The Steps Of Forming Of Solid Solution Noted (PZT-PSN-YMN) And Structural Characterization Of These Ceramic Materials

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ABSTRACT

This work is aimed to synthesize nano ceramic material of general formula short **PZT-PSN-YMN** of structure perovskite near the morphotropic phase boundary. These ceramics worked out by solid way, we present the preparation and the different stages of reaction mechanism of formation. Then we will detail the different techniques of analysis applied to this compound; we begin by the X-ray diffraction in the following by analysis spectroscopic (FTIR), laser particle size distribution and analysis by scanning electron microscopy (SEM).. These studies help us to accumulate as much information on the microstructure, the average particle size for all materials studied ceramic is less than 0.1µm. this value decreases after the heat treatment , beginning of forming the phase : $PbTiO_3$ from the calcination temperature 450 ° C ,$PbZrO_3$ from the calcination temperature 550 ° C and the formation and stabilization of the solid solution $Pb(Ti,Zr)O_3$ noted PZT at the temperature 900 °C.
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Keywords: ceramic, materials, formation, X-ray diffraction, solid way, solid solution.

1. INTRODUCTION

The A ceramic is an inorganic material, non-metallic, consolidated after its shaping under high temperatures.
Ceramics are inorganic materials, obtained following the shaping of a powder and a high-temperature heat treatment. They are very hard and very rigid (although withstand very high voltages), they are resistant to heat, abrasion, chemicals and corrosion. Their main disadvantage is fragile (easily breaks under a load). These general properties derived from the nature of their chemical bonds, their crystalline state and their microstructure. [1]
PZT is a material from the family of ferroelectric ceramics that once polarized have good piezoelectric characteristics. [2]
The first piezoelectric materials based on lead zirconium titanate (PZT) have been developed as early as 1954. The excellent piezoelectric properties of these ceramics have been demonstrated by Jaffe, Roth and Mazullo. [3]
Today the PZT used in the manufacture of many ferroelectric transducers. In fact, because more efficient, they have replaced in many cases the barium titanate ceramics $BaTiO_3$ [4] .The lead zirconate titanate of (PZT) are made from a binary mixture of $PbTiO_3$ and $PbZrO_3$. Indeed mixing $PbTiO_3$ ferroelectric and anti-ferroelectric $PbZrO_3$, miscible in all proportions, form solid solutions PZT ($PbZr_{1-x}$ Ti_xO_3) with piezoelectric and dielectric characteristics are clearly superior to those of the initial compounds. [5]
The solid route by calcination : This method consists in subjecting the powder mixtures (oxides or carbonates):
1. Thermal cycle during which they will by diffusion phenomenon, solid phase react and form the desired crystalline phase or form a mixture of different phases of the starting mixture.
2. The solid route by mechanical activation (dry grinding)
The preparation of PZT powder by the above methods (by a liquid or solid route) requires the calcination step, but there is another method called mechanical activation, in this technique the calcining operation is neglected and the product is recovered by the dry grinding of mixture of the oxides. [6]
Technical or mechanical dry grinding activation was successful for the synthesis of lead-based powders as PMN, PZN and PZT is a new technique that has appeared recently (since 1999). It is formed by the same step as the synthesis by

solid channel and uses the same raw materials, but in this technique the mixed after drying the powders is subjected to a dry grinding of several hours (> 25 hours) in a planetary mill vibrating balls, this operation is called mechanical activation after Lee and Kong [7], they showed that the two main advantages of this method are: the first is the transformation mixture powder PZT perovskite structure material that is done directly without passing through intermediate phases: $PbTiO_3$, $PbZrO_3$. The second advantage is that the reaction between the oxide is complete and the obtained powder of very fine particles. [6]
Synthesis by solid route is the industrial process as widely used as it is very economical and more direct . [2]

This part of work describes the manufacturing process of new type materials: **PSN-PZT-PYMN** and their reaction mechanism, all preparations were made at temperatures not exceeding 800°C, it gives then the results of the study radio crystallographic. In this work, the main purpose is to study the reaction sequences of formation of solid solution of perovskite structure in the presence of doping NiO, Sm_2O_3, Y_2O_3, MoO_3 and Nd_2O_3. We present the preparation and the different stages of the formation reaction of the solid solution. Then we will detail the different techniques of analysis applied to this compound, we begin first by X-ray diffraction, in the following by analysis spectroscopic (FTIR), Laser particle size distribution and analysis by scanning electron microscopy (SEM).

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2. PREVIOUS WORK

Several studies were conducted by different researchers [14] in order to show the reactions that occur during formation of ceramics. In general the results reported in dif- ferent studies show that lead titanate $PbTiO_3$ is the first reaction product to be formed [14-15]. However, when using a submicron ZrO_2 powder prepared chemically, the formation of $PbZrO_3$ is earlier than that of PT. This PZ, the intermediate product, was not observed in most other work, with the exception of Ohno *et al.* [15], which reveal its formation and reaction with PT to form the PZT solid solution and also Yamaguchi *et al.* who reported the possible formation of PZ but only under certain conditions.

The reaction sequence according to some researchers: Mori *et al.* [16] proposed two reaction steps:

$PbO + ZrO_2 + TiO_2 \rightarrow (PbTiO_3 + ZrO_2)ss$

$(PbTiO_3 + ZrO_2)ss \rightarrow Pb(Zr_{1-x}, Ti_x)O_3$

Speri [8] proposed a three step process:

$PbO + TiO_2 \rightarrow PbTiO_3$

$PbTiO_3 + PbO + ZrO_2 \rightarrow (PbO)ss$

$(PbO)ss + PbTiO_3 + ZrO_2 \rightarrow Pb(Zr_{1-x}, Ti_x)O_3$

(PbO)ss is a solid solution of tetragonal ZrO_2 containing PbO and $PbTiO_3$.

Hankey and Biggers [18] presented a reaction sequence consistent with Speri, but at different temperatures for each reaction step. Kingon, Terblanche and Clark [17] proposed a process of homogenization; they confirmed the formation of PbO ss in special experimental conditions, the final step in a reaction intermediate of PZT rich in $PbTiO_3$ PZT with rich $PbZrO_3$.

Matsio and Sasaki [19] were proposed:

$PbO + TiO_2 \rightarrow PbTiO_3$

$PbTiO_3 + PbO + ZrO_2 \rightarrow PbTiO_3 + (PZ_xT_{1-x})$

$PbTiO_3 + (PZ_xT_{1-x}) \rightarrow PZT$

Biggers and Venkataramani [20] reported the reaction sequence for two sources of ZrO_2 synthesized and commercial a different reaction sequence occurred which depends on the ZrO_2 used. ZrO_2 synthesized gives the formation of an intermediate phase $PbZrO_3$ and training of PZT at 500°C. ZrO_2 the introductory commercial formation of a phase webmail $PbTiO_3$ and the formation of PZT to 800°C. Chandratreya [21] has reported on the reaction mechanisms of the formation of PZT solid solution. He found that the $PbTiO_3$ forms between 450°C and 600°C and the PZT is formed above 700°C against any $PbZrO_3$ formation was detected.

3. EXPERIMENTAL PROCEDURE

The synthesis of a new ceramic material **PSN-PZT-PYMN** from a mixture of oxide is mainly in a few steps: The amount of starting materials required for the synthesis is calculated and then weighed and mixed with acetone for 6 h for homogenization. In later dried at 100°C in an oven for 12 h. The powder of the initial mixture is manually ground with a glass mortar for 4 h, and then the powder is compacted in the form of pellets 2 g mass. The pellets obtained are brought to the calcinations at tem- peratures of about 450°C,550°C,650°C, 750°C and 800°C in a programmable oven and under an ambient atmosphere with a heating rate of 2°C/min to a temperature maintained constant for two hours. Cooling the resulting materials is slow. No weight change was observed. The starting materials are basic oxides , their characteristics are summarized in **Table 1**:

Table 1. Characteristics of starting materials

Product	The molar mass (g / mol)	Chemical purity (%)	Supplier
PbO	223.20	99%	Biochem
ZrO_2	123.224	99%	Biochem
TiO_2	79.87	99%	Biochem
Sm_2O_3	348.70	99.9%	Alfa Aesor
Nd_2O_3	265.82	99.5%	Strem chemicals
Y_2O_3	225.82	99.6%	Alfa Aesor
MoO_3	143.94	99.6%	Alfa Aesor
NiO	74.71	99.6%	Strem chemicals

3.1 Analysis by « X-Ray Diffraction »

The various diagrams of X-ray diffraction were obtained using a Bruker-AXS D8 diffractometer installed at the Laboratory of RX (University of Biskra. ALGERIA)

equipped with a copper anticathode. In order to have a monochromatic radiation, the device is equipped with a monochromator which selects the wavelength corresponding to the Kα radiation of copper: 1.5405 A. To perform the measurements, the voltage applied by the generator is 40 kV and the current is 40 mA. The diffractograms are recorded at room temperature, and 2 theta between 10° and 90°.

The diffraction pattern of the powder mixed oxides uncalcined (room temperature). This chart shows the characteristic lines of basic oxides PbO, ZrO_2 and TiO_2 without secondary phases that indicate the absence of any reaction between these oxides during milling. The doping oxides are in very small quantities in the initial mixture; no characteristic peak appears on this diagram.

The results of the X-ray diffraction for the powder before calcination and after calcination at different temperatures(450-550-650-750-900) are shown in **Figure 1-2-3-4-5**

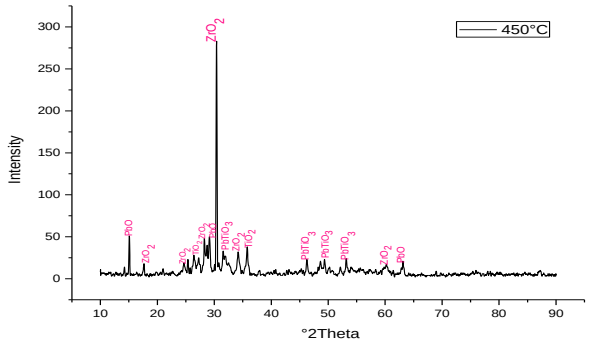

Figure 1. Diffraction pattern of X-ray powder calcinated at 450°C

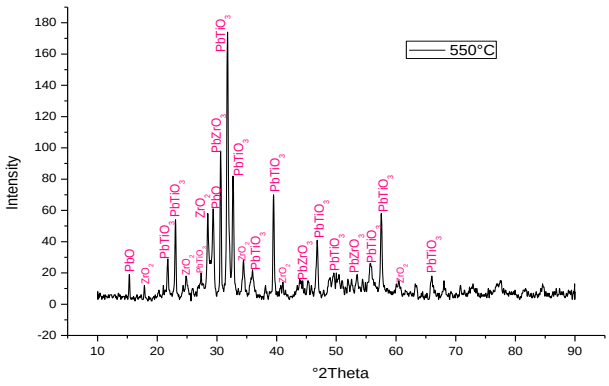

Figure 2. Diffraction pattern of X-ray powder calcinated at 550°C

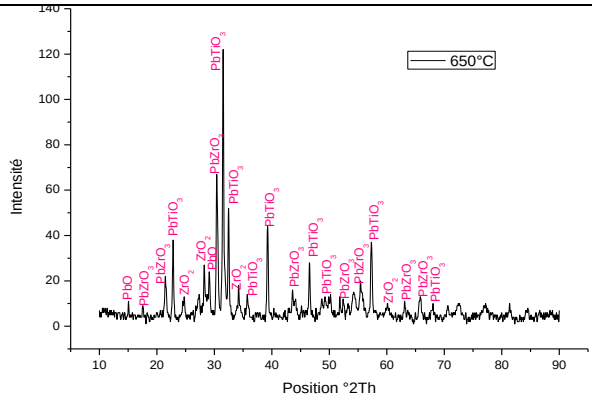

Figure.3. Diffraction pattern of X-ray powder calcinated at 650°C

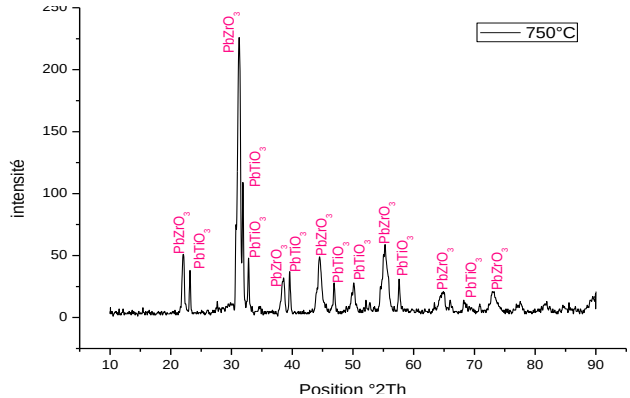

Figure.4. Diffraction pattern of X-ray powder calcinated at 750°C

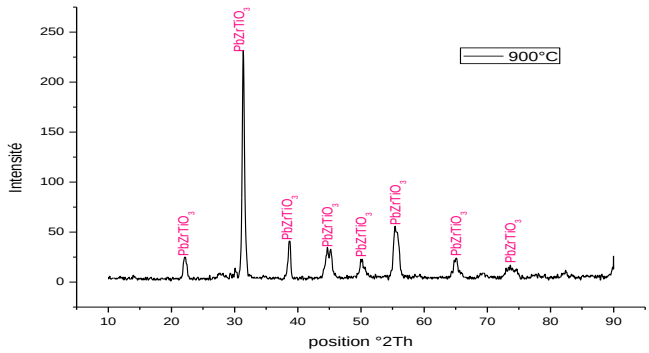

Fig.5. Diffraction pattern of X-ray powder calcinated at 900°C

All existing phases of 450 ° C to 900 ° C obtained from their relative intensities located in the diffraction X-ray diffractograms are summarized in **Table 2**.

Table 2. The existing phases in each calcined powder.

calcining temperature	Existing phases
Uncalcinated	PbO, ZrO_2, TiO_2
Calcinated at T = 450°C	PbO, ZrO_2, TiO_2, $PbTiO_3$ (traces)
Calcinated at T = 550°C	PbO, ZrO_2, $PbTiO_3$,$PbZrO_3$ (traces)
Calcinated at T = 650°C	PbO, ZrO_2, $PbTiO_3$,$PbZrO_3$
Calcinated at T = 750°C	$PbTiO_3$, $PbZrO_3$
Calcinated at T = 900°C	PZT

View the results observed from this **table 2**, it is proposed reaction mechanism of formation of the solid solution: Before calcination the existence of bases oxides (PbO, ZrO_2, TiO_2) without any traces of doping.

at T= 450°C : $PbO + TiO_2 \rightarrow PbTiO_3$ (traces)

at T = 550°C : $PbO + ZrO_2 \rightarrow PbZrO_3$ (traces)

at T = 650°C : $PbO + TiO_2 \rightarrow PbTiO_3$ (SS)

at T = 750°C : $PbO + ZrO_2 + TiO_2 \rightarrow PbZrO_3 + PbTiO_3$

at T=900°C : $PbZrO_3 + PbTiO_3 \rightarrow PZT$

3.2. Analysis by Infrared Spectroscopy in Fourier Transmission "FTIR"

The different spectra FTIR were obtained using a Shimadzu spectrophotometer type FTIR-8400S PC that is used to obtain IR spectra with a resolution of 1 cm^{-1}. Laboratory of Chemistry (University of Biskra, Algeria). Analysis of the calcined powder at a temperature of 750°C by infrared spectroscopy in Fourier transmission mode (FT) in the range of 400 - 4000 Cm^{-1} shows an absorption band between 450 and 800 Cm^{-1}. This band is characteristic of the MO bond [8] and a second peak at 1400 Cm^{-1} is a characteristic of the solid solution $PbTiO_3$. M. Zaghete *et al.* [8] also studied the formation of the PZT. Quantitative determination by infrared spectroscopy performed on our powders with different calcinations temperature (450°C-550°C-650°C-750°C-900°C) shows the existence of two peaks with a vibrational absorption band between 450 Cm^{-1} and 800 Cm^{-1} and the second peak around 1400 cm^{-1}(**Figure 6)**, the latter is a characteristic of the solid solution of $PbTiO_3$. Moreover, we can see clearly the gradual disappearance of the peak as a function of temperature presented in **Figure 7** This also confirms our results suggested by X-rays.

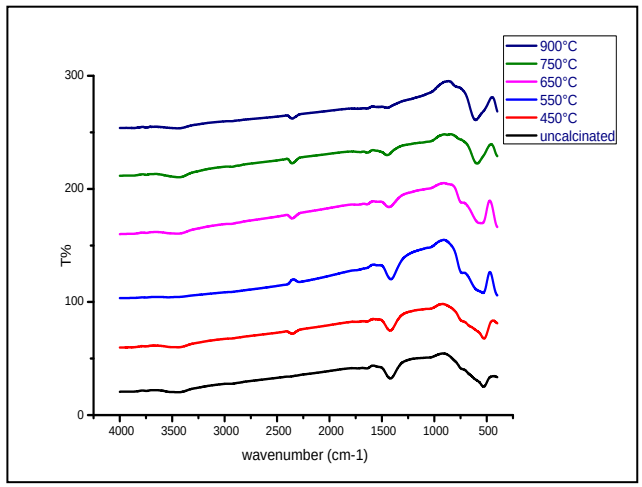

Figure. 6 Infrared absorption spectra as a function of temperature of calcinated

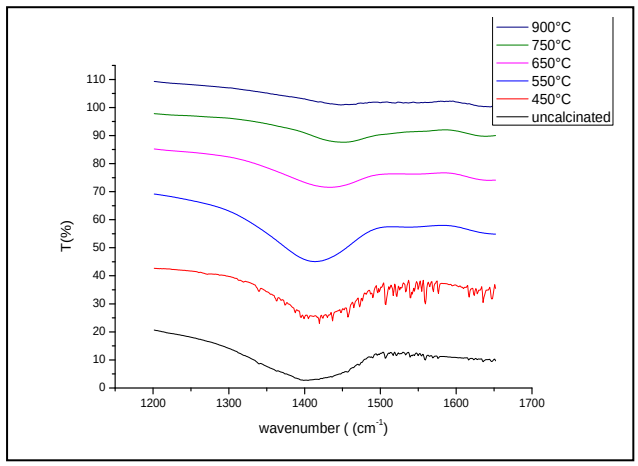

Fig.7 The appearance and disappearance of the band M-O-M with the calcination temperature

3.3. Laser particle size distribution

The particle size measurements are performed in liquid method. The powder is suspended in 600 ml of water by adding sodium hexametaphosphate (dispersant) and is dispersed by ultrasound for 15 minutes.

The particle size of the powder is an essential parameter for the study of the morphology of the material, the grains should be fine enough for practical reasons: to facilitate the homogeneous melting of the entire material, avoid high retention of air in the material and finally prevent the grains from sticking to each other, apart from the surface, which may cause brittleness of the finished part. The average particle size for all materials studied ceramic is less than 0.1µm. this value decreases after the heat treatment (calcination) .we took as an example the uncalcined powders and those calcined at 550-650-750-900 ° C as shown in the following **table3** and **figures 8-9-10-11-12**

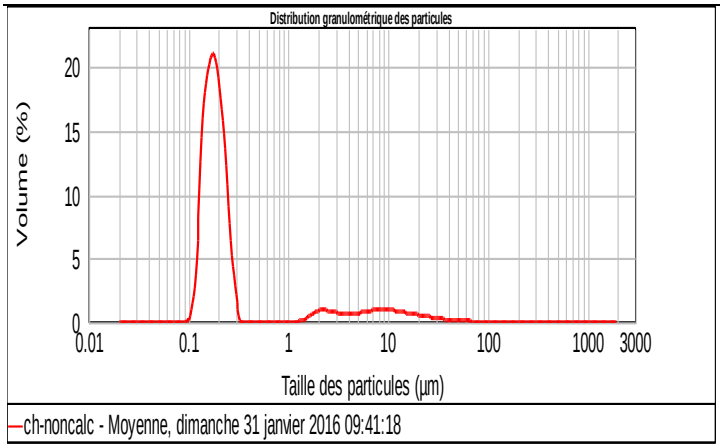

Figure 8 Particle size distribution curve of the particles for non-calcined powder

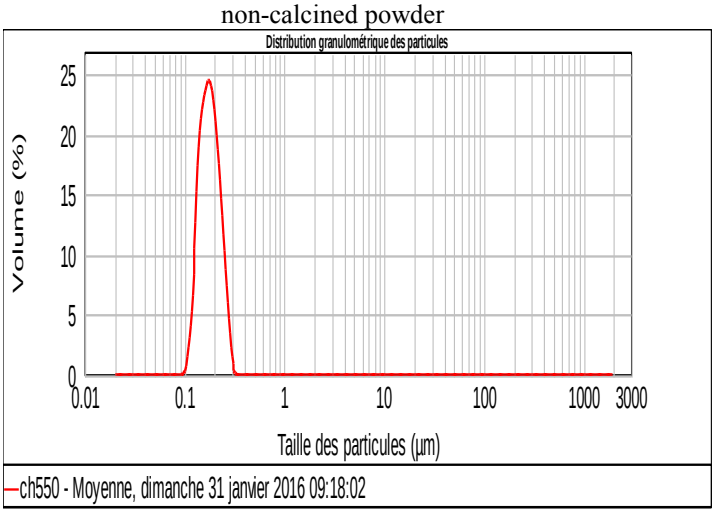

Figure 9 Particle size distribution curve of the particles for powder calcined at 550 °C

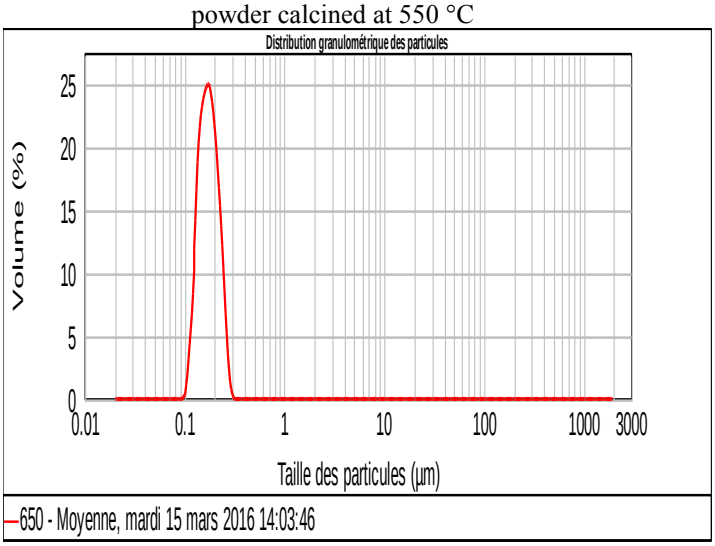

Figure 10 Particle size distribution curve of the particles for powder calcined at 650 °C

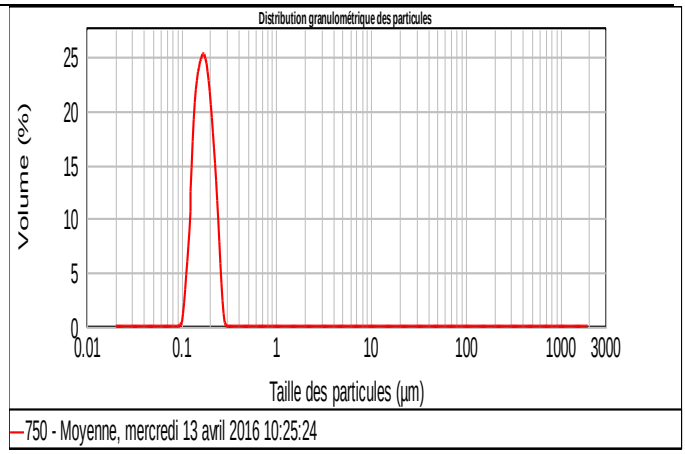

Figure 11 Particle size distribution curve of the particles for powder calcined at 750 °C

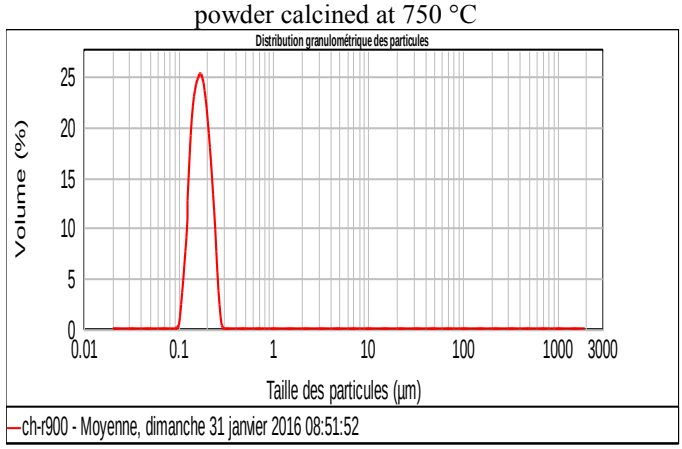

Figure 12 Particle size distribution curve of the particles for powder calcined at 900 °C

Table 3. The average grain size for the uncalcined powder and calcined at 550-650-750-900 ° C

calcining temperature	D(0.5) µm	D(0.9) µm
Uncalcinated	0.189	3.380
Calcinated at T = 550°C	0.177	0.239
Calcinated at T = 650°C	0.173	0.231
Calcinated at T = 750°C	0.172	0.228
Calcinated at T = 900°C	0.171	0.227

3.4 Analysis by Scanning Electron Microscopy (SEM)

The SEM is a complementary technique of analysis and sample characterization in solid state. When scanning the sample by the electron beam, multiple interactions occur : absorption and electron energy loss, using an appropriate detection technique that can transform into an electrical signal the result of the interaction electron-material. The scanning electron microscope (SEM) analysis uses mainly secondary electrons which are usually coupled with that of backscattered electrons for "images" of the sample. Secondary electron mode, the information obtained concerning the topography of the sample while backscattered electron mode gives information about the variation of the composition.

The SEM provides information on the shape and size of grains after sintering. It also qualitatively assesses the

presence of porosity and secondary phases. We also present the **Figure 13** image corresponding to sample sintered at 1150°C. In **Figure14** the image of the sample sintered at 1180°C. For the sample (doped with 2% Sm, 2% Nd), this composition is doped with 4% in site A, there is a grain growth. Grain distribution is uniform over the almost entire surface of the sample. The average grain size increases with increase in the sintering temperature of 1.71 µm at 1150°C up to 3.6 µm at 1180°C. It is important to note, for all samples, that no parasite phase was observed on the SEM micrographs.

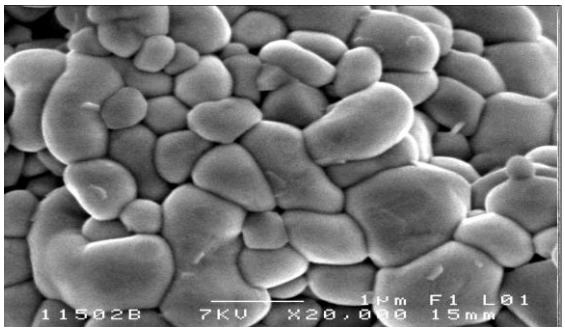

Figure. 13 Scanning electron micrographs of the composition sintired at 1150°C.

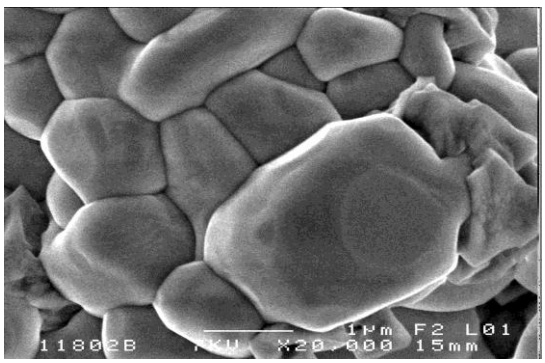

Figure. 14 Scanning electron micrographs of the composition sintired at 1180°C.

2. CONCLUSION

Our work is devoted to the synthesis of the solid solution type PZT and the structural characterization .Note the following points for the formation of the PZT solid solution: gradual decrease of the intensities of characteristic peaks of basic oxides PbO, TiO_2, ZrO_2 at temperatures between 400 ° C and 650 ° C and total disappearance of these peaks to 750 ° C. The gradual emergence of $PbTiO_3$ characteristic peaks at 450 ° C and maximum training to 650 ° C. The gradual emergence of $PbZrO_3$characteristic peaks at 550 ° C and maximum training to 750 ° C.A total of the solid solution formation Pb (Zr, Ti) O_3 (PZT) to 900 ° C.

The quantitative determination by IR spectroscopy carried out on our powders at various calcinations temperature showing the existence of two vibration bands : an absorption band between 450 cm $^{-1}$ and 800 cm $^{-1}$ that can be assigned to the link M-O and the second band at 1400 Cm^{-1} is characteristic of the solid solution $PbTiO_3$ kind. There is the progressive disappearance of the peak as a function of the calcination temperature until total disappearance at T = 900 ° C "formation of the solid solution PZT".

From “Laser particle size distribution “The grain distribution for all of the synthesized powder is homogeneous (nearly uniform without the existence of aggloméras). There is a slight decrease in average grain size with increasing the heat treatment temperature (calcination).

The SEM provides information about the shape and size of grains after sintering. The average grain size increases with increase in the sintering temperature of 1.71µm at 1150°C up to 3.6 µm at 1180°C. For samples which are doped in A site with 10% and 20% respectively, shows that the grain distribution is fairly uniform over the entire surface of the sample. The composition is less dense and therefore more porous. It is important to note, for all samples, no parasite phase was observed on the SEM micrographs.

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