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Dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $(Pb_{1-x}La_x)(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ ceramics prepared by columbite route

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Abstract

The role of the La-addition on the A-site of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) on the phase formation, microstructure and dielectric properties was investigated. Ceramic samples were obtained from PMN and $(Pb_{1-x}La_x)(Mg_{1+x/3}Nb_{2-x/3})O_3$ (PLMN) nanopowders synthesized by the columbite method using MgO and Mg-carbonate precursors. An influence on the degree of crystallinity and phase purity was found particularly in the PMN ceramics. Typical relaxor properties characterised by a diffuse phase transition with a maximum around 270 K and relaxation in the kHz range were observed. The incorporation of La induces the formation of a short range nanopolar ordered superstructure, thus modifying the dielectric relaxation properties, strongly depressing the permittivity. The observed behaviour is discussed in terms of microstructural characteristics induced by the Mg-precursor and of La-incorporation in the PMN perovskite unit cell.

Keywords: Microstructure-final; Dielectric properties; Niobates; Perovskites; Relaxor

1. Introduction

The relaxor ferroelectric lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3}O_3)$, designated PMN and synthesized for the first time by Smolenskii and Agranovskaya[1] in 1959, exhibits excellent dielectric properties (permittivity values >10000) and a high electrostrictive coefficient, making the ceramics related to this compound very promising candidates for applications as multilayer capacitors, sensors and actuators.[2–4] The main feature of the PMN, from electrical point of view, is a broad maximum dielectric peak, which indicates a diffuse phase transition associated with compositional fluctuations on the B-site sublattice of the perovskite structure.[5,6] Another obvious trend is the decrease of the magnitude of this maximum correlated with its temperature increase as frequency increases.

A problem in the fabrication of pure PMN is the formation of a stable pyrochlore second phase, detrimental for the dielectric permittivity of the ceramics. An innovative approach in this sense was proposed by Swartz et al.[2] who minimized the amount of the pyrochlore phase (<5 wt.%) using the so-called “columbite precursor method”. This route consists in the precalcining of a stoichiometric mixture of MgO and Nb_2O_5 in order to form $MgNb_2O_6$ (columbite), which subsequently reacts with PbO.

We showed earlier[7] that the nature of the magnesium precursor could play a role in both the formation mechanism and purity of the perovskite PMN phase.

Despite of a great number of papers which refer to the study of structural modifications induced by lanthanum used as dopant on Pb^{2+} sites in the perovskite lattice,[8–13] there are only a few reported data, regarding the dielectric properties of the related $(Pb_{1-x}La_x)(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ (PLMN) ceramics.[6,14]

The aim of this work is to study the influence of the magnesium precursor on both the microstructure and dielectric behaviour of PMN and PLMN ($x = 0.2$) ceramics obtained by the “columbite” route.

2. Experimental

The starting materials were reagent-grade PbO, La_2O_3, MgO, $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ and Nb_2O_5 powders. Synthesis of

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Table 1
Chemical, structural and microstructural characteristics of samples isothermally treated at 1200 °C/4 h

Sample	Composition	Mg-precursor	Lattice parameter, *a* (Å)	Unit cell volume, *V* ($Å^3$)	*Z*	Relative density, ρ_r (%)
PMN1	$Pb(Mg_{0.33}Nb_{0.66})O_3$	MgO	4.048	66.3318	1	95.02
PMN2	$Pb(Mg_{0.33}Nb_{0.66})O_3$	$(MgCO_3)_4\cdot Mg(OH)_2\cdot 4H_2O$	4.047	66.2826	1	94.80
PLMN1	$Pb_{0.8}La_{0.2}(Mg_{0.4}Nb_{0.6})O_3$	MgO	8.050	521.6601	8	85.09
PLMN2	$Pb_{0.8}La_{0.2}(Mg_{0.4}Nb_{0.6})O_3$	$(MgCO_3)_4\cdot Mg(OH)_2\cdot 4H_2O$	8.045	520.6887	8	74.07

PMN and La-modified PMN samples was carried out by the "columbite" method presented elsewhere.[7] The composition of the samples is presented in Table 1.

The calcined powders with polyvinyl alcohol (PVA) added as binder, were pressed into pellets of 10 mm diameter and ~3 mm thickness, which were then sintered for 4 h in air at 1200 °C. Sintering was performed inside closed platinum crucibles and the pellets were covered with powders of the same composition to minimize the lead loss during the thermal treatments.

The phase composition and the structural parameters of the samples were studied by X-ray diffraction (XRD) with a Brucker-AXS D8 diffractometer, using Ni-filtered Cu Kα radiation. The lattice unit cell parameters have been determined by the least squares method, based on the position of nine or ten well defined diffraction lines.

The perovskite powders morphology and the microstructural features of the ceramics were investigated by SEM using JEOL JSM-6400 and Hitachi S2600N equipments. The sinterability of PMN and PLMN ceramics was estimated by means of the values of relative density calculated as ratio between the apparent density determined by the hydrostatic method and the theoretical density.

For the electric measurements, Ag-Pb electrodes were deposited on the plane-parallel polished surfaces of the ceramics followed by annealing in air at 500 °C for 12 h. The dielectric measurements were performed with an impedance analyzer Solartron SI1260 for temperatures of 30–200 °C with a heating/cooling rate of 0.5 °C/min in the frequency range 10–10^6 Hz.

3. Results and discussions

The room temperature X-ray diffraction patterns of ceramics sintered at 1200 °C indicate that the well crystallized perovskite PMN phase starts to decompose, so that small amount of pyrochlore phases were detected in this case (Fig. 1a and b). This process was reported also in the literature[7] and is more obvious for PMN2 composition. Fig. 1c and d shows the XRD patterns of La-modified PMN samples sintered in the same conditions as pure PMN. One can notice that the La additive induces a short range ordering pointed out by supplementary (1 1 1), (3 1 1) and (3 3 1) diffraction peaks, corresponding to a superstructure formation. Although La incorporation into the perovskite lattice determines a unit cell shrinkage because of the smaller ionic radius of La^{3+} compared with Pb^{2+} (1.14 Å versus 1.20 Å), due to the superstructure formation, the effective lattice parameters of the ordered structures are twice than those of the disordered PMN structures. The values of the lattice parameters and unit cell volume for the compositions considered are presented in Table 1. Taking into account that the PLMN1 and PLMN2 X-ray diffraction patterns are quite similar we concluded that for the La-modified samples the influence of Mg precursor is less obvious than in the case of pure PMN samples.

SEM analyses were performed on the surface of the pellets sintered at 1200 °C. The SEM micrographs of the PMN1 and PMN2 samples show heterogeneous microstructures with bimodal grain size distribution. This feature is more obvious for PMN2 (Fig. 2), where groups of 4–6 smaller grains with an average size of ~4 μm are located between larger grains (of ~15 μm). One can notice the lack of any inter- or transgranular porosity and perfect triple grain junctions. The PMN samples present also a good densification, having high relative density values of ~95% (Table 1).

The micrographs of PLMN samples show that lanthanum influences dramatically the microstructure (Fig. 3). One can observe the inhibiting effect of the lanthanum used as additive on the grain growth process and, consequently, a relative homogenous microstructure, with intergranular porosity, and finer grains (of ~3 μm) than those ones of similar, non-modified samples was formed. In the case of PLMN2 specimen this effect induced by lanthanum is even more pregnant and resulted in a higher porosity because of the microstructure disturbance, mainly in the grain boundary regions (Fig. 3). These observations are sustained by the relative density values, significantly lower for the PLMN samples comparing with pure PMN, especially when magnesium carbonate was used as precursor (Table 1).

The real part of the dielectric constant vs. temperature at a few frequencies is comparatively shown in Fig. 4 (samples PMN1–2)

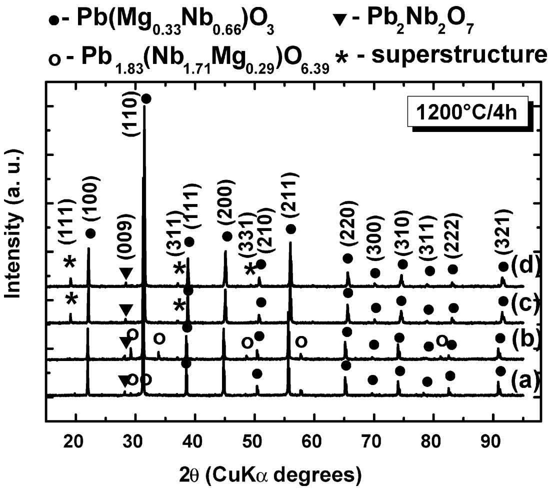

Fig. 1. X-ray diffraction patterns obtained for the sintered ceramics: (a) PMN1, (b) PMN2, (c) PLMN1 and (d) PLMN2.

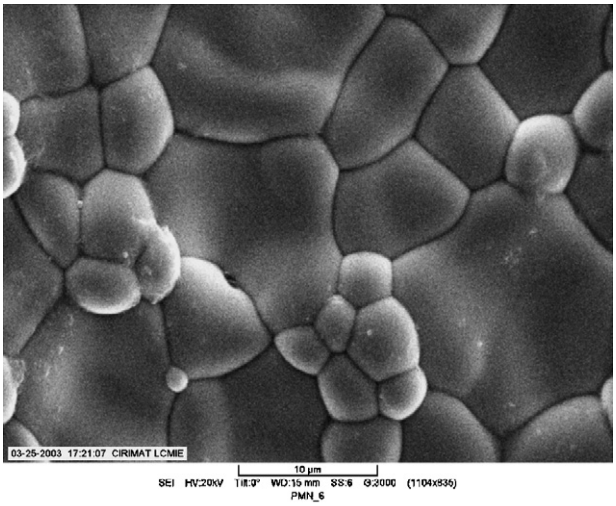

Fig. 2. Surface SEM image of PMN2 ceramic sample sintered at 1200 °C for 4 h.

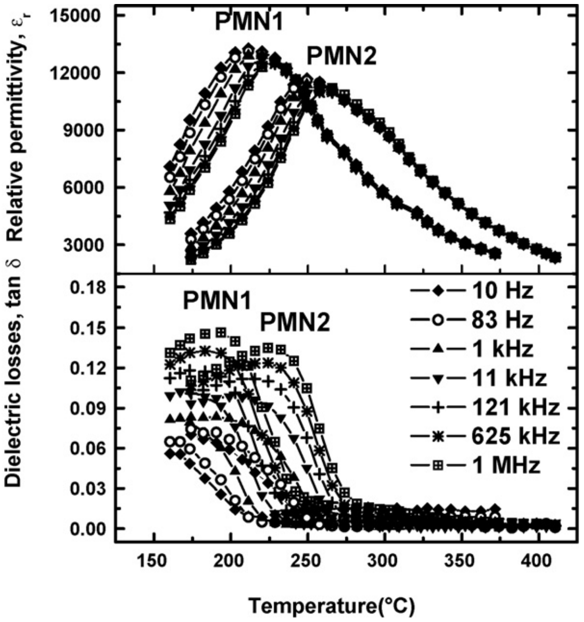

Fig. 4. Relative permittivity and dielectric losses vs. temperature and frequency for PMN samples.

and Fig. 5 (PLMN1–2). PMN ceramics have excellent dielectric properties with low losses: tan $\delta < 2\%$ in the temperature range 300–450 K and <16% at T_m and high values of the permittivity for PMN1 and PMN2, respectively: ∼6000 and ∼9000 at room temperature and ∼13,500 and ∼12,000 at the temperature corresponding to the maximum permittivity T_m. Both samples present relaxor character with diffuse phase transition and permittivity dispersion in the kHz range for $T < T_\mathrm{m}$. It is interesting to note that $\varepsilon(T)$ dependences of PMN1–2 present a shift of T_m: from 210 to 230 K (PMN2) and from 250 to 265 K (PMN1) when the frequency is ranging from 10 Hz to 1 MHz. This shift can be explained as coming from the compositional differences between PMN1 and PMN2 (secondary phases in PMN2) and from the microstructural characteristics, particularly the degree of crystallinity and grain size. The presence of a few very large grains (Fig. 2) can cause an increasing of T_m.

Due to more similar microstructures, the dielectric data of PLMN1–2 do not present such an evident shift. By comparison with dielectric data of PMN, the presence of La causes a strong reduction of permittivity.[6] This is explained by the fact that in PLMN, increasing positive charge provided by La facilitates the growth of 1:1 chemically ordered regions, which most probably are not ferroelectric in nature[10] and thus, are causing a diminishing of the permittivity by comparison with PMN. A further reduction of ε is determined by the small grain size and by the poor densification (even lower for PLMN2). In spite of lower density values, the dielectric losses are <2% in the investigated temperature range.

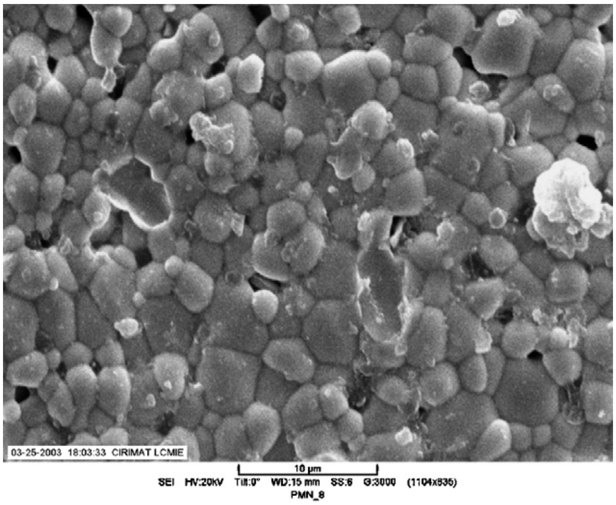

Fig. 3. Surface SEM image of PLMN2 ceramic sample sintered at 1200 °C for 4 h.

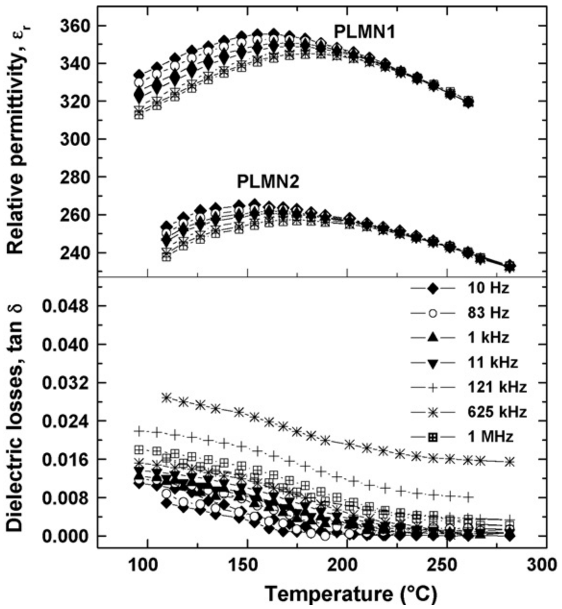

Fig. 5. Relative permittivity and dielectric losses vs. temperature and frequency for PLMN samples.

4. Conclusions

The PMN samples sintered at 1200 °C exhibit high crystallinity, high densification ($\rho_r \sim 95\%$) and excellent dielectric properties. Higher amount of secondary pyrochlore phases was detected in the PMN2 sample. The compositional and microstructural differences determines, for all the investigated frequencies, a clear shift of ~40 K for the temperature of the permittivity maximum, T_m, towards higher values, causing higher permittivity and lower dielectric losses at room temperature for the PMN2 specimen.

From both phase composition and structural point of view, in the lanthanum modified samples, the influence of magnesium precursor is less obvious, than in the case of pure PMN ceramics; the presence of lanthanum in the perovskite PMN lattice determines the increase of the short range ordering accompanied by the doubling of the unit cell parameter and inhibits the grain growth process, affecting the ceramics sinterability. From electrical point of view, the lanthanum addition ($x = 0.2$) caused a strong flattening of the $\varepsilon(T)$ characteristic. For both PLMN samples T_m is similar at the same frequency, which means that the precursor type seems to have almost no effect on the ferroelectric relaxor properties. The higher dielectric permittivity of the PLMN1 sample is probably due to the slightly higher density of this sample. The low values of dielectric losses indicate good insulating properties for lanthanum modified lead magnesium niobates.

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