

# Synthesis of PMN pyrochlore free ceramics via a modified mixed oxide method

Pouya Moetakef · Z. Ali Nemati

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**Abstract** A modified mixed oxide method which is based on a two step reaction sintering process was designed to obtain single phase PMN ceramics. In this regard, pyrochlore phase formation during calcination process at different calcination temperatures was studied to determine the best soaking temperature for the first step in the specified method. In other words, the calcination temperature in which the least pyrochlore phase produced was chosen as the first step soaking temperature. The results showed that by utilizing this new method, single phase PMN ceramics with a high relative density of 98% can be synthesized successfully using conventional mixed oxide starting materials.

**Keywords** Lead magnesium niobate · Mixed oxide method · Pyrochlore · Relaxor ferroelectric

## 1 Introduction

Lead magnesium niobate (PMN) is a relaxor ferroelectric with the composition of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  which exhibits high dielectric constant, excellent voltage stability, low sintering temperature and good electrostrictive effect [1, 2]. These properties make it suitable for applications such as multilayer capacitors, electrostrictive actuators, electromechanical transducers and electro-optic devices [2–5]. One of the major problems facing the applications of PMN ceramics is the production of Lead Niobate based pyrochlore phase with low dielectric constant [2, 6, 7] (about 130 in comparison

with 20,000 for single-phase perovskite structure) during the heating process. The presence of pyrochlore phase can degrade dielectric properties of PMN-based ceramics. It is known that the conventional mixed oxide method would result in multi-phase ceramic system [5]. Many studies have been conducted to produce PMN single-phase of perovskite type material. There are several fabrication routes that can be utilized to fabricate PMN pyrochlore free ceramic. One is the mechanical activation [4, 5, 8] of starting materials, in which the product would be pyrochlore free due to the low temperature synthesis. However, this method is very time consuming and requires high energy mills. Another fabrication method for production of pyrochlore free PMN is the sol-gel method [9, 10]. Unfortunately, the starting materials are very sensitive and can not be used widely. Another method that utilizes high temperature but produces low amount of pyrochlore in the ceramic was introduced by Swartz and Shroud as columbite route [11–13]. In this method, columbite ( $\text{MgNb}_2\text{O}_6$ ) was synthesized from MgO and  $\text{Nb}_2\text{O}_5$  and then the resulting columbite was mixed with PbO to form PMN. This method would result in very low pyrochlore phase production. Therefore, some authors tried to modify this route to obtain single-phase material [3, 14].

Some data are available on mixed oxide route of production of single-phase ceramic by using other types of oxide materials [15–17]. But, still more work is required to obtain pyrochlore free PMN using traditional oxide materials.

The aim of the present work is to produce PMN pyrochlore free ceramic by a modified mixed oxide method which is based on a two step sintering process without calcination. Therefore, pyrochlore phase formation during heating process was studied to determine the best condition for the first step (soaking temperature) which leads to minimum pyrochlore phase in the system.

P. Moetakef · Z. A. Nemati (✉)  
Materials Science and Engineering Department,  
Sharif University of Technology,  
Tehran 11365-9466, Iran  
e-mail: nemati@sharif.edu

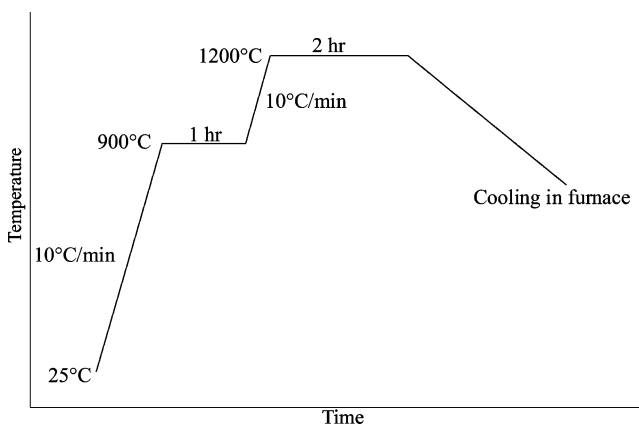
## 2 Experimental procedure

Laboratory grade PbO (Merck, 99.0%), MgO (Merck, 98.0%) and Nb<sub>2</sub>O<sub>5</sub> (Merck, 99.9%) powders were used as starting materials. These materials were weighted in the stoichiometric ratio. Then the mixture of starting materials without any additives was milled for 90 minutes at the speed of 1,000 rpm by a disc mill (Siebtechnik T100) with tungsten carbide discs and vial. The mixed materials were calcined from 500 to 900 °C with the heating rate of 10 °C/min for 3 h. Another batch of milled materials was pressed (in disc shape with diameter of 10 mm and thickness of 2 mm) and then placed in an alumina crucible and sintered directly in a two step process, as shown in Fig. 1. The atmosphere was controlled by adding trace of pure PbO powder into the alumina crucible. In the first step the mixture was heated to 900 °C with the heating rate of 10 °C/min and then soaked in that temperature for 1–2 h and then heated again with the same heating rate to 1200–1250 °C and sintered for 2 h. Different conditions that samples were prepared under the modified method have been presented in Table 1. After sintering procedure, the sintered specimens were polished to remove the lead rich layer on the sample.

The XRD patterns, obtained from calcined powder and sintered ceramic pellets, were recorded at room temperature with CuK $\alpha$  radiation, in a Bruker D-4 diffractometer. Diffraction intensity was measured between 4 and 70°, with a 2 $\theta$  step of 0.02° for 5 s per point. The amount of pyrochlore phase was determined by using Eq. 1 [6, 7].

$$\% \text{Pyrochlore} = 100 * \frac{I_{\text{pyr}}}{I_{\text{pyr}} + I_{\text{Perovs}}} \quad (1)$$

Where  $I_{\text{pyr}}$  and  $I_{\text{Perovs}}$  are values of major intensities for pyrochlore (222) and perovskite (110) phases respectively. Differential thermal analysis (DTA, Netzsch) was also carried out to study the phase change during heating pro-



**Fig. 1** Two step sintering route designed to produce pyrochlore free PMN ceramic

**Table 1** Different conditions used for the preparation of PMN samples via two step sintering process.

Sample code	First step temperature (°C)	First step soaking time (h)	Second step temperature (°C)	Second step soaking time (h)
SM01	900	1	1200	2
SM02	900	1	1250	2
SM03	900	2	1250	2

cess from room temperature to 1100 °C with heating rate of 5 °C/min.

Density of the sintered ceramics was measured by Archimedes method. Microstructure characterization was carried out on the milled powder and fracture surface of specimens using scanning electron microscopy (SEM, Philips XL30) and average particle/grain size of powder and sintered specimens were estimated by a linear intercept method on SEM micrographs.

In order to measure the electrical properties, the sintered samples were coated with silver based paste and then fired at 200 °C for 10 min to burn the polymer part of paste and leave the pure silver on sample's both surfaces. For electrical measurements, a LCR meter (CHY 41R) was used; data being collected at 1 kHz. Runs were taken in 0.1–0.2 °C steps in proximity to the transition temperature. In order to achieve thermal equilibrium, samples were left at the preset temperature for at least 5 s between measurements. Experiments were performed from –23 up to 10 °C in air. The dielectric constant was calculated from Eq. 2 [18].

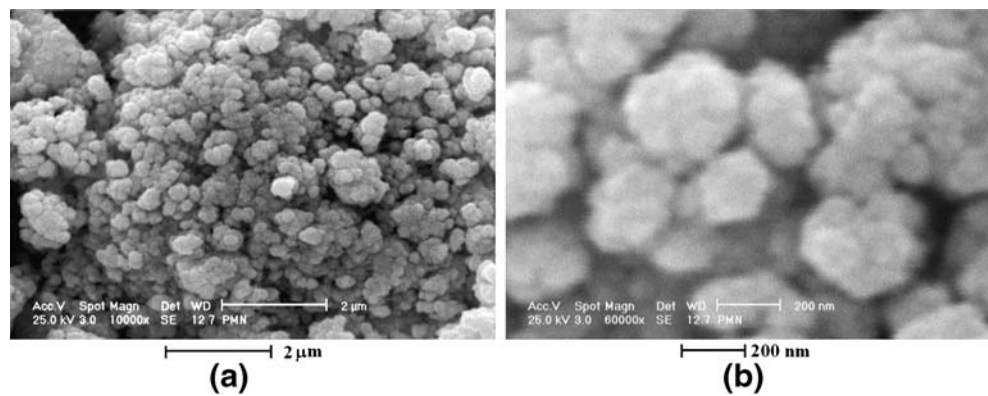
$$K = \frac{C \cdot h}{A \cdot \epsilon_0} \quad (2)$$

Where,  $K$  is the dielectric constant,  $C$  is the measured capacitance of the sample,  $h$  is the thickness of sample,  $A$  is the area of the sample's surface and  $\epsilon_0$  is the dielectric permittivity of vacuum ( $\epsilon_0=0.08854$  pF/cm).

## 3 Results and discussion

The SEM micrographs of milled powder have been shown in Fig. 2. It can be seen that this powder consist of very fine particles, exhibiting a rounded morphology. The finer the particles become the more surface energy they gain and this would lead to agglomeration of particles. In the pressing procedure high packing was seen which is due to the crushing of agglomerates with low amount of energy and this would suggest that the agglomerates are loose and would crush with low energy. The average particle size estimated from these micrographs was below 50 nm. This nano sized powder mixture was used as starting material.

**Fig. 2** SEM micrographs of starting materials mixture after milling for 90 min at (a) 10,000× and (b) 60,000× magnification

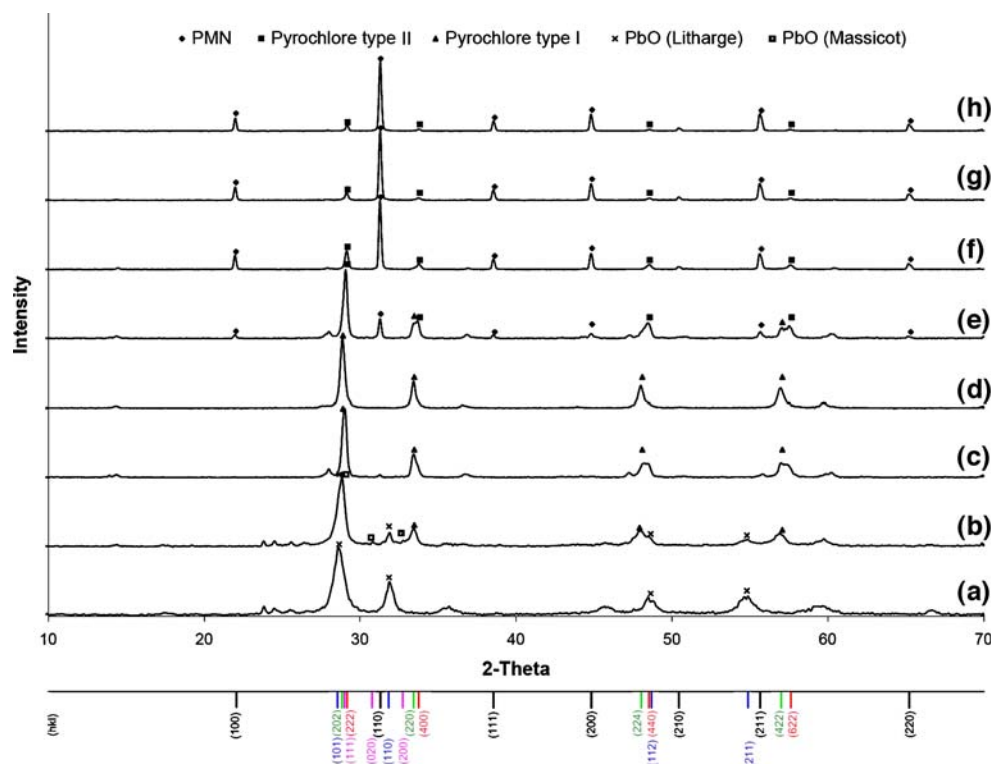


The XRD patterns with different calcination temperatures for starting materials are shown in Fig. 3. It can be seen that the perovskite structure was produced above calcination temperature of 750 °C. In the XRD patterns, two types of pyrochlore phases were detected. The first type of pyrochlore phase (Pyrochlore phase type I) with composition of  $Pb_3Nb_2O_8$  (JCPDS card 30–712) has been detected in powders calcined at low temperatures (below 750 °C). The second type (pyrochlore phase type II) with more complex composition of  $Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}$  (JCPDS card 37–71) has been detected in powders calcined at higher temperatures (above 750 °C). The same results were reported earlier by other authors [6, 7]. The patterns show that with calcination temperature of 500 °C the reaction is not complete and mixture of residual PbO (Litharge, JCPDS card

5–561 and Massicot, JCPDS card 38–1477) and pyrochlore phase type I can be detected. As the calcination temperature raises the amount of pyrochlore type I phase increases to 100% in 700 °C. Above this temperature pyrochlore type I degrade in favor of pyrochlore type II and perovskite PMN (JCPDS card 27–1199) forms [7]. With further increase in calcination temperature the amount of perovskite structure increases to about 92% at 900 °C. The amount of detected pyrochlore and perovskite phases in different calcination temperatures has been shown in Table 2. As it can be seen in this work, by utilizing the calcination in mixed oxide method the pyrochlore free PMN can not be produced.

The DTA curve for starting materials has been shown in Fig. 4. This curve shows an exothermic peak at 291 °C which thought to be due to the transformation of orthorhom-

**Fig. 3** XRD patterns of (a) as milled powder and calcined powders at (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 750 °C, (f) 800 °C, (g) 850 °C and (h) 900 °C for 3 h



**Table 2** Amount of perovskite and pyrochlore phases at different calcination temperatures.

Calcination temperature (°C)	Perovskite phase (%)	Pyrochlore phase (%)
700	0	100
750	23.0	77.0
800	78.2	21.8
850	90.5	9.5
900	92.2	7.8

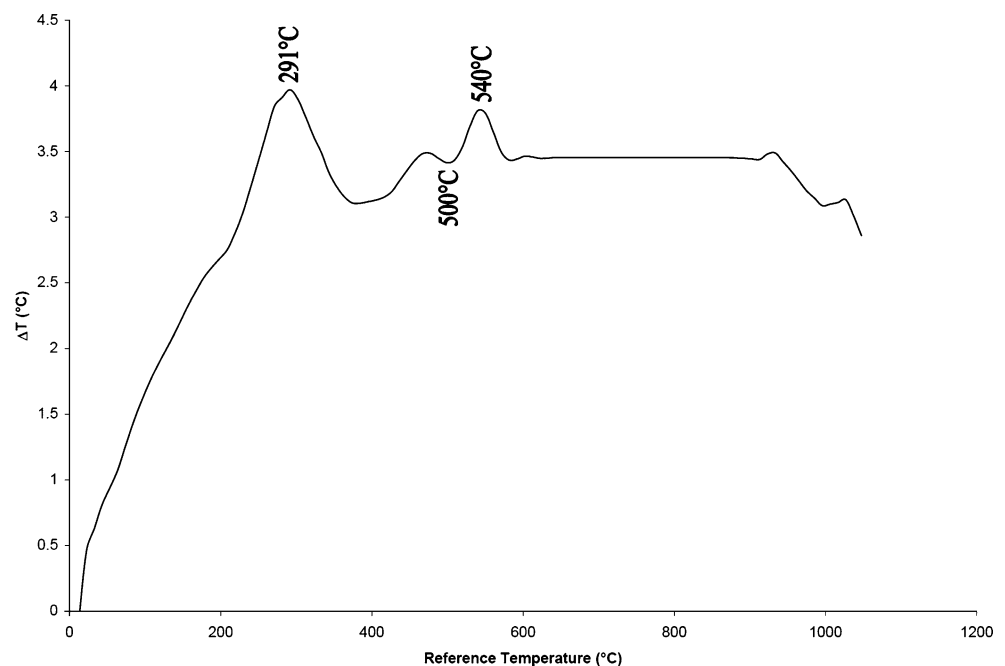
bic PbO (yellow) to tetragonal PbO (red). Lead monoxide occurs in two polymorphic forms. The tetragonal  $\alpha$ -form which called Litharge is red and stable up to 500 °C and the orthorhombic  $\beta$ -form PbO which called Massicot is yellow and stable at elevated temperatures [7]. During milling process orthorhombic PbO became metastable and remain in the same condition. Therefore, above 291 °C the metastable phase began to transform to stable tetragonal PbO. This fact can be proved by studying the XRD pattern of the sample calcined at 500 °C which show little amount of residual Massicot. Therefore, it can be concluded that at higher temperatures close to 500 °C orthorhombic PbO began to form by transformation from tetragonal PbO which can be seen in Fig. 4 by an endothermic peak. Another exothermic peak is presented at 540 °C which could be due to the formation of pyrochlore phase type I. Interestingly, similar results were reported earlier by Mergen and Lee [7].

As the best results was obtained in powder calcined at 900 °C (Fig. 3, i.e. minimum amount of pyrochlore phase

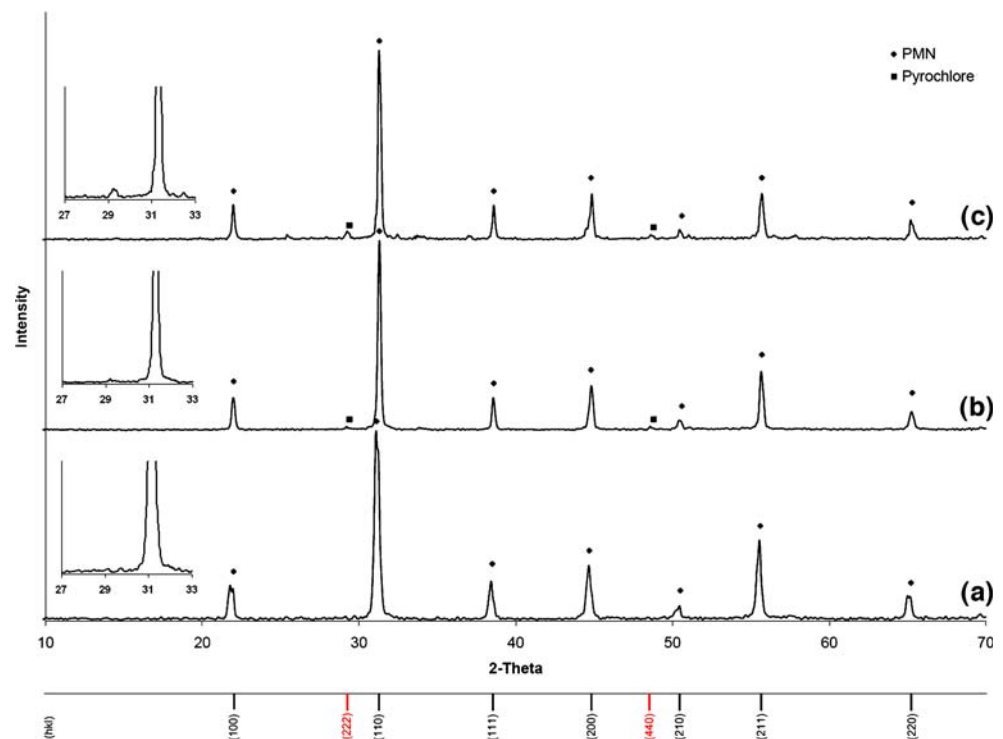
in the calcined powder), this temperature was selected as the soaking temperature for the modified mixed oxide method. The XRD patterns of specimens prepared by the modified mixed oxide route have been presented in Fig. 5. As it can be seen, pyrochlore phase was not detected in the specimen sintered at 1200 °C, while the other samples (Table 1) show very little amount of pyrochlore phase. This is related to the heat treatment conditions. The concept beyond this fact suggest that in the first soaking temperature of 900 °C, PMN would form partially because of the low soaking time and the reaction would complete in the sintering process. During sintering process, no additional pyrochlore phase would form. Therefore, pyrochlore phase would not form from decomposition of PMN and this would lead to a pure phase.

Increase in the soaking time at 900 °C shows an increase in the amount of pyrochlore phase (i.e. by increasing soaking time from 1 to 2 h the amount of pyrochlore phase would be nearly doubled) due to the production of pyrochlore phase in the first step period. As it can be seen in Fig. 5, higher sintering temperature may also result in pyrochlore phase production which could be due to the decomposition of PMN to pyrochlore phase at higher temperatures. The relative amount of perovskite and pyrochlore phases for these specimens has been presented in Table 3.

The SEM micrographs of sintered specimens via the modified mixed oxide method have been shown in Fig. 6 at different conditions. It can be seen that by increasing the sintering temperature, the average grain size of specimens increase which is due to the grain growth process at higher temperatures [Fig. 6(b) and (c)]. By increasing the sintering

**Fig. 4** DTA curve of starting mixed oxide mixture

**Fig. 5** XRD patterns of sintered specimens prepared by modified mixed oxide method (a) SM01, (b) SM02 and (c) SM03



temperature the density of the specimen would also be decreased. This could be due to the pyrochlore phase formation and PbO evaporation at higher temperatures. On the other hand, increase in the soaking time at 900 °C showed the positive effect on density but the chance of pyrochlore phase formation increased which suggest that it could be the cause of grain size reduction. Similar results were reported by other authors [6].

The measured dielectric properties of the sintered pyrochlore free sample are shown in Fig. 7. As it can be seen, the maximum value of 81,000 for dielectric constant at Curie temperature (0 °C) has been obtained. This value is much higher than the values reported earlier by other authors in the literature who synthesized pyrochlore free PMN ceramic via other methods [15, 19, 20]. Also, the curve in Fig. 7 shows a non relaxor but a very high normal piezoelectric behavior for the PMN synthesized by this route. This observed behavior

could be resulted from the new preparation route or the compositional inhomogeneity of the sample. Figure 5 shows a splitting of the peaks for this sample, which suggests compositional inhomogeneity in the sample. Comparing the peaks to standard ones, it can be found that the major part of the sample show a shifted PMN composition (i.e. taller peaks are shifted from standard peaks). Therefore, it can be concluded that this new composition of PMN exhibits normal piezoelectric behavior with very high dielectric properties at Curie temperature. Also, the dielectric values obtained at room temperature and –23 °C are comparable with other authors' reports. This suggests that the part of the sample with standard composition is responsible for this relaxor behavior and high dielectric properties at room temperature and –23 °C. Thus, it can be said that this sample shows a mixed relaxor and normal piezoelectric behavior at Curie temperature.

**Table 3** Properties of the specimens prepared by modified mixed oxide method sintered at different conditions.

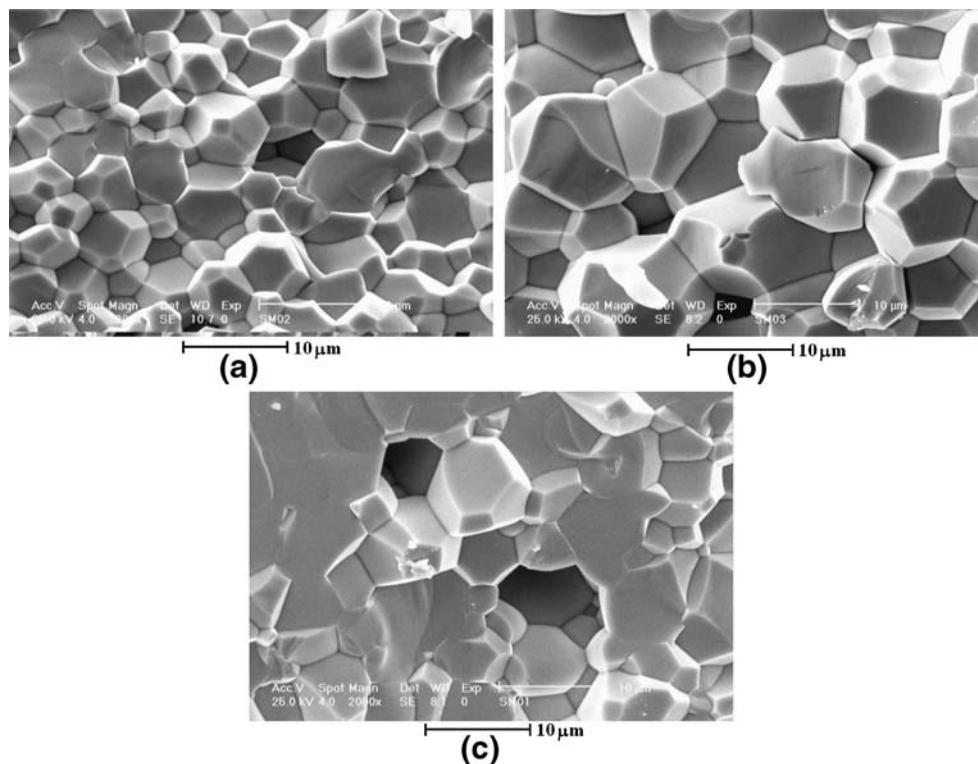
Sample code	Perovskite phase (%)	Pyrochlore phase (%)	Density (g/cm <sup>3</sup> )	Relative density (%)	Grain size (μm)
SM01	100	0	8.03	98.77	4.67
SM02	97.1	2.9	7.84	96.52	8.6
SM03	95	5	8.05	99.06	6.28

#### 4 Conclusion

Two types of pyrochlore phases can produce at different conditions. The pyrochlore phase type I with the composition of Pb<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub> would form at lower temperatures (below 750 °C) while at 750 °C this phase transform to the pyrochlore phase type II with the composition of Pb<sub>1.83</sub>Nb<sub>1.71</sub>Mg<sub>0.29</sub>O<sub>6.39</sub> and PMN perovskite phase. By increasing calcination temperature, the amount of perovskite phase



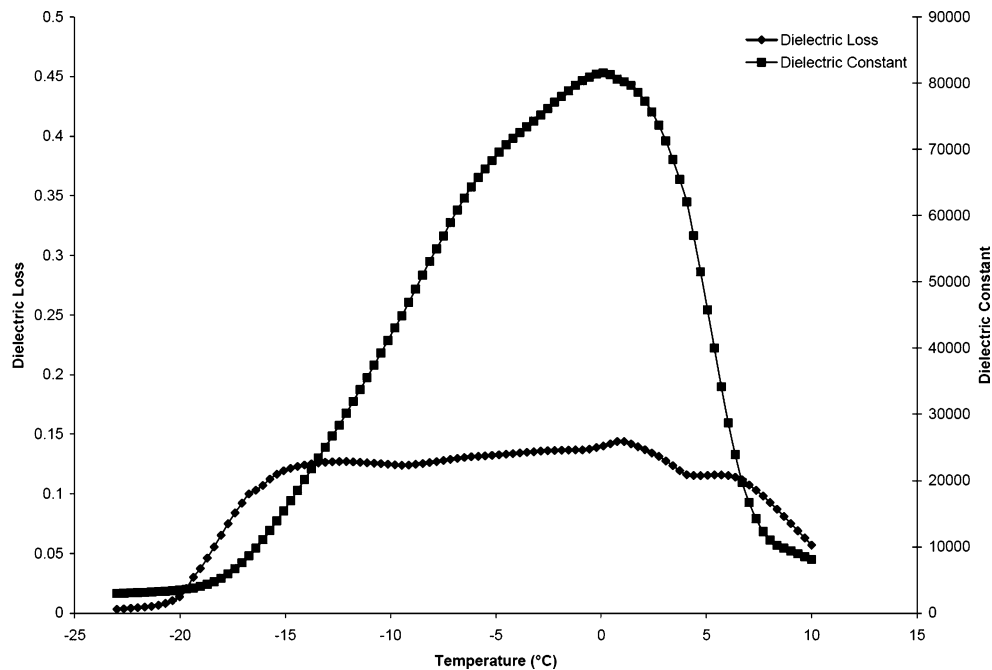
**Fig. 6** SEM micrographs from the fracture surface of sintered specimens prepared by modified mixed oxide method, (a) sample SM01, (b) sample SM02 and (c) sample SM03



increases to 92.2% at 900 °C. Producing the least amount of pyrochlore phase, this temperature was chosen as the first step temperature for the two step sintering process. In this method, the pressed pellets were heated up to 900 °C and remained for 1 h and then heated up again to 1200 °C for 2 h to complete sintering process. By use of this method,

a single phase PMN perovskite phase was prepared successfully with a high relative density of 98.76%. So, this modified method can be used to synthesize single phase PMN ceramic using traditional metal oxides, and it was found that the calcination process has negative effect on the production of single phase PMN ceramic in the mixed oxide method.

**Fig. 7** Dielectric constant and loss tangent of the sintered pyrochlore free sample (SM01) as a function of temperature



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