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Structural phase, and morphological characterization of a new based on oxide ceramic material

A. Aouragh[a]*, T-A. Chinar[b], A. Boutarfaia[a] and A. Meklid[a]

[a]*Laboratory of Applied Chemistry, Department of Science Matter, University of Mohamed Kheider, 07000, Biskra, Algeria.*
[b]*Laboratory of Analytical Sciences Materials and Environment, Department of Chemistry, University of Larbi ben M'Hidi, 04000, Oum El Bouaghi, Algeria.*

Corresponding author: email: abdellatif_chimie_05@yahoo.fr

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Abstract

The main objective of this work is based on the synthesis, structural and physical characterization of a new ceramic material of PZT type and perovskite structure ABO_3, We are interested in the study of the ternary system $Pb_xCa_{1-x}[(Mn_{1/3}, Nb_{2/3})_{0.06}(Mg_{1/3}, Nb_{2/3})_{0.06}(Zr_{0.50}, Ti_{0.50})_{0.88}]O_3$ abbreviated PZT-CMMN with $0.95 \leq x \leq 0.98$.

A site substitution was carried out in order to improve its physical properties. The samples chosen for this study were prepared using solid synthesis methods. Heat treatment was applied to these compositions at different temperatures: 1100 ° C, 1150 ° C, 1180 ° C, 1200 ° C and 1230 ° C successive order , to optimize the sintering temperature .The product possess better physical properties when density of the materials are maximized.Such as: Scanning electron microscopy (SEM), X-ray diffraction (DRX), and IR analysis, have been carried out on the samples.

Keywords: Perovskite, PZT, DRX, PZT-CMMN, MEB, Sintering.

1. Introduction

Lead Zirconate-Titanate (PZT) piezoelectric ceramics of general formula $Pb(Zr_{1-x}Ti_x)O_3$ are used in very numerous applications including pulse generators, ultrasonic transducers, sensors, actuators[1-4], motors piezoelectric and in various fields such as medicine, aeronautics, electronics, electrical engineering... etc [5-10]. The extent of these fields of application is due to their dielectric and piezoelectric properties.

Numerous works carried out in recent years on PZT piezoelectric ceramics attest to the importance of these materials near the morphotropic phase boundary (FMP). Where the two phases coexist and exhibit the most student values of the dielectric constant and coupling factor. This boundary separates the two ferroelectric phases, one of which is tetragonal and the other of which is rhombohedral. Studies have shown that dopants lead to the displacement of this border [11].

This study aims to improve the electrical properties of ceramics. These properties are generally improved by the addition of one or more cations which will replace Pb^{2+} in site A and / or couple (Zr^{4+} / Ti^{4+}) in site B of the perovskite structure [12]. Substitutions in the crystal lattice called doping [13]. In fact any change by doping by means of metal oxides or by substitution of the elements moves the morphotropic border to the right or to the left [10]. Various methods are used to locate the corresponding compositions at the morphotropic phase boundary of PZT-type ceramics and its derivatives (addition of dopants)[14]. Among these methods used for the investigation: X-ray diffraction analysis and analysis by study of physical properties (measurement of dielectric, piezoelectric and electromechanical properties). The objective of this work consists in the synthesis of the solid solution, to study the morphological and structural characterization of the quaternary system and the study of the dielectric and piezoelectric properties of this solid solution of general formula:

$Pb_xCa_1[(Mn_{1/3},Nb_{2/3})_{0.06}(Mg_{1/3},Nb_{2/3})_{0.06}(Zr_{0.50},Ti_{0.50})_{0.88}]O_3$
abbreviated in the PZT-CMMN suite.

2. Experimental part

The experimental protocol adopted Many synthetic routes exist for the formation of perovskite structures. The choice of one of these routes depends on the use of oxides because they directly affect the morphology of the solid and therefore its properties [15].

The preparation of powders is an important step in the shaping processes. The objective is to obtain a powder which makes it possible, on the one hand, to obtain the desired microstructure, generally dense and homogeneous, during the shaping and on the other hand, which ensures satisfactory densification during sintering [16], After the preparation of the powders by one of the shaping processes, this makes it possible to obtain the desired microstructure and ensures satisfactory densification during sintering [17].

The synthesis of the samples was done by the ceramic method (by the solid way), the chemical formula of the samples is:

$Pb_xCa_{1-x}[(Mn_{1/3},Nb_{2/3})_{0.06}(Mg_{1/3},Nb_{2/3})_{0.06}(Zr_{0.50},Ti_{0.50})_{0.88}]O_3$

with $0.95 < x < 0.98$.

The sample preparation process will be described in six steps: starting with weighing and stirring, then grinding, followed by shaping, followed by calcination and finally sintering.

After weighing the products according to the desired compositions, the products are mixed intimately, in an acetone medium in a beaker by a magnetic stirrer facilitating the stage of homogenization of the powder of the mixture for a period of two (02) hours. The paste obtained is dried at 80 ° C in an oven for two (02) hours also, then ground in a glass mortar for six 06 hours. We obtain fine particles, which promotes phase formation by solid / solid diffusion more quickly.

To facilitate reactions in the solid state, our mixtures are compacted by a manual press in a cylindrical mold with a diameter of 13 mm and a thickness varying according to the force applied. Note that a few drops of polyvinyl alcohol (PVA) can be added if necessary to facilitate compaction. The powder obtained after grinding is compacted in the form of pellets under a pressure of around 350 Kg / cm2. Then, a preliminary calcination at 900 ° C is carried out for two (02) hours with a heating rate of 04 ° C / min. The mixture is ground a second time for four (04) hours, and then it is rapidly ground in the form of pellets at a pressure of 3×10 3 kg / cm ^{2}. These pellets are agglomerated at different fermentation temperatures (1100 ° C, 1150 ° C, 1180 ° C, 1200 ° C and 1230 ° C) for two (02) hours.

It is important to note that weight loss is possible by evaporation of PbO which is very volatile at temperature T ° ≥ 900 ° C. To limit this phenomenon, we introduce it into an atmosphere rich in $PbZrO_3$ where the PbO is maintained with its powder to minimize and reduce this loss during sintering [9, 18]. The pellets are metallized by a thin layer of silver on both sides.

2.2. Characterization techniques

The powder diagram was recorded on a MiniFlex600 'Rigaku' diffractometer

using the copper K_α radiation (λ_{Cu} Kα: 1.540600 A °) and the diffraction patterns are recorded in the angular domain 10 ° ≤ 2θ ≤ 90 ° which is sufficient for the identification of the different phases.

The morphology of the materials was observed by conventional JSM 6400 microscope with thermionic gun with tungsten filament.

3. Results

The synthesis of our ceramic samples was done by the ceramic method (the solid way), defined in detail in the previous part. And the different compositions prepared for our study are mentioned in the following table:

Table 1: Different prepared compositions of PZT-CMMN

SN	Matrix
1	$Pb_{0.98}Ca_{0.02}[(Mn_{1/3},Nb_{2/3})_{0.06}(Mg_{1/3},Nb_{2/3})_{0.06}(Zr_{0.50},Ti_{0.50})_{0.88}]O_3$
2	$Pb_{0.97}Ca_{0.03}[(Mn_{1/3},Nb_{2/3})_{0.06}(Mg_{1/3},Nb_{2/3})_{0.06}(Zr_{0.50},Ti_{0.50})_{0.88}]O_3$
3	$Pb_{0.96}Ca_{0.04}[(Mn_{1/3},Nb_{2/3})_{0.06}(Mg_{1/3},Nb_{2/3})_{0.06}(Zr_{0.50},Ti_{0.50})_{0.88}]O_3$
4	$Pb_{0.95}Ca_{0.05}[(Mn_{1/3},Nb_{2/3})_{0.06}(Mg_{1/3},Nb_{2/3})_{0.06}(Zr_{0.50},Ti_{0.50})_{0.88}]O_3$

SN: Sample number

3.1. Analysis of PZT-CMMN ceramics

3.1.1. The density

- ✓ Evolution of the density as a function of the sintering temperature:

The study of the density is essential in order to optimize the sintering temperature. The quality of the material increases with increasing density and these increases with increasing sintering temperature [19]. The optimum sintering temperature is determined from the density diagram as a function of the temperature d = f (T). The maximum density corresponds to the product of better electrical quality (low dielectric loss). Figure 1 shows the density curves of all samples as a function of the sintering temperature:

The same appearance is observed for all of the curves: the density is minimum for a sintering temperature 1180 ° C, it begins to increase until reaching a maximum value at a sintering temperature T = 1200 ° C then it decreases to 1230 ° C which means that the optimum sintering temperature is 1200 ° C. The increase in density implies a decrease in the number and size of pores, so the volume of the mesh decreases and consequently the structure becomes more compact.

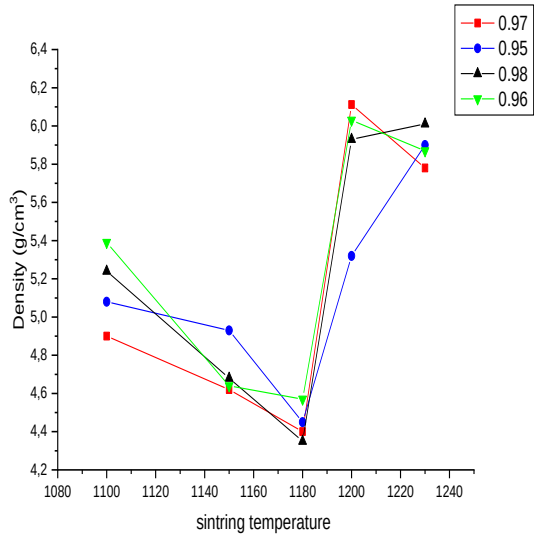


Figure 1. Evolution of the density as a function of the sintering temperature

The increase in density means that we have a compact structure, this means a smaller mesh volume and a decrease in the number and size of pores. The optimum sintering temperature corresponds to the evaporation-recondensation balance of the following reaction:

PbO → PbO (steam) → Pb (steam) + 1/2 O_2 (steam).

The optimum sintering temperature depends on several factors such as: the addition of impurities, the sintering speed, the holding time as well as the amount of $PbZrO_3$ added to minimize the volatilization of PbO[20].

- ✓ Evolution of the density according to the composition:

The evolution of the density of the different samples of PZT-CMMN sintered at 1100, 1150, 1180, 1200 and 1230 ° C as a function of the lead rate (Pb) is illustrated in Figure 2.

The density increases with increasing Pb concentration, and takes maximum values at 1200 ° C, at this temperature the density reaches a maximum value of 6.1211 g / cm3 (96.36% of theoretical density) at Pb= 97%.

3.1.2. Porosity

- ✓ Evolution of the porosity as a function of the sintering temperature:

The monitoring of the variation of the porosity as a function of the sintering temperature for the 97% sample is reported on the curve of Figure 3.

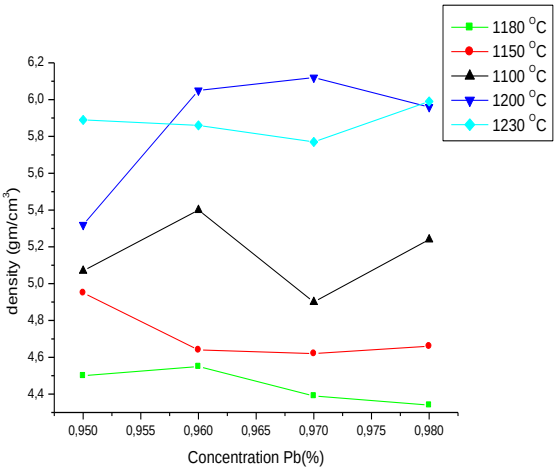


Figure 2. Evolution of the density as a function of the lead rate.

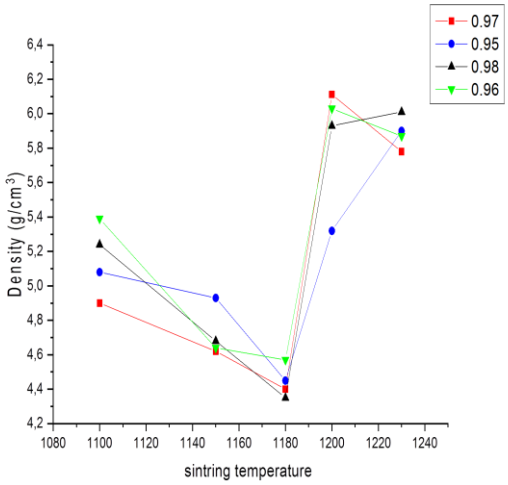


Figure 3. Evolution of the porosity as a function of the sintering temperature.

We find that the shape of the porosity curve is the opposite of that of density. The same behavior observed for the set of sintered samples at different sintering temperatures. The porosity decreases when the sintering temperature increases until reaching a minimum which corresponds to the maximum density at 1200 ° C., which confirms that the temperature optimum sintering is 1200 ° C.

- ✓ Evolution of the porosity as a function of the composition:

Figure 4 shows the variation in porosity as a function of the Pb concentration of dopants for samples of sintered ceramics at 1200 ° C.

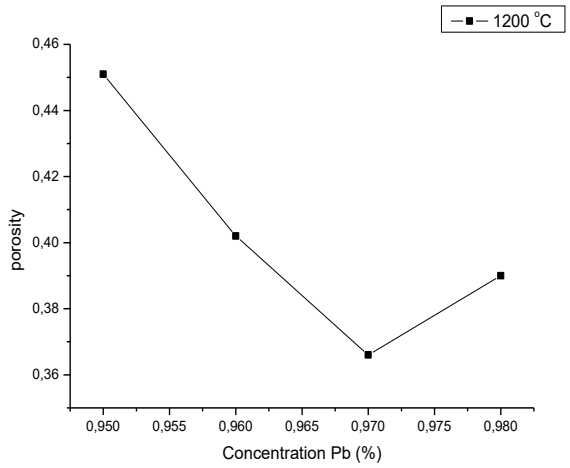


Figure 4. Evolution of the porosity as a function of the lead rate.

We note that the shape of the porosity curve is the opposite of that of the density, it decreases to a minimum for the sample where the doping rate equal to 97%, which corresponds to the maximum density then it increases.

3.2. Structural and morphological analysis of PZT-CMMN ceramics:

3.2.1. DRX analysis

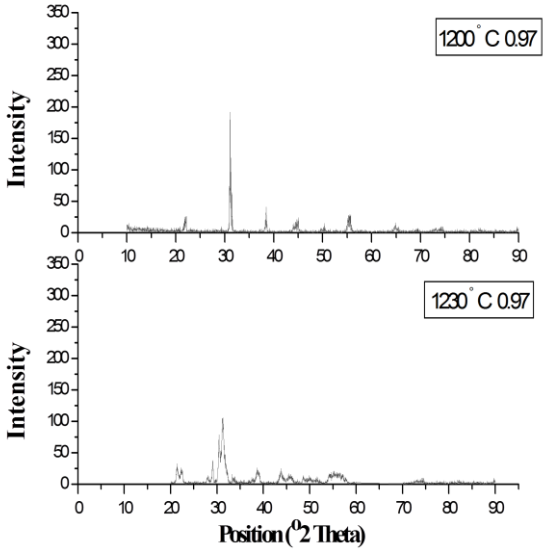
The sintered compounds PZT-CMMN are carefully ground, then analyzed by X-ray diffraction to establish the crystallographic phases: Tetragonal, Rhombohedral and Tetragonal-Rhombohedral [21, 22].

The X-ray results concerning our series of sintered compositions at 1100, 1150, 1180, 1200 and 1230 ° C doped at 97% are illustrated in Figure 5 and in Table 2.

Table 2: Nature of the crystallographic phases of the composition 97%.

Temperature (°C)	Nature of the phases
1100	T+R
1150	T+R
1180	T+R
1200	T+R
1230	T

The X-ray results concerning our series of sintered compositions at 1100, 1150, 1180, 1200 and 1230 ° C doped at 97% are illustrated in Figure 5.



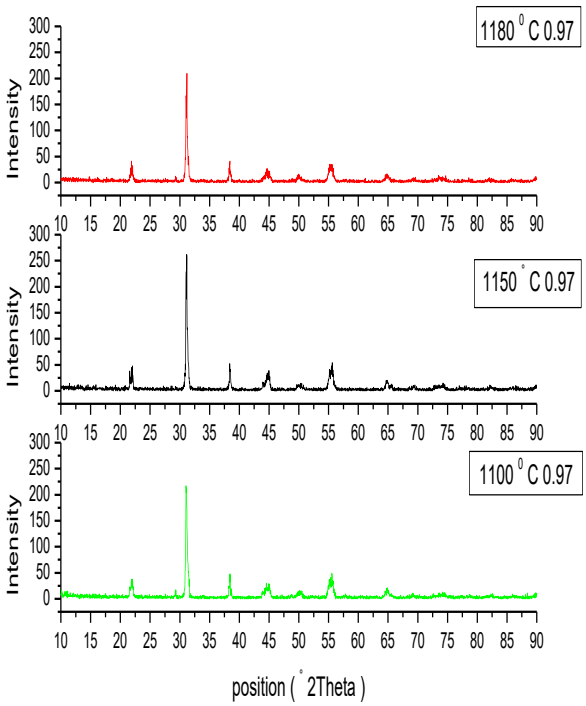


Figure 5. X-ray spectra of PZT-CMMN ceramics of composition 97%.

The X-ray results concerning the PZT-CMMN compositions with x = 95, 96, 97 and 98% sintered at 1200°C. are illustrated in FIG. 6 and in Table 3.

Table 3: Nature of the crystallographic phases at an optimal sintering temperature of 1200 ° C.

Composition (%)	Nature of the phases
0.98	T+R
0.97	T+R
0.96	T+R
0.95	T

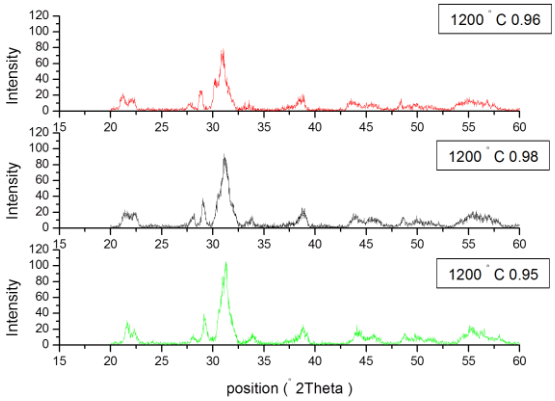


Figure 6. X-ray spectra of PZT-CMMN ceramics at optimal sintering temperature 1200 ° C.

Examination of the X-ray diffraction spectra of the different samples of the PZT-CMMN solid solution showed the coexistence of the two tetragonal and rhombohedral ferroelectric phases. The coexistence of the phases (T + R) is characterized by the peaks (002) T, (200) T and (200) R in the range 43-45 ° in both Figure 5 and Figure 6.

In the angular intervals 2θ: [21-23], [43-46] and [54-57] we observe the peaks corresponding to the perovskite phase. From these results and according to the comparison with the ASTM files, it can be said that the PZT phase obtained is the tetragonal phase in both Figure 5 and Figure 6.

At high sintering temperature, the coexistence of the phases (T + R) is stable. So our results have been limited to the only temperature 1200 ° C in Figure 6. We also observed the presence of the pyrochlore phase in the 2θ interval: [28-30] in the 97% dopant at sintering temperature 1180 ° C and 1230 ° C in Figure 5 and in the 95% and 96% dopant at sintering temperature 1200 ° C in Figure 6.

- ✓ Evolution of the mesh parameters of PZT-CMMN as a function of the sintering temperature:

Taking into account our interest in changes in the mesh parameters as a function of temperature, we studied the influence of the sintering temperature (1100, 1150 and 1180 and 1200 and 1230 ° C) on the mesh parameters of the two tetragonal and rhombohedral structures near the phase morphotropic border. From the characteristic lines: (200) T, (002) T, (200) R, the mesh parameters and the distortion ratio cT / aT were determined. And shows an illustration of the evolution of the mesh parameters (a_R, a_T and c_T) and the variation of the distortion ratio c_T / a_T as a function of the sintering temperature in Figure 7.

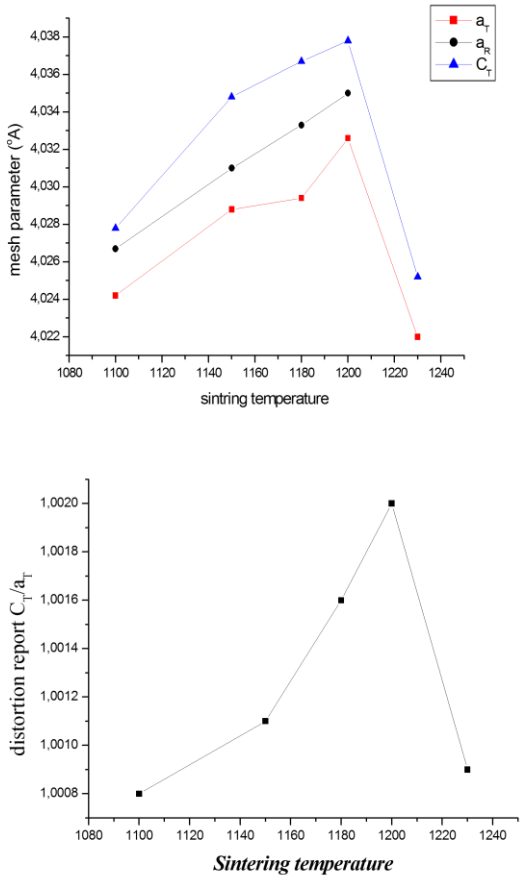


Figure 7. Evolution of the mesh parameters and the distortion ratio as a function of the sintering tempurature

It can be seen that the value of the mesh parameters a_R, a_T and c_T and the ratio c_T / a_T increases up to the optimum sintering temperature 1200 ° C and decreases at 1230 ° C.

- ✓ Evolution of the mesh parameters of PZT-CMMN according to the composition:

At a fixed temperature at 1200 ° C, we have studied the evolution of the mesh parameters of the PZT-CMMN solution as a function of the Pb composition: Figure 8.

We note that the mesh parameters are very sensitive to the variation in the composition of the dopants. The three parameters a_T, a_R and c_T increase up to the 97% dopant and then decrease. The variation of these parameters is related to the distortion of the tetragonal-rhombohedral structure, defined by the c_T / a_T ratio, which increases when the concentration of dopants increases.

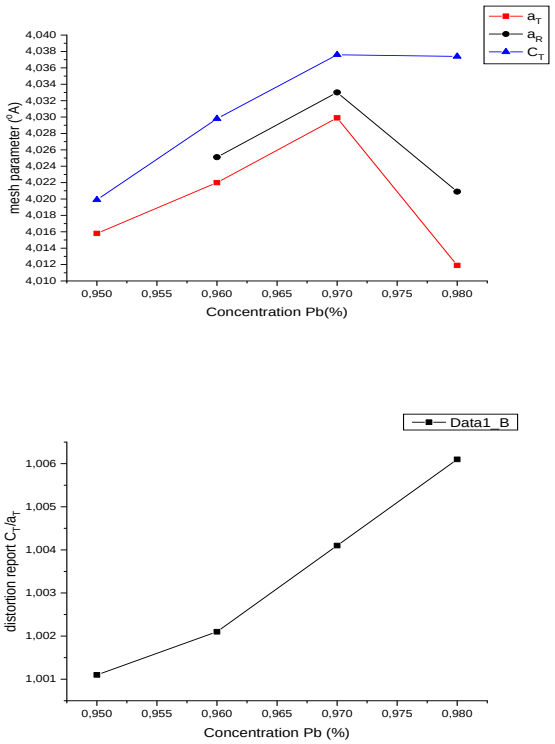


Figure 8. Evolution of the mesh parameters and the distortion ratio as a function of the composition.

3.2.2. SEM analysis

For the two 97% doping samples at sintering temperature 1180 ° C. and 1200 ° C., it is observed that the distribution of the grains is uniform over the entire surface of the compositions, the average grain size generally increases with increasing temperature. sintering. and over the entire surface of the micrographs we observe:
- The grain distribution is uniform.
- There is a slight variation in average grain size between [1.61-6.42] µm.
- The presence of the secondary pyrochlore phase because it is remarkable for its pyramidal shape. Observations by SEM scanning electron microscopy show dense ceramics and a narrow and homogeneous distribution of grains whose size is around 1.61 µm [23].

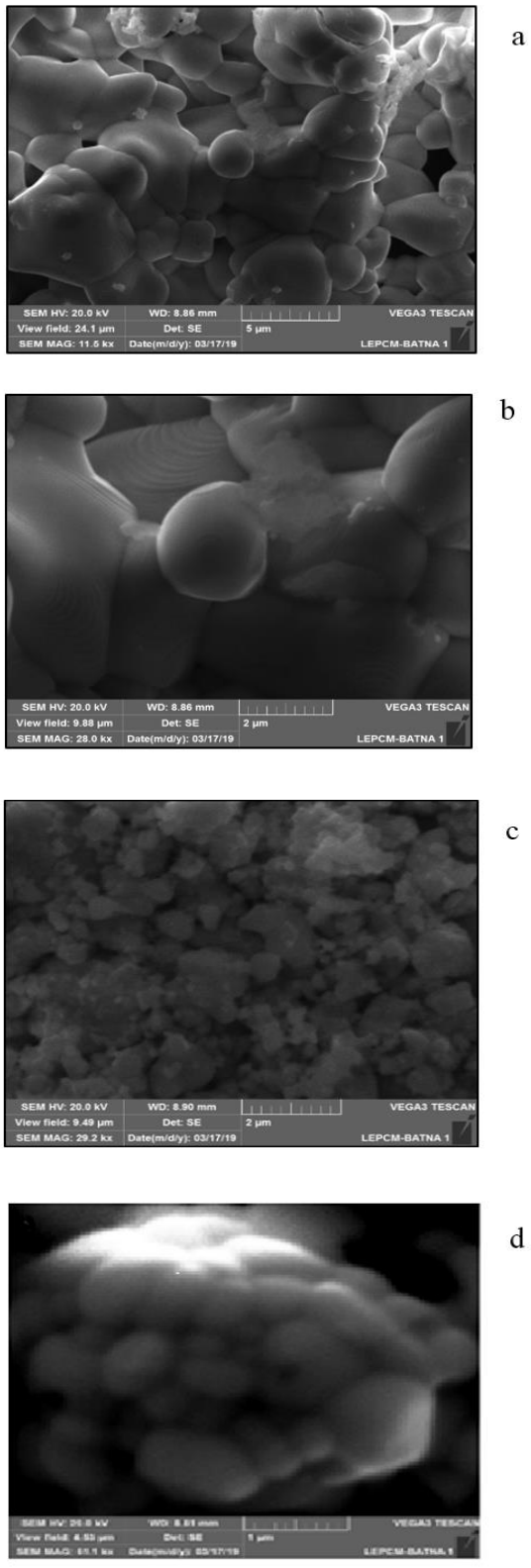


Figure 9. SEM micrographs for the 0.97% sample at different sintering temperatures. (a) 1180 °C; (b) 1150 °C; (c) 1200 °C; (d) 1230°C

4. Conclusion

The objective of this work is part of the study of piezoelectric ceramics of PZT type and of ABO_3 perovskite structure. The interest presented for PZT type piezoelectric ceramics has led us to synthesize new materials which open up many interesting perspectives.

To achieve our objective, the development and synthesis of our ceramics by the "so-called classical method" is implemented. It requires relatively little equipment. A heat treatment at different temperatures (1100 ° C, 1150 ° C, 1180 ° C, 1200 ° C and 1230 ° C) is applied to these samples to monitor and observe their behavior.

Finally, different analysis techniques were used for the morphological and structural identification of this material, among them: X-ray diffraction (DRX), and scanning electron microscopy (SEM). The different analysis methods used made it possible to draw the following conclusions:

-The observations by SEM scanning electron microscopy show dense ceramics and a narrow and homogeneous distribution of the grains whose size is of the order of 1.65µm - 2.14 µm.

-The grain distribution is almost uniform over the entire surface of the sample, the average grain size increases with increasing sintering temperature and increasing Ca rate. To form a denser solution and almost non-porous at 1200 ° C. For all the samples, it is noted that no parasite phase such as pyrochlore is observed on the SEM micrographs. This observation is confirmed by X-ray diffraction (XRD).

-The X-ray diffraction study confirmed the existence of the PZT phase at 900 ° C. The diffractograms of the various samples fried at 1200 ° C. show that the PZT phase is of tetragonal and rhombohedral structure. The mesh parameters of the phase (T + R) (a_R, a_T, c_T) are sensitive to the percentage percentage of lead.

-The second composition (0.97) is the best because it has a higher density and a lower porosity, the average grain size is also higher.

Following the results found it can be said that the PZT 3% composition has better densification and this is confirmed by analysis (DRX) on the one hand, and on the other hand deserves the study of these piezoelectric and dielectric properties to know if tunable industrial applications.

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