

PHASE STRUCTURE, MICROSTRUCTURE AND DIELECTRICS PROPERTIES OF NEW CERAMIC MATERIAL NEAR THE MORPHOTROPIC PHASE BOUNDARY

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ABSTRACT

This article investigates the sintering temperature effect on microstructure and dielectric properties of a new ceramic material : $Pb_{0.96}Sm_{0.02}Nd_{0.02}[(Zr_{0.55}Ti_{0.45})_{1-2x,x}(Y_{2/3}Mo_{1/3})_x(Y_{2/3}Ni_{1/3})]O_3$ of perovskite structure , such that $x = \{0.01,0.03,0.05,0.07,0.1\}$. In order to study well this system and delimiting the composition close to the morphotropic phase boundary (FMB) in which the tetragonal and rhombohedral phases coexist, we varied the dopants ratio for that various compositions were prepared by conventional solid state process. A thermal treatment was applied to these compositions at different temperatures (1100, 1150, 1180°C), in order to optimize the sintering temperature where the density of ceramics is maximum. We present the preparation and the different stages of the formation 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, analysis by scanning electron microscopy (SEM) and finally the study of physical properties (dielectrics). These studies help us to accumulate as much information on these materials.

KEYWORDS: Ceramic; Microstructure; dielectrics.

1 INTRODUCTION

The lead zirconate titanate materials $Pb(Zr_xTi_{1-x})O_3$ (PZT) of a perovskite-type represented by the formula ABO_3 , have been extensively used for the piezoelectric applications such as capacitors, sensors, actuators and other high piezoelectric devices. In the PZT materials, the dielectric, the ferroelectric, and the electromechanical characteristics have been modified when several substitutions were being done on the A- or/and B-sites, and also by varying the ratio of Zr/Ti [1-2]. Since the discovery of the behavior of the relaxor in $Pb(Mg_{1/3},Nb_{2/3})O_3$ [3], $Pb(Zn_{1/3},Nb_{2/3})O_3$ [4], and $Pb(Ni_{1/3},Nb_{2/3})O_3$ [5], the studies of the ferroelectrics of the relaxor with $Pb(B^{1/3}, B^{2/3})O_3$ -type perovskites have attracted much attention because of their excellent dielectric and electromechanical properties.

In a conventionally prepared PZT ceramics with compositions near the morphotropic phase boundary (MPB), the tetragonal, and the rhombohedral phases always coexist [5]. The width and the properties of the Coexistence region are associated with the occurrence of the compositional fluctuation of Ti^{4+} and Zr^{4+} ions in the PZT materials [6]. The compositional fluctuation, which is due to a non uniform distribution of Titanium and Zirconium ions, leads to a broad variation in the dielectric constant accompanied with a Zirconium concentration in the MPB region [7]. The width of this coexistence region and the

structure of the PZT ceramics were greatly affected by the firing time and temperature [8]. The selection of dopants or substitutions to tailor some physical properties of PZT was based on many factors which are the following: 1) charge neutrality, 2) tolerance factors, 3) ionic radius, and 4) solubility/ miscibility. The substitution of lanthanides and the different doped material at Pb-sites and Zirconium at the Ti-sites with a different ratio of Zr/Ti have produced many solid solutions with interesting properties for wide industrial applications. The dopant can improve the sintering process, produce ceramics with high specific mass, reduce the lead oxide evaporation, and prevent the formation of second phases [9].

Besides, dopants also engender the substitution of A or B cations of ABO_3 perovskite structure. Ions of higher valence, such as Nb^{5+} , cause vacancies in the A cation called lead vacancies; and the lower valence ions, as Fe^{3+} , result in vacancies [10]. The additives that increase the amount of oxygen vacancies cause a small reduction of the unit cell dimensions, increase the internal stress; and, consequently, increase the coercitive field.

Therefore, the additives that accept electrons are called hardener additives. The material doped with iron presents lower dielectric constant, and loses constant when the mechanic quality factor is increase [11]. Therefore, according to [12] the vacancies of oxygen generated by the addition of iron are suppressed when there are niobium and

iron equimolar compositions. In a polycrystalline system, dielectric and piezoelectric properties are dependent on both intrinsic and extrinsic mechanisms [13,14]. Intrinsic contributions are from the relative ion or cation shift that protects the ferroelectric crystal structure.

In this study, $\text{Pb}_{0.96}\text{Sm}_{0.02}\text{Nd}_{0.02}[(\text{Zr}_{0.55}\text{Ti}_{0.45})_{1-2x},x(\text{Y}_{2/3}\text{Mo}_{1/3}),x(\text{Y}_{2/3}\text{Ni}_{1/3})]\text{O}_3$ piezoelec ceramics were investigated near the MPB by varying the ratio of dopant . The purpose of this work was to study the phase structure, the dielectric properties of these ceramics near the MPB in detail.

2 EXPERIMENTAL PROCEDURE

The polycrystalline samples with a general compositional formula $\text{Pb}_{0.96}\text{Sm}_{0.02}\text{Nd}_{0.02}[(\text{Zr}_{0.55}\text{Ti}_{0.45})_{1-2x},x(\text{Y}_{2/3}\text{Mo}_{1/3}),x(\text{Y}_{2/3}\text{Ni}_{1/3})]\text{O}_3$, such that $x = \{0.01,0.03,0.05,0.07,0.1\}$ were being prepared by a conventional dry ceramic method to form the solid solution . The reagent grade oxide of Pb_3O_4 , ZrO_2 , TiO_2 , NiO , Y_2O_3 , Sm_2O_3 , MoO_3 and Nd_2O_3 were used as starting materials in a stoichiometric ratio.

The powders were, first, ball milled for Six hours; and then, calcined at 800°C for two hours at the following heating and cooling rates: $2^\circ\text{C}/\text{min}$. After calcination, the mixture was, first, ball milled for Six hours; and then, after drying, the powders were pressed into discs of a diameter of thirteen millimeters and of a thickness of about one millimeter. The compacted discs were being sintered at a temperature ranging from 1100°C - 1180°C for two hours in air. To prevent PbO volatilization from the pellets, a PbO atmosphere was controlled with a bed of PbZrO_3 powder placed in the vicinity of the pellets.

The X-ray diffraction (XRD, Simens D500) was used to determine the crystalline phases present in the powder. The compositions of PZT phases were identified by the analysis of the peaks [(002)T, (200)R, (200)T] in the twenty range 43° - 46° . The Cu K radiation with a step of 0.01° was used. The bulk densities of the sintered ceramics were being measured by the Archimedes method. The micrographs of the fractured samples were taken on a JEOL scanning electron microscope. The average grain size of the samples was determined from the micrographs by the linear intercept technique. To investigate the electrical properties, the electrodes were made by applying a silver paste on the two major faces of the sintered disks followed by a heat treatment at 750°C for thirty minutes. The dielectric constant was calculated from the capacitance at a frequency of one kHz. It was measured at temperatures ranging from 25°C to 400°C with a heating rate of one $5^\circ\text{C}/\text{minute}$ by using an impedance analyzer (HP 4192A, Hewlett-Packard).

3 RESULTANTS AND DISCUSSIONS

Sintered powders were examined by X-ray diffractometry to ensure phase purity and to identify the phases and lattice constants of the materials. The co-existence of tetragonal

and rhombohedral phases near the morphotropic phase boundary implies the existence of compositional fluctuation. The compositional fluctuation can in principle be determined from the width of the X-ray diffraction peaks. A morphotropic phase boundary « co-existence region » was observed [shown by duplicated (200) peaks]. it has been reported in the literature [5,6] that the splitting of these reflections into triplets takes place in conventionally prepared ceramics due to compositional fluctuations leading to the co-existence of the tetragonal and rhombohedral phases (T+R).The X-ray diffraction patterns of $\text{Pb}_{0.96}\text{Sm}_{0.02}\text{Nd}_{0.02}[(\text{Zr}_{0.55}\text{Ti}_{0.45})_{1-2x},x(\text{Y}_{2/3}\text{Mo}_{1/3}),x(\text{Y}_{2/3}\text{Ni}_{1/3})]\text{O}_3$ materials ($x = 0.01$, 0.03 , 0.05 , 0.07 and 0.1), represented by samples A1,A2 ,A3 ,A4 and A5 are given in(figure 1).

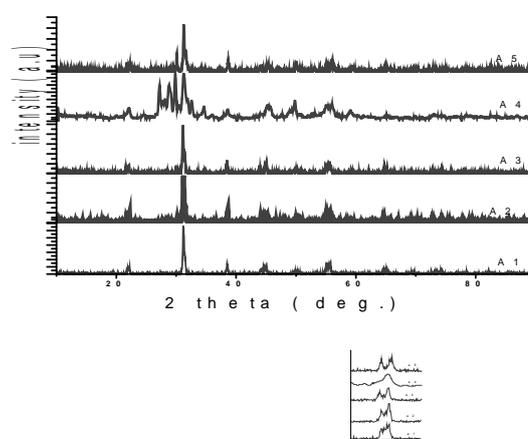


Figure 1: XRD patterns obtained by $\text{Pb}_{0.96}\text{Sm}_{0.02}\text{Nd}_{0.02}[(\text{Zr}_{0.55}\text{Ti}_{0.45})_{1-2x},x(\text{Y}_{2/3}\text{Mo}_{1/3}),x(\text{Y}_{2/3}\text{Ni}_{1/3})]\text{O}_3$ after crushing the pellets at 1180°C for 2 h : (A1) $x=0.01$; (A2) $x= 0.03$; (A3) $x=0.05$; (A4) $x=0.07$; (A5) $x=0.1$.

Triplet peaks around $2\theta = 45^\circ$ indicate that the specimen consists of a mixture of tetragonal and rhombohedral phases. so the morphotropic phase boundary (MPB) of solid solution is located at $x = x = 0.07$ (A4 sample) and at $x=0.01$ (A1 sample).

It is shown that the tetragonal structure can be formed up to $x_T < 44$. While the rhombohedral structure becomes stabilized for $x_R > 45$, however, at $x = 44-45$ tetragonal and rhombohedral phases coexist .The width $x = x_T - x_R$ of the co-existence region from our work is close to that obtained by others [15, 16, 17].

The variation of the lattice parameters as a function of sintering temperature could be explained by the enhancement of cation diffusion . and consequently by the homogenization of the micro composition .The variation in the lattice parameters of the identified phase composition shows that the values of the cT/aT ratio have decreased .

Figure2 shows the lattice parameters variations for the composition $\text{Pb}_{0.96}\text{Sm}_{0.02}\text{Nd}_{0.02}[(\text{Zr}_{0.55}\text{Ti}_{0.45})_{1-0.02},0.01(\text{Y}_{2/3}\text{Mo}_{1/3}),0.01(\text{Y}_{2/3}\text{Ni}_{1/3})]\text{O}_3$ As a function

of sintering temperature. This can be explained by microscopic compositional fluctuations occurring in these perovskite materials, which cannot provide a real homogeneity in the solid solutions, which determine the co-existence of tetragonal and rhombohedral phases. [15]

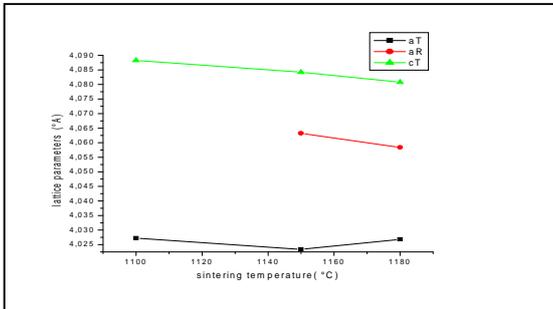


Figure 2: Lattice parameters variations for both coexisting ferroelectric phases as a function of sintering temperature.

(Figure3) shows scanning electron micrographs of the specimens sintered at 1100, 1150 and 1180 °C respectively. From these images, it can be deduced that the decrease of porosity with increasing sintering temperature, is due to a decrease in the number and size of the pores.

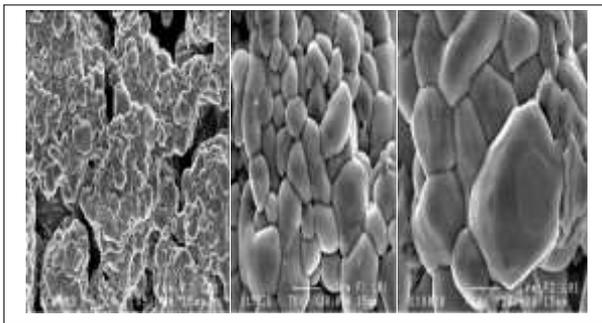


Figure 3: Scanning electron micrographs of polished and chemically etched of: $\text{Pb}_{0.96}\text{Sm}_{0.02}\text{Nd}_{0.02}[(\text{Zr}_{0.55}\text{Ti}_{0.45})_{1-0.02,0.01}(\text{Y}_{2/3}\text{Mo}_{1/3}),0.01(\text{Y}_{2/3}\text{Ni}_{1/3})]\text{O}_3$ sintered at 1100, 1150 and 1180 °C respectively From left to right

(Figure4a) describes the micro structural evolution. Grain size increases with increasing sintering temperature. A uniform microstructure was obtained at 1150 and 1180 °C. While the average grain size was 12-14 μm. This was caused by coexistence of the two phases in these materials. (Figure4b) describes the microstructure evolution with the dopants percentage of the specimens sintered at 1150 °C. Grain size increases with increasing the dopants percentage.

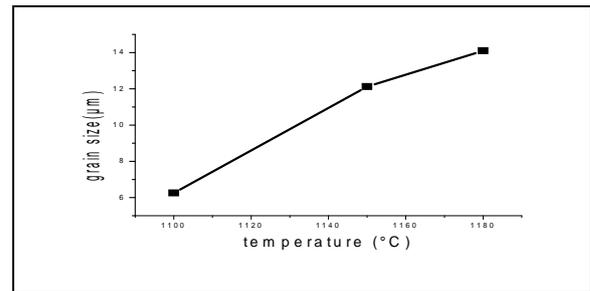


Figure 4a: Grain size versus sintering temperature

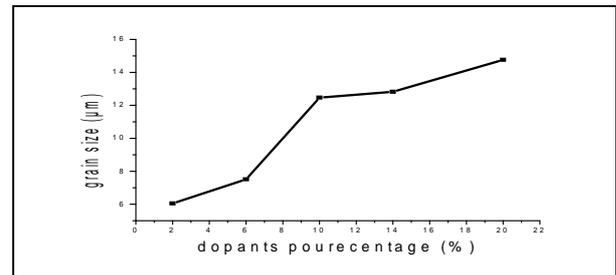


Figure 4b: Grain size evolution with the dopants percentage of the specimens sintered at 1150 °C

Measures of the change in the dielectric constant as a function of temperature is a main objective to determine and compare the temperature of electric transition ferro-para spiked samples.

(Figure5) shows the evolution of the dielectric constant as a function of temperature for 1 kHz as frequency of measurement, the results are given for the sintering temperatures 1100, 1150, 1180 °C. The graphs below show the different samples retain virtually the same speed regardless of the sintering temperature. dielectric constant increases with temperature in the range of ferroelectricity, it passes through a maximum which corresponds to the Curie temperature, and then decreases in the area where the ceramic is not ferroelectric.

Note that the sample of the composition A4, has a dielectric constant value of up to 33283.7954 at sintering temperature to 1100 °C and the sample composition A5, its dielectric constant is 33664.0442 at sintering temperature to 1100 °C. The sample of the A3 composition, the dielectric constant is 120000 at the sintering temperature 1150 °C. The sample A4 of the composition, its dielectric constant is 49179.0849 at sintering temperature to 1180 °C. The maximum dielectric activity can be explained by the presence of several directions of spontaneous polarization on the existence of both rhombohedral and tetragonal structures [18-19].

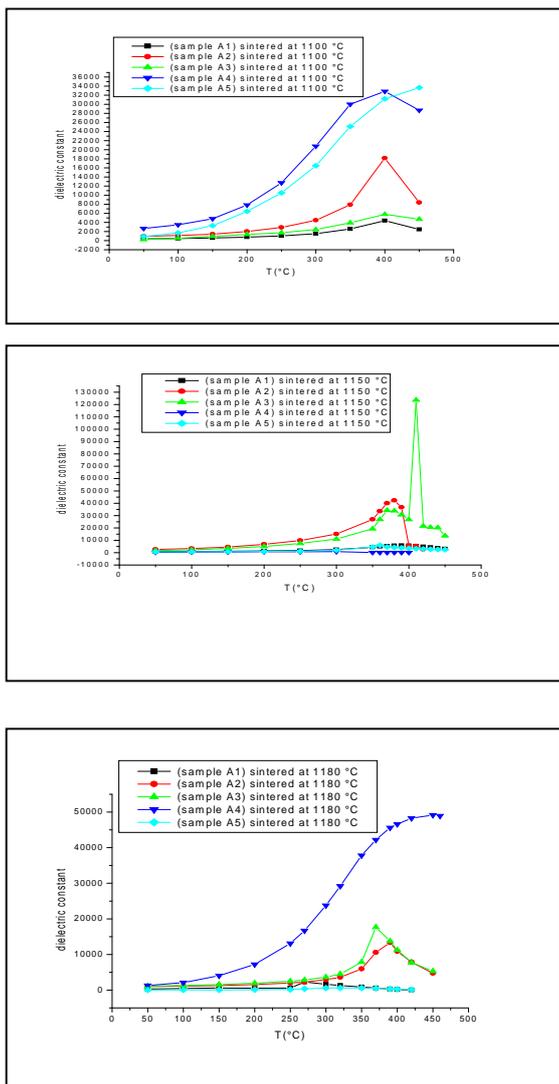


Figure 5: Evolution of the dielectric constant as a function of temperature for all the samples

This constant decreases gradually with increasing frequency Figure 6, It reaches a maximum value at small values of frequency which explained by existence of different polarization models [20, 21].

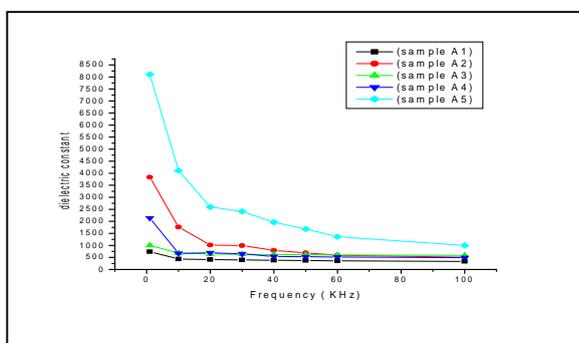


Figure 6: Frequency dependence of ϵ' for all samples sintered at 1180°C .

THE DENSITY

The study of the density is necessary to optimize the optimum temperature sintering. Figure 7 shows the variation of density as a function of sintering temperature, it is seen that there is an increase in density, so the optimum temperature of sintering is 1180 ° C for A1,A2,A3,A4,A5. The quality of the material increases with increasing density and it increases with increasing the sintering temperature [15].

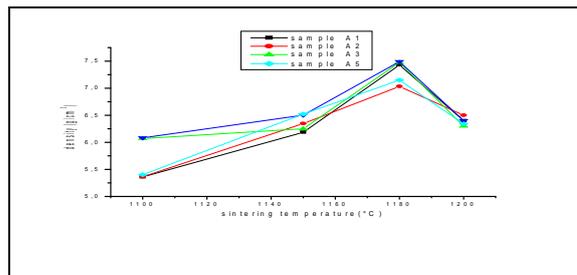


Figure 7: versus of density with the sintering temperature

4 CONCLUSION

The aim of this study was to investigate the structure and the behavior of the electrical properties in $Pb_{0.96}Sm_{0.02}Nd_{0.02}[(Zr_{0.55}Ti_{0.45})_{1-2x}x(Y_{2/3}Mo_{1/3})_x(Y_{2/3}Ni_{1/3})]O_3$ ($x = 0.01, 0.03, 0.05, 0.07$ and 0.1).

The XRD results reveal that the morphotropic phase boundary (MPB) of solid solution is located at $x = 0.01, 0.07$. It was found that the MPB is not a narrow and vertically straight boundary but a region whose width depends on the sintering and the dopants percentage.

The effect of sintering temperature on the density has been studied in order to achieve the optimum sintering temperature. This temperature (1180 ° C) is the maximum value of the density, so the minimum value of the porosity and also corresponds to the product of better quality. The lattice parameter of both the tetragonal and rhombohedral structures varies with the sintering temperature.

The SEM provides information about the shape and size of grains after sintering. It 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, that no parasite phase was observed on the SEM micrographs and a uniform microstructure was obtained 1180 °C. The average grain size was 12-14 μm . This was caused by coexistence of the two phases in these materials.

The grain size increases with increasing the temperature. The lattice parameters and the density increased with increase of the sintering temperature. The dielectric constant of the sintered samples decreased with increase in the frequency. The effects of the sintering temperature on the dielectric properties can be attributed to the change in

the bulk density and the grain morphology.

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