Sol−Gel Synthesis and Characterization of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) Ferroelectric Perovskite

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The synthesis of lead magnesium niobate perovskite by sol−gel methods has been investigated and conditions established for preparing a transparent gel after curing at room temperature. The decomposition of the gel has been studied by DTA/TG and XRD; crystallization of metallic Pb and a pyrochlore phase occur before the formation of the desired PMN phase. Compositions yielding X-ray-pure PMN have been established. Microscopic studies show the presence of pure phases in some samples studied. The composition of the PMN phase was determined by electron probe microanalysis; departures from the ideal stoichiometry occur.

Introduction

Lead magnesium niobate, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), is an important relaxor ferroelectric material with a high dielectric constant and a high electrostrictive strain coefficient. Its high permittivity ϵ', small temperature coefficient dϵ'/dT, and relatively low firing temperature have made it a promising candidate material for multilayer ceramic capacitors. A significant problem exists, however, in the preparation of this material: it is very difficult to prepare phase pure, without the presence of a pyrochlore impurity phase which degrades the dielectric properties. Depending upon the processing conditions, the amount of pyrochlore phase varies. A few methods have been reported[1−3] in which phase-pure PMN, with the perovskite structure, has been synthesized but the temperature of reaction is quite high. Swartz and Shrout[1] prepared PMN at 800 °C using columbite precursor (MgNb$_2$O$_6$), which was in turn, prepared at 1000 °C. But even with this procedure, a small amount of pyrochlore was observed.

The addition of an excess of MgO and/or PbO to PMN-based ceramics has been shown to have a beneficial effect to reduce the amount of, and even eliminate, the pyrochlore phase.[2,4−7] Wang et al.[8] reported that pure PMN can be fabricated by the addition of excess MgO, whereas excess PbO did not yield phase-pure PMN. Columbite was reacted with PbO with and without excess MgO or PbO. The powders were calcined at 800 °C/4 h, pressed into disks, and fired in covered alumina crucibles. The pellets, with and without excess MgO, were buried in stoichiometric, calcined PMN powder. Pellets with excess PbO were buried in PMN−2% PbO powder. All pellets were sintered at 1200 °C/1 h. This method gave better reproducibility of PMN fabrication but the prereaction step added complexity, and thus, cost to the process.

The sol−gel method is widely employed to prepare ceramic oxides at low temperature. Such routes, which lead to homogeneous stoichiometric and high purity fine particles, offer great flexibility because of the large variety of organic precursors that are available. Because of that, there is considerable interest in making electroceramics by sol−gel processes and they offer numerous potential advantages for PMN formation compared to solid-state routes.[9−14]

Chaput et al.[11] obtained PMN by a sol−gel technique using alkoxide precursors. They first prepared niobium and magnesium ethoxides and by progressive dissolution of magnesium ethoxide into niobium ethoxide, the double-metal alkoxide, Mg[Nb(OEt)$_6$]$_2$, was obtained.

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(1) Swartz, S. L.; Shrout, T. R. *Mater. Res. Bull.* **1982**, *17*, 1245.
(2) Swartz, S. L.; Shrout, T. R.; Schulze, W. A.; Cross, L. E. *J. Am. Ceram. Soc.* **1984**, *67*, 311.
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(12) Ravindranathan, P.; Komarneni, S.; Roy, R. *J. Am. Ceram. Soc.* **1990**, *73*, 1024.
(13) Ramamurthi, S. D.; Payne, D. A. *J. Am. Ceram. Soc.* **1990**, *73*, 2547.
(14) Francis, L. F.; Payne, D. A. *J. Am. Ceram. Soc.* **1991**, *74*, 3000.

The lead precursor was prepared by reacting pure lead acetate with sodium isopropoxide but because this reaction was incomplete and leads to the oxoalkoxide Pb$_4$O(O-i-Pr)$_6$, they proposed to obtain Pb(O-t-Bu)$_2$ by reaction between Pb[N(SiMe)$_2$]$_2$ and 2t-BuOH in hexane. To overcome problems associated with conventional drying and to eliminate the liquid−vapor interface inside pores, evaporation of the solvent was carried out under hypercritical conditions; phase pure PMN was obtained after firing at about 700 °C.

Ravindranathan et al.[12] used the sol−gel route to make structurally diphasic (nanocomposites) xerogels of PMN which served as precursors for obtaining pure PMN at low temperatures. X-ray diffraction data showed that the amount of perovskite phase formed from the structurally diphasic PMN gels increased on increasing the quantity of PMN used as a seed and there was also a significant lowering of the formation temperature to 675 °C. Phase-pure PMN was obtained after firing the diphasic gel for 50 h. Ramamurthi et al.[13] and Francis et al.[14] prepared some Pb-perovskite compounds by a sol−gel process in which 2-methoxyethanol was used as solvent. The processing conditions and the reactions that occur during solution preparation were extensively studied using spectroscopic techniques.

In summary, it appears to be difficult to prepare single-phase PMN by solid-state synthesis but the sol−gel methods used so far involve many steps and usually involve refluxing the mixtures with a large quantity of solvents.

To overcome some of the problems mentioned above, we have investigated the synthesis of PMN by a simple sol−gel method at room temperature using a minimum quantity of solvent; slow drying leads to a monolithic gel, thereby avoiding many of the problems that often arise on drying due to accelerated evaporation. This work also has the aim of investigating the range of MgO, PbO, and Nb$_2$O$_5$ compositions in which PMN is obtained as a single phase; even though off-stoichiometric compositions are usually used to synthesize PMN, it is generally assumed that the product has the ideal stoichiometry Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. We, therefore, have used electron-probe microanalysis, EPMA, to perform accurate cation analyses of the PMN phase in sintered ceramics.

Solvents such as MeOH, EtOH, and BuOH, are usually used in sol−gel syntheses; 2-methoxyethanol is also extensively used in the synthesis of perovskite materials and is beneficial in assisting the dissolution of carboxylate precursors such us lead acetate.[15] The key reactions leading to the formation of the precursor species are hydrolysis and condensation of the alkoxide reagents, leading to formation of metal−oxygen−metal (M−O−M) bonds.

Experimental Section

Sol−Gel Synthesis. A multicomponent alkoxide solution was prepared by mixing lead acetate [Pb(CH$_3$COO)$_2$·3H$_2$O (99.9% (ACS), Merck)], anhydrous magnesium acetate [Mg-(CH$_3$COO)$_2$ (pure grade, Quimidroga)], and niobium ethoxide [Nb(OC$_2$H$_5$)$_5$ (99.9+% Nb, Strem Chemicals)]. The solvents

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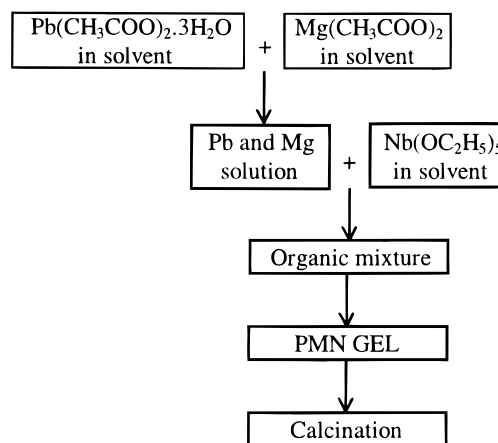
Figure 1. General preparation scheme of the samples.

**Table 1. Composition and Quantity of Precursors for Samples Prepared**

samples	PbO/Pb(CH$_3$COO)$_2$·3H$_2$O		MgO/Mg-(CH$_3$COO)$_2$		Nb$_2$O$_5$/Nb-(OCH$_2$CH$_3$)$_5$	
	mol %	weight (g)^a	mol %	weight (g)^a	mol %	weight (g)^a
1	60	1.1664	20	0.1458	20	0.6523
2	59	1.1993	24	0.1830	17	0.5807
3	56	1.2138	29	0.2348	15	0.5250
4	48	1.1735	40	0.3668	12	0.4923

^{a} Weight of the precursors: calculated quantities for preparing 1 g of final product.

which were investigated with the objective of preparing a transparent solution, were 2-methoxyethanol [CH$_3$OCH$_2$CH$_2$-OH (Prolabo)], methanol [CH$_3$OH (distilled, Villaran Química S.A)], and ethanol [CH$_3$CH$_2$OH (absolute, extra pure 99%, Normasolv)]. The general scheme for preparation is shown in Figure 1; in Table 1 are given the compositions of the samples prepared: 1, based on PMN stoichiometry; 2, 3, and 4 with an excess of Pb and Mg over the PMN stoichiometry.

Ethanol was the first solvent which was tested, but neither lead acetate nor niobium ethoxide were soluble in it. Second, 2-methoxyethanol was tested. Although Ramamurthi et al.[13] prepared a solution by first refluxing 1 mol of lead acetate trihydrate with 8 mol of methoxyethanol at ∼118 °C, and then repeated distillations were conducted to remove the byproducts. In our working conditions at room temperature, lead acetate did not dissolve, but on adding lead acetate to a solution of magnesium acetate in 2-methoxyethanol, a transparent solution was obtained. This solution was added dropwise to the stirred niobium ethoxide solution in 2-methoxyethanol at room temperature; after a few minutes, a white gel was obtained.

Although processes based on 2-methoxyethanol[15,16] are considered to be sol−gel processes in which M−O−M bonds are formed by hydrolysis and condensation of the alkoxide reagents another key reaction with the use of this solvent is the alcohol exchange:

$$M(OR)_x + xR'OH \rightarrow M(OR')_x + ROH$$
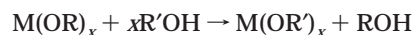
In this sense, the following reactions could be described in our system. First:

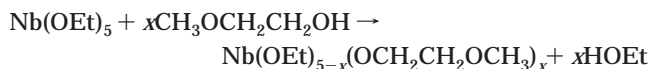$$Mg(ac)_2 + xCH_3OCH_2CH_2OH \rightarrow [Mg(solv)]^{2+} + ac(solv)$$

where solv = CH$_3$OCH$_2$CH$_2$OH and ac = CH$_3$COO$^-$. The formation of CH$_3$COO$^-$ could explain the dissolution of Pb-(ac)$_2$ when it was added to the solution of magnesium acetate

(16) Budd, K. D.; Dey, S. K.; Payne, D. A. *Brit. Am. Ceram. Soc. Proc.* **1985**, *36*, 107.

by forming a $[Pb(ac)_{2+x}]^-$ complex. Second:

$$Nb(OEt)_5 + xCH_3OCH_2CH_2OH \rightarrow$$
$$Nb(OEt)_{5-x}(OCH_2CH_2OCH_3)_x + xHOEt$$

where $OEt = CH_3CH_2O^-$. However, since this reaction results in the generation of a certain amount of ethanol, the 2-methoxyethanol was undried prior to use and the lead acetate contained water of crystallization, it is possible that H_2O from the sources contributed to the explaination of the precipitation of Nb(V) hydrous oxides.[17]

Because the resulting gel was not transparent and 2-methoxyethanol is a known teratogen,[15] the effect of replacing the 2-methoxyethanol by methanol was studied.

On addition of niobium ethoxide to methanol a white precipitate was observed, probably caused by the hydrolysis of Nb(V) ions, because undried methanol was used or because there are alcohol exchange reactions that form insoluble species. However, this precipitation could be prevented by adding acetylacetone. Acetylacetone (acacH) is a rather strong chelating ligand that has often been reported in the sol−gel literature as a stabilizing agent for nonsilicate metal alkoxide precursors. Complexing ligands such as acacH lead to less-hydrolyzable M−acac bonds.[18] The procedure used to prepare gels with methanol as solvent was as follows:

The niobium ethoxide (2.0, 1.8, 1.6, and 1.5 mmol) was added to a mixture of methanol (62.5 mmol) and acetylacetone (2.8 mmol). Separately, lead acetate (3.1, 3.2, 3.2, and 3.1 mmol) was added to a vessel with 62.5 mmol of methanol and stirred continuously until dissolution of the lead acetate. To this solution, the magnesium acetate (1.0, 1.3, 1.6, 2.6 mmol) was added with continued stirring, followed by dropwise addition of the niobium ethoxide solution. The solution hydrolyzed and was cured at room temperature; gelation occurred within 2 days. The resulting alkoxide gel was allowed to dry at room temperature for 2−3 weeks. Since this method using methanol as solvent gave transparent gels, it was used for all subsequent work and for all the results presented here.
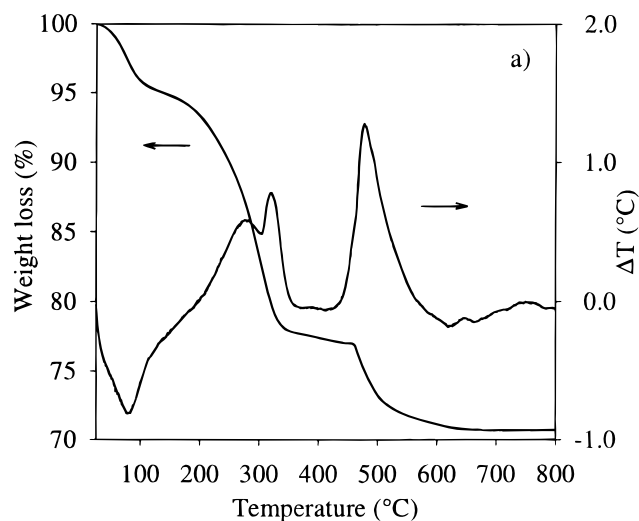
Characterization. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out on samples placed in an alumina crucible using a Mettler Toledo model SDTA 851^e over the temperature range 25−800 °C. All experiments were carried out in air at a heating rate of 5 °C min^{-1}.

For phase analysis by X-ray powder diffraction (XRD), a SIEMENS D5000 diffractometer with Cu Kα_1 radiation was used. Data were collected by step-scanning from 10 to 60°2θ with a step size of 0.050°2θ and 1 s counting time at each step. The goniometer was controlled by the "SIEMENS DIFFRACT *plus*" software, which also determined the positions and intensities of diffraction peaks.

On the basis of the DTA/TG results and associated XRD analysis, a procedure for firing the dried gels was devised. They were heated in air at 10 °C min^{-1} to 650 °C/2 h to ensure the total removal of organic material and then heated at 5 °C min^{-1} to 800 °C and held at 800 °C for 4 h. Samples were cooled and then removed from the furnace, crushed, pressed into pellets, and reheated at 800 °C for 3 h. Both powders and pellets were heated in Au foil. After each heating stage, the phase purity was determined by XRD.

Scanning electron micrographs were taken on a scanning electron microscope (SEM) Leica, Leo 440 model, equipped with a spectrometer for energy dispersion of X-ray (EDX), using the following operation parameters: acceleration voltage 20 kV, measuring time 100 s, working distance 25 mm, counting rate 1.2 kcps. The samples for microstructural and microanalysis determination were deposited in an aluminum holder and coated by graphite film.

Electron probe microanalysis (EPMA) was employed to determine the homogeneity and stoichiometry of sintered

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(18) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007.

Figure 2. DTA/TG analysis of PMN (sample 1), in the range 25−800 °C, in air, at heating rate of 5 °C min^{-1}.

pellets. Small pieces of the pellet were mounted in resin blocks, polished, carbon-coated, and analyzed using a Cameca SX51 EPMA with an accelerating voltage of 20 kV and a beam current of 60 nA. For accurate elemental analysis, grains of dimensions at least 2−3 μm were selected; the inner regions of these grains were analyzed with an instrumental spot size of ~1 μm. To assess sample homogeneity and the possible presence of minority phases, elemental maps for Pb, Mg, Nb, and O were produced for regions of the sample of overall dimensions 50 × 50 μm.

Chemical analysis of Pb and Mg were performed by Service Central D'Analyse of C.N.R.S. (Vernaison, France).
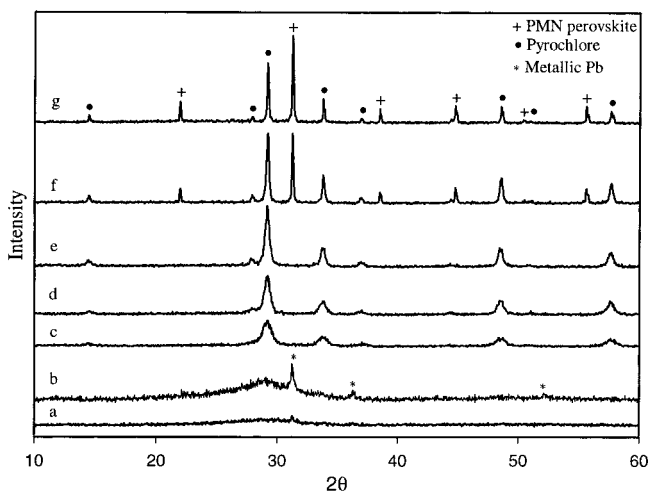
Results and Discussion

A range of dried transparent gels, with the starting compositions given in Table 1 were obtained after curing at room temperature for 2 weeks. To determine appropriate conditions for firing these gels to remove organic matter and to obtain the desired PMN products, DTA/TG and XRD experiments were carried out.

Figure 2 shows the results of DTA/TG analysis of dried PMN gel, sample 1, in the range 25−800 °C. The TG data show stepwise weight loss in three stages, from room temperature to ~100 °C, from ~200 to ~300 °C and from ~460 to 650 °C. The DTA data show an endothermic band that commences almost immediately on heating and peaks at about 80 °C. This band is assigned to loss of water and evaporation of solvent, consistent with the loss of weight by TG over the same temperature range. A doubled exotherm occurs over the range ~200−320 °C followed by a second exotherm at ~450−600 °C. These also correspond to the two higher temperature weight losses in the TG data and are attributed to the desorption of physisorbed water an the decomposition/combustion of the organic groups. Finally, there is some evidence of two small, broad exotherms around 650 °C and at ~700−800 °C without weight losses by TG.

An XRD analysis was performed for as-dried sample 1 heated in DTA/TG apparatus at 10 °C min^{-1} at 600 and 650 °C. The XRD patterns show only broad peaks of pyrochlore (Figure 3 c,d). To investigate the nature of any possible changes at ~650 °C a second sample was then heated by DTA under the same conditions but the temperature was held constant at 650 °C for 2 h. At

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Figure 3. XRD data of sample 1 fired at different temperatures: (a) 400 °C, (b) 450 °C, (c) 600 °C, (d) 650 °C, (e) 650 °C for 2 h, (f) 800 °C, and (g) 1000 °C.

the end of this thermal treatment, the sample was cooled rapidly to room temperature. XRD showed the presence of only pyrochlore phase (Figure 3e). The exotherm at ~750 °C could be assigned to PMN perovskite crystallization according to the XRD results (Figure 3f).

To study the phase evolution of sample 1 on heating, XRD was carried out after heating at 400, 450, 600, 650, 800, and 1000 °C with results shown in Figure 3. At 400 and 450 °C, the diffractograms indicate an amorphous sample with some peaks assigned to metallic lead.[19] At 600 and 650 °C some peaks corresponding to the pyrochlore phase[20] appear. At 800 and 1000 °C, the diffraction peaks are assigned to a mixture of pyrochlore and PMN[21] phases.

To confirm the XRD results of samples fired at 450 °C, SEM and EDX were used, with the results shown in Figure 4. These confirmed the presence of metallic Pb and therefore, indicated that Pb^{2+} can be reduced during removal of organic material. Comparison of the DTA/TG and XRD results shows that the gel decomposition is a complex multistep process. In addition to the three weight loss steps seen by TG, a sequence of crystallization reactions occurs involving formation of Pb, pyrochlore, and PMN.

To determine whether any compositional changes occurred during the various stages of synthesis, chemical analysis of Mg and Pb contents was performed by Service Central D'Analyse of C.N.R.S. (Vernaison, France) on sample 1, before and after firing at 800 °C/4 h. The results (Table 2) indicated a gradual reduction in Pb/Mg ratio, both during sample preparation and subsequent thermal treatment. This could explain the large discrepancy between the starting composition of the gel and the cationic composition of the PMN final product. The reasons for the compositional changes are not fully understood and are currently under investigation.

Since the XRD results showed that perovskite PMN was the final phase to appear, crystallizing above 650 °C, the following heat treatment schedule was adopted.

(19) JCPDS: pattern 04-0686.
(20) JCPDS: pattern 37-0071.
(21) JCPDS: pattern 27-1199.

The gels were fired in air at 10 °C min^{-1} to 650 °C/2 h to ensure the total removal of organic material, heated at 5 °C min^{-1} to 800 °C and held at 800 °C for 4 h. Samples were cooled and then removed from the furnace, crushed, pressed into pellets, and reheated at 800 °C for 3 h.

XRD results on both pelleted and powdered samples of four compositions fired at 800 °C showed PMN perovskite with or without some pyrochlore, these results are shown in Figure 5. Compositions 3 and 4 were X-ray-pure PMN-whereas 2 and, especially 1, also contained pyrochlore. The amount of PMN was estimated approximately from the intensities of the strongest peaks in the perovskite (110) and pyrochlore (222) patterns using the equation:

$$\% \text{ PMN perovskite} = \frac{I_{\text{perovskite}}}{I_{\text{perovskite}} + I_{\text{pyrochlore}}} \times 100$$

Results are summarized in Table 3. Of course, for accurate analysis, a calibration curve would be required for this method.

EPMA results on pelleted samples 2, 3, and 4 are summarized in Table 4 and Figures 6 and 7. These samples were phase-pure PMN by X-ray diffraction. EPMA of samples 2 and 3 indicated the presence of only one phase having a stoichiometry very close to that expected for ideal PMN, with composition PbMg$_{0.33}$Nb$_{0.66}$O$_3$. In sample 4, EPMA indicated the presence of two phases. The majority one had the stoichiometry of PMN and the minority phase was PbO. The composition of the PMN phase, taken from the average of a number of grains, was fairly close to the ideal PMN stoichiometry (PbMg$_{0.33}$Nb$_{0.66}$O$_3$) in each case (Table 4). Data were normalized to a Pb content of unity, but for sample 3 this resulted in a oxygen content significantly greater than 3. Possibly the data should be normalized to an oxygen content of 3, or to a B cation content of unity, given that there is no space within the perovskite structure for interstitial cations or anions.

The data in Table 4 do indicate slight departures from the ideal stoichiometry of PMN, in particular a Pb deficiency in sample 3. To investigate the homogeneity of ceramic samples at the micrometer level, the elemental analyses are presented as histograms in Figures 6 and 7.

In Figure 6, the number of grains is given as a function of B/A (i.e., [Mg + Nb]/Pb) ratio. For samples 2 and 4, the composition is closely centered on the 1:1 ratio, although with slightly more scatter for sample 4. Sample 3, however, is clearly deficient in Pb. The compositional distribution in the B sites, given by the ratio Mg/Nb, is shown in Figure 7; sample 3 is Mg-rich, sample 2 is Nb-rich, and sample 4 is inhomogeneous but is mainly Nb-rich. At this stage, we do not wish to overinterpret the results and speculate on the mechanisms of charge balance that are needed to accommodate, for example, deficiency of Pb but excess of Mg (sample 4) or deficiency of Mg/excess of Nb (sample 2). The results do clearly indicate, however, that PMN is not simply a line phase with the fixed stoichiometry Pb(Mg$_{0.33}$Nb$_{0.66}$)O$_3$ but is, instead, capable of significant compositional variation. None of those samples in
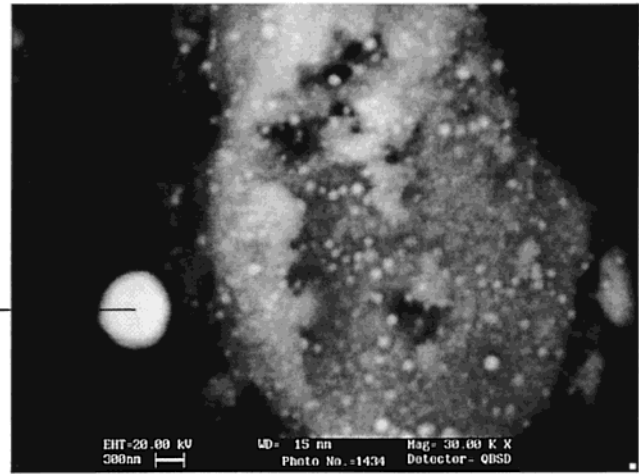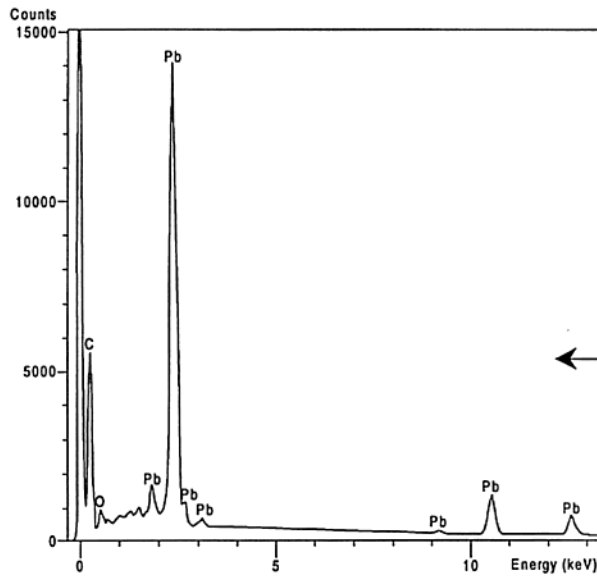
Figure 4. SEM analysis of a sample of gel, number 1, fired at 450 °C, by XRD the sample contained metallic Pb and an amorphous phase. The approximately circular region was shown by EDX to be pure Pb.

Table 2. Chemical Analysis Data for Sample 1 (ideal composition moles of Pb/moles of Mg = 3.0)

	unfired sample	fired sample
% in moles Pb^{2+}	0.31	0.20
% in moles Mg^{2+}	0.11	0.08
moles Pb^{2+}/moles Mg^{2+}	2.8	2.5
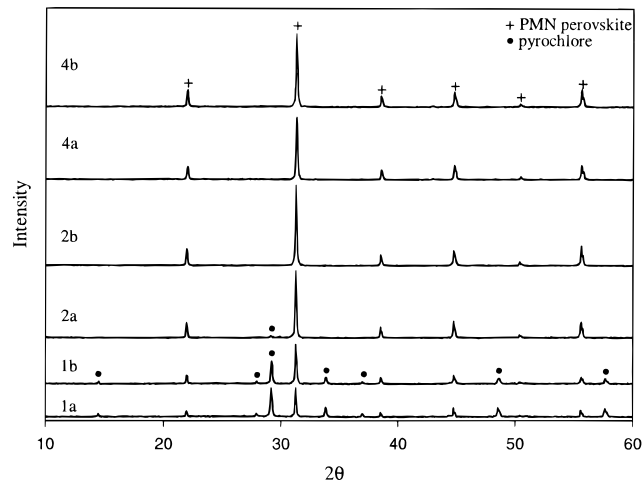
Figure 5. XRD data of samples 1, 2, and 4: (a) powder and (b) pellets.

Table 3. XRD Results of Samples Fired at 800 °C

	% PMN	
sample	powder	pellet
1	50	65
2	94	100
3	100	100
4	100	100

Figures 6 and 7 appear to have the stoichiometric composition.

Conclusions

A sol−gel synthesis procedure has been devised which leads to transparent PMN gels after curing at room temperature. After heating certain gel compositions at

Table 4. EPMA Results on Pelleted Samples Fired at 800 °C

	atomic %			
sample	Mg	Nb	Pb	phase[a]
2	6.17	13.74	19.79	$PbMg_{0.32}Nb_{0.68}O_{3.02}$
	6.53	13.43	19.96	
	6.43	13.47	20.01	
	6.21	13.52	20.12	
	6.38	13.53	19.93	
	6.51	13.47	19.91	
	6.50	13.42	20.02	
	6.27	13.72	19.72	
	6.29	13.53	20.04	
	6.30	13.44	20.17	
3	7.56	13.21	19.32	$PbMg_{0.36}Nb_{0.69}O_{3.09}$
	6.97	13.38	19.62	
	7.62	13.15	19.37	
	8.45	13.05	18.71	
	7.61	13.19	19.30	
	7.10	13.42	19.42	
	6.44	13.43	20.06	
	6.76	13.50	19.62	
	6.40	13.65	19.72	
	6.96	13.40	19.52	
	6.52	13.42	20.00	
	7.01	13.46	19.44	
4	6.28	13.37	20.32	$PbMg_{0.32}Nb_{0.67}O_{3.00}$
	6.20	13.64	19.92	
	6.79	13.52	19.56	
	6.34	13.55	19.95	
	6.33	13.54	19.98	
	6.35	13.66	19.75	
	6.91	13.34	19.74	
	6.35	13.31	20.35	
	6.26	13.38	20.33	
	0.01	0.21	49.63	PbO
	0.02	0.14	49.72	
	0.00	0.22	49.62	
	0.01	0.06	49.88	

[a] Compositions are normalized to a Pb content of unity. Oxygen contents are calculated, assuming valence states of 2+, 2+, and 5+ for Pb, Mg, and Nb, respectively.

800 °C, the product by XRD and EPMA was single-phase PMN perovskite. Metallic Pb and pyrochlore phase were both detected by XRD as intermediates during decomposition of the gel.
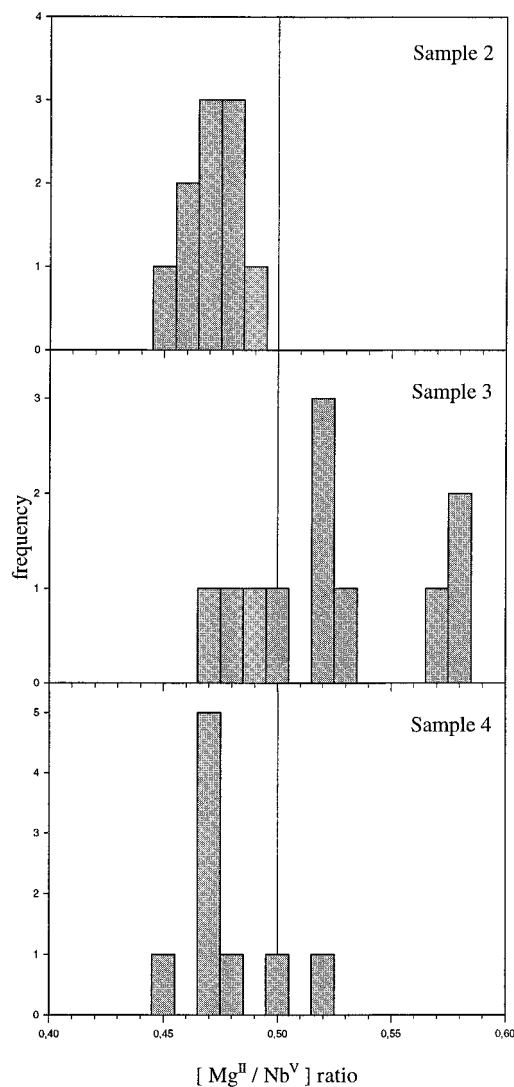
The novelty of the new synthesis method is that the process is one-stage, the gel product is obtained at room
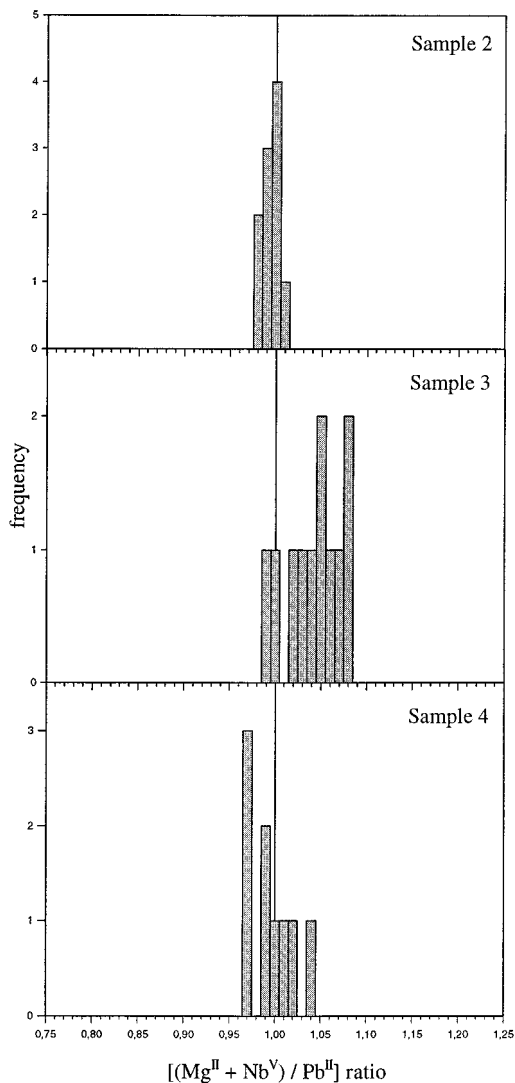
Figure 6. $(B + B')/A$ molar ratio in the PMN phase.

Figure 7. B/B' molar ratio in the PMN phase.

temperature and the method can be utilized for the preparation of thin film PMN products. During the synthesis and firing stages, compositional changes occurred and, in agreement with various reports in the literature, it was found that an excess of PbO and MgO were necessary to obtain a single-phase PMN product after the final heat treatment.

EPMA is a valuable technique for characterizing PMN ceramics, for both detecting the presence of second phases not detected by XRD and for giving accurate elemental analysis, at the micron level, throughout the samples. The PMN product had an average composition which corresponded to the "ideal" stoichiometry Pb-(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, but EPMA showed a small variation in composition, both in the Pb:(Mg + Nb) ratio and the Mg:Nb ratio.

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