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Effects of additives on perovskite formation in sol–gel derived lead magnesium niobate

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Abstract

The effects of ionic compounds (PbO, $BaTiO_3$, $PbTiO_3$, MgO) and covalent compounds (SiO_2, GeO_2, and B_2O_3), individually or as mixtures, on perovskite formation in sol–gel derived lead magnesium niobate, $PbMg_{0.33}Nb_{0.67}O_3$ (PMN) were studied. The ionic additives were coprecipitated with the PMN while the covalent compounds were added as fine particulates. At a level of 10 mol% additive per mol of PMN, additions of PbO, $BaTiO_3$, $PbTiO_3$, as alkoxide solutions, increased perovskite formation from 82% to 90, 91 and 87% respectively. A combination of PbO (10–15 mol%) and $BaTiO_3$ (8–9 mol%) increased perovskite formation further to 98%. The addition of 9 mol% MgO alone (also as an alkoxide solution) decreased perovskite formation to 77%, but a combination of PbO (10 mol%) and MgO (5 mol%) increased perovskite formation to 100%. The chemical effects of ionic compounds can be partially explained via the Goldschmidt tolerance factor. Compositions with high tolerance factors (>0.9) exhibited high (>90%) perovskite formation. Additions of 5 mol% GeO_2, SiO_2, and H_3BO_3 to modified PMN (14 mol% PbO and 9 mol% $BaTiO_3$), resulted in significant decreases in perovskite formation, from 98% to 86, 80, 50%, respectively, when heated to 980°C for 8 h. The reduction in perovskite for undoped PMN, however, was nearly double (62% perovskite) when 5 mol% SiO_2 was added. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lead magnesium niobate; Sol–gel; Additives; Perovskite; Tolerance factor

1. Introduction

Lead magnesium niobate, $PbMg_{0.33}Nb_{0.67}O_3$ (PMN) is a relaxor ferroelectric which possesses a high dielectric constant (~20,000) and has been studied extensively for actuator and capacitor applications [1]. However, the formation of low dielectric constant (~200) pyrochlore phase ($Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}$) during the synthesis and loss of PbO at high (up to ~1300°C) sintering temperatures has limited the full use of this material. Extensive research has been performed to prepare pyrochlore free PMN from solid state reactions of constituent oxides. Shrout and Halliyal [2] have reviewed the problems associated with pyrochlore formation. Swartz and Shrout [3] reported the elimination of the pyrochlore phase via the formation of a columbite structure of $MgNb_2O_6$ first, then reacting it with PbO to form PMN. Other researchers obtained perovskite PMN by using ultra pure starting materials [4], adding excess MgO (2–10%) [5,6], excess PbO [7] or 4 to 5 mol% $BaTiO_3$ [8].

Low temperature firing (below 950°C) which would allow the use of less expensive silver palladium electrodes generally requires sintering aids which lead to lowering and aging of the dielectric properties of PMN. However, lower sintering temperatures have been achieved for many sol–gel derived materials due to the homogeneous mixing of metal oxide precursors (metal alkoxides) as solutions and the high activity of the resulting powders. Two research groups (Payne [9] and Roy [10]) have reported perovskite PMN formation at 800 and 775°C respectively from sol–gel method.

The objective of this study was to determine the effects of chemical additives on perovskite formation in sol–gel derived PMN. The selected additives were ionic compounds, e.g. PbO, $BaTiO_3$, $PbTiO_3$, and MgO, and covalent compounds, e.g. B_2O_3 (added as H_3BO_3), SiO_2 and GeO_2, individually or as mixtures. The ionic compounds are some which have been reported to increase perovskite formation or stability, while the covalent compounds are those which might be present in glasses used as sintering aids. The results are summarized and discussed in the following sections.

2. Experimental

2.1. Solution synthesis

PMN was synthesized according to the method of Roy group [10] with some modifications. To a 2 l three neck flask

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equipped with thermometer, stirrer and argon purge, 178.55 g (0.8 mol) of lead oxide (Hammond Lead Products, Inc.) was added and purged with argon overnight. Acetic acid (Fisher Scientific, 410.74 g, 6.8 mol) was added into the flask (carefully due to the resulting exothermic reaction). The mixture was heated to 130°C to distil out water and acetic acid (about 270 g total over a 4 h period). After the solution was cooled below 40°C, 1025.07 g of methoxyethanol was added into the flask, the solution was then again heated to 130°C to distil out methoxyethylacetate and methoxyethanol (about 300 g distillate) until the pH of the solution was ~8.2 at room temperature. Magnesium ethoxide (Gelest Inc., 30.28 g, 0.27 mol) and niobium ethoxide (Cerac Chem. Co., 168.75 g, 0.53 mol) were added into the solution. There was a slight exotherm and the solution became cloudy. The solution was heated to 130°C until about 50 g of distillate (ethanol) was collected. Approximately 25% (weight of metal by weight of solution) clear solution was obtained.

2.2. Powder preparation

In a crystallization dish equipped with a magnetic stirrer, 10 g of deionized water was added to 100 g of the above PMN solution; gelation occurred quickly. The gel was dried at 130°C for 18 h and calcined at 350°C for 18 h to prepare the PMN precursor powder. X-ray diffraction showed a weakly crystalline pyrochlore structure after the 350°C calcine as shown in Fig. 1. The calcined powder was heated from room temperature to 100°C at 1°C/min, from 100 to 500°C at 5°C/min, held at 500°C for 1 h, then heated from 500 to 980°C at 5°C/min, and held at 980°C for 8 h.

2.3. Additives on PMN

Additions of lead oxide, barium titanate, and magnesium oxide to PMN were performed in solution using lead acetate in methoxyethanol, barium titanium alkoxide solution (Gelest Inc.) and magnesium ethoxide in methoxy ethanol respectively. The additive solutions were mixed with the base PMN sol for 1 h prior to gelation. Gelation and powder preparation were carried out as described above for the PMN powder.

A modified PMN powder containing lead oxide (14 mol%) and barium titanate (9 mol%) was used to study the chemical reactions with silica (precipitated from tetraethoxy silane), and boron oxide doped (23% by weight) silica (precipitated from tetraethoxysilane and boron trimethoxide), germanium oxide (Gelest Inc.) and boric acid (Aldrich). The modified PMN powder and 1–10 wt.% additive were milled overnight in ethanol using a 60 ml polypropylene bottle half filled (~70 g) with high purity zirconia balls (5 mm diameter). The powder was then dried at 60°C overnight, and heated from room temperature to 100°C at 1°C/min, from 100 to 500°C at 5°C/min, held at 500°C for 1 h, then heated from 500 to 980°C at 5°C/min, and held at 980°C for 8 h.

2.4. X-ray diffraction study

A Philips automated powder diffraction system APD 3720 was used to examine the X-ray diffraction of heat treated powders. The relative amounts of perovskite and pyrochlore phases are determined using system software which compared relative intensities of known X-ray patterns for $Pb(Mg_{0.33}Nb_{0.67})O_3$ and $Pb_{1.83}NB_{1.71}Mg_{0.29}O_{6.39}$.

2.5. Tolerance factor (t) calculation

The tolerance factor (t) of each composition was calculated according to Goldschmidt [11] equation, $t = (R_A + Ro)/(2)^{0.5}(R_B + Ro)$, where R_A, R_B and Ro are the ionic radii

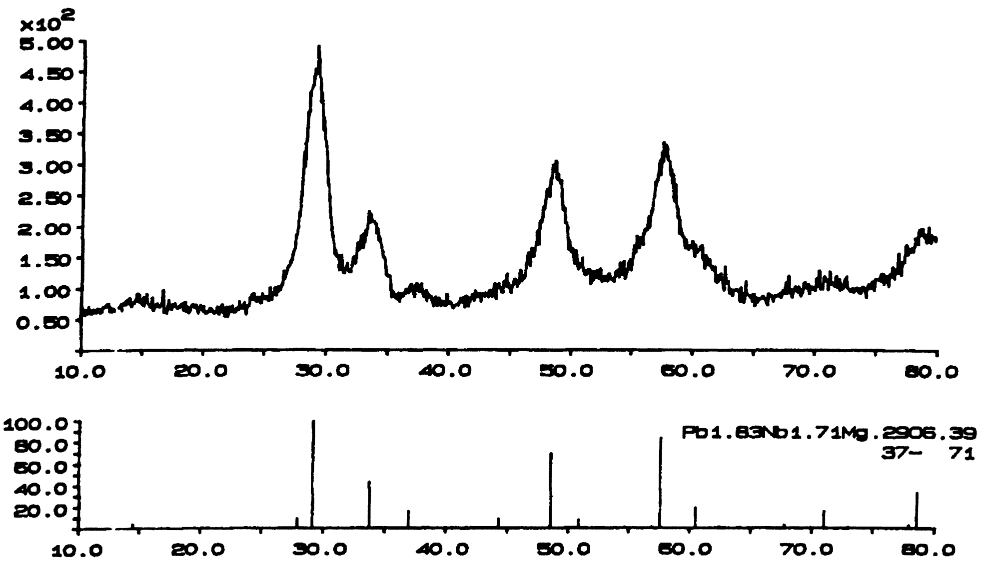

Fig. 1. X-ray diffraction pattern for sol–gel derived PMN calcined at 350°C which exhibits a weakly pyrochlore crystal structure.

Table 1
Ionic radii of selected ions

Ion	Ionic radius (Å)
Ba^{+2}	1.34[a]
Pb^{+2}	1.20[a]
O^{-2}	1.26[b]
Nb^{+5}	0.69[a]
Mg^{+2}	0.74[a]
Ti^{+4}	0.61[a]

[a] F.S. Galasso, Structure, Properties and Preparation of Perovskite Type Compounds, Pergamon Press, 1969, pp. 41–45

[b] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley, 1988, pp. 1386–1388.

of cation A, cation B and anion oxygen respectively. The value of each ionic radius is listed in the Table 1.

3. Results and discussion

We have carried out the quantitative study of chemical effects on perovskite formation of sol–gel derived PMN. Goldschmidt [11] tolerance factor (*t*) of cubic perovskite structure was used to explain the chemical effects of ionic compounds PbO, MgO, $BaTiO_3$, $PbTiO_3$. The tolerance factor is an indication of how tightly the atoms are packed in the cubic structure of ABO_3 compound. The factor is related to the ionic radii of atoms and is defined as the following:

$$t = (R_A + Ro)/(2)^{0.5}(R_B + Ro)$$

where R_A, R_B and Ro are the ionic radii of large cation A, small cation B, and of oxygen anion respectively. The most stable cubic perovskite structure of ABO_3 is formed when its tolerance factor is equal to 1.000.

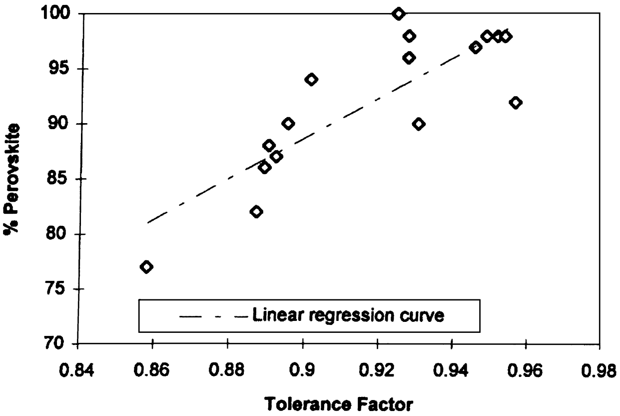

Fig. 2. Observed perovskite content vs. Calculated tolerance factor for PMN modified with PbO, $PbTiO_3$, MgO and $BaTiO_3$ (data from Table 2).

Barium titanate has a tolerance factor of 0.986 and exhibits stable 100% perovskite structure. For PMN, we assume Pb is a large cation and Mg and Nb are small cations. The ionic radius of Pb (1.20) is smaller then that of Ba (1.34) but the ionic radii of Mg (0.74) and Nb (0.69) are larger than that of Ti (0.61), thus the tolerance factor of PMN is reduced to 0.887 and exhibits only 82% perovskite. From the tolerance factor formula, the % perovskite of PMN can be increased by adding high tolerance factor compounds such as $BaTiO_3$ and $PbTiO_3$ or by increasing the amount of a large radius cation such as lead ion.

Table 2 lists the calculated tolerance factor and the corresponding percentage of perovskite formation observed by X-ray diffraction for PMN with and without ionic additives. Fig. 2 is a graphical representation of these data. $PbTiO_3$ is not as effective as PbO or $BaTiO_3$ in increasing perovskite formation. A 90% perovskite was obtained when 10% (by mol) or more of $BaTiO_3$ or PbO was added into the

Table 2
Effect of ionic chemicals on the perovskite formation of sol–gel PMN (powder heated to 980°C for 8 h)

Sample	Mol% of Chemical per mol of PMN				Tolerance factor (*t*)	% Perovskite
	PbO	MgO	PT	BT		
1	0	0	0	0	0.887	82
2	10	0	0	0	0.930	90
3	16	0	0	0	0.956	92
4	0	9	0	0	0.858	77
5	0	0	3	0	0.889	86
6	0	0	12	0	0.892	87
7	0	0	0	3	0.890	88
8	0	0	0	8	0.895	90
9	0	0	0	16	0.901	94
10	10	5	0	0	0.924	100
11	15	5	0	0	0.945	97
12	8	0	0	8	0.927	96
13	8	0	14	8	0.927	98
14	14	0	0	9	0.951	98
15	13	0	0	13	0.948	98
16	14	0	0	17	0.953	98

PMN. The amount of perovskite formation can be further increased to 98% by adding a mixture of PbO and $BaTiO_3$.

The sol–gel PMN with excess MgO (9 mol%) exhibited low perovskite formation (77%), which can be explained on the basis of a low tolerance factor of 0.858. This does not agree with observations for PMN prepared from mixed oxides. Schulze et al. [5,7] showed that the fabrication of 100% perovskite PMN required excess MgO (at least 5 mol%). The observed percentage of perovskite differences between the sol–gel derived PMN and oxides derived PMN may be explained on the basis of a difference in the distribution of the excess MgO and its interaction in the formation of PMN. For the PMN prepared from oxides, the excess MgO was added as part of the columbite precursor $MgNb_2O_6$. The precursor helped to prevent the formation of lead niobate pyrochlore from Pb and Nb. Schulze observed that after sintering, excess MgO existed as inclusions both as the grain boundary and within the perovskite grain. For sol–gel PMN, excess MgO was added homogeneously as an alkoxide solution. The excess is mixed on an atomic level in a material which has exhibited a weakly pyrochlore structure after drying at 350°C (Fig. 1). Since the more stable pyrochlore phase is already present, the excess MgO is ineffective in preventing its formation. In addition, the incorporation of MgO in the perovskite structure decreases its tolerance factor over that of the stoichiometric PMN and one would expect the observed decrease in perovskite formation.

The combination of excess PbO and MgO in the sol–gel PMN generated a higher perovskite formation (97–100%) than the PMN containing excess PbO only (92% perovskite); this cannot be accounted for basis on the tolerance factor. The reaction kinetics are not considered in the calculation of Goldschmidt tolerance factor. The addition of MgO may react with niobium preferably to form the columbite precursor of $MgNb_2O_6$. This precursor prevents the excess of PbO to react with niobium and to form lead niobate pyrochlore. Thus, the combination of excess of PbO and MgO on the perovskite formation of PMN cannot simply be explained by the tolerance factor.

The combination of excess lead oxide and $BaTiO_3$ or a combination of excess PbO, $BaTiO_3$ and $PbTiO_3$ in PMN also exhibited high perovskite formation (98%) which can be attributed to their higher tolerance factors (>0.927). Although the tolerance factor cannot explain every case studied in this report (88% success rate), the factor can serve as an initial prediction tool before performing actual experimental works.

To study the potential impact of glass additives present in sintering aids such as those present in the sealing glass used by Srikanth and Subbarao [12], B, Si and Ge were added to the PMN precursor powder modified with PbO (14 mol%) and $BaTiO_3$ (9 mol%). As discussed earlier, the PMN precursor powder is a poorly crystalline pyrochlore which, without additives, is not completely converted to perovskite upon heating to 980°C.

Srikant and Subbarao [12] used a sealing glass (Corning 7555) to lower the sintering temperature of oxides derived $0.93PMN\text{-}0.07PbTiO_3$ (PMN-PT). They reduced the sintering temperature from 950°C/4 h to 750°C/30 min. The sealing glass contains 60–80% (by weight) PbO, 10–30% B_2O_3, 1–20% SiO_2, 1–20% Al_2O_3 and 1–20% ZnO. Despite the high lead content of the glass, they found that pyrochlore formed at as low as 1% (by weight) glass at 700°C (20% pyrochlore after 4 h) and the amount of pyrochlore increased with time, temperature and glass content. Even at as low level as 3% (by weight) glass, 4 h at 800°C reduced the perovskite content to 0%. It was postulated that the destabilization of the perovskite phase could be attributed to the gradual depletion of MgO from the PMN-PT through the action of B_2O_3, SiO_2 or Al_2O_3. They showed that, with additions of MgO (MgO substituting 10 and 20% of the glass phase respectively), pyrochlore formation could be significantly reduced or eliminated. However, fired densities were reduced to less than 90% which may have changed the distribution of the glass or indicated a change in the glass

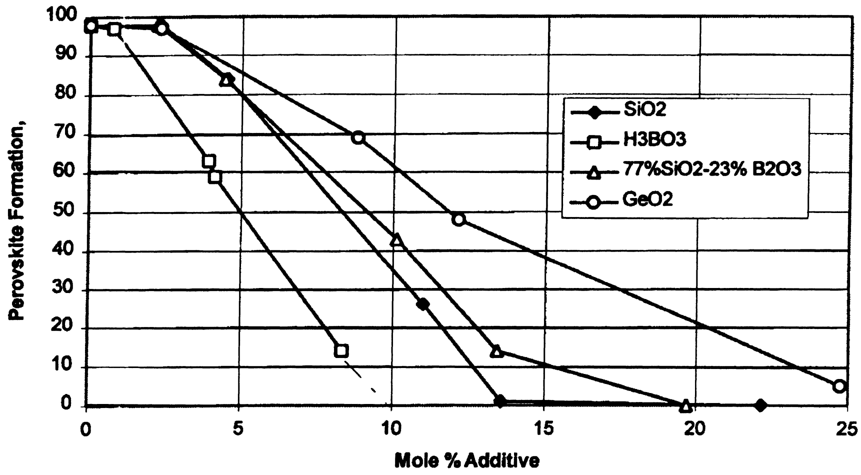

Fig. 3. Effects of covalent additives on perovskite formation in PMN doped with PbO (14%) and $BaTiO_3$ (9%).

viscosity. Both factors could affect the reaction kinetics.

Fig. 3 shows how the addition of covalent compounds such as B_2O_3 (as H_3BO_3), SiO_2, B_2O_3 (23% by weight) doped silica, and GeO_2 reduced perovskite formation of modified PMN, which was 98% perovskite when heat treated without the additives. At 5 mol% concentration, addition of GeO_2, SiO_2 and H_3BO_3 significantly decreased the perovskite formation from 98% to 86, 80 and 50% respectively. For comparison, undoped PMN exhibited 62% perovskite when it was combined with 5 mol% SiO_2. This level of additive roughly corresponds to the combined amounts of B and Si in the Pb glass used by Srikanth and Subbarao. The sample produced 100% pyrochlore in the 0.93PMN-0.07PT after 4 h at 800°C. The sol–gel powder began as a weakly pyrochlore phase (Fig. 1) and was heated nearly 200°C higher for an additional 4 h. The results indicated that a homogeneous addition of the PbO and $BaTiO_3$ in the sol–gel PMN produced a material much more resistant to destabilization. The improved stability may be explained in part by the work of Hirata and Yamaguchil [13]. For interfacial reactions between $BaTiO_3$ and Pb substituted $BaTiO_3$ with a PbB_2O_3 glass, the rate of reaction was governed by the solubility of the Pb and Ba in the glass. Because the Pb is more soluble than Ba, the Pb is reacted with glass instead of $BaTiO_3$. In our work, in addition to the increased tolerance factor, the addition of Ba to the PMN may reduce the rate of PMN reacting with the glass forming additives. Thus the weakly pyrochlore precursor powder was allowed to convert to perovskite before reacting with the covalent compounds. Also a Ba rich shell may develop, which is increasingly resistant to destabilization. As Hirata and Yamaguchi point out, however, the interfacial reactions are also dependent upon glass volume, composition and distribution. Additional work would be required to determine the exact nature of the improved stability.

The B_2O_3 doped silica did not have a greater impact that the pure silica in destabilizing PMN perovskite even though B_2O_3 alone had the greatest impact. At the 5 mol% level, it had the equivalent perovskite content of 80% and continued to have a similar trend as the pure SiO_2 curve at higher additive levels. Several explanations are available for this observation. First, the B_2O_3 may have reacted with absolute ethanol during milling to form volatile boron ethoxide which may have been lost during drying of the slurry or during the high temperature calcine. Thus, the remaining silica exhibited behaviour similar to the pure silica doped PMN. A second explanation is that boric acid melts at ~176°C and may have become more homogeneously distributed around the PMN powder than would a higher melting point B_2O_3 or borosilicate compounds, and as a result the reaction kinetics were significantly enhanced.

4. Conclusions

The chemical effects on the perovskite formation of sol–gel derived PMN has been studied. The addition of ionic compounds such as lead oxide, magnesium oxide, barium titanate and lead titanate or their mixture, to PMN increased the formation of perovskite. The results were explained by invoking the Goldschmidt tolerance factor of perovskite structure. Compositions with a high tolerance factor (>0.9) exhibit high (>90%) perovskite formation. The addition of covalent compounds such as boric acid, silica, boron oxide doped silica and germanium oxide, or their mixture, destabilized the PMN perovskite and reduced the formation of perovskite. Boron had the greatest impact on reducing perovskite formation followed by SiO_2 and GeO_2. The B_2O_3 doped silica did not have an impact as as great as pure silica in destabilizing PMN perovskite even though B_2O_3 alone had the great impact. This may be the result of a more uniform distribution of the lower melting point boric acid or possible loss of boron from the borosilicate due to the formation of volatile boron ethoxide. The PMN doped with PbO and $BaTiO_3$ showed a significant improvement in perovskite formation (80%) compared to undoped material (62%) for a 5 mol% addition of SiO_2.

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