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Pyrochlore phase and microstructure development in lead magnesium niobate materials

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Abstract

Microstructure characteristics of powder and sintered samples of lead magnesium niobate (PMN) have been compared and related to the presence or not of pyrochlore phase. Two kinds of samples obtained from two different batches of powders, batch A and B, containing 1 and 0 vol.% of pyrochlore phase respectively, were analysed. The two powders show the same morphology. The sintered samples, with pyrochlore content around 13 vol.% for samples from batch A and 0 vol.% for samples from batch B, exhibit totally different microstructures The grain size increases drastically from about 1 μm for samples with pyrochlore to 4–5 μm for pyrochlore free samples although starting from powders with same granulometry. The maximum dielectric constant of samples as fired, ground and annealed were measured and related to microstructures and amount of pyrochlore. On the basis of these results and data reported in literature, mostly relating dielectric properties to stoichiometry of the starting powder, it has been hypothesised that different sintering mechanisms come into play and govern the microstructure. Consequently the dielectric properties obtained were correlated to the sintering mechanism occurred rather than to the absolute value of pyrochlore phase present, as it's commonly accepted.

Keywords: Dielectric properties; Microstructure-final; Perovskites; PMN; Powders-solid state reaction; Pyrochlore

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1. Introduction

Electrical properties of lead based magnesium niobate ceramics (PMN) have been investigated since the end of 1960s.[1,2] However the widest investigation on the processing parameters, microstructural, dielectric and electrostrictive properties has been concentrated in the 1980s.[3] In these years the main attention was turned to the development of a simple and reproducible fabrication technique. PMN ceramics are relaxor ferroelectric materials with the perovskite structure, that exhibit good dielectric and electrostrictive properties. They are useful for applications such as multilayer capacitors, electrostrictive actuators, components working by induced piezoelectric effect. The main problem in their fabrication is the formation of a lead niobate-based pyrochlore phase with low dielectric constant (≅200 compared to 20 000 for PMN single crystal[4]) during the heating processes. The more widespread and efficient method to synthesise an almost phase-pure perovskite was introduced by Swartz and Shrout in 1982[5] and is well known as the columbite method. Unlike the conventional mixed oxides method, where all the starting oxides are mixed together, MgO and Nb_2O_5 are pre-calcined to form the columbite, $MgNb_2O_6$, prior to reaction with PbO. Following this route, the formation of pyrochlore, rising from the direct reaction of Nb_2O_5 with PbO during the calcination of the powder, is prevented.[6] Nevertheless the pyrochlore can be formed by decomposition of the PMN perovskite phase, as a consequence of PbO volatilisation during the sintering process; therefore, the control of PbO stoichiometry during the synthesis steps is extremely important.

In order to understand the correlations between microstructure, sintering mechanism and dielectric properties it is worthwhile to review the results reported in literature.

Swartz et al.,[7] discussing the dielectric properties of PMN ceramics on the base of process parameters like calcination/sintering temperature and powder composition, showed that the transition temperature increases and maximum dielectric constant (ε_{max}) decreases when sample composition moves from PMN + 2 vol.% $MgNb_2O_6$ to stoichiometric PMN to PMN + PbO, i.e. compositions in defect, stoichiometric and in excess of

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PbO. It was also noted that the increase in grain size due to an increase in the sintering temperature, up to 1270°C, is coupled with a decrease in the transition temperature and density as well as to an increase in $\varepsilon_{\max}$. Moreover, the excess MgO determines an increase in grain size coupled with a decrease of transition temperature and an increase in maximum dielectric constant. The detrimental effect over the dielectric constant of excess PbO, was shown in some other works.[8,9] An excessive amount of PbO, coming from the packing atmosphere of PMN-PT ceramics, results in the decrease of the maximum dielectric constant.[10] Studying the role of excess magnesium oxide and lead oxide in terms of microstructure and electrical properties of PMN, Wang et al. [11] showed that the grain size and the maximum dielectric constant increase moving from PMN with excess PbO to stoichiometric PMN to PMN with excess MgO. At the same time they show that the percentage of pyrochlore detected in the as fired samples is zero for samples with excess MgO whilst it increases of some units per cent upon addition of PbO. The detrimental effect of excess PbO on the dielectric constant is attributed to the formation of a PbO-rich grain-boundary phase with low dielectric constant (PbO dielectric constant ≅20).[2,4,11,12] This phase usually coexists with the pyrochlore phase,[13] that differs from the stoichiometric PMN composition for a defect in PbO and MgO content. In fact the Pb/Nb stoichiometric ratios are 1.5 for PMN, 1.15–1.25 for pyrochlore, the Mg/Nb stoichiometric ratios are 0.5 for PMN, ≅0.15 for pyrochlore.[4,14] Otherwise, the incremental effect of excess MgO on the dielectric constant, is attributed either to a reduction of the pyrochlore formation or to an increase of the grain sizes with a consequent reduction of the volume of the grain boundaries that lowers permittivity.[7,15] Villegas et al.[16–18] discuss the role of excess PbO in the evolution of secondary phases (free PbO and pyrochlore) in the PMN-PT sintered samples; the presence of a rich PbO liquid phase which dissolves perovskite grains is the cause of the formation of a pyrochlore phase layer at the top surface, through a process of migration and vaporization of this liquid phase towards the top air surfaces.

The aim of this work is to further improve the understanding of the role played by the pyrochlore phase in the PMN sintered samples properties. Pyrochlore, in a quantity of some units %, seems not to be sufficient to justify the decrease of the dielectric properties, as it is commonly accepted, but it is most probably that a signal of a different sintering mechanism occurred that is reflected in the final microstructure.

2. Experimental procedure

Reagent-grade starting powders of PbO (Aldrich, 99.99%), Nb_2O_5 (Aldrich, 99.99%) and MgO (Carlo Erba, 99%) were used as raw materials in a stoichiometric amount to synthesize PMN ceramics with the columbite method.[5] The slurry containing MgO, as received (batch A) or pre-dried at 800°C for 30 min (batch B)[19] and Nb_2O_5 was ball milled for 24 h, dried and calcined at 1000°C for 6 h. The so obtained columbite ($MgNb_2O_6$) batches were added to the PbO/water suspension, ball milled for 24 h, dried and calcined in a covered alumina crucible at 800°C for 4 h. The calcined powders added with 1 wt.% of polivinylalchol (PVA) were dry ground using an agate mortar, passed through 100-mesh sieves and pressed into disks (25 mm in diameter and 2 mm thick) by die pressing at 50 MPa and isostatic pressing at 150 MPa. The disks were then supported on ZrO_2 setters and fired in a closed alumina crucible sealed with $PbZrO_3$ (PZ) powder to minimize the PbO volatilization. The particle size of the powders was determined by particle size analyzer (Sedigraph, Micromeritics 5100). Sintering was performed at 1150°C in air for 1 h. The density of the sintered samples was determined by the Archimede's method in deionized water. The microstructure of the polished and fracture surfaces of the sintered samples was investigated by Scanning Electron Microscopy (SEM) coupled with an energy-dispersive X-ray spectrometer (EDS). The average grain size was measured from the micrographs using a linear intercept technique. All calcined powders and sintered disks were analyzed using X-ray diffractometry (XRD). The relative amount of perovskite and pyrochlore phase was determined using the formula:[5]

$$\%\text{pyrochlore} = 100 \times I_{\text{pyro}}/\left(I_{\text{pyro}} + I_{\text{perov}}\right)$$

where I_{pyro} and I_{perov} are the intensity of the major X-ray peaks of pyrochlore (222) and perovskite (110) phases. Samples for dielectric measurements were prepared from the sintered pellets by screen printing silver electrodes and heating at 750°C for 15 min. Dielectric measurements were performed with a HP 4194A Impedance Analyser with a temperature control chamber (B-M-A, Inc., Model AT-102XC). Dielectric constant and dissipation factors were measured at 0.1, 1, 10 and 100 kHz as the sample were cooled through the transition range (80 to −30°C) at a rate of 2°C/min. The parameters used for analysis of dielectric data were the maximum dielectric constant at 1 kHz and the temperature at which this maximum occured (T_m). The dielectric constants were not corrected for porosity.

3. Results and discussion

3.1. Microstructure and phase formation

The main characteristics of PMN powders and sintered bodies of the samples obtained from two different batches of powder are summarized in Table 1. The perovskitic phase from batch A (calcined powder from columbite prepared with as received MgO), contains 1 vol.% of pyrochlore phase, while that from batch B, (calcined powder from columbite prepared with predried MgO) is 100% pure. The presence of pyrochlore in batch A arises from a slight magnesium deficiency caused by the presence of volatile substances in the as received MgO powder.[20] Apart from the presence of pyrochlore, the two powders show the same morphology and very similar particle size distribution and mean particle diameter (d_{50}). The sintered samples show a very high density, near to the theoretical one (8.01 g/cm^3 for sample I and 8.13 g/cm^3 for sample II), while they differ substantially in the pyrochlore content, which is 13 vol.% in sample I and absent in sample II. Another significant difference between the samples is the mean grain size that decreases drastically from 4 to 5 μm for sample II without pyrochlore to about 1 μm for sample I with pyrochlore even if both the samples start from powders with the same granulometry. Sample II also reveals better dielectric properties being its ε_{max} higher than 15000 in comparison with sample I ($\varepsilon_{max} \cong 13\,000$).

The microstructures of the samples I and II are shown in Fig. 1a and b respectively. Two large angular grains are shown in Fig. 1a. The EDS analysis reveals that the elongated dark inclusion corresponds to MgO whilst the trapezoidal grain is typical of pyrochlore phase. A small grain corresponding to MgO is also shown in Fig. 1b. It can be hypothesized that the microstructure of sample I, characterized by a smaller grain size with a narrow distribution, large pyrochlore grains on the surface and large discrete MgO inclusions, is the result of a liquid phase sintering mechanism promoted by an excess of PbO. The crystallization of MgO big grains confirms the presence of PbO not involved in the formation of the perovskite phase. The formation of a liquid phase during sintering can be only attributed to PbO as well as the weight loss, being the PbO melting point (889°C) lower than that of other components (MgO, Nb_2O_5, $MgNb_2O_6$ m.p. >1100°C). This phase promotes a liquid phase sintering process that decreases the densification temperature[21] but at the same time undergoes PbO volatilization with consequent formation of pyrochlore. This mechanism can be activated in the presence of excess PbO or when there is free PbO not involved in the formation of the perovskite phase. Starting from a stoichiometric composition (batch B) or in excess MgO it can be supposed that there is not free PbO liquid phase. The microstructure shown in Fig. 1b, referred to in sample II, is totally different. It is evident that the coarsening of big grains over small grains is through a process coherent with a solid state sintering mechanism. In this case a better control of stoichiometry, starting from the purification of the raw materials, results in the formation of pure PMN phase with very few and small MgO inclusions. The X-ray diffractograms of a sample I pellet, as fired and ground (grinding depth ≅ 0.5 mm) are shown in Fig. 2a and b respectively. It can be seen that a grinding depth

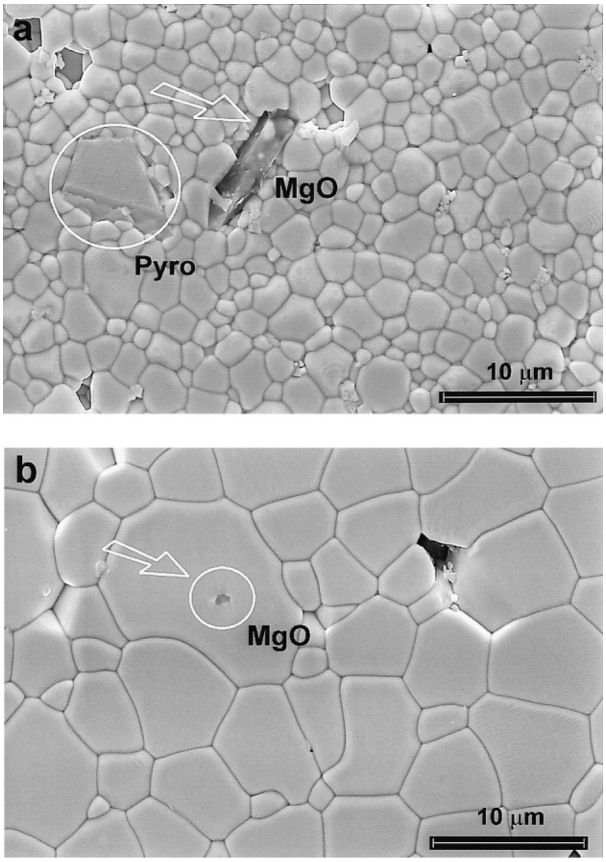

Fig. 1. SEM morphology of (a) polished surface of sample I, starting from powder of batch A and (b) polished surface of sample II, starting from powder of batch B.

Table 1
Phase composition and physical properties of perovskitic starting powders and sintered pellets

Sample	Batch	Powder properties		Sintered pellet properties			
		Pyroclore (vol.%)	d_{50} (μm)	Density (g/cm^3)	Mean grain size (μm)	Pyroclore (vol.%)	ε_{max}[a]
I	A	1	1.7	7.96	1.6	13	13057
II	B	0	1.6	7.88	4.6	0	15633

[a] ε_{max} calculated at 1 kHz

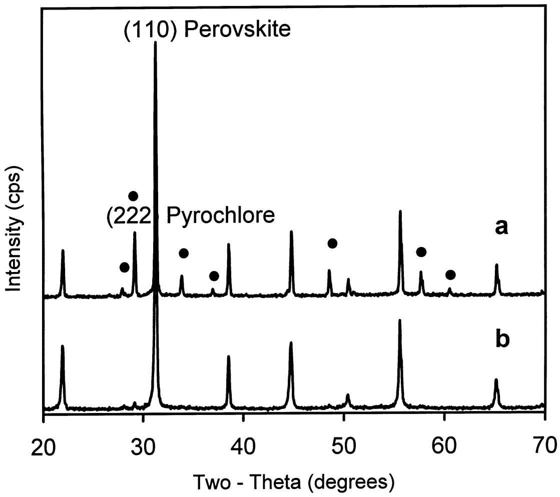

Fig. 2. XRD patterns of sample I, as sintered (a) and ground (b) (grinding depth: 0.5 mm); the pyrochlore phase peaks are marked.

of about 0.5 mm is sufficient to eliminate almost all the pyrochlore phase (from 13 to 1.5 vol.%). The presence of a pyrochlore concentration gradient is also revealed by SEM microstructure shown in Fig. 3a and b, where large pyrochlore grains are found only near the surface. In Table 2 some physical constants referred to as samples I and II, as fired, grounded and annealed at the sintering temperature for 1 h are reported. The annealing treatment slightly increases the grain size in both cases, from about 1.6 to 2.0 μm for sample I and from 4.6 to 5.5 μm for sample II. Nevertheless, in the case of sample I, the pyrochlore phase is formed again, as can be also shown in Fig. 3c. The removal of the pyrochlore phase at the beginning of the annealing process is not enough to promote a different mechanism that would lead to bigger grain sizes (about 5 μm). The mechanism that takes place depends on the presence or not of enough liquid PbO phase to promote liquid phase sintering and create a pyrochlore phase layer at the top surface through a process of migration and vaporisation. This PbO liquid phase can be available if there is an excess PbO or if the PbO present is not fully involved in the formation of the perovskite phase. It can be due to a non homogeneous mixing of the starting oxides, a lower reactivity of magnesium as regards to niobium or to the presence of pyrochlore in the starting powder and so the PbO did not react again.

3.2. Dielectric properties

The typical relaxor behavior[22,23] with the characteristic dispersive frequency dependence of the dielectric maxima is shown in Fig. 4, for sample II. The same behavior has been observed in all samples. The dielectric constants and dissipation factors are compared in Figs. 5 and 6. The T_m are about the same for all samples measured (about $-8°C$) whilst the samples from batch A

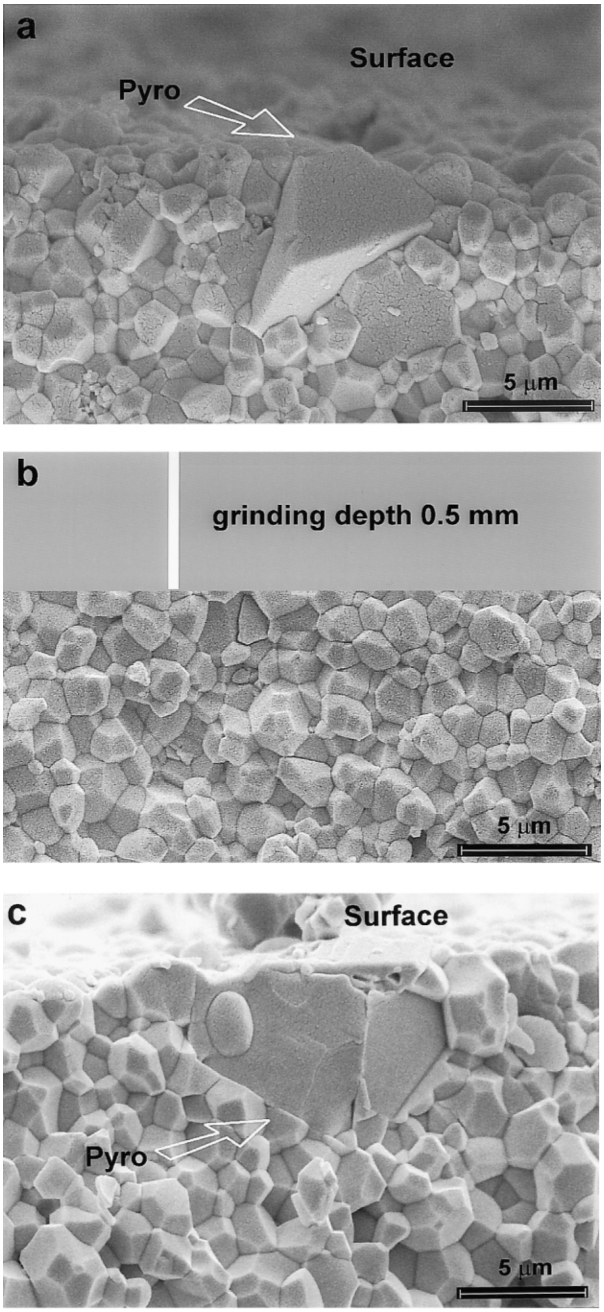

Fig. 3. SEM morphology of (a) the surface layer, (b) inner layer after grinding and (c) after annealing of sample I.

Table 2
Phase composition, mean grain size and density of PMN sintered, ground and annealed samples

		Pyroclore (vol.%)	Mean grain size (μm)	Density (g/cm³)
Sample I:	as fired	13.0	1.6	7.96
	ground	1.5	1.6	7.96
	annealed	15.0	2.0	7.93
Sample II:	as fired	0.0	4.6	7.88
	annealed	0.0	5.5	7.86

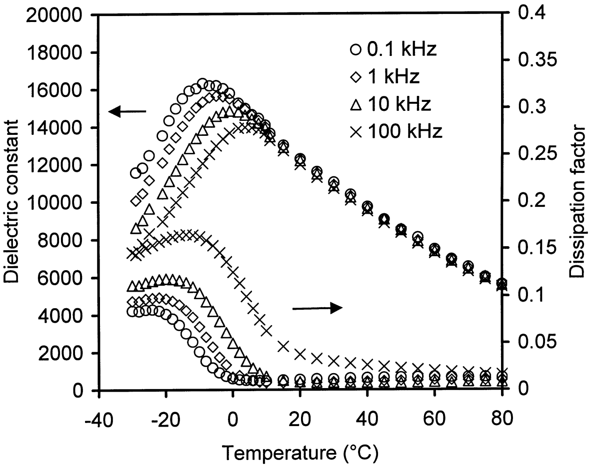

Fig. 4. Dielectric constant and dissipation factor as a function of temperature and frequency for sample II.

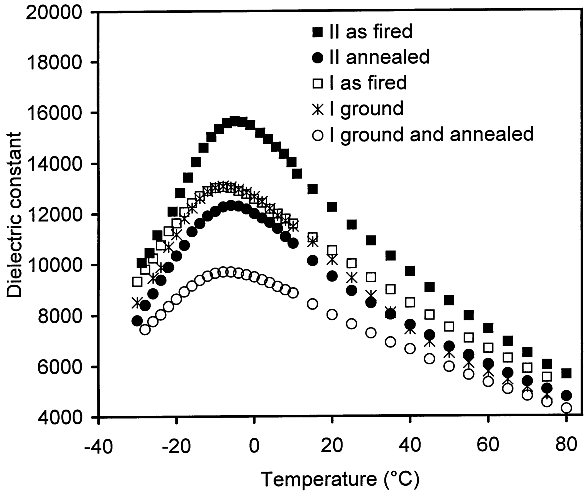

Fig. 5. Comparison of dielectric constants as a function of temperature for samples I and II as sintered and upon grinding and annealing (at 1 kHz).

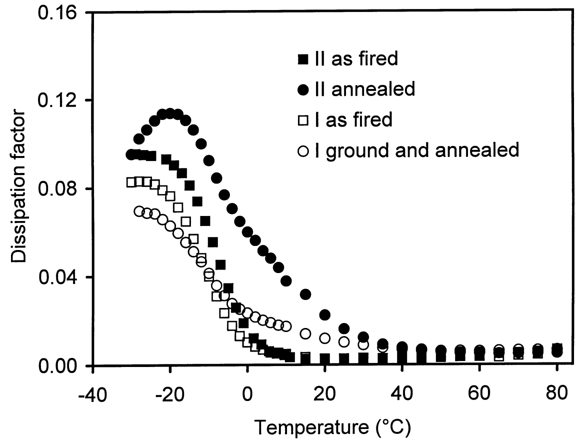

Fig. 6. Comparison of dissipation factors as a function of temperature for samples I and II as sintered and upon grinding and annealing (at 1 kHz).

show a slight increase in the diffuseness of the phase transition (see slopes of the dissipation factors in Fig. 6). The maximum dielectric constant of sample II as fired (15633) is higher than that of sample I (13057). The maximum dielectric constant of sample I ground (13088) does not increase after reducing the quantity of pyrochlore phase and it remains lower than the dielectric constant of sample II starting from powder without pyrochlore. This result confirms that the presence of the pyrochlore phase is not the only responsible for the decreasing of dielectric properties because its removal doesn't increase the maximum dielectric constant. It was already demonstrated by Chen and Harmer[4] that characterised lead magnesium niobate-pyrochlore diphasic mixtures and found that the material retains relaxor properties and a high dielectric constant ($\varepsilon_{\max} = 14\,500$) up to a 18 vol.% of pyrochlore content in the perovskite structure. The annealing treatment decreases the maximum dielectric constant in both cases (sample I ground and annealed, 9687; sample II annealed 12327) in despite of the increase of the mean grain size. Actually, the dielectric properties are more influenced by microstructure and evolution of grain boundary phase than by pyrochlore phase or by grain size itself.

4. Conclusions

The presence of a few percentage of pyrochlore phase in the calcined powder promotes differences in the grain size and in the dielectric constant of the sintered bodies. They are lower for sample with pyrochlore. Sample I, starting from a pyrochlore impure perovskitic phase, is characterised by smaller grain sizes with a narrow distribution and large pyrochlore grains on the surface. Sample II, starting from a pyrochlore free perovskitic phase, shows big grains, coarsened over small grains. These microstructures are typical of two different sintering mechanisms, a liquid phase sintering mechanism in the case of sample I, a solid phase sintering mechanism in the case of sample II. The presence of pyrochlore phase is associated to the presence of free PbO, available to activate a liquid phase sintering mechanism and to promote the formation of further pyrochlore phase. The kind of sintering mechanism involved influences the microstructure and consequently the dielectric properties. As already demonstrated stoichiometric samples (sample II) show higher dielectric constants in comparison to samples with pyrochlore involved (sample I). Nevertheless the presence or not of pyrochlore in the sintered samples is not the cause of lowering dielectric properties but the consequence of a different sintering mechanism leading to a different microstructure. The hypothesis of a liquid phase sintering mechanism could justify a bigger amount of glassy phase in the grain boundary with a consequent lowering of dielectric properties in the sample starting with pyrochlore. Further investigations will be carried out in order to better characterise the grain boundary phase.

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