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RESEARCH ARTICLE

SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF PEROVSKITE CERAMICS SYSTEM PFN-PMN

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ABSTRACT

The classical solid state method was developed to prepare solid-solution x PFN + (1-x) PMN, shows a good homogenization of the starting products. The powder was heat treated at 300°C and then calcined at 850°C. The products were characterized by XRD, microstructure of the samples was analyzed with scanning electron microscope (SEM), and dielectric measurements were performed using an impedance analyser (LCR, HP 4284 A) in the frequency range from 100 Hz to 2 MHz.

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INTRODUCTION

The perovskite ferroelectric materials are characterized by a very high dependence their properties with the electrical field, mechanical and thermal of constraints applied and the procedure for their preparation. Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ noted (PMN), is a relaxor ferroelectric material with a high dielectric constant and a large electric field induced (Swartz *et al*., 1984; Nomura and Uchino,1982; Uchino, 1986; Shrout and Halliyal, 1987 and Chen and Harmer, 1990). Pure perovskite PFN phase has been reported to be difficult to obtain because of the pyrochlore which appears during to sintering process (Synthesis by Hydrothermal Process and Characterizations of PFN Phase, 2013). At room temperature the PFN is ferroelectric; Pb^{2+} in site A and Nb^{5+} in site B favor the electric order. Its spontaneous polarization associated with ferroelectricity is caused by lattice distortion. The Fe^{3+} in octahedral sites B provides the magnetic moment of the magnetic order. In this material, the angle B–O–B is clause to $\theta = 180°$, facilitating magnetic ordering via an indirect exchange interaction between the Fe ions through the O ions. This is the basis of coexistence of ferroelectric and ferromagnetic order in this ferro electromagnetic material (Alvareza *et al*., 2007).

Ananta and Thomas developed two-stage mixed oxide synthetic routes for the preparation of single phases of lead-based complex perovskite PMN and PFN and two complexes perovskite compounds at selected compositions in the PMN–PFN pseudo-binary system were prepared and characterized (Ananta and Thomas,1999; Jun *et al*., 1998). $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) have received considerable attention since the late 1970 and have been applied recently in multilayer ceramic capacitors (MLCCs) and electrostrictive actuators (Uchino, 1986; Swartz *et al*., 1984). Lead magnesium niobate (PMN) and lead iron niobate (PFN) are the ferroelectric ceramics having perovskite structure. Both of these compounds have high dielectric constant (10 000–20 000) and the change of their dielectric constant with respect to temperature is gradual, showing diffused phase transition peaks at -120°C (PMN) and 110°C (PFN) respectively (Dhirendra Mohan *et al*., 2001). In the present paper we describe. The preparation of solid solution x PFN + (1-x) PMN ceramics, obtained from a classical solid process mixing PbO, MgO, Nb_2O_5 and Fe_2O_3. The phases formation of the perovskite PFN-PMN and the effect of the sintering temperature on the microstructure and the electrical properties will be presented and discussed.

Procedure experimental

PMN and PFN phases perovskite are developed by using solid oxides PbO, MgO, Fe_2O_3 and Nb_2O_5 taken in stoichiometric amounts according to the following reactions.

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$$3PbO + MgO + Nb_2O_5 \rightarrow 3Pb\,(Mg_{1/3}Nb_{2/3})\,O_3 \quad \text{Noted (PMN) (1)}$$
$$4PbO + Fe_2O_3 + Nb_2O_5 \rightarrow 4Pb\,(Fe_{1/2}Nb_{1/2})\,O_3 \quad \text{Noted (PFN) (2)}$$

The oxides were mixed and ground in an agate mortar for 1 hour to have a uniform distribution. The resulting mixture was placed in a nacelle and a heat treated to 300°C for 2h. After removing the product from the oven, we proceed to another mill for 30 min. The mixture solid solutions xPFN + (1-x)PMN, is obtained after we calcined products at 850°C with a step of 5°C/mn for 4 hours. The different types of systems have been developed for compositions x = 0; 0.1; 0.3; 0.5; 0.7; 0.9 and 1

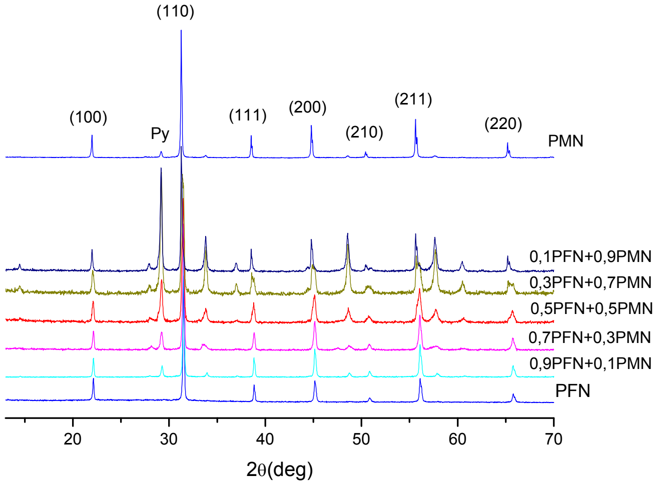

Figure 1. XRD spectrum of the system xPFN + (1-x) PMN treated at 850°C for 4 h

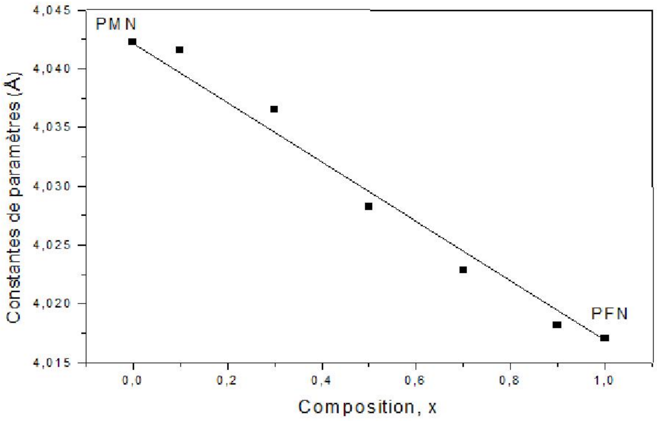

Figure 2. Variation of the parameter (a) of the system x PFN + (1-x) PMN

RESULTS AND DISCUSSION

Analysis of formed phases

The XRD pattern of the solid solution x PFN + (1-x) PMN system with different compositions x are shows in Figure.1. In the sample of x = 0, the XRD patterns appearance of intense peaks a large proportion of the perovskite phase PMN[$Pb(Mg_{1/3}Nb_{2/3})O_3$] from the peak characterize of the pyrochlore $Pb_{1.38}Nb_{1.71}Mg_{0.29}O_{6.39}$ at peak 29.2°. The magnesium substituted in the niobium during the synthesis of PMN.

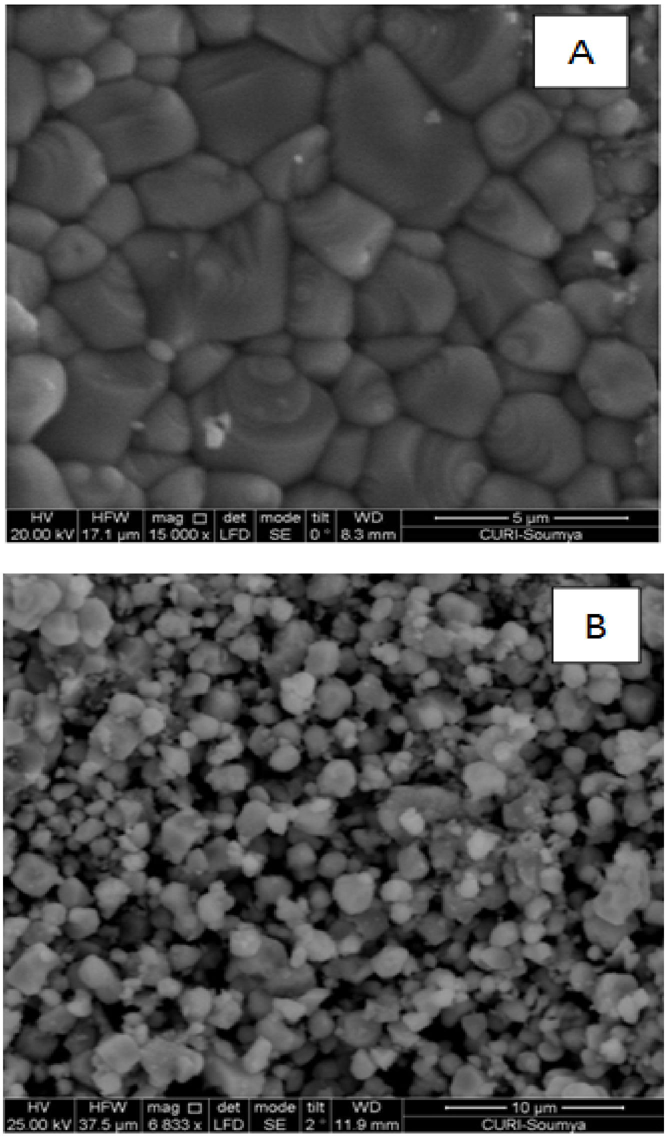

Figure 3. Microstructure of the PFN (A) and PMN (B) samples heat treated at 850°C/4 h

For x = 1, there is the characteristic peaks of pure perovskite phase PFN. The intensity of diffraction peaks changed depending on temperatures and maximum perovskite phase was obtained at 850°C. For x = 0.9, we note that in addition to the lines of the PFN stage, the appearance of a characteristic line pyrochlore $Pb_{1.5}Nb_2O_{6.5}$ of the position 2θ = 29.2593° studied by ROTH (Roth, 1959), indexed in a cubic lattice parameter neighbor.

From x = 0.7 we notice to the presence of the perovskite phase, the appearance of two phases pyrochlore $Pb_6MgNb_{10}O_{32}$ and $Pb_{2.29}Nb_2O_{7.29}$. [The change in x values effect the formation of pyrochlore phase in this temperature range]. The study of the variation of the parameter a in the cubic lattice function of x in the xPFN + (1-x) PMN system, indicates that it decrease linearly with increasing x (Fig. 2). This parameter changes from 4.0425Å for x = 0 (PMN) to 4.0175Å for x = 1 (PFN). In the solid solution xPFN + (1-x)PMN is noted that the perovskite phase evolves according to x, at the expense of the pyrochlore phase.

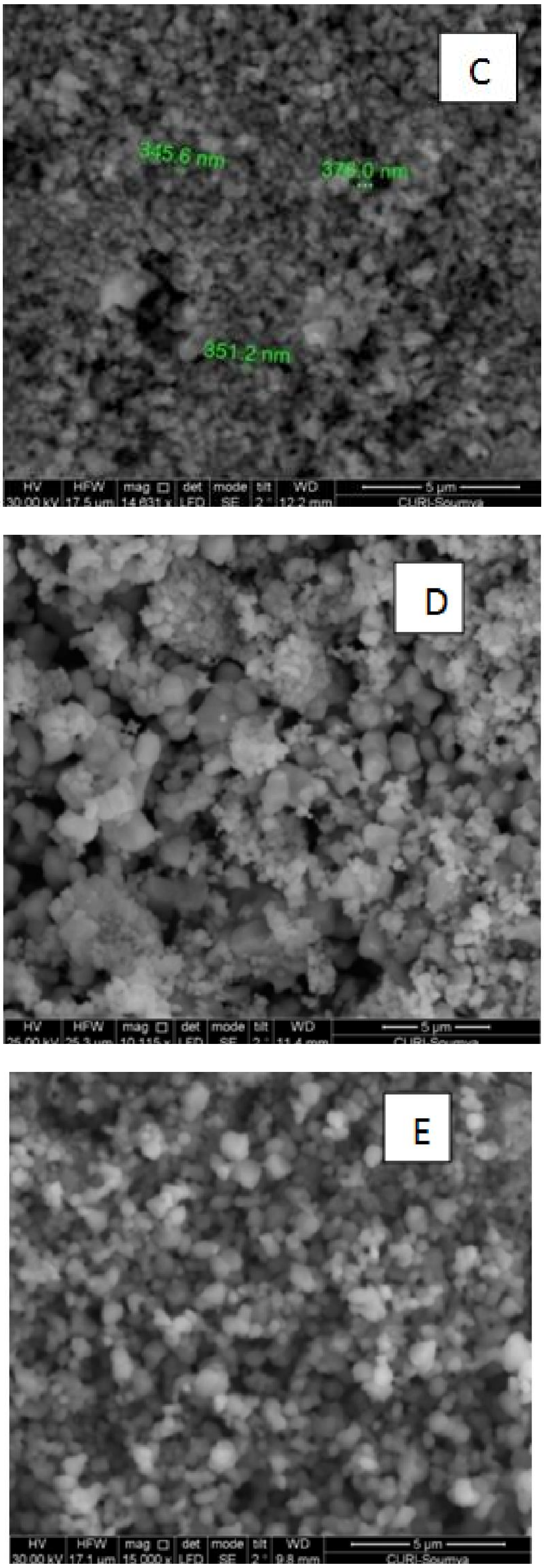

Figure 4. Microstructure of the system x PFN + (1-x) PMN heat treated at 850°C/ 4h

A consideration of the structural variations accompanying the pyrochlore–perovskite transformation can give insight into how the relative permittivity might be changed from unit cell to unit cell (Faruk Ebeoglugil and ErdalCelik, 2015).

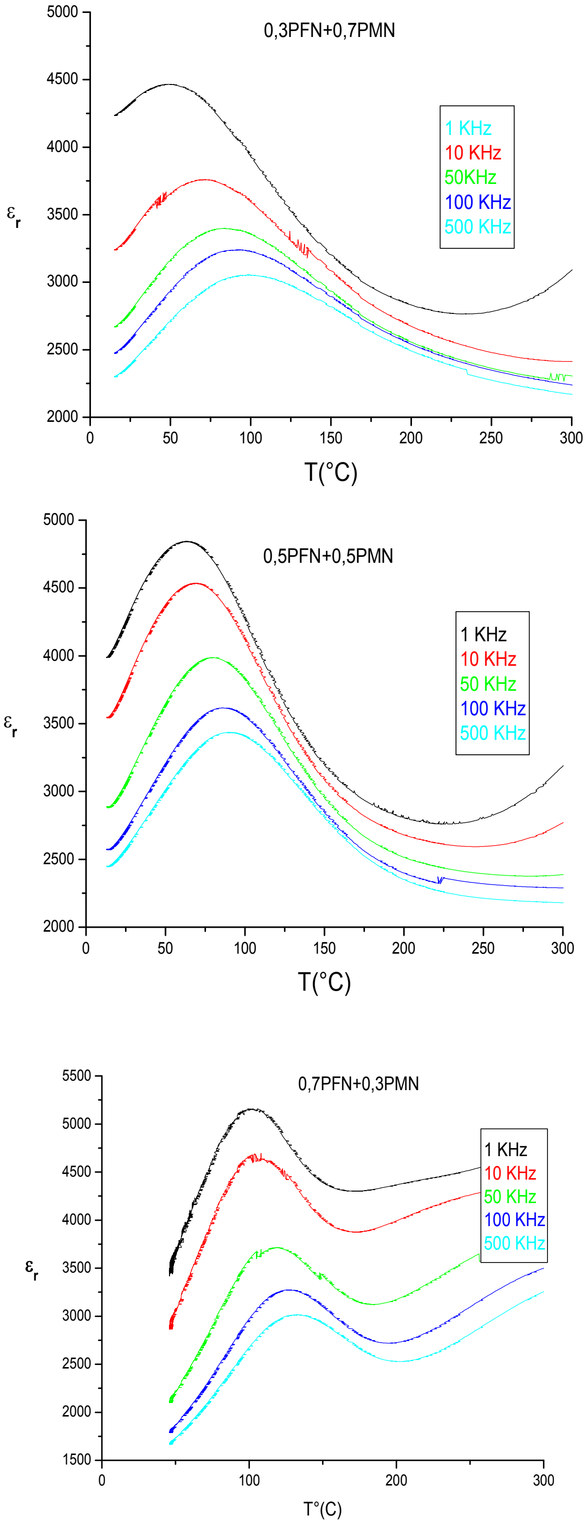

Figure 5. Relative permittivity values of the as a function of temperatures for different frequency

Microstructure analysis

SEM Images of the microstructure of the PFN (A) and PMN (B) heat treated at 850°C for 4 hours are presented in Figure 3. These images shows a relatively compact structure with a non uniform shape and grain site, the latter varying between 2 and 4, 4 µm (A).

The micrograph B shows an ultrafine particle size and homogeneous. The average grain size is of the order of 0.5µm. We also note a relative abundance of pores. This result is in agreement with the results of XRD which showed that at 850°C/4H, the phase obtained is formed of a mixture of a peaks pyrochlore and a perovskite. For the system x PFN + (1-x) PMN, the SEM image, was limited to the study of three samples (A: 0.3PFN + 0.7PMN; B: 0.5PFN+ 0.5PMN; C: 0.7PFN + 0.3PMN).

Figure 4 shows various micrographs obtained for compounds C, D and E which show the existence of changes in the morphology of the grain sizes which have spherical shapes. Other studies have shown that the grain size also changes some properties such as the dielectric constant and the Curie temperature of which is increased if the grain size increases (Kinoshita and Yamaji, 1976; Martirena and Burfoot, 1960; Zouhairi *et al.*, 2012).

Dielectric Properties

Dielectric constant spectra of the ceramics are displayed in figures 5. Relative permittivity of x PFN + (1-x) PMN is maximums at about transition temperature (T_c), relative permittivity decrease with increasing frequency. Table 1 gives values of the parameters ε_r and the temperature, T_m, of the maximum of the permittivity ε_r, for a frequency of 1 KHz. The transition increases as x increases, it is 46°C (x = 3), 62°C (x = 5) and 98°C (x = 7). The behavior of the dielectric relaxation is observed for the three samples (x = 0.3, 0.5 and 0.7). This is due to the nonlinearity of T_c, it is obvious the transition varies with frequency. Smolensky considers relaxor ferroelectrics, as homogeneous and domainoïdes, which have different values Curie temperature above and below the transition temperature. Dielectric demeanour of the samples was also studied with the Uchino's law:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m}\left[1 + \frac{(T - T_m)^{\gamma}}{2\delta^{\gamma}}\right] \qquad [18]$$

δ and γ are the diffuse and relaxor parameters, respectively.

Table 1. Comparison of ε_r and T_m corresponding to samples of x PFN + (1-x) PMN

	PFN[15]	0.3PFN+0.7PMN	0.5PFN+0.5PMN	0.7PFN+0.3PMN
ε_r	5500	4465	4842	5153
T(°C)	102	51	62	98

Table 2. δ and γ values for the samples PMN-PFN heated at 850°C

	0.3PFN+0.7PMN	0.5PFN+0.5PMN	0.7PFN+0.7PMN
δ	12.853	10.369	10.967
γ	1.67	1.87	1.90

The linear fit was performed for the various curves, to determine the parameters δ and γ (Fig). The samples show a diffuse character of the ferro to praelectric transition. Values of γ are characteristic of a diffuse character as 1< γ < 2 (Table).

Conclusion

The PFN-PMN system was synthesized from PbO, Fe_2O_3, MgO mixed with Nb_2O_5 at 850°C for 4 h by the classical solid state method. Lattice parameters of the system decreased continuously with increasing PFN content, from 4.0425 Å (PMN) to 4.0175Å (PFN). SEM micrographs revealed non uniform shape and grain size estimated to vary from 0.5 to 4.4µm. A clear diffuse character, together with a relaxation process, was observed on the thermal variation of the permittivity. Pure perovskite PFN is available, whereas phase pure PMN is not achievable in this temperature, the system PFN-PMN phase evolves according to x, at the expense of the pyrochlore phase.

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