

Effect of excess Mg and Excess Nb incorporation into the B-site of pyrochlore in the Pb-Mg-Nb-O system

A. MERGEN

Eti Holding A.Ş., AR-GE Dairesi Başkanlığı, İstanbul Yolu Üzeri, Ankara, Turquía

In the Pb-Mg-Nb-O system, excess Mg and excess Nb incorporation into the B-site of PMN pyrochlore were investigated along the compositions of $\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$ where $x=0.1, 0.2, 0.3, 0.4, 0.522$ and $\text{Pb}_{1.83}\text{Mg}_{0.29-x}\text{Nb}_{1.71+x}\text{O}_{6.39+1.5x}$ where $x=0.1, 0.2, 0.29$ respectively. Excess Mg incorporation led to the formation of perovskite and excess Nb resulted in formation of $\text{Pb}_2\text{Nb}_2\text{O}_7$ monoclinic pyrochlore. The densities of the PMN pyrochlore-PMN perovskite mixtures decreased with an increase in Mg concentration. The relative permittivity of the mixtures increased with decreasing pyrochlore content. The effect of pyrochlore on the permittivity follows the Weiner's mixture rule up to a pyrochlore content of 50 vol%.

Key Words: Pyrochlore, Lead magnesium niobium oxide, dielectric properties.

Efectos del exceso de Mg y exceso de incorporación de Nb en posición B de pirocloro en el sistema Pb-Mg-Nb-O

Se investigó la incorporación en lugares B de pirocloro PMN de un exceso de Mg y un exceso de Nb. En el sistema Pb-Mg-Nb-O2 las composiciones analizadas fueron $\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$ donde $x=0.1, 0.2, 0.3, 0.4, 0.522$ y en $\text{Pb}_{1.83}\text{Mg}_{0.29-x}\text{Nb}_{1.71+x}\text{O}_{6.39+1.5x}$ donde $x=0.1, 0.2, 0.29$. El exceso de Mg condujo a la formación de perovskita y el exceso de Nb resultó en la formación del pirocloro monoclínico, $\text{Pb}_2\text{Nb}_2\text{O}_7$. La densidad de la mezcla de PMN pirocloro-perovskita disminuye con el aumento de la concentración de Mg. La permitividad dieléctrica de las mezclas aumenta con la disminución del contenido de pirocloro. El efecto del pirocloro sobre la permitividad sigue la regla de mezclas de Weiner hasta contenidos de pirocloro del 50%.

Palabras clave: Pirocloro, niobato de magnesio y plomo, propiedades dieléctricas.

1. INTRODUCTION

The crystal structure of mineral pyrochlore, $(\text{Ca}, \text{Na})_2(\text{Nb}, \text{Ta})_2(\text{OH}, \text{F})_7$, was first determined by von Gaertner (1) to belong to the space group $\text{Fd}\bar{3}\text{m}$ (No. 227). The simple pyrochlore structure is face centred cubic and there are eight molecules per unit cell. For a stoichiometric pyrochlore structure ($\text{A}_2\text{B}_2\text{X}_6\text{Z}$ where A and B are cations and X and Z are anions) there are 88 atoms in a unit cell: 16 A cations in position (c), 16 B cations in position (d), 8 Z anions in position (a), and the remaining 48 X anions in position (f).

Pyrochlore crystal structures can be classified as normal and defect types. Pyrochlores are not limited to the ideal $\text{A}_2\text{B}_2\text{X}_6\text{Z}$ stoichiometry and by removing combinations of A and Z ions, a variety of defect structures can be produced with the general formula $\text{A}_{1-2}\text{B}_2\text{X}_6\text{Z}_{0-1}$ (such as $\text{A}_2\text{B}_2\text{X}_6$, AB_2X_6). Defect pyrochlore oxides, e.g. MSbTeO_6 ($\text{M}=\text{K}, \text{Rb}, \text{Cs}, \text{Tl}, \text{Ag}$) and $\text{Tl}(\text{NbTe})\text{O}_6$, are of great interest because of their potential as ionic conductors (2).

Single phase pyrochlores have a wide range of possible applications due to their various electrical, magnetic, dielectric, optical and catalytic properties (3). Pyrochlore oxides can be used as electronic materials since their electronic behaviour varies widely from insulating through semiconducting to metallic with a few compounds exhibiting a semiconductor-to-metal transition (4, 5, 6). Pyrochlores can be used in solid state devices

such as high permittivity ceramics ($\text{Cd}_2\text{Nb}_2\text{O}_7$, $\text{Ln}_2\text{Ti}_2\text{O}_7$), thermistors ($\text{Bi}_2\text{Ru}_2\text{O}_7$), thick film resistors and materials for screen printing (many Pb and Bi containing precious metal pyrochlores) and switching elements ($\text{Cd}_2\text{Os}_2\text{O}_7$, $\text{Ca}_2\text{Os}_2\text{O}_7$) (3). In addition, some nonferroelectric pyrochlores may serve as technologically useful dielectrics in applications such as temperature-stable and temperature-compensating dielectrics or microwave dielectrics. For example; $\text{Pb}(\text{Cd})\text{BiM}^{\text{VI}}\text{SbO}_7$ (where $\text{M}^{\text{VI}}=\text{Ti}, \text{Zr}, \text{Sn}$) (7), pyrochlore compounds in the $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ system (8, 9) and lead based non-ferroelectric pyrochlores ($\text{Pb}_{1.83}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ and $\text{Pb}_2\text{FeWO}_{6.5}$) (10).

On the other hand, pyrochlore phases occur intergranularly or as isolated grains in many electrical ceramic microstructures and often degrade the desired properties of the ceramics. One of these electrical ceramics is $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ relaxor ferroelectric. The formation of lead magnesium niobate perovskite is often accompanied by the occurrence of a secondary pyrochlore phase (11, 12). PMN pyrochlore phase exhibit a low dielectric constant (around 130) (13) and it is commonly believed that the presence of such pyrochlore phase significantly degrades the dielectric properties of PMN-based ceramics. Several innovative techniques have been developed to produce pyrochlore free PMN ferroelectrics such as columbite method and chemical processing routes (11, 14).

Perovskite-pyrochlore diphasic mixtures containing different amounts of pyrochlore were produced by Chen and Harmer (15) and their dielectric properties were studied. They controlled the amount of pyrochlore second phase by changing the Mg/Nb ratio (specifically changing the Nb concentration), from near pure PMN perovskite to near pure pyrochlore. As the Nb content increases, $\text{Pb}_3(\text{Mg}_{(1-x)}\text{Nb}_{(2+x)})\text{O}_{9+3x/2}$ ($x=0$ to 0.625), the pyrochlore phase increases linearly up to 100% pyrochlore and the maximum dielectric constant of PMN decreases continuously. The intrinsic effect of isolated pyrochlore phase on the dielectric properties of PMN can be described by the isolated Wiener's mixture rule even for amounts up to 18 vol%. Chen and Harmer (15) concluded that other factors such as lattice impurities and intergranular phases could be considered besides the presence of pyrochlore phase since isolated grains of pyrochlore alone cannot account for the low values of dielectric constant.

The present work investigates dielectric properties of pyrochlore-perovskite diphasic mixtures, which were obtained by incorporating Mg into the B-site of pyrochlore while simultaneously decreasing Nb on this site. The density relations of pyrochlore-perovskite diphasic mixtures with Mg incorporation and sintering temperature were studied. In addition, the dielectric properties of the pyrochlore-perovskite mixtures were also investigated. Moreover, the incorporation of Nb^{5+} cation into the B-site of pyrochlore was examined along with a composition expressed by $\text{Pb}_{1.83}\text{Mg}_{0.29-x}\text{Nb}_{1.71+x}\text{O}_{6.39+1.5x}$ where $0.1 \leq x \leq 0.29$ using XRD.

2. EXPERIMENTAL

In the Pb-Mg-Nb-O system, $\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$ where $x=0.1, 0.2, 0.3, 0.4, 0.522$ and $\text{Pb}_{1.83}\text{Mg}_{0.29-x}\text{Nb}_{1.71+x}\text{O}_{6.39+1.5x}$ where $x=0.1, 0.2, 0.29$ compositions were produced using conventional solid state reaction of PbO (99.9%), Nb_2O_5 (99.5%) and MgO (99%) powders, supplied from Aldrich Chemical Company Ltd., UK. The details of sample preparation techniques have been described in earlier work (16). Calcined powders were sintered at temperatures of between 1150-1300°C for 2 h with a heating and cooling rate of 5 K min^{-1} . Densities of the sintered pellets were measured by a mercury displacement method based on Archimedes principle.

Sintered pellets were examined using a Philips powder diffractometer with Cu $K\alpha$ radiation. Microstructures of sintered pellets were investigated on thermally etched samples using a scanning electron microscope (SEM, Joel 6400). The dielectric constant and dissipation factor ($\tan \delta$) were measured using a HP4284A precision LCR meter. Prior to the dielectric measurements, samples were polished to obtain parallel surface and electroded with a silver paste, which was sintered at 550°C for 30 min.

3. RESULTS AND DISCUSSION

3.1 Effect of Excess Mg ($\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$; $x=0.1, 0.2, 0.3, 0.4, 0.522$)

The pyrochlore phase formed in PMN perovskite ceramics have the formula of $\text{Pb}_{1.83}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ (13, 17). Mg incorporation into the B-site of PMN pyrochlore instead of Nb led to formation of PMN perovskite phase ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$). XRD analysis of pellets containing different amounts of excess Mg

sintered at between 1150-1300°C for 2h revealed that both Mg content and sintering temperature significantly affect the percentage of perovskite phase formed within pyrochlore (Figure I). As the mole percent of excess Mg increases (i.e. as the x increases in the $\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$ composition), the amount of perovskite phase linearly increases finally reaching to 100% perovskite phase at $x=0.522$. This is in agreement with the other results obtained in the literature (11, 18, 19). Excess Mg favours the formation of perovskite, which contains higher Mg concentration than pyrochlore. Table I gives the percentage of perovskite phase formed within pyrochlore according to the Mg concentration and sintering temperature. The values were derived from the XRD data by measuring the major x-ray peak intensities and using the following equation (11, 16):

$$\% \text{Perovskite} = \frac{I_{\text{Pr}}}{I_{\text{Pr}} + I_{\text{Py}}} \times 100 \quad [1]$$

where I_{Pr} is the relative intensity of (110) of perovskite phase and I_{Py} is the relative intensity of (222) of pyrochlore phase.

As can be seen from Table I, sintering temperature also affect the percentage of perovskite phase formed within pyrochlore as observed by the previous researchers (11, 20). However, Mg concentration has a more pronounced effect on the formation of perovskite phase. The values in parenthesis in Table I gives the percentage of perovskite calculated from the atomic compositions which indicates that both experimental and calculated values are in a good agreement (16).

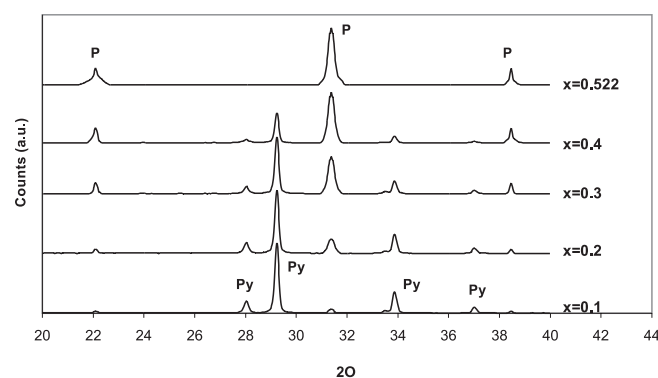


Figure I. XRD of pure and Mg rich PMN pyrochlore sintered for 2h at 1200°C indicating that as the amount of excess Mg (or x in $\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$ composition) increases the amount of perovskite phase increases. Py=Pyrochlore, Pr=Perovskite.

TABLE I. PERCENTAGE OF PEROVSKITE PHASE FORMED WITHIN PYROCHLORE AS A FUNCTION OF MG CONCENTRATION AND SINTERING TEMPERATURE

T, °C	X=0.1		x=0.2		x=0.3		x=0.4		x=0.522	
	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
1150	2	-	17	21	44	44	64	67	98	95
1260	5	4	20	27	49	49	71	72	99	100
1300	8	6	28	29	53	51	79	74	100	102

(Exp=Experimental, Cal=Calculated).

3.2 Effect of Excess Nb ($\text{Pb}_{1.83}\text{Mg}_{0.29-x}\text{Nb}_{1.71+x}\text{O}_{6.39+1.5x}$; $x=0.1, 0.2, 0.29$)

The solubility of Nb into the B-site of pyrochlore was examined along the composition expressed by $\text{Pb}_{1.83}\text{Mg}_{0.29-x}\text{Nb}_{1.71+x}\text{O}_{6.39+1.5x}$ where $x=0.1, 0.2, 0.29$. XRD patterns of Nb doped samples indicate that as Nb incorporation into the pyrochlore increases $\text{Pb}_2\text{Nb}_2\text{O}_7$ (PN) monoclinic pyrochlore starts to form along with cubic PMN pyrochlore (Figure II). At $x=0.29$, at which value the formula becomes $\text{Pb}_{1.83}\text{Nb}_2\text{O}_{6.83}$, all PMN pyrochlore transformed to PN pyrochlore with formation of a small amount of Nb_2O_5 . From these results it can be concluded that incorporation of Nb instead of Mg in the PMN pyrochlore led to formation monoclinic PN pyrochlore. The other conclusion that can be derived from these results is that MgO is soluble in the PN pyrochlore on the Nb site as found by Wakiya et al. (21) who determined that the solubility of MgO into $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ cubic pyrochlore was around $x=0.24$ in the composition of $\text{Pb}_{(3+3x)}\text{Mg}_x\text{Nb}_{(2+x)}\text{O}_{6.5}$ resulting with a formula of $\text{Pb}_{1.86}\text{Mg}_{0.24}\text{Nb}_{1.76}\text{O}_{6.5}$.

3.3 Densification of PMN Pyrochlore-PMN Perovskite Mixtures

Theoretical densities of PMN pyrochlore-PMN perovskite diphasic mixtures formed when x was varied between 0.1-0.522 in the composition $\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$ were calculated from their relative amounts obtained from XRD, and from their theoretical densities by using the following formula (22).

$$\rho_{\text{TD}} = V_{\text{Pr}} \times \rho_{\text{Pr}} + V_{\text{Py}} \times \rho_{\text{Py}} \quad [2]$$

where ρ_{TD} is the theoretical density of the pyrochlore-perovskite mixture, V_{Pr} and V_{Py} are volume fractions of the perovskite and pyrochlore phases and ρ_{Pr} and ρ_{Py} are theoretical densities of perovskite and pyrochlore compounds (7.22 g/cm^3 for pyrochlore and 8.13 g/cm^3 for perovskite).

In Figures IIIa and b calculated theoretical densities of pyrochlore-perovskite diphasic mixtures for different Mg concentrations and sintering temperatures are compared. As the Mg concentration and sintering temperature increase the calculated theoretical density of the mixture increases. This is due to the increase in the amount of perovskite phase, which has a larger theoretical density than pyrochlore, at higher Mg concentrations and sintering temperatures. Comparing Figures IIIa and b it is clear that the slope of the curves in Figure IIIa are larger than in Figure IIIb. This implies that the theoretical density of the mixture is more dependent on the Mg concentration than sintering temperature. This is because Mg concentration is more effective in forming the perovskite phase.

Relative bulk densities of diphasic pyrochlore-perovskite mixtures are compared in Figure 4. In general, densities decrease with increasing Mg concentration and increase with sintering temperature. At a sintering temperature of 1150°C there is little variation in density with Mg concentration (Figure IVa). However, at 1260°C and 1300°C relative density is strongly dependent on the Mg concentration. These results imply that Mg incorporation by replacing the Nb cation on the B-site of the PMN pyrochlore reduced densification of the mixtures. The reason for this is not fully understood but it may be associated with an increase in PbO evaporation as the

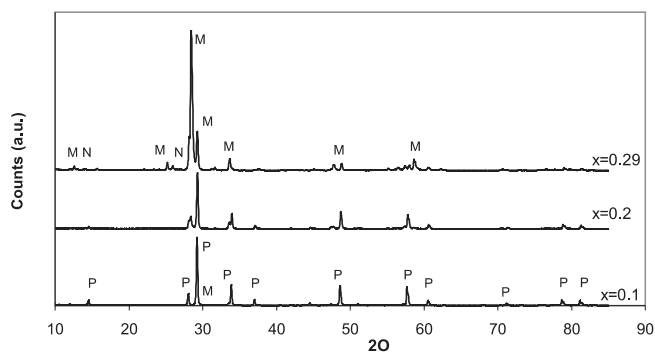


Figure II. XRD results of $\text{Pb}_{1.83}\text{Mg}_{0.29-x}\text{Nb}_{1.71+x}\text{O}_{6.39+1.5x}$ where $x=0.1, 0.2$ and 0.29 indicating that Nb incorporation into the B-site of PMN pyrochlore (P) instead of Mg led to the formation of $\text{Pb}_2\text{Nb}_2\text{O}_7$ monoclinic pyrochlore (M). ($\text{N}=\text{Nb}_2\text{O}_5$)

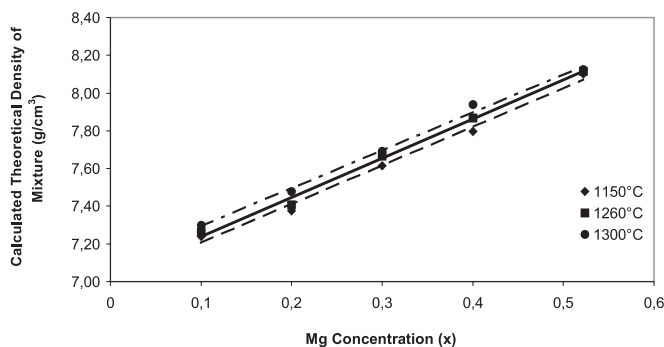


Figure III. Calculated theoretical density of pyrochlore-perovskite diphasic mixtures a) for different Mg concentrations, x , and b) at different sintering temperatures.

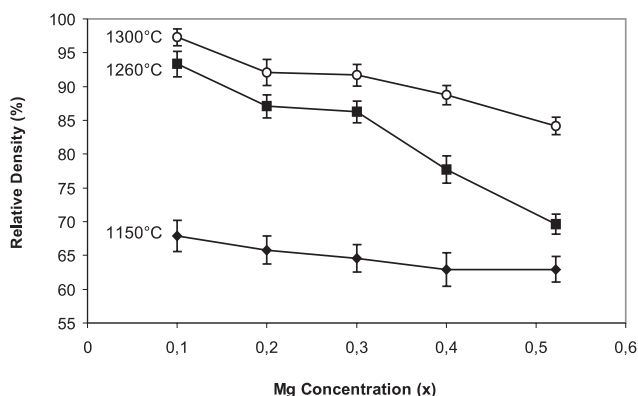


Figure IV. % relative densities of pyrochlore-perovskite diphasic mixtures a) for different Mg concentrations, x , and b) at different sintering temperatures.

excess MgO concentration increases since excess MgO might cause nonstoichiometric starting compositions leading to lead oxide loss causing density decrease. Weight losses in the pellets with $x=0.3$ were recorded after sintering and it was found that there was around 2.55% and 2.81% weight loss at sintering temperatures of 1260°C and 1300°C respectively. Ling et al. (23) prepared nonstoichiometric PMN perovskite compositions which transformed to stoichiometric PMN after sintering with the excess MgO appearing as inclusions and evaporation of excess PbO. Lattice parameter measurements (16) showed that pyrochlore and perovskite compositions invariably had consistent unit cell values at different Mg concentrations and sintering temperatures suggesting that both phases retain their stoichiometry. Another reason for the density decrease with Mg concentration could be the low reactivity of refractory MgO. As Figure IV indicates at higher Mg concentrations the mixture density is always lower.

3.4 Phase Distribution in PMN Pyrochlore PMN Perovskite Mixtures

Microstructural examination of PMN pyrochlore-PMN perovskite mixtures reveal that when excess Mg content is low, the perovskite phase is generally exist as isolated minor phase (Figure Va). Figure Va indicates that perovskite phase generally dispersed at the pyrochlore grain boundaries and rarely within the grains. When the amount of excess Mg increases, the amount of perovskite phase also increases and becomes interconnected (Figure Vb). When $x=0.4$ ($\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$), in other words when the volume percent of perovskite reaches to around 80%, the pyrochlore phase becomes the minor phase and perovskite forms the matrix (Figure Vc). At Mg concentration of $x=0.522$ only single phase perovskite grains were obtained (Figure Vd). The size of perovskite grains were around 1 μm .

3.5 Dielectric Properties of PMN Pyrochlore-PMN Perovskite Mixtures

When an electric field is applied across a dielectric material, which contains more than one phase, the lines of flux will tend to concentrate in the phase with the greatest dielectric permittivity (24). The relative permittivity (dielectric constant) for such a mixture will depend on the relative permittivities of each phase, the volume fraction of phases, the phase distribution and the shapes of each component.

The effect of PMN pyrochlore on the dielectric properties of PMN perovskite was investigated between room temperature and 120°C. Figure VI shows the relative permittivity and dissipation factor of these mixtures between 30-120°C.

Figure VIa indicates that at 100 kHz the dielectric constant of the mixture strongly depends on the amount of pyrochlore. While pyrochlore content decreases the dielectric constant of the mixture increases. For example, when $x=0.1$, i.e. when there is ~92 vol% of pyrochlore, the relative permittivity has the lowest values and when $x=0.522$, i.e. when there is no detectable pyrochlore within XRD limits, the relative permittivity has the highest values between 30-120°C. This is due to the low dielectric constant of PMN pyrochlore. The same result was also observed by Chen and Harmer (15) who measured dielectric properties of perovskite-pyrochlore mixtures at temperatures of between -150°C and 150°C and observed that increasing the pyrochlore concentration in a perovskite

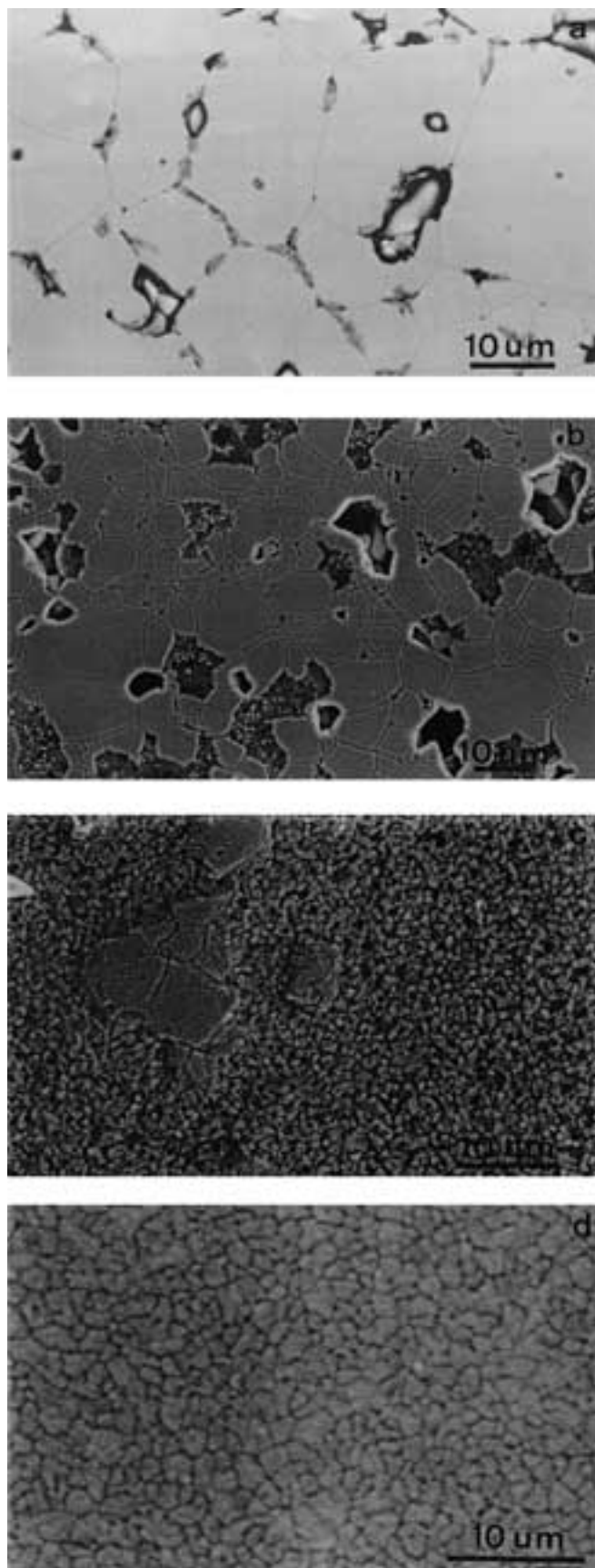


Figure V. Secondary electron image of $\text{Pb}_{1.83}\text{Mg}_{0.29+x}\text{Nb}_{1.71-x}\text{O}_{6.39-1.5x}$ with a) $x=0.1$, b) $x=0.2$, c) $x=0.4$ and d) $x=0.522$ which sintered 2h at 1300°C and reveal that perovskite is a minor phase at $x=0.1$ and becomes single phase at $x=0.522$. (p=pyrochlore, r=perovskite).

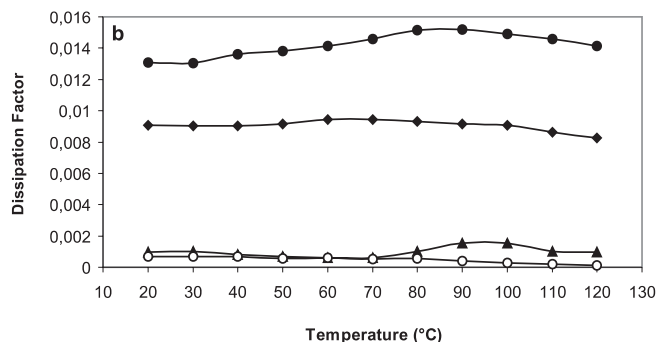
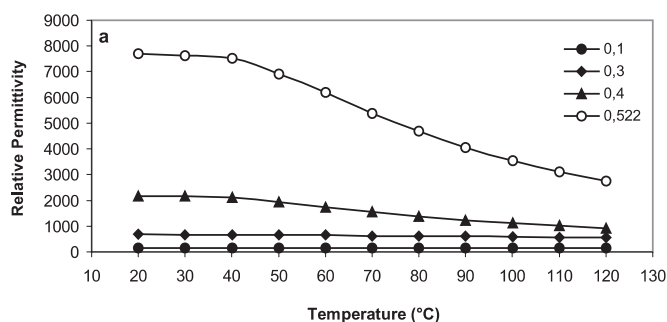


Figure VI. Dielectric properties of pyrochlore-perovskite diphasic mixtures and pure PMN perovskite ($x=0.522$) as a function of temperature at 100 kHz a) relative permittivity and b) dissipation factor.

matrix decreased the maximum dielectric constant (K_{max}) of the mixture. In addition, Yan et al. (25) established a correlation between decrease in dielectric constant and presence of pyrochlore using dielectric and XRD data and concluded that residual pyrochlore phase can significantly reduce the dielectric constant of PMN perovskite.

In Figure VIIb the dielectric loss of pyrochlore-perovskite mixtures is variable between 30-120°C at 100 kHz but it is smaller than 0.016 for all mixtures. Increasing perovskite percentage (going from $x=0.1$ to $x=0.522$) decreased the dielectric loss so that as for $x=0.522$ $\tan\delta$ was lower than 0.001. The low dielectric loss is typical of PMN perovskites above 20-30°C (10, 26, 27).

The effect of pyrochlore on dielectric properties can be predicted using a mixture rule. In this study, two mixture rules developed by Wiener (24, 28) and Lichtenecker (15, 24) were applied to pyrochlore-perovskite mixtures. Wiener's mixture rule can be applied using the following formulae for a diphasic solid containing an isolated spheroidal minor phase :

$$K_m = \frac{K_{Py}(3 - 2V_{Pr})}{V_{Py}} \quad (\text{for } V_{Pr} \ll V_{Py}) \quad [3]$$

$$K_m = \frac{2K_{Pr}(1 - V_{Py})}{2 + V_{Py}} \quad (\text{for } V_{Pr} \gg V_{Py}) \quad [4]$$

where K_m is the dielectric constant of the mixture, K_{Pr} is the dielectric constant of pure PMN perovskite (taken as 7595 in this study), K_{Py} is the dielectric constant of the pure PMN pyrochlore phase (taken as 130) and V_{Pr} and V_{Py} are volume fractions of perovskite and pyrochlore. Figure VII shows the dielectric constant of the mixture plotted as a function of the percent pyrochlore present with both experimental and Wiener's mixing rule. The isolated Wiener's mixing rule fits the data well up to 50 vol% of pyrochlore. In addition, Wiener's mixing rule also fits the data well for the other end of the scale (up to 28 vol% of perovskite). This is in agreement with the SEM observations of minor pyrochlore phase with $x \geq 0.4$ (high dielectric constant region) and minor perovskite phase with $x=0.1$ (low dielectric constant region). Chen and Harmer (15) applied the same mixture rule for perovskite-pyrochlore mixtures and determined that it fits the data well up to a minor phase content of 18 vol%, from both ends of the scale (i.e. when there is less than 18 vol% of pyrochlore or perovskite). Although Chen and Harmer (15) used the peak dielectric constants for the mixtures rules, in the present study

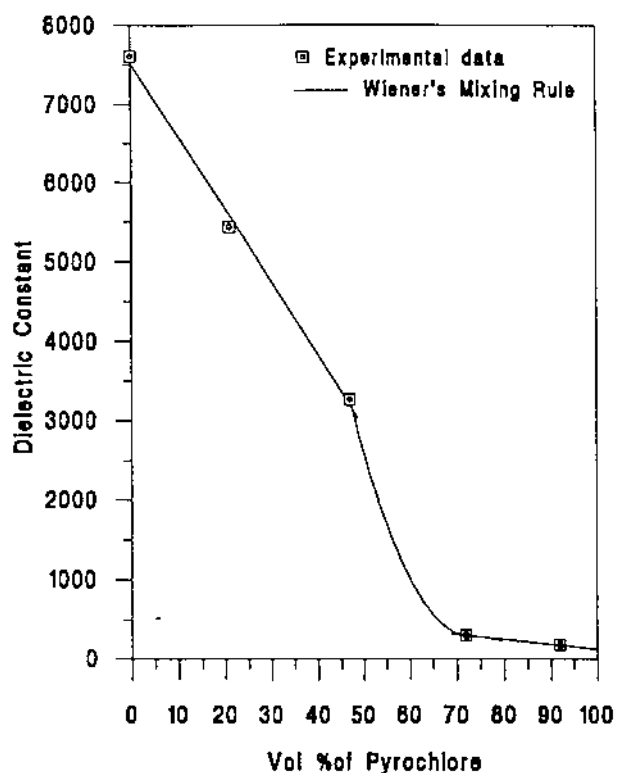


Figure VII. Dielectric constant of pyrochlore-perovskite mixture as a function of vol% of pyrochlore; both experimental and theoretical data calculated using Wiener's mixture rule are given.

room temperature values were used since the peak dielectric constants of the mixtures could not be determined.

In Lichtenecker's mixture rule it is assumed that components in the mixture could be represented by layers of material normal and parallel to the applied field or to the capacitor plates. The following general formula was used for calculations :

$$K_m^n = \sum_i V_i \cdot K_i^n \quad \text{or} \quad K_m^n = V_{Pr} K_{Pr}^n + V_{Py} K_{Py}^n \quad [5]$$

where V_i and K_i are the volume fraction and dielectric constant of each phase i and n is constant and has the values -1 and

+1. When $n=+1$ layers of material are parallel to the applied field and the structure corresponds to elements of capacitance in parallel i.e. parallel mixing is applicable and when $n=-1$ layers of material are normal to the applied field and the structure corresponds to the capacitance of elements in series i.e. series mixing is applicable. In any real polycrystalline system there is a combination of both parallel and series mixing (24). For an equal amount of series and parallel mixing i.e. as n approaches to zero the formula becomes:

$$\log K_m = \sum_i V_i \log K_i \quad [3]$$

In Figure VIII the predictions for series ($n=-1$), parallel ($n=+1$) mixing and logarithmic mixing ($n=0$) are compared and an n value of -0.20 was obtained for a reasonable empirical fit with the experimental results. Chen and Harmer (15) also applied this rule for their mixtures and found the best fit for an n value of 0.25 . The difference between these two results is thought to be due to the different dielectric constants used for the mixture rules since Chen and Harmer (15) used peak dielectric constants and room temperature values were used in this study.

Although these results show that the pyrochlore phase has a detrimental effect on the dielectric properties of PMN perovskite, the work done by Chen et al. (28) suggested that factors other than pyrochlore, such as lattice impurities and the presence of intergranular second phase may also be important. They prepared two PMN perovskite compositions from high purity powders (HPP) and from low purity powders (LPP) and found that although PMN perovskite prepared from HPP contained a higher amount of pyrochlore than PMN perovskite prepared from LPP it had a higher dielectric constant. This is attributed to the intergranular second phases in the LPP. Minor Mg-rich and Mg-Nb phases were also observed in the pyrochlore-perovskite mixtures prepared in the present study using SEM and TEM (16). For example, MgO has a dielectric constant of 9.7, which is much lower than the dielectric constant of pyrochlore. Gupta and Kulkarni (20) reported that phases which have dielectric constant of lower than the pyrochlore, such as PbO ($K \sim 20$), will have higher effect on the dielectric constant of PMN perovskite than the pyrochlore.

4. CONCLUSIONS

1. Mg incorporation into the B-site of PMN pyrochlore led to the formation perovskite phase and by increasing excess Mg content from 0.1 to 0.522, diphasic mixtures from near pure pyrochlore to near pure perovskite were obtained.

2. The density of the mixtures decreased with increasing Mg content and increased with sintering temperature.

3. Relative permittivity of the mixtures decreased with an increase in pyrochlore content and dissipation factor of the mixtures increased with pyrochlore content.

4. The isolated Wiener's mixing rule fits the data well up to 50 vol% of pyrochlore.

5. In Lichtenecker's mixture rule, the experimental results gives reasonable empirical fit at an n value of -0.2 .

6. The incorporation of Nb into the B-site of PMN pyrochlore instead of Mg resulted in formation of $Pb_2Nb_2O_7$ monoclinic pyrochlore and all PMN pyrochlore transformed to monoclinic pyrochlore at a value of 0.29 with formation of a small amount of Nb_2O_5 .

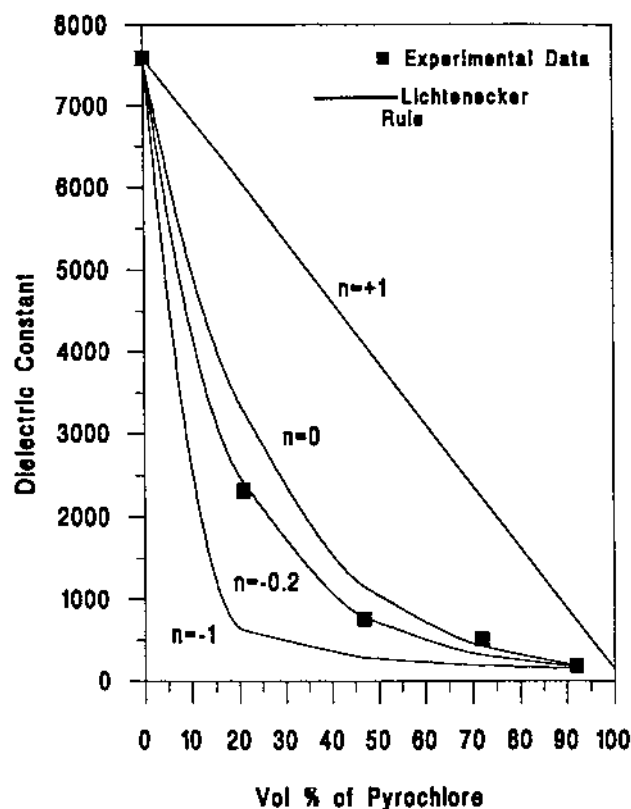


Figure VIII. Dielectric constant of pyrochlore-perovskite mixture at different pyrochlore % with comparison theoretical Lichtenecker's mixture rule ($n=+1$ parallel mixing, $n=-1$ series mixing and $n=0$ logarithmic mixing). A reasonable empirical fit was obtained for an n value of -0.2 .

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Recibido: 10.04.02

Aceptado: 16.09.02



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