

Fabrication of Pyrochlore-free Lead Magnesium Niobate Ceramic from Nanopowder Precursors via Single Step Sintering

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Abstract

Lead magnesium niobate, $\text{Pb}^{2+}\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN), is one of the most widely investigated relaxor ferroelectric materials with a perovskite structure. The excellent relative permittivity of PMN (~20,000) over the operational temperature range, electrostrictive properties and low dielectric loss make it a promising electroceramic material for multilayer ceramic capacitors (MLCCs), sensors, electromechanical transducers, electro-optic applications, electrostrictive actuators and fuel injectors for automobile engines. In the present study, a high density single-phase lead magnesium niobate ceramic with the highest peak dielectric constant reported so far, has been synthesized and sintered simultaneously via a modified mixed oxide route, using nanopowder precursors and single-step sintering. Appropriate amounts of PbO, Nb₂O₅ and MgO for stoichiometric PMN were dry-milled using a disc mill with tungsten carbide discs, for 90 min at 1000 rpm. The mixed nanopowder was sintered at 1200 °C in air and PbO atmospheres. By comparison, samples sintered in air, gained pyrochlore structure, while those samples sintered in PbO atmosphere had pure perovskite structure. Pellets sintered for 2.5 h exhibited best dielectric properties with peak dielectric constant of 18,672 at the frequency of 1 kHz at -13 °C. The dielectric properties, phase formation, densification, and microstructure of the samples were investigated. It has been proven that sintering the stoichiometric pellets in air results in the formation of pyrochlore phase. The results obtained from dielectric measurement of the samples, also indicated positive effect of grain growth on dielectric properties.

Introduction

The excellent relative permittivity of PMN (~20,000) over the operational temperature range, electrostrictive properties and low dielectric loss make it a promising electroceramic material for multilayer ceramic capacitors (MLCCs), sensors, electromechanical transducers, electro-optic applications, electrostrictive actuators and fuel injectors for automobile engines. There has been a great deal of interest in the preparation of single-phase PMN powders as well as in the sintering and dielectric properties of PMN-based ceramics [1-3].

In general, the overriding aim of any materials processing technique is to achieve a final product with

consistent properties. In practice, the level of consistency obtained is often a matter of compromise, it being largely a consequence of the economics of fabrication and characterization.

The main problem in fabrication of pure perovskite PMN ceramics is formation of the unwanted pyrochlore phase with low dielectric constant (~200) which decreases the dielectric and electromechanical performances of the resulting material. The pyrochlore phase is the major product at the initial stages of the solid-state reactions between the three constituent oxides, owing to the preferential reaction between Nb₂O₅, a large amount of PbO and a small amount of MgO. With the increasing reaction temperature and time, pyrochlore further combines with the remaining PbO and MgO to yield the perovskite PMN. The residual pyrochlore phase, together with the main perovskite, is a consequence of low MgO reactivity and intrinsic inhomogeneity of the reacting mixture. Furthermore, the heating treatment at temperatures above 900 °C can lead to the formation of pyrochlore phase as a consequence of PbO loss by evaporation, if samples are not fired in a saturated PbO atmosphere [4-7].

In the present study, an attempt has been made to fabricate full dense single-phase PMN ceramic with the best dielectric properties by employing modified mixed oxide route. High energy milling was used to reduce the size of powder down to nanoscale, followed by calcination within the single-step sintering of PMN. Phase formation, densification, microstructure, and dielectric properties of the samples have also been investigated.

Experimental

The modified mixed oxide route was employed for the synthesis of PMN powder. Starting raw materials were reagent-grade PbO (99%, Merck), Nb₂O₅ (99.9%, Merck) and MgO (98%, Merck). Appropriate amounts of PbO, Nb₂O₅ and MgO for stoichiometric PMN were dry-milled using disc mill (Siebtechnik T100) with tungsten carbide discs, for 90 min at 1000 rpm. Morphology and size of the milled powder was observed using transmission (TEM, CM200 FEG, Philips, Netherlands) and scanning (SEM, Philips XL30, Netherlands) electron microscopy. The green pellets (10 mm dia, 3 mm thickness) were obtained by

uniaxial pressing of the powder at 800 MPa in a steel cylindrical die. After ejection of compacts from die, the green density of the pellets (64 ± 0.5 of theoretical density) was measured by water immersion method.

Pellets were then sintered isothermally at 1200 °C up to 3 h with heating rate of 10 °C min⁻¹ in closed alumina crucibles with amount of PbO powder, in order for the atmosphere to be saturated with PbO. Sintering of some other samples also carried out in air for the comparison of results. The density of sintered PMN pellets was also measured by water immersion method. Microstructures were observed by SEM. The phase formation of sintered PMN ceramics was analyzed by X-ray diffraction (XRD, PW3710-based Philips diffractometer) at 2θ between 25° and 40° with a step size of 0.02°. The relative amounts of perovskite and pyrochlore phases were determined from XRD pattern of the samples by measuring the major peak intensities for the perovskite phase ($I_{perov.}$) and pyrochlore phase ($I_{pyro.}$) related to (110) and (222), respectively. The following approximation (Eq. (1)), was used:

$$\% \text{ perovskite} = 100 \times I_{perov.} / (I_{perov.} + I_{pyro.}) \quad (1)$$

Dielectric properties were measured by LCR meter (HP-4174 Hewlett-Packard) at 1 KHz.

Results and Discussion

Fig. 1 shows the TEM micrograph of oxides mixture after milling. Size of the mixed powder was also estimated by SEM to be in the range of 50 - 80 nm which is in good agreement with TEM micrographs (30-70 nm). As it is seen in Fig. 1, milling has been done properly and the oxides are mixed perfectly, however, no PMN phase was observed in the X-ray diffraction of as-milled powder.

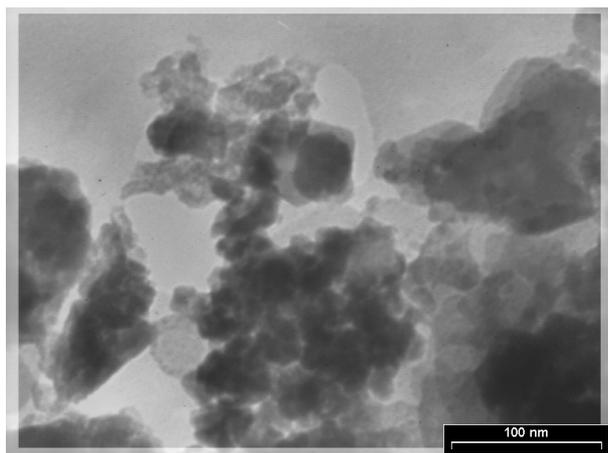


Fig. 1 TEM micrograph of oxides mixture after milling

The relative density, average grain size, amount of perovskite phase of samples (samples No. 1-5) sintered for different soaking times and in different atmospheres, are listed in Table 1. Weight loss of PMN ceramics during sintering procedure can be thought of as a measure of the degree of PbO volatilization. This was

analyzed by recording the weights of the pellets before and after sintering. By employing the PbO atmosphere powder during the sintering process, the level of weight loss can be limited to less than 5% in the system. The XRD profile of PMN ceramics sintered at 1200 °C for 2, 2.5 and 3 h, in PbO atmosphere are shown in Fig. 2. The major peak (222) of pyrochlore phase at $2\theta = 29.2^\circ$ is not found in the pattern for samples No. 1 and 2. It indicates that our modified mixed oxide route is simple and effective in producing pyrochlore-free PMN ceramics.

Table 1 Sintering behavior of mixed oxide nanopowder.

Sample No.	Sintering temp. (°C)	Soaking time (h)	Density (%)	Weight loss (%)	Grain size (μm)	Perovskite phase (wt%)
1 ⁺	1200	2	97.2	0.3	0.5-3	100
2 ⁺	1200	2.5	98.5	1.7	1-5	100
3 ⁺	1200	3	98.2	2.9	2-6	98.5
4 [*]	1200	1	97	5.9	----	14
5 [*]	1200	2	96.5	7.8	----	3.5

The samples have been sintered in PbO atmosphere⁺ and air^{*}.

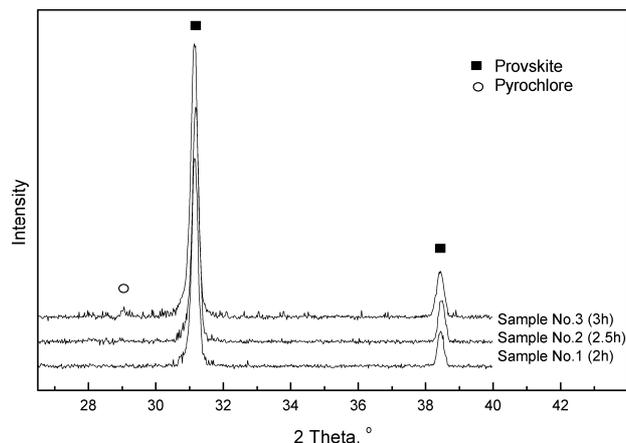


Fig. 2 The XRD profile of PMN ceramics sintered at 1200°C for 2, 2.5 and 3h, in PbO atmosphere.

The smaller the starting particle size, the larger the specific surface area, the higher driving force for densification and reactivity of starting powders. Furthermore, the low intrinsic reactivity of MgO will be compensated. Thus, the time and temperature required for the calcination reaction and then sintering will decrease. Calcination reaction was carried out during heating up to soaking temperature, then sintering started and completed after 2.5 h. In Fig.3, microstructure of PMN ceramics sintered in PbO atmosphere at 1200 °C for 2.5 h, confirm results of XRD patterns and no pyrochlore phase is found in these micrographs. However the advantage of SEM here lies in its ability to reveal microstructural features often missed by X-ray diffraction, such as MgO and PbO inclusions. The average grain size was determined from the SEM

images using the ImageJ software. Although, our crucibles were sealed, after the 2.5 h of soaking time, the PbO atmosphere began to effuse out of the system and resulted in evaporation of PbO from the pellets, reduction of relative density of the sample (see Table 1), destabilizing the perovskite phase and formation of pyrochlore phase by the following decomposition reaction at temperatures above 900 °C:



Therefore, the major peak of pyrochlore appeared in XRD pattern of sample No. 3. Despite some papers which have reported the fabrication of pyrochlore-free PMN ceramics by sintering stoichiometric pellets in air, present results for samples No. 4 and 5 show formation of pyrochlore phase up to 96.5%. According to reaction mentioned above, it is impossible to prepare pyrochlore-free PMN ceramics by sintering stoichiometric pellets in air.

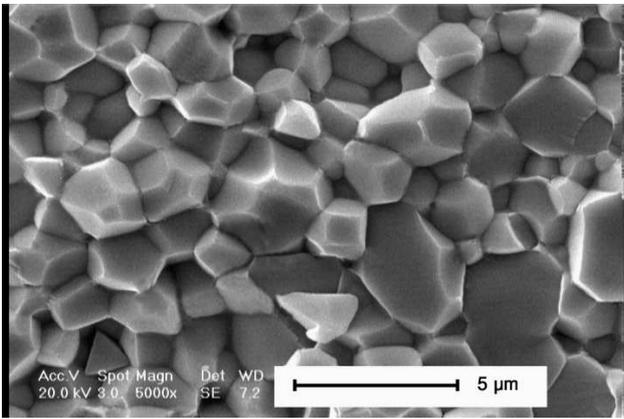


Fig. 3 SEM image of PMN ceramics sintered at 1200°C for 2.5 h in PbO atmosphere

The temperature dependence of dielectric constant for samples sintered in PbO atmosphere at 1 kHz is shown in Fig. 4. The dielectric constant values were corrected for porosities by using a relation $K = K_{\text{measured}} \times (\text{theoretical density/sintered density})$. Sample No. 2 exhibits higher maximum dielectric constant due to its pyrochlore-free structure and its larger grain size than that of sample No. 1.

The increase in dielectric constant with grain size can be explained by the influence of low-permittivity grain boundaries. The dielectric constant in PMN ceramics is reported to depend on grain size and also on grain boundary thickness following a relation given below (Eq. (3)):

$$\frac{1}{K} = \frac{1}{K_{\text{crystal}}} + \frac{1}{R \cdot K_{\text{GB}}} \quad (3)$$

K = maximum dielectric constant of ceramic sample.

K_{crystal} = maximum dielectric constant of PMN crystal.

R = ratio of grain size to grain thickness.

K_{GB} = dielectric constant of grain boundary phase.

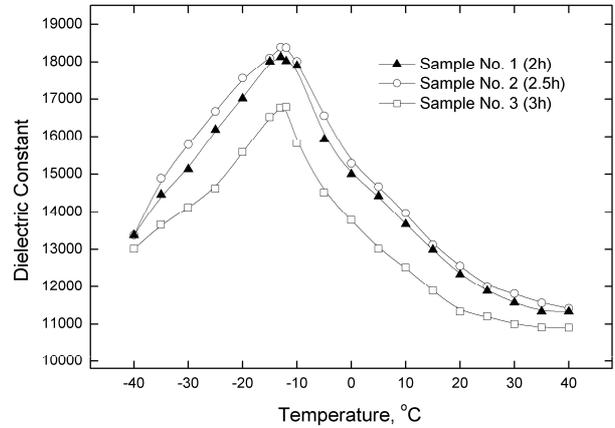


Fig. 4 The temperature dependence of dielectric constant at 1 kHz of PMN ceramics sintered at 1200 °C for 2, 2.5 and 3h, in PbO atmosphere

It is reported that grain boundary phase is made of lead based material. In the sample No. 3, formation of pyrochlore phase has reduced dielectric constant. Increasing the sintering time, and thus PbO loss, would change the stoichiometry of PMN and the transition temperature would be expected to decrease.

Conclusions

A high density single-phase PMN ceramic with the peak dielectric constant of 18672 at the frequency of 1kHz at -13 °C, has been synthesized and sintered simultaneously via modified mixed oxide route by using mixed oxide nanopowder, omitted calcination step and single step sintering. The results revealed that our modified mixed oxide route is effective in producing pyrochlore-free PMN ceramics. It has been proven that sintering the stoichiometric pellets in air results in the formation of pyrochlore phase. The results obtained from dielectric measurement of the samples, also indicated positive effect of grain growth on dielectric properties.

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