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Study of the relaxor ferroelectric properties of the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ ceramic

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The relaxor ferroelectric properties of the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ (PMNT) system are presented. The diffuse phase transitions are analyzed using the Smolenskii-Isupov and the *Spin-Glass* superparaelectric theories. Dielectric permittivity curves as function of temperature and frequency as well as the $\ln f$ dependence with the reciprocal temperature are reported. The samples were sintered using the conventional ceramic technique.

Keywords: Relaxor ferroelectric; dielectric properties; diffuse phase transitions

Se presentan las propiedades de ferroeléctrico relajador del sistema cerámico $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ (PMNT). Las transiciones de fase difusa son analizadas utilizando la teorías de Smolenskii-Isupov y la teoría de vidrio de espín superparaeléctrico. Se reportan las curvas experimentales de permitividad dieléctrica en función de la temperatura y de la frecuencia así como la dependencia en $\ln f$ de inverso de la temperatura. Las muestras fueron preparadas utilizando la técnica convencional de preparación de cerámicas.

Descriptores: Ferroeléctrico relajador; propiedades dieléctricas; transiciones de fase difusa

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1. Introduction

There are many ferroelectric materials that due to their peculiar dielectric behavior are known as relaxor ferroelectrics [1]. Among them, we can find a number of complex perovskites of the type $A(B'_xB''_{1-x})O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is one of them. Solid solutions of relaxor PMN and the first order ferroelectric, $PbTiO_3$ (PT), exhibit many attractive properties for dielectric and electrostrictive applications [2]. The high dielectric constant, over broad temperature ranges, close to room temperature make systems like $PMN_{1-x}T_x$ very attractive for multilayer capacitor (MLC) and actuator applications. Several previous investigations on the dielectric properties, such as maximum dielectric permittivity (ε_{max}) [2], diffuseness (the effective width of the maxima) and aging, have been shown to be dependent on the processing conditions, in particular, the role of stoichiometry and grain size on the above mentioned properties. Choi *et al.* [3] reported the existence of a *morphotropic phase boundary* (MPB) at 35% Ti content separating the pseudo-cubic and tetragonal phases as well as the role of the $PbTiO_3$ ($T_c \sim 490$°C) in the dielectric properties.

In this work, a study of the relaxor ferroelectric properties of the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ solid solutions is presented. For such purpose, measurements of the dielectric permittivity as a function of temperature and frequency were performed and the diffuse phase transitions are analyzed using the Smolenskii-Isupov and the Spin-Glass superparaelectric theories.

2. Experimental procedure

The conventional ceramic method was utilized to prepare the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ solid solutions. The culombite precursor technique with excess magnesium oxide [4] was used to prevent the formation of pyrochlore phases [5] that depress the dielectric properties of lead oxide based ferroelectric ceramics [6]. The samples were prepared with high purity reactives (E. Merk, Darmstadt, Germany): PbO (> 99%), MgO (> 97%), Nb_2O_5 (> 99.9%) y TiO_2 (> 99%). The MgO powders with a 5% excess and the Nb_2O_5 were calcined at 1000°C for 4 hours with a 10°C/min heating rate, to form the $MgNb_2O_6$ culombite structure. These powders were then ground and properly mixed with PbO and TiO_2, calcined at 800°C for 2h and finally sintered at 1200°C for 2h with a heating rate of 1°C/min. The behavior of the dielectric permittivity as a function of temperature and frequency was measured with the help of a lock-in amplifier in the range of 25 to 350°C and 500 Hz to 100 kHz, respectively.

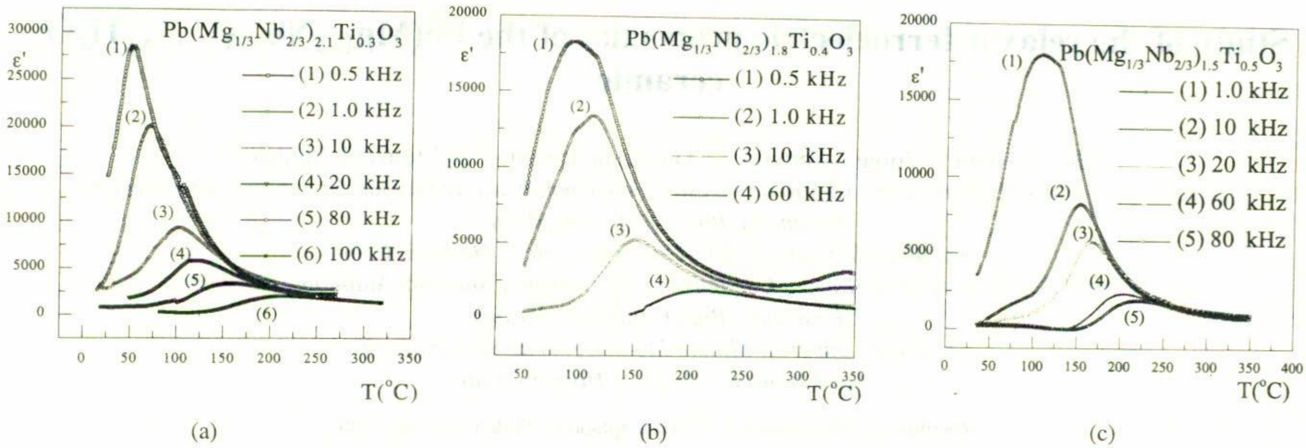

FIGURE 1. ε' *vs.* T curves at different frequencies for a) the $PMN_{2.1}T_{0.3}$ sample; b) the $PMN_{1.8}T_{0.2}$ sample; and c) the $PMN_{1.5}T_{0.5}$ sample.

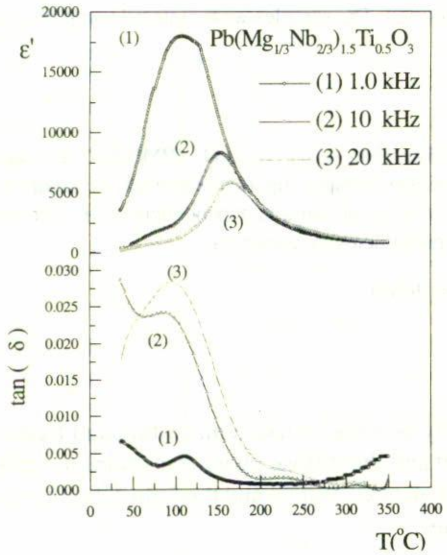

FIGURE 2. Dependence of the permittivity and dielectric losses as function of temperature and frequency for $PMN_{1.5}T_{0.5}$ sample.

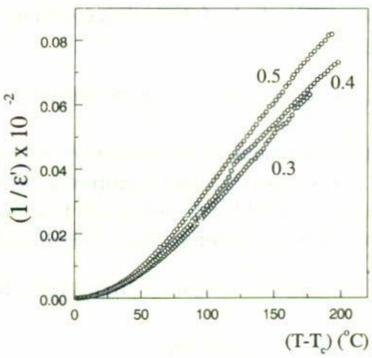

FIGURE 3. The curve of the reciprocal dielectric permittivity as a function of $T - T_c$ shows a non Curie-Weiss behavior.

3. Results and discussion

The dielectric response of the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ system with $x = 0.3, 0.4$ and 0.5 is shown in Figs. 1a, 1b and 1c where it can be seen that the dielectric permittivity decreases with the measuring frequency and its peak shifts toward higher temperatures. The non- coincidence between corresponding peaks of the permittivity and dielectric loss is shown in Fig. 2 as an evidence of the diffuse phase transition.

In Figs. 1a, 1b and 1c it can also be observed that, as the Ti concentration is incremented, the shifts of the dielectric permittivity maxima toward higher temperatures for higher frequencies becomes smaller, reflecting thereby a remission of the relaxor character of the system.

The above-described behavior of these ceramics may be explained in terms of the Smolenskii-Isupov theory by noticing that, when the doping of the sample increases, the Ti^{+4} cations tend to occupy the B crystallographic sites of the perovskite structure increasing therefore the cationic disorder.

However, as the Ti concentration is increased, a limit is reached where electrostatic and elastic forces act in such a way that higher order is introduced in the structure of the material, losing, therefore, the relaxor characteristics. This phenomenon can also be explained with the help of the phase diagram where, as the Ti content is increased the relaxor behavior of the material decreases and transforms into a normal ferroelectric system beyond the morphotropic phase boundary [1]. In the tan δ *vs. temperature* curves for different frequencies presented in Fig. 2, some anomalies possibly corresponding to conduction phenomena are observed for $T \gg T_c$. The analysis of these results is currently being performed and will be the subject of a future publication.

Figure 3 shows the $1/\varepsilon'$ *vs* $(T - T_c)$ curves for the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ samples at 1 kHz, where a the *Curie-Weiss* Law no longer holds in its classical form $1/\varepsilon \sim C(T\text{-}T_c)$. For ferroelectric materials with diffuse phase transition, such law must be modified and takes the form

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon'_{\max}} + \frac{(T - T_c)^2}{2\varepsilon'_{\max}\delta^2},$$

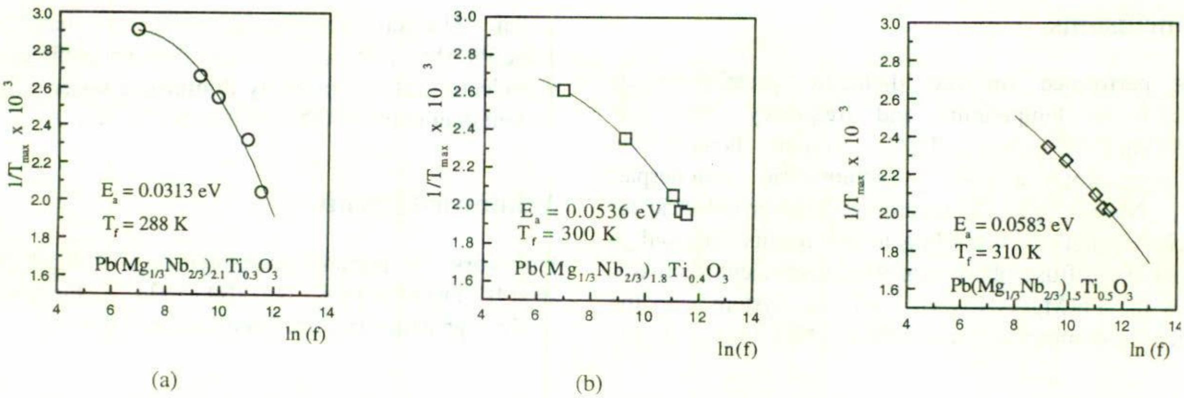

FIGURE 4. The reciprocal of the dielectric permittivity maxima temperature as a function of the measuring frequency.

TABLE I. The values of the diffuse phase coefficient obtained from the slope of the $1/\varepsilon' - 1/\varepsilon'_{max}$ *vs.* $(T - T_c)^2$ curve for the non stoichiometric PMN-PT system are presented.

% Ti(x)	δ
(0.3)	38.51
(0.4)	35.20
(0.5)	29.67

where ε'_{max} is the dielectric permittivity maximum, T is the temperature and T_c is the Curie temperature. δ is a measure of the width of the diffuse phase transition, assuming a Gaussian distribution of the Curie temperatures [7]. Table I shows how the diffuse phase transition coefficient δ decreases with the Ti content. It is also worth noticing that, as the Ti concentration increases, the system moves in the phase diagram toward the morphotropic region showing a lesser diffuse character due to an increase in order and grain size (Shrout *et al.* [6]). This fact essentially means that the polar microregions will get smaller and therefore the normal phase will be larger.

Within the framework of the super-paraelectric theory [1], the dispersion of the permittivity maxima may be modeled by the Volger-Fulcher relation [8]. Figures 4a, 4b and 4c shows the dependence of the temperature of the dielectric permittivity maxima with frequency. A very good agreement between the experimental data and the values obtained with the Volger-Fulcher expression is evident. This result leads us to believe that the relaxor behavior of this system is similar to a spin-glass system with a polarization fluctuation around the freezing point.

Energy activation values E_a for each of the studied composition are shown in Fig. 5 where it can be noticed that E_a increases as the Ti concentration increases in agreement with the Smolienskii-Isupov theory that states that, as the Ti content increases, the relaxor properties of the system tend to disappear. This behavior may be explained by expressing E_a

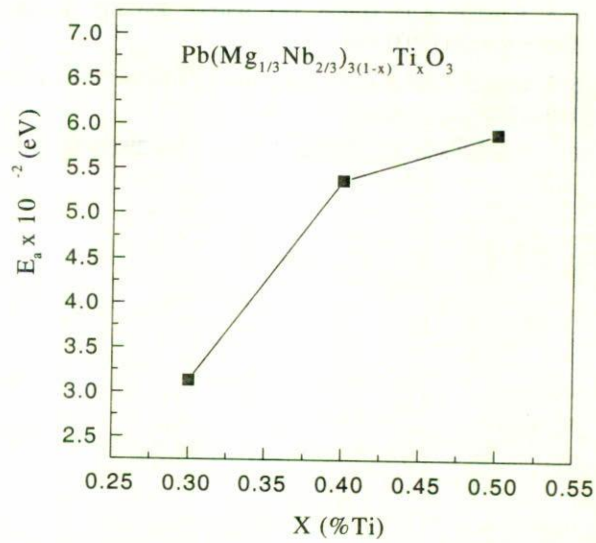

FIGURE 5. Variation of the activation energy with the Ti content (x) for the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ system.

as

$$E_a = E_{ani} \cdot V_c,$$

being E_{ani} the anisotropy energy of a ferroelectric material and V_c the volume of the clusters. With the increase in the Ti content, the tetragonality of the unit cell increases affecting the contribution of the clusters to the dielectric relaxation. That is, in a pseudo-cubic structure, the polar clusters inside the grain are randomly oriented whereas in the tetragonal case such randomness is less likely to exist due to increase in the anisotropy of the system. A pre-exponential factor $f_o = 10^{11}$ Hz was obtained for all compositions.

From the experimental results and the application of the above mentioned theories it can be said that a $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ relaxor system has been obtained where the relaxor properties diminish with the Ti content The diffuse phase transition coefficient is obtained from the Smolenskii-Isupov theory and the activation energies from the superparaelectric spin-glass theory.

4. Conclusions

Studies performed on the dielectric permittivity as a function of temperature and frequency show that the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ system behaves in a similar way as its stoichiometric counterpart $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ regarding their ferroelectric relaxor characteristics. According to the results obtained in this work the diffuse phase transition coefficient decreases faster in the $Pb(Mg_{1/3}Nb_{2/3})_{(1-x)}Ti_xO_3$ system with the Ti content as compared to the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ system. The activation energy, on the other hand, is larger in the $Pb(Mg_{1/3}Nb_{2/3})_{(1-x)}Ti_xO_3$ system implying that the ferroelectric relaxor property diminishes faster with the Ti content than in the $Pb(Mg_{1/3}Nb_{2/3})_{3(1-x)}Ti_xO_3$ system.

Acknowledgments

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