



The Formation of Doped PZT Solid Solution and Its Structural Characterization

Kribaa O. Keltoum^{1*}, Louiza Zenkhri², Ahmed Boutarfaia¹

¹ Applied Chemistry Laboratory, University of Biskra, Box 145 RP, Biskra 07000, Algeria

² Valorisation and Promotion of Saharan Resources Laboratory (VPRS), Chemistry Department, Faculty of Mathematics and Material Sciences, Kasdi Merbah University, Ouargla 30000, Algeria

Corresponding Author Email: oumkeltoum.kribaa@univ-biskra.dz

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ABSTRACT

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The main objective of this work is the synthesis, structural and morphological characterization of ceramics materials. Abbreviated PZT-PYN. Ferroelectric ceramics of general formulation $Pb(Zr_xTi_{1-x})O_3$ are massively used in many fields such as medicine or aeronautics because of their dielectric and electromechanical properties, although the electronic properties of doped PZT are much better compared to undoped PZT. Samples selected for this study were prepared by solid way. The thermal treatment called calcination was applied to these compositions is carried around: 450°C, 550°C, 650°C, 750°C, and 900°C for two hours with a Vitesse of 2°C / min., then sintered at different temperatures: 1100°C, 1150°C, 1180°C, successively to optimize the sintering temperature where the product is better physical quality. Different techniques of characterization were used such as scanning electron microscopy (SEM), x-ray diffraction (XRD) analysis, and Energy-dispersive spectrometric, which showed that the response is optimal for the compositions included in the morphotropic phase boundary, achieves excellent properties.

1. INTRODUCTION

Lead zirconatetitanate is carefully designed because of its better properties, as well known [1, 2], and is widely used in the electronics industry because of its piezoelectric properties. Various means, such as transducers and integrated circuits for microelectronic applications use this type of ceramic [3]. This material has been the subject of extensive studies since the miscibility of lead titanate and zirconate was discovered in 1950 [4]. Lead zirconatetitanate (PZT) is known with perovskite structure (ABO_3) in which A-site is busy by the Pb^{2+} ions and the B site by Zr^{4+} and/or Ti^{4+} ions [5]. The addition of different dopants in the matrix (PZT) is the way to improve the different properties, to synthesize new ceramic materials for better applications. For these reasons, many researchers have studied the composition of PZT modified by substitution at sites A and B [6-8], use dopants to improve the electrical and mechanical properties of ceramic materials. The properties of the PZT samples are related to the nature of dopants, composition, and the method of synthesis [9]. Various methods are used to locate the compositions corresponding to the morphotropic phase boundary of PZT-type ceramics and its derivatives (addition of dopants), among which: X-ray diffraction analysis [10, 11]. The theoretical thermodynamic analysis [12, 13]. Measurements of dielectric and piezoelectric properties [14-16].

In the present work, PYN-PZ-PT ceramics have been prepared by using the solid-state reaction method. The structural, morphological, and spectroscopic properties have been investigated and well discussed.

2. EXPERIMENTATION

2.1 Starting products

The starting products were basic oxides and were commercial powders: PbO (99% Biochem), ZrO_2 (99% Biochem), TiO_2 (99% Biochem), Y_2O_3 (99.6% Alfa Aesor), NiO (99.6% Stream chemical). Titanium Dioxide TiO_2 : is a white amorphous powder with a melting point of 2000°C. Rutile TiO_2 has a quadratic structure and crystal lattice parameters $a = 4.59 \text{ \AA}$ and $c = 2.96 \text{ \AA}$. Zirconium Oxide ZrO_2 : with good hardness, good resistance to thermal shock and corrosion, low thermal conductivity and a low coefficient of friction. The mesh is monoclinic with crystal lattice parameters $a = 5.14 \text{ \AA}$, $b = 5.20 \text{ \AA}$ and $c = 5.21 \text{ \AA}$, $\beta = 80.45^\circ$. Its melting point is 2700°C. Lead monoxide PbO : is a yellow or red crystalline powder obtained by heating lead in the presence of air with an orthorhombic structure ($a = 5.489 \text{ \AA}$, $b = 4.755 \text{ \AA}$, $c = 5.891 \text{ \AA}$) or quadratic red solid ($a = 3.9729 \text{ \AA}$, $c = 5.0192 \text{ \AA}$), and which has a melting temperature of 888°C. There is a transition from red oxide to yellow at 587°C, has a molecular weight of 223.20 g/mol and a density of 9.53 g/ml. The compound is not very soluble in water, insoluble in alcohol. The compound is a weak oxidizing or reducing agent. Nickel oxide NiO : crystallizes in the NaCl type structure. It is obtained by the pyrolysis of divalent nickel compounds such as $Ni(OH)_2$, $Ni(NO_3)_2$ or $NiCO_3$. NiO is non-stoichiometric (the Ni/O ratio is slightly different from 1) $a = 424 \text{ pm}$, mesh volume: $V = 7.62 \cdot 10^{-29} \text{ m}^3$. Its melting temperature is approximately 2852°C [17-22].

2.2 Development

The raw materials are oxid: PbO, ZrO₂, and TiO₂. An ideal powder can be described as being formed from small grains, mixing and grinding are essential steps in the manufacturing cycle, it is also during this operation that a uniform distribution of the precursors is obtained [23].

The powders are weighed according to the stoichiometric quantities provided by the reaction equation.

Pb [(Zr_{0.52}, Ti_{0.48})_{1-x}, x(Y_{1/2}, Ni_{1/2})]O₃ powders are mixed in an acetone medium for four hours using a magnetic stirrer to obtain a homogeneous mixture [24]. The mixture is then dried for two hours at 90°C in an oven. The grinding is done in a glass mortar for six hours. The powder obtained then undergoes a first heat treatment called calcination. It can take place in different atmospheres [25].

The heat treatment is carried out from 450°C to 900°C for two hours in a programmable oven (Nabertherm) with a temperature rise slope of 2°C / min.

Regrinding: After the heat treatment, the powder is reground introduces the grains' size, to homogeneity and to hemease its reactivity.

The particle size of the powder is an essential parameter for the materials morphology study, the grains must be quite fine for practical reasons: to facilitate the homogeneous melting of all the material, to avoid a strong retention of air in the material and finally, to prevent the grains from sticking to each other, except on the surface. The average particle size in our ceramic materials is reduced after heat treatment (calcination) as shown in Table 1:

Table 1. The average particle size

The starting products	D (0.5) μm
TiO ₂	24.293
ZrO ₂	14.723
PbO	37.533
PZT powder	D (0.5) μm
PZT calcined at 450°C	0.180
PZT calcined at 550°C	0.173
PZT calcined at 750°C	0.172
PZT calcined at 900°C	0.171

The powder is then subjected to a heat treatment at a high temperature (1100,1150 and 1180°C) to obtain the desired phases [26]. In order to obtain a denser product (At these temperatures, we have the highest density values, which leads to the most compact structure) with better physical quality.

Table 2. Matrix for each composition

Sample	Matrix	doping rate
S1	Pb [(Zr _{0.52} ,Ti _{0.48}) _{1-0.01} ,0.01(Y _{1/2} , Ni _{1/2})]O ₃	1%
S2	Pb[(Zr _{0.52} ,Ti _{0.48}) _{1-0.03} ,0.03(Y _{1/2} , Ni _{1/2})]O ₃	3%
S3	Pb [(Zr _{0.52} ,Ti _{0.48}) _{1-0.05} ,0.05(Y _{1/2} , Ni _{1/2})]O ₃	5%
S4	Pb [(Zr _{0.52} ,Ti _{0.48}) _{1-0.07} ,0.07(Y _{1/2} , Ni _{1/2})]O ₃	7%
S5	Pb [(Zr _{0.52} ,Ti _{0.48}) _{1-0.10} ,0.10(Y _{1/2} , Ni _{1/2})]O ₃	10%

The crystalline phases analysis of the powders was carried out on X-ray diffraction θ/2θ Siemens D 5000 diffractometer. The diffractograms were acquired with K_α radiation from copper on and counting times between 2 and 10 s. The samples analyzed are presented in the form of powders. The device used is from mark RIGAKU MINIFLEX 600 (Table 2).

FT-IR spectroscopy was carried out by Shimadzu FTIR-

8400S. Sample preparation consisted of mixing 0.001g of PZT powder with 0.2g of potassium bromide (KBr), compressed to form a tablet and then placed on the specimen holder to be analyzed at a range of 400 to 4000 cm⁻¹ at 4 cm⁻¹ resolution.

Energy dispersive x-ray systems are often attachments to scanning electron microscopy instruments. Typically scanning electron microscopy provides the visual analysis and energy dispersive x-ray provides the elemental analysis for this characterization, samples were prepared in discs. For doing 0.45g of the material powder was pressed using a Specac hydraulic press with a load pressure of 2.5 tons.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD)

X-ray diffraction results for powderS3: Pb [(Zr_{0.52},Ti_{0.48})_{1-0.05},0.05(Y_{1/2}, Ni_{1/2})]O₃ calcined at different temperatures are shown in Figure 1.

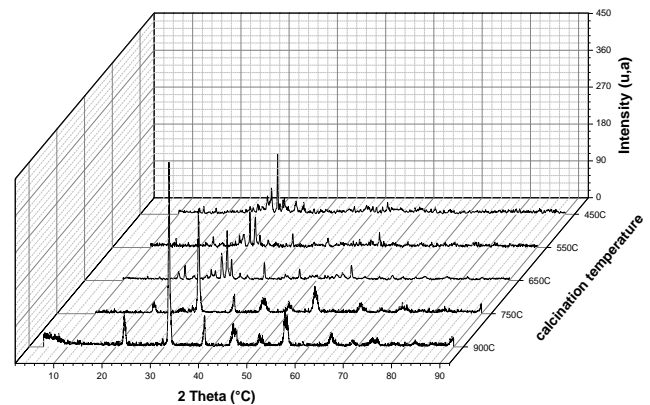


Figure 1. X-ray diffraction diagram of the calcined powder (S3)

The existing phases obtained in the diffractograms of X-ray diffraction were followed by their characteristic peak of intensity in the A.S.T.M.

Pattern List

450°C

Ref.Code	Compound Name	Chem. Formula
98-006-2842	Litharge	PbO
98-000-9754	Minimu	Pb ₃ O ₄
98-016-4736	Zirconium Oxide	ZrO ₂
98-004-0180	Massicot	PbO

550°C

Ref.Code	Compound Name	Chem. Formula
98-002-9117	Macedonite	PbTiO ₃
98-006-0135	Massicot	PbO
98-006-2845	Litharge	PbO
98-009-4566	Anatase, nanocrystal.	TiO ₂
98-009-2091	Zirconia (nanocrystal)	ZrO ₂

650°C

Ref.Code	Compound Name	Chem. Formula
98-016-5498	Lead Titanate	PbTiO ₃
98-008-7587	Lead Zirconate	PbZrO ₃
98-006-0900	Baddeleyite	ZrO ₂
98-007-7648	Lead(IV) Oxide	PbO ₂
98-065-7748	Titanium Oxide	TiO ₂

750°C

Ref.Code	Compound Name	Chem. Formula
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98-024-6571	Lead Zirconium Titanate	PbTi _{0.48} Zr _{0.52} O ₃
98-016-2044	Lead Titanate	PbTiO ₃
98-006-2845	Litharge	PbO
98-004-0180	Massicot	PbO
98-009-3126	Zirconia	ZrO ₂
98-009-7282	Minium	Pb ₃ O ₄
98-008-7587	Lead Zirconate	PbZrO ₃
98-006-9331	Rutile	TiO ₂

900°C

<u>Ref.Code</u>	<u>Compound Name</u>	<u>Chem. Formula</u>
98-024-6570	Lead Zirconium Titanate	PbTi _{0.48} Zr _{0.52} O ₃

The results obtained admit the formation of PbTiO₃ begins from 550°C and that of PbZrO₃ from 650°C while the appearance of the PZT solid solution from 750°C with the persistence of the base oxides, whereas at a temperature of 900°C, the stabilization of PZT solid solution is noted without base oxides or intermediate products.

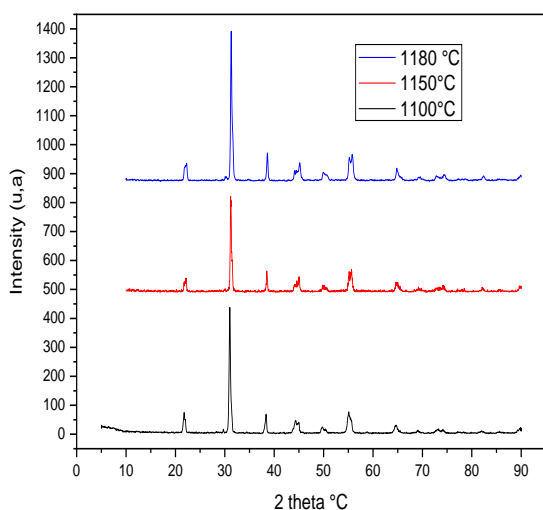


Figure 2. X-ray diffraction diagram of the sintered powder (S3)

From the diagrams in Figure 2, we derive the following information:

At T=1100°C

<u>Ref.Code</u>	<u>Compound Name</u>	<u>Chem. Formula</u>
98-009-7059	Lead Zirconium Titanate	PbTi _{0.48} Zr _{0.52} O ₃

Relevant parameters of Lead Zirconium Titanium Oxide

Density (calculated)/ g/cm³: 8,0045
 Space group (No.): P 4 mm (99)
 Lattice parameters: a/ Å: 4,043000 b/ Å 4,043000
 c/ Å: 4,132000, alpha/°: 90 beta/°: 90 gamma/°: 90
 V/ 10⁶ pm³: 67,54105

At T=1150°C

Pattern List

<u>Ref.Code</u>	<u>Compound Name</u>	<u>Chem. Formula</u>
98-009-7060	Lead Zirconium Titanate	PbTi _{0.48} Zr _{0.52} O ₃
98-007-5312	Zirconium Yttrium	Zr _{0.84} Y _{0.16} O _{1.92}

Relevant parameters of Lead Zirconium Titanium Oxide

Density (calculated)/ g/cm³: 8,0835
 Space group (No.): P 4 mm (99)
 Lattice parameters: a/ Å: 4,017000b/ Å: 4,017000 c/ Å: 4,142000, alpha/°: 90 beta/°: 90 gamma/°: 90V/ 10⁶pm³:

66,83652

Formula sum: Zr_{0.84}Y_{0.16}O_{1.92}

Density (calculated)/ g/cm³: 5,9427

Space group (No.): P 42/n m c (137)

Lattice parameters: a/ Å: 3,635000b/ Å: 3,635000 c/ Å: 5,141000 alpha/ °: 90 beta/ °:90gamma/ °: 90V/ 10⁶ pm³: 67,92919

At T=1180°C

Pattern List

<u>Ref.Code</u>	<u>Compound Name</u>	<u>Chem. Formula</u>
98-024-6569	Lead Zirconium Titanate	PbTi _{0.48} Zr _{0.52} O ₃

Relevant parameters of Lead Zirconium Titanium Oxide

Density (calculated)/ g/cm³ 8,0918

Space group (No.): P 4 mm (99)

Lattice parameters: a/ Å: 4,030(7 b/ Å: 4,030(7 c/ Å: 4,110(8)
 alpha/ °: 90 beta/ °: 9 gamma/ °: 90 V/ 10⁶ pm³: 66,76814

The structure of PZT-YN (Pb [(Zr_{0.52},Ti_{0.48})_{1-0.05},0.05(Y_{1/2},Ni_{1/2})]O₃) studied is stable, this stability is due to the reduction of the distortion ratio c_T/a_T from the sintering temperature 1100°C to the optimum temperature 1150°C (Figure 3).

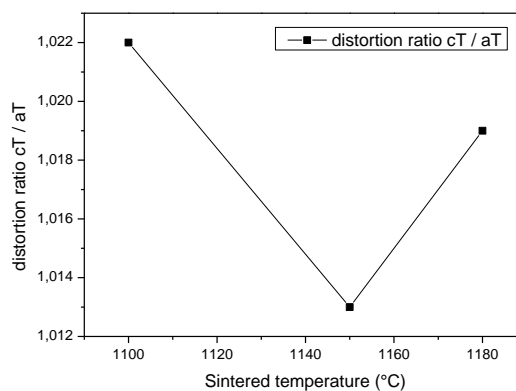


Figure 3. Evolution of the distortion ratio of the “S3” sample as a function of the sintering temperature

3.2 Energy dispersive spectrometric analysis (EDS)

This analysis allows the identification of the elements constituting our ceramic as well as the observation or not of secondary phases. The analysis results for the samples are shown in Figures 4 and 5.

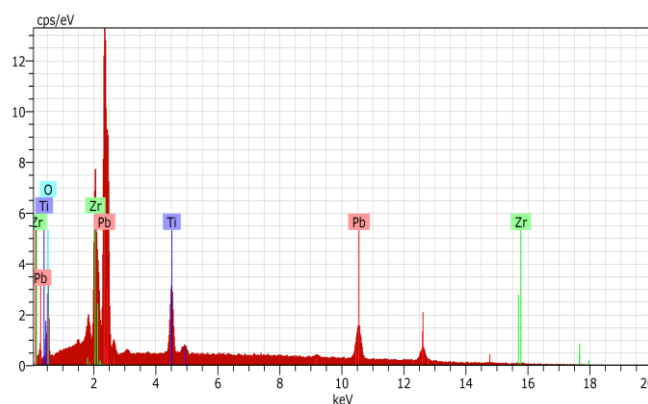


Figure 4. EDS spectrum for composition S3 calcined at 900°C

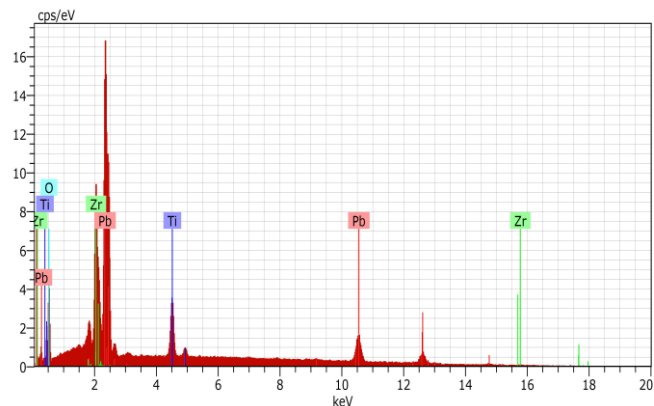


Figure 5. EDS spectrum for composition S3 sinter at 1180°C

We can observe the peaks detecting main elements of "Pb, Zr, Ti, O" for the two samples with an excess of Pb. As regards the dopants, the device could not detect them. The cause may be the low rate. The absence of the peaks representing the impurities was also observed for the two samples. This observation is confirmed by the phase diagrams analyzed by X-rays and by the photographs taken by the scanning electron microscope.

According to Figure 6, distribution of the grains is almost uniform on the whole of the surface of sample, the grain size increases with increasing heat treatment temperature to form more dense and non-porous solution at a temperature of 1150 and 1180°C in Figure 6 (c and d), the increase of grain size is due to the decrease in oxygen vacancies and with increasing the dopants percentage in the PZT [27].

In the follow-up process:

In perspective, it will be interesting in the continuation of this research to carry out dielectric and piezoelectric measurements for the elaborated powders, according to their composition and calcination temperature to better improve their applications in the industrial and medical fields.

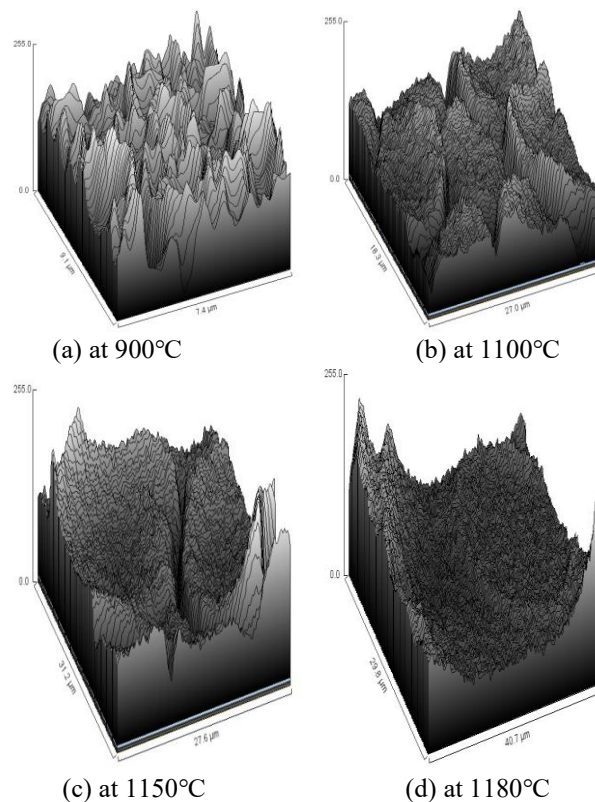
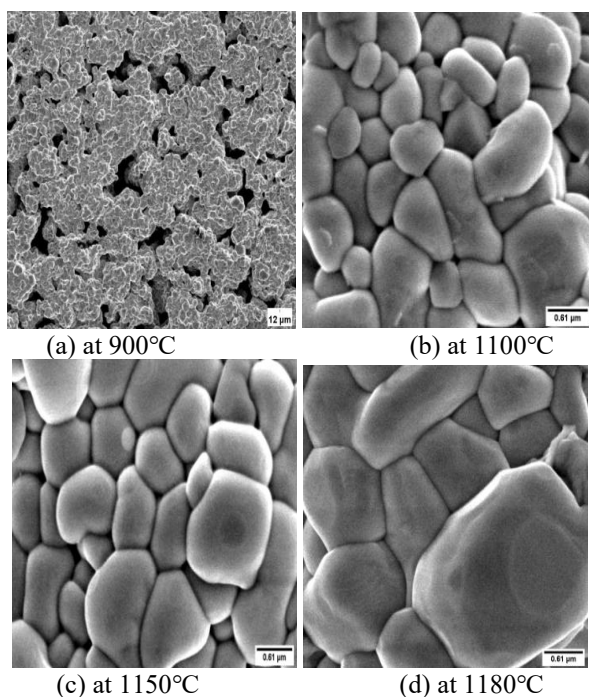


Figure 6. Scanning electron microscope photographs for S3 composition treated at different temperatures

4. CONCLUSION

Our work is devoted to the synthesis the solid solution of PZT- PYN by the solid route and their characterization from a structural point of view. The mechanism of formation of the solid solution of lead zirconate-titanate PZT, of the perovskite structure by a doped matrix, has been studied using several experimental techniques such as X-ray diffraction, energy dispersive spectrometric analysis, and Scanning electron microscopy.

The following essential points should be noted for the formation of the PZT solid solution:

The gradual decrease in the intensities of the characteristic peaks of the basic oxides PbO, TiO₂, ZrO₂. The gradual appearance of characteristic peaks of PbTiO₃ from 550°C, of the characteristic peaks of PbZrO₃ from 650°C, and Pb [(Zr_{0.52},Ti_{0.48})_{1-0.05},0.05(Y_{1/2}, Ni_{1/2})]O₃ from 750°C. Total formation of the solid solution (PZT-PYN) at 900°C.

The grain distribution is almost uniform over the entire surface of the sample, the average grain size increases significantly with increasing sintering temperature. To form a more dense and non-porous solution at a temperature of 1180°C. The structure of PZT-PYN studied is stable, this stability is due to the reduction of the distortion ratio CT/ aT from the sintering temperature 1100°C to the optimum temperature 1150°C.

For all samples, it is noted that no parasite phase such as pyrochlore is observed on the SEM micrographs, X-rays and Energy Dispersive Spectrometric Analysis (EDS) confirm these results.

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