Obtention of a non stoichiometric PMN-PT ferroelectric system

A. Fundora, J. Portelles, A. Pentón, and F. Calderón
Departamento de Ciencia de Materiales, Universidad de la Habana
Habana 10400, Cuba

J.M. Siqueiros, R. Machorro, and G.A. Hirata
Instituto de Física, Universidad Nacional Autónoma de México, Laboratorio de Ensenada
Apartado postal 2681, 22800 Ensenada, Baja California, Mexico

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The obtention of a non stoichiometric PMN-PT system has been studied. The influence of different $PbZrO_3$ atmospheres in the sintering process of $3(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 + xPbTiO_3$ (PMN-PT) solid solution has been investigated and measured by thermoelectric analysis at 1 kHz. Values lower than those for the stoichiometric PMN-PT system have been obtained for T_c. X-ray diffraction (XRD) was performed in the samples for structural analysis and phase identification.

Keywords: Perovskite, ferroelectric

Se presenta el estudio de la obtención de un sistema PMN-PT no estequiométrico. Se investiga la influencia de diferentes atmósferas de $PbZrO_3$ en el proceso de sinterizado de la solución sólida de $3(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 + xPbTiO_3$ (PMN-PT) y se caracteriza mediante análisis termoeléctico a 1 kHz. Se reportan valores de la temperatura crítica T_c inferiores a los obtenidos para el sistema estequiométrico de PMN-PT. Se utilizó la técnica de difracción de rayos X (XRD) para análisis estructural e identificación de fases en las muestras.

Descriptores: Perovskita, ferroeléctrico

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1. Introduction

Relaxors based on the perovskite $3(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 + xPbTiO_3$ solid solutions exhibit excellent dielectric properties and are of current interest for multilayer capacitor fabrication [1]. The preparation of a pure perovskite phase of PMN by the conventional mixed oxides method without the formation of an associated pyrochlore phase is a very difficult task. Due to the low dielectric constant of the pyrochlore phase [2], the dielectric constant of the sample will decrease with respect to that of a pure perovskite. Swartz and Shrout [3] developed a method to process pure PMN perovskite by precalcining the mixture of MgO and Nb_2O_5 to form $MgNb_2O_6$ which has a columbite structure and then reacting it with PbO to from PMN. The addition of excess MgO to PMN-based ceramics has been shown [4–6] to have a beneficial effect to reduce and even eliminate the presence of the pyrochore phase.

The aim of this work was to obtain a non stoichiometric PMN-PT system by the ceramic conventional method using columbite precursor method with 5% mole excess MgO and measure its properties. The atmosphere influence in the sintering process has been studied by thermoelectric analysis (TEA) and XRD.

2. Experimental Procedure

The non stoichiometric ceramics $3(1-x)\mathrm{PMN} + x\mathrm{PT}$ ($x = 0.1$–0.4) were prepared by the standard ceramic method. The first stage was the formation of columbite $MgNb_2O_6$ with 5% mole excess MgO [7]. The samples were sintered at 1200°C for 2h under different concentrations of $PbZrO_3$ as atmosphere. The effect of the different preparation atmospheres on the dielectric properties was studied at 1kHz using a BM 509 RLC meter controlled by a personal computer. The heating rate was maintained at 1°C/min.

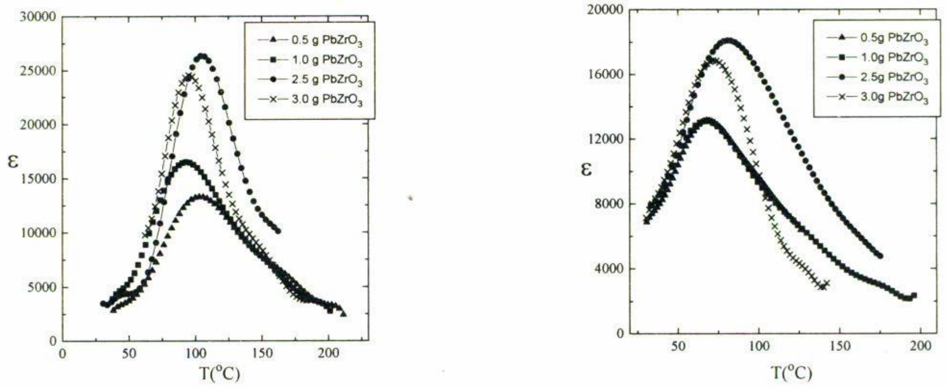
3. Results and Discussion

Figure 1 shows temperature dependence of the dielectric permittivity for $x = 0.3$ and 0.4, respectively. The maximum value of the dielectric permittivity increases with the $PbZrO_3$ concentration in the sintering atmosphere as it is varied from 0.5 to 2.5 grams but decreases slightly for 3.0 g of $PbZrO_3$. These results agree with similar reports on stoichiometric PMN:PT ceramics where the excess or deficit of PbO leads to the formation of a pyrochlore phase. Analogous results were obtained for compositions with $x = 0.1, 0.2$

Table I shows the values of the maximum dielectric constant $\varepsilon_{\max}$ and the transition temperature (T_c) for sintered

TABLE I. Composition (x% of PT), T_c, $\varepsilon_{\max}$, lattice constants and calculated deformation parameter of non stoichiometric PMN:PT systems.

x (%PT)	T_c(°C)	$\varepsilon_{\max}$	a (Å)	c (Å)	$(a^2c)^{1/3}$ (Å)	Deformation parameter, δ
0.1 (3%)	8	11 000	4.042	4.045	4.042	0.000742
0.2 (8%)	27	16 000	4.038	4.052	4.042	0.002470
0.3 (12%)	57	18 000	4.035	4.055	4.041	0.003460
0.4 (18%)	91	26 000	4.030	4.057	4.038	0.004700



(a) (b)

FIGURE 1. The temperature dependence of the dielectric constant for (a) $x = 0.4$ and (b) $x = 0.3$.

TABLE II. Composition (x% of PT) and corresponding T_c of stoichiometric PMN:PT systems.

x (% PT)	T_c
3	15
8	40
14	70
22	120

samples with a 2.5 g atmosphere. As the titanate content is decreased in the samples, T_c takes lower values; these results agree with similar reports in stoichiometric PMN:PT ceramics but, for each composition, ($x = 0.1$–0.4), the corresponding T_c is a little lower than that of the stoichiometric PMN:PT system, since the amount of PT by percent is very small compared with PMN. For instance, when $x = 0.1$ it will be 3% mole of PT into the PMN. Table II shows the transition temperature values of the stoichiometric PMN:PT system in the analyzed concentration range.

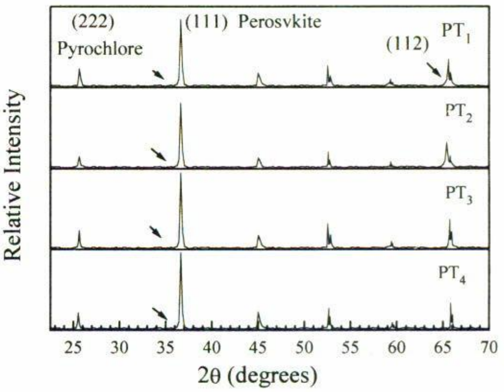


Figure 2. X-ray diffraction patterns of $3(1-x)$PMN $+x$PT materials sintered at 1200°C for 2 h, with a 2.5 g PbZrO$_3$ atmosphere. ($x = 0.1$ {PT$_1$}, $x = 0.2$ {PT$_2$}, $x = 0.3$ {PT$_3$}, $x = 0.4$ {PT$_4$}).

X-ray diffraction analysis of the sample was performed in a HZG-4 universal diffractomenter using the Kα Cobalt line scanning continuously at 2°/min in a 20°–70° range for 2θ. The X-ray diffraction patterns of $3(1-x)\mathrm{PMN}+x\mathrm{PT}$ materials ($x = 0.1$–0.4), represented by samples PT$_1$, PT$_2$, PT$_3$ and PT$_4$ respectively, are shown in Fig. 2. In these patterns, the absence of the (222) characteristic diffraction peaks of the pyrochlore phase is confirmed, as opposed to those of the solid solution reported by Wang and Schulze [7]. However, we must point out that under the conditions prevailing during the measurements, it was impossible to detect the presence of a phase under 5% of relative abundance. From the X-ray results reported in Fig. 2, a systematic shift toward larger angles of the diffraction peaks was determined as the PT relative concentration was increased. In Fig. 3 the shift in the angular position of the (112) peak with the PT can be observed for all studied compositions with an estimated uncertainty in the position of the peak of $2\theta_{\mathrm{err}} = 0.04°$. From this shift, an increase of the tetragonality of the cell with the PT concentration can be qualitatively inferred. According to the percent content of PT on PMN, samples PT$_1$, PT$_2$ and PT$_3$ should be pseudo-cubic but our samples exhibit

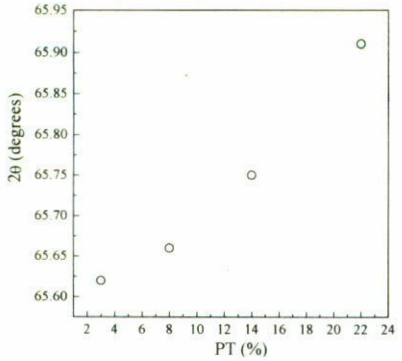


Figure 3. Dependence of the position of the (112) peak with the PT concentration.

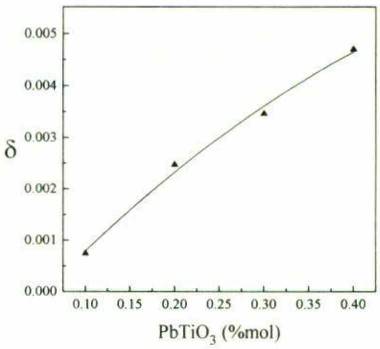


Figure 4. The compositional dependence of the deformation parameter δ.

a tetragonal structure. This results disagrees with those reported by Choi *et al.* [8], Shrout *et al.* [9] and Ho *et al.* [10] who claim that stoichiometric PMN:PT with these compositions has a pseudo-cubic structure. In Table I, high values for $\varepsilon_{\max}$ for all compositions as well as an increase in $\varepsilon_{\max}$ with PT concentration can be observed. This fact strongly supports the non existence of the pyrochlore phase since, for the PMN based systems, the dielectric constant decreases with the pyrochlore concentration. The lattice parameters c, a and cell volume (a^2c) are calculated from the XDR patterns and are shown in the Table I. In the same table, a new parameter related to the lattice constant of the tetragonal crystal structure, defined according to:

$$\delta = \frac{\left[c - (a^2c)^{1/3}\right]}{(a^2c)^{1/3}} \tag{1}$$

is also reported against the PT content. This is called the *deformation parameter* δ by Fesenko *et al.* [11].

When the deformation parameter is different from zero $(\delta \neq 0)$ these materials are ferroelectric in the tetragonal phase and are paraelectric in the cubic phase also present our materials. On the other hand, the pseudo-cubic PMN materials show remarkable ferroelectricity at low temperatures $(T < -10°\mathrm{C})$ and crystals with cubic symmetry exhibit $\delta = 0$.

Finally, Fig. 4 shows the compositional dependence of the deformation parameter with the lead titanate molar concentration.

4. Conclusion

The non stoichiometric PMN-PT system was obtained by the columbite precursor method with 5% mole excess of MgO. These materials have a pure perovskite phase which is evidenced by X-ray diffraction analysis and the samples show good ferroelectric properties. Dielectric analysis suggests that the decrease in the dielectric constant for the higher PT concentrations is attributed to presence of a pyrochlore phase. The deformation parameter δ, is found to be very suitable to describe the compositional dependence of the ferroelectric properties. The transition temperatures found for the non stoichiometric PMN:PT system are lower than those of the stoichiometric PMN:PT system with the same amount of PT in PMN.

Acknowledgments

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