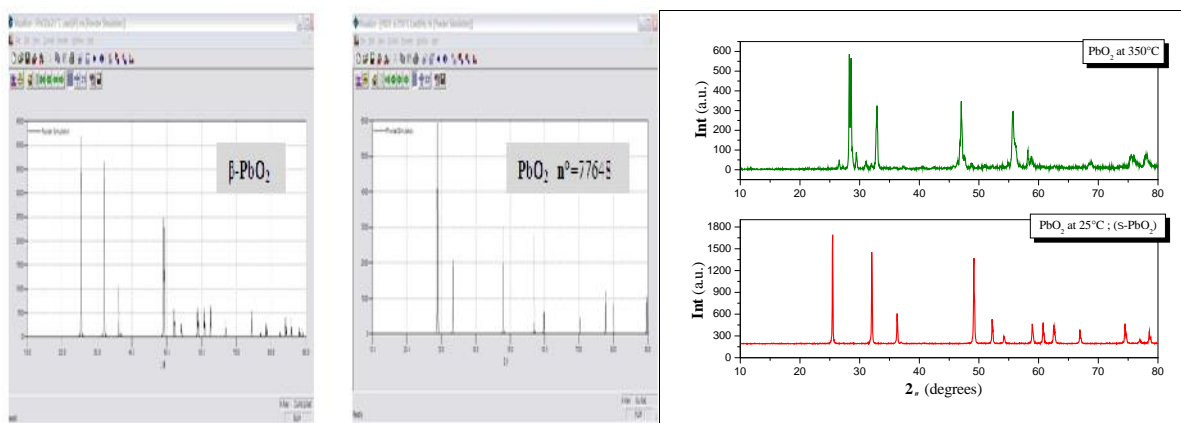

Fig.3. XRD patterns of PbO_2 at room temperature and after calcination at 350°C.

The diffraction patterns of X-ray α-PbO$_2$ at room temperature and calcined at 350°C, justified by their file ICSD (Inorganic Crystal Structure Data Base) n^o = 77648 gave the bass find (Crystallographica DLL: Dynamic Link library-version 2.0.1.4 -2004).

- The third step is evidenced by a very important DTA endotherm at 465 °C, which can be attributed to the first decomposition of PbO$_2$ (HP) to Pb$_3$O$_4$ with heat generation according to the following reaction:

$$3\ PbO_2\ (HP) \longrightarrow Pb_3O_4 + O_2 + Q$$
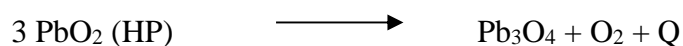
- The next step corresponds to the second decomposition, Pb$_3$O$_4$ to PbO, which corresponds to an endothermic peak at 541°C [7].

$$Pb_3O_4 \longrightarrow 3\ PbO + \tfrac{1}{2}\ O_2 + Q$$

This double decomposition also appears on the thermogravimetric curve, two weight losses 5% and 6% are observed at 465°C and 541°C respectively. To confirm that this double loss is due only to the decomposition of α-PbO$_2$ we have analyzed lead dioxide by TG/ATG (Fig. 4.).
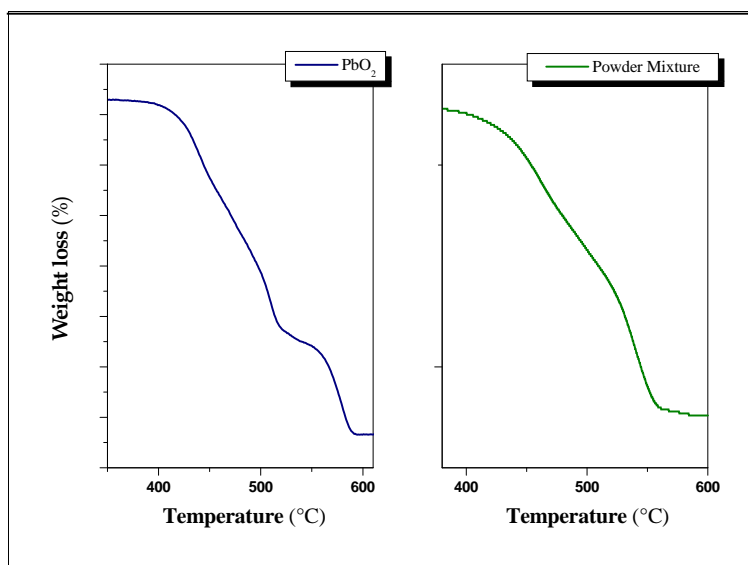

Fig.4. Thermogravimetric analysis of the as-prepared samples: α-PbO$_2$ (a), Powder mixture (b).

Similarly, XRD measurements lead to the following conclusions:

- Between 25°C and 400 °C, we observed the total disappearance of the characteristic peaks of tetragonal α-PbO$_2$ and the emergence of the cubic HP-PbO$_2$ [8] as shown in Fig. 5. (b).

➕ Between 400 °C and 536 °C the characteristic lines of Pb_3O_4 appears in the XRD pattern (Figs. 5 (b and c)).

The XRD diagram of the mixture calcined at 536 °C (Fig. 5 (d)) shows the characteristic lines corresponding to the formation of nascent PbO, including the peak centered at 35.74°. JSPDS files allowed us to identify these characteristic peaks.
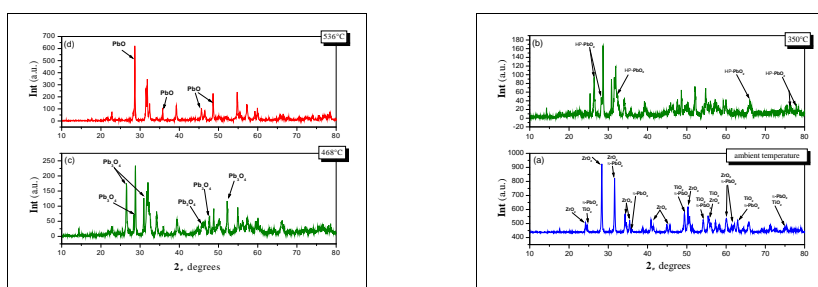

Fig. 5. X-ray diffraction patterns of powder mixture at the room temperature (a); and calcined at: 350°C (b), 468°C(c) and 536°C (d).

➕ The fifth stage starts from 562 °C. It is characterized by a broad and intense exothermic peak associated with a decrease in the slope of the TG curve.

The greater reactivities of TiO_2 compared to that of ZrO_2 and that of lead oxide obtained from the decomposition of Pb_3O_4 certainly promotes the formation of $PbTiO_3$ (Fig. 6.).
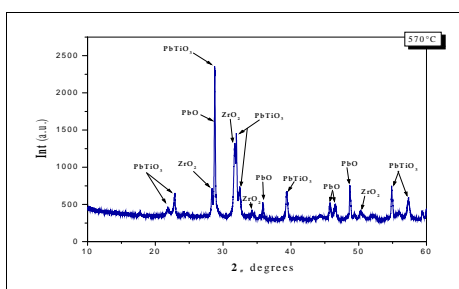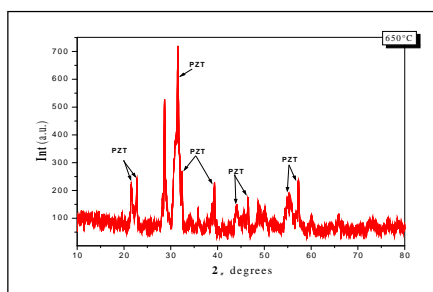

Fig.6. X-ray diffraction patterns of standard reactants calcined at 570 °C.

At higher temperature, solid solutions of lead titanate $(PbTiO_3)_{ss}$ are formed, probably resulting from the inter-granular contact between $PbTiO_3$-PbO, and ZrO_2-$PbTiO_3$. A small amount of unreacted PbO and zirconia is likely to diffuse in the $PbTiO_3$ perovskite structure. This assumption is justified by the variation of the linear parameters of the tetragonal $PbTiO_3$ as a function of temperature (Table 1), which are calculated from the interreticular distances (d_{100}, d_{001}) that corresponds respectively to a_T and c_T.

Table 1. Lattice parameters (X-ray diffraction data) as a function of temperature

Settings	540°C	570°C
a_T (°A)	3.895	3.892
c_T (°A)	4.122	4.065
c_T/ a_T (°A)	1.058	1.044

After heating the powder at 650°C, the diffraction peaks of the PbO_2, and ZrO_2 $(PbTiO_3)_{ss}$ phases decrease while the intensity of the PZT main lines increases (Fig. 7.).

Fig.7. X-ray diffraction patterns of standard reactants calcined at 650 °C.

Vibrational spectroscopy based on infrared transmission has been used to characterize samples obtained at different calcination temperatures. Absorption spectra evidence two peaks of vibration. The first one is located between 460 cm^{-1} and 800 cm^{-1} and is considered by several authors [9-10] as metal-oxygen (M-O) stretching vibration. This is the case Zaghetti *et al* who have also studied the formation of the PZT with a ratio of 53/47[9]. The second peak around 1400 cm^{-1} is characteristic of the solid solution of $PbTiO_3$. Indeed, we can see clearly the gradual disappearance of the peak as a function of temperature, as shown in Fig. 8. As this disappearance involves the formation of PZT, this confirms the conclusion of the XRD study.
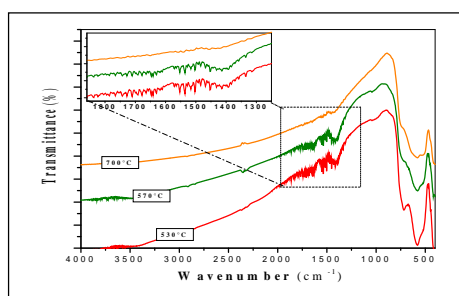
Fig.8. IR bands for PZT powder calcined at 540°C, 570°C and 700°C.

However, the TG-DTA curve of Figure 3 indicates that the PZT cannot be obtained as a pure phase at 700°C. This is probably due to the volatilization of small amounts of lead oxide (PbO liquid phase) at temperatures above 750°C. However, the XRD patterns of powders calcined at 700 ° C, 750 ° C and 850 ° C allow confirming this hypothesis (Fig. 9.).
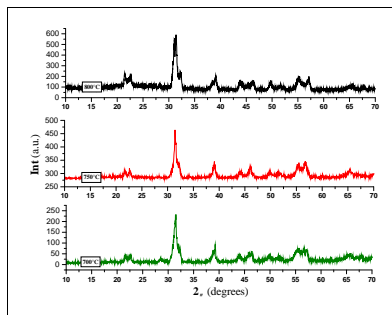

Fig.9. X-ray diffraction patterns of powder mixture calcined at 700 °C, 750 °C and 800°C.

4. CONCLUSION

PZT ceramics have been synthesized using -PbO$_2$ as a starting material in association to standard TiO$_2$ and ZrO$_2$ powders. From thermal and diffraction measurements, the reaction sequencecanbedescribedasfollows:

1. Phase change from   -PbO$_2$ to PbO$_2$ (highpressure).

2. The transformation of PbO$_2$ (HP) into PbO and Pb$_3$O$_4$.

3. The formation of solid solution of PbTiO$_3$, perovskite structure.

4. The diffusion of Pb^{2+} and Zr^{4+} in PbTiO$_3$ structure.

5. The formation of PZT solid solution.

The use of lead dioxide in the batch seems to enhance the diffusion of Pb^{2+} and Zr^{4+} in PbTiO$_3$ structure. In addition, it makes the formation of PZT phase possible at low temperature because the PbO originating from the decomposition of   -PbO$_2$ is more reactive than commercial PbO.

5. REFERENCES

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