Chem. Mater. **2004,** *16,* 5365−5371

Polyethylene Glycol-Based New Solution Route to Relaxor Ferroelectric $0.65Pb(Mg_{1/3}Nb_{2/3})O_3-0.35PbTiO_3$

K. Babooram and Z.-G. Ye*

Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, V5A 1S6, Canada

Received May 31, 2004. Revised Manuscript Received September 20, 2004

A new soft chemistry route has been developed for the synthesis of relaxor ferroelectric lead magnesium niobate−lead titanate solid solution (0.65PMN−0.35PT). The method uses a poly(ethylene glycol) (PEG) and methanol mixture as solvent. It allows reactions to be performed at room temperature without using an excess amount of the lead starting material to compensate for lead oxide loss during ceramic sintering as is usually the case in conventional synthesis. The effect of using a triol molecule, 1,1,1-tris(hydroxymethyl)ethane (THOME), which serves as a complexing agent in binding together the metal ions in the precursor solution, has also been studied. Pure perovskite phase was obtained in ceramics sintered at a relatively low temperature of 1040 °C as compared to 1250 °C in solid-state reactions. A high dielectric constant (at 1 kHz) of above 5000 is found at room temperature and the value reaches ~27 000 at the Curie temperature. Ferroelectric hysteresis loops are displayed on a ceramic with an average grain size of 2 μm, giving rise to a remnant polarization (P_r) of 21 $\mu C/cm^2$ and a coercive field (E_c) of ~7.5 kV/cm.

I. Introduction

The solid solutions between the relaxor ferroelectric lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), and the normal ferroelectric lead titanate, $PbTiO_3$ (PT), abbreviated as (1−x)PMN−xPT (or PMNT), have gained a lot of interest as potential candidates for dielectric and piezoelectric devices, such as multilayer capacitors, sensors, and actuators.[1−4] While the solid solutions with lower PT contents give rise to materials with high dielectric constants and low remnant polarization suitable for dynamic random-access memory (DRAM) devices, those with higher PT contents have relatively low dielectric constants and high remnant polarization at room temperature. Compositions around the morphotropic phase boundary (MPB) exhibit typical ferroelectric properties, with a large spontaneous polarization and a low coercive field, showing great potentials for advanced electromechanical applications both in the forms of electroceramics and thin or thick films.[5] Recently, single crystals of (1−x)PMN−xPT solid solutions have been found to exhibit electromechanical performance superior to that of the $(1-x)PbZrO_3-xPbTiO_3$ (PZT) ceramics[6,7] which have been intensely used for decades as piezoelectric materials for transducers and actuators.[8]

Although most research to date has been concentrated on compounds based on the PZT system because of its high remnant polarizations, certain drawbacks such as fatigue and aging have deviated attention toward other materials in the quest for better properties.[9] In that respect, the (1−x)PMN−xPT system stands as a potential candidate as its ceramics have been reported to show high dielectric, piezoelectric, and electrostrictive properties.

One of the challenges in making PMN−PT compounds is to suppress and avoid the formation of a pyrochlore phase which is thermodynamically more stable and kinetically more favorable than the perovskite phase but functionally undesirable because it impairs the dielectric properties of the materials.[10]

Solid-state reactions have been widely used to prepare mixed oxide powders and ceramics, but the failure to achieve homogeneity and single phase in some final products has given rise to several powderless processing methods which use liquid precursors rather than powders as starting materials.[11] These methods have gained interest because they offer such advantages as control of homogeneity, stoichiometry, and purity, leading to increased reactivity.[12] Among the various routes to homogeneous multicomponent oxides that have recently

---

* Corresponding author. Fax: 1-604-291-3765. E-mail: zye@sfu.ca.

(1) Cross, L. E. *Ferroelectrics* **1987**, *76*, 241. Cross, L. E. *Ferroelectrics* **1994**, *151*, 305. Ye, Z.-G. *Key Eng. Mater.* **1998**, *155−156*, 81. Ye, Z.-G. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6* (1) 35.

(2) Noheda, B.; Cox, D. E.; Shirane, G.; Gao, J.; Ye, Z.-G. *Phys. Rev. B* **2002**, *66*, 054104. Ye, Z.-G.; Noheda, B.; Dong, M.; Cox, D.; Shirane, G. *Phys. Rev. B.* **2001**, *64*, 184114.

(3) Choi, S. W.; Shrout, T. R.; Jang, S. J.; Bhalla, A. S. *Ferroelectrics* **1989**, *100*, 29.

(4) Shrout, T. R.; Chang, Z. P.; Kim, N.; Markgraf, S. *Ferroelectric Lett.* **1990**, *12*, 63.

(5) Park, J. H.; Kang, D. H.; Yoon, K. H. *J. Am. Ceram. Soc.* **1999**, *82* (8), 2116.

(6) Service, R. F. *Science* **1997**, *275*, 1878.

(7) Park, S.-E.; Shrout, T. R. *J. Appl. Phys.* **1997**, *82* (4), 1804.

(8) Jaffe, B.; Cook, W. R.; Jaffe, H. *Piezoelectric Ceramics*; Academic Press: London, 1971.

(9) Francis, L. F.; A Payne, D. *J. Am. Ceram. Soc.* **1999**, *74* (12), 3000.

(10) Nijmeijer, A.; Kruidhof, H. *J. Am. Ceram. Soc.* **1997**, *80* (10), 2717.

(11) Gülgün, M. A.; Nguyen, M. H.; Kriven, W. M. *J. Am. Ceram. Soc.* **1999**, *82* (3), 556.

(12) Payne, D. A. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 311.

10.1021/cm049134s CCC: $27.50

been developed, the polymeric precursor method has drawn a lot of attention.[13] Pioneered by Pechini in the 60s, this method provides a simple way to oxide powders by first making a solution containing all the cations in the form of polymer−cation complexes in the desired stoichiometry and then firing this solution to drive off any organic moeties and to form the target oxides.[14] The chelation and entrapment of the cations by the polymer chains give rise to oxide powders with better chemical homogeneity and smaller particle size. This is explained by the fact that chelation considerably lowers the mobility of the cations and thereby stabilizes them against precipitation,[15] which is the key requirement to form a stable precursor solution to be used for depositing thin films.

Several researchers reported the synthesis of multicomponent ceramic oxides via the oxidation of poly(ethylene glycol)− or poly(vinyl alcohol)−cation complexes.[11,13,15−17] The Pechini method, which uses α-hydroxycarboxylic acids such as citric and lactic acids together with polyhydroxyl alcohols such as ethylene glycol to make a polymer resin, has been modified to some extent to the use of water-soluble sources such as metal nitrates and chlorides. This has now become a very common method because these inorganic salts are more stable than the corresponding alkoxides and, hence, easier to handle. Another way of forming extended structures in solution is by cross-linking the cations using a molecule with multiple binding sites. Sriprang and co-workers[18] demonstrated this through a triol-based route to PZT thin films in which 1,1,1-tris(hydroxymethyl)ethane (THOME) was used as the complexing agent. However, to the best of our knowledge, no application of such technique has been made to the synthesis of complex perovskites such as the (1−x)PMN−xPT systems. Commonly, sol−gel processes using alkoxides require refluxing at temperatures usually above 100 °C to allow for hydrolysis and condensation reactions to take place and to form the cross-linked structures.

In this paper, we report the sol−gel synthesis of 0.65PMN−0.35PT ceramics using a mixture of poly(ethylene glycol)-200 and methanol as the solvent for the starting materials. The PMN/PT ratio of 65/35 was chosen because this composition lies in the morphotropic phase boundary (MPB) region where a rhombohedral, a monoclinic, and a tetragonal phases were recently found in the (1−x)PMN−xPT phase diagram.[2] For compositions around the MPB, anomalously high pyroelectric and dielectric properties were demonstrated which could be of high interest for thin-layer devices.[3,4] Single crystals of the MPB composition exhibit excellent piezoelectric properties.[6,7] With the increase of the PT content from zero to the MPB compositions, the ferro-/paraelectric phase transition temperature (T_C) increases from −15 to above 150 °C, which is interesting for many applications.[3,19,20] Using the polymer/alcohol mixture, we are able to perform a room-temperature reaction to make the precursor solution as well as to obtain the pure (pyrochlore-free) perovskite phase for the PMN−PT ceramics. Furthermore, this new route to PMN−PT ceramics does not require the use of any excess of the lead starting material, which was necessary in all conventional and most soft chemistry syntheses to compensate for lead oxide loss during sintering at high temperatures. We also study the mechanism of the calcinations of the gel and the effects of using the triol molecule in the sol−gel synthesis on the phase formation and properties of the PMN−PT ceramics.

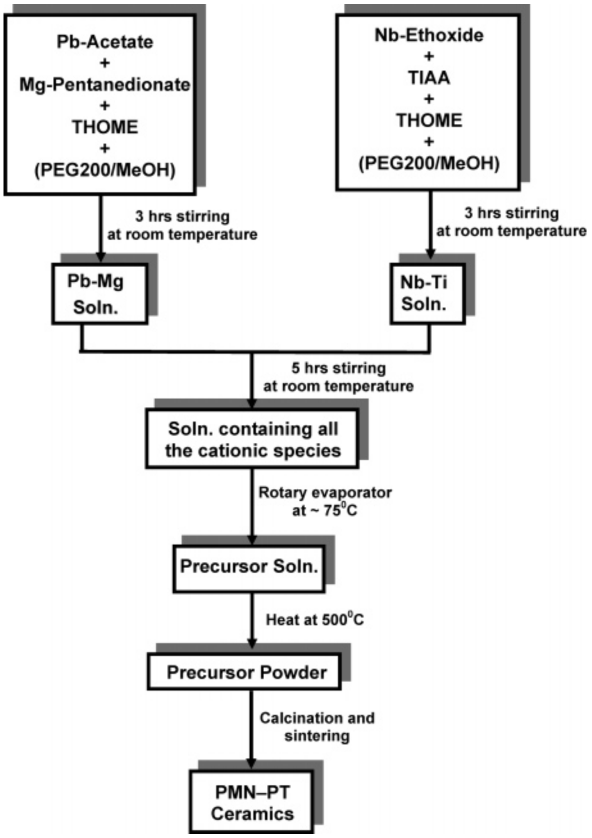

Figure 1. Flowchart for the preparation of the precursor solutions and the ceramics of 0.65PMN−0.35PT.

II. Experimental Procedure

(1) Preparation of 0.65PMN−0.35PT Ceramics. Ceramics of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3-0.35PbTiO_3$ (0.65PMN-0.35PT) solid solution were synthesized by the method outlined in Figure 1. Stoichiometric amounts (corresponding to the 0.65PMN−0.35PT composition) of lead acetate trihydrate [$Pb(O_2C_2H_3)_2\cdot 3H_2O$, 2.3898 g, 6.30 mmol], magnesium 2,4-pentanedionate dihydrate [$Mg(O_2C_5H_7)_2\cdot 2H_2O$, 0.3564 g, 1.38 mmol], and 1,1,1-tris(hydroxymethyl)ethane (THOME) [$C(CH_2OH)_3CH_3$, 0.3785 g, 3.15 mmol] were mixed with an excess of poly(ethylene glycol)-200 (PEG200) and methanol mixture (PEG200/MeOH at a 1:2 volume ratio). In a separate reaction flask, niobium ethoxide [$Nb(OCH_2CH_3)_5$, 0.8687 g, 2.73 mmol], titanium di-isopropoxide bis-acetyl acetonate (TIAA) [$Ti(O_2C_5H_7)_2(OCH(CH_3)_2)_2$, 1.0701 g, 2.94 mmol], and THOME

---

(13) Uekawa, N.; Sukegawa, T.; Kakegawa, K.; Sasaki, Y. *J. Am. Ceram. Soc.* **2002**, *85* (2), 329.

(14) Pechini, M. P. U.S. Patent 3 330 697, 1967.

(15) Nguyen, M. H.; Lee, S-J.; Kriven, W. M. *J. Mater. Res.* **1999**, *14* (8), 3417.

(16) Uekawa, N.; Endo, M.; Kakegawa, K.; Sasaki, Y. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5485.

(17) Shimizu, Y.; Murata, T. *J. Am. Ceram. Soc.* **1997**, *80* (10), 2702.

(18) Sriprang, N.; Kaewchinda, D.; Kennedy, J. D.; Milne, S. J. *J. Am. Ceram. Soc.* **2000**, *83* (8), 1914.

(19) Udayakumar, K. R.; Chen, J.; Schuele, P. J.; Cross, L. E.; Kumar, V.; Krupanidhi, S. B. *Appl. Phys. Lett.* **1992**, *60* (10), 1187.

(20) Lu, Y.; Jin, G.-H.; Cronin-Golomb, M.; Liu, S.-W.; Jiang, H.; Wang, F.-L.; Zhao, J.; Wang, S.-Q.; Drehman, A. J. *Appl. Phys. Lett.* **1998**, *72* (23), 2927.

(0.1766 g, 1.47 mmol) were also mixed with an excess of PEG200/MeOH (1:2) mixture. Both of these reaction mixtures were kept under stirring condition at room temperature for about 3 h before they were mixed together and further stirred for about 5 h to give a clear and homogeneous yellow solution. The latter was then dried in a rotary evaporator to remove all organic volatiles and to form a viscous solution, which was then heat-treated in a high-temperature furnace at 500 °C for 2 h at a heating and cooling rate of 300 °C/hr. At this point, a light yellow powder was obtained and it was ground in acetone and pressed into pellets, which were then calcined for a period of 8 h in a Pt/Al_2O_3 double crucible setup containing Pb_3O_4 as a PbO source to prevent any lead oxide loss from the sample during this process. The same reaction was also performed but without the triol molecule to study the possible difference on the properties of the ceramics. The samples containing the triol were named PEG(S)T, and those without the triol, PEG(S).

(2) Characterization of the 0.65PMN−0.35PT Ceramics. Powder X-ray diffraction (XRD) patterns were obtained on a Philips powder diffractometer using Cu Kα radiation (40 kV, 35 mA) to check the phases formed. The decomposition pathways of the precursor solutions were observed by thermogravimetric and differential thermal analyses (TG/DTA) on a Seiko Exstar 6300 TG/DTA Thermal Analyzer. The precursor solutions were oxidized by heating from room temperature to 1000 °C at a heating rate of 5 °C/min. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Bomem MB spectrometer to monitor the transformation of the precursor solutions during the thermal reactions leading to the oxides. The grain size of the ceramics was imaged using scanning electron microscopy (SEM) on a Bausch and Lomb Nanolab 2100 SEM equipment, and the dielectric permittivity was measured as a function of temperature within a frequency range of 10^2−10^6 Hz on a computer-controlled impedance analyzer (Solartron 1260) in conjunction with a dielectric interface (Solartron 1296). Ferroelectric hysteresis measurements were performed on an RT66A standard ferroelectric testing system.

III. Synthesis of 0.65PMN−0.35PT Ceramics

III. (a) Sol−gel Synthesis. The main challenge at the beginning of this work was to find a proper solvent that would be able to dissolve all the starting materials, especially the magnesium 2,4-pentanedionate which is very difficult to dissolve in such solvents as 2,4-pentanedione, pure methanol, and ethanol. Finally, a 1:2 volume ratio of poly(ethylene glycol) (PEG200) and methanol mixture proved to be successful in obtaining a homogeneous solution mixture containing all four cationic species. An interesting feature here is that this precursor solution to the target PMN−PT ceramics was formed at room temperature by simple mixing and stirring conditions, thus avoiding the reflux and distillation steps usually required in sol−gel reactions. Moreover, the sol is not moisture sensitive and shows very good stability against precipitation, which makes it a very promising stock solution for depositing thin films. One common practice in the synthesis of lead-based ceramic oxides is to use an excess amount of lead starting material to compensate for any loss in terms of PbO during the calcining and sintering processes at high temperatures. In this respect, another benefit of this solvent system is that it allows the synthesis of the PMN−PT compound of pure perovskite phase without the need for an excess amount of the lead acetate. However, an excess of the PEG200/methanol mixture is necessary to keep the solutions from precipitating during the synthesis process.

The triol molecule, 1,1,1-tris(hydroxymethyl)ethane (THOME), was initially employed in the synthesis of the precursor solutions with a view to improving the quality of metal oxides because of its high metal-complexing ability, as demonstrated by Sriprang et al.[18] who observed an improvement in the quality of lead zirconium titanate thin films when THOME was used in the sol−gel synthesis of the precursor solution. At the same time, it is also well known that poly(ethylene glycol) also chelates and entraps metal ions very efficiently in solution and this helps in the formation of the pure phase of multicomponent ceramic oxides when the solution is fired at high temperatures.[11] On the basis of this consideration, we also performed the reactions without THOME to study its role in the synthesis process of the 0.65PMN−0.35PT ceramics, which resulted in ceramics containing about 5% pyrochlore phase, with considerably lower dielectric constant and remnant polarization values (see Section V).

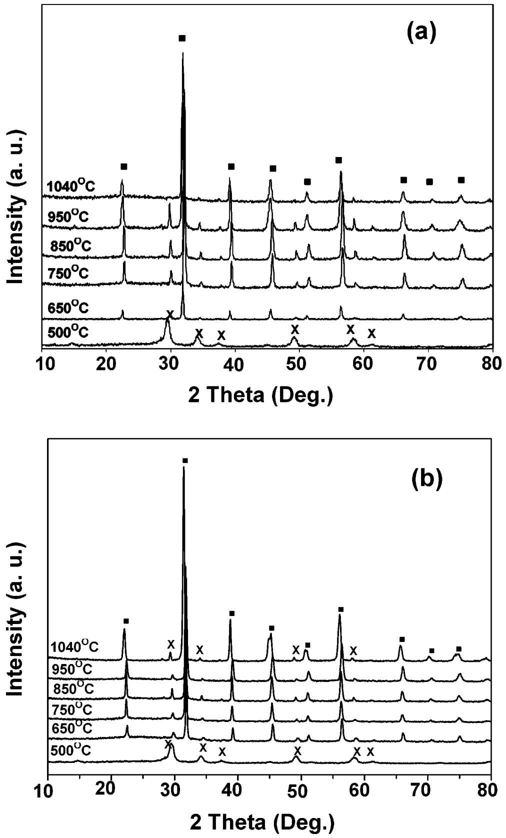

Figure 2. X-ray diffraction spectra at room temperature of the (a) PEG(S)T and (b) PEG(S) precursor powders calcined at different temperatures for a period of 8 h.

III. (b) X-ray Diffraction (XRD). The formation of different phases in all the samples was monitored using X-ray powder diffraction. As can be seen from the XRD patterns in Figure 2a and 2b, the PEG(S)T and PEG(S) powders are already in the crystalline form after treatment at 500 °C, with the presence of a pyrochlore phase. In PEG(S)T (Figure 2a), as temperature is increased further, the perovskite phase grows at the expense of the pyrochlore one, until a pure perovskite phase is obtained for the pellet calcined at 1040 °C. A very good ceramic density of ∼96% of the theoretical value was obtained after sintering at 1140 °C for 8 h. For the PEG(S) samples, the perovskite phase also takes over the pyrochlore phase as the temperature is increased above 500 °C, but as can be seen from Figure 2b, a small amount of pyrochlore phase still subsists after heat

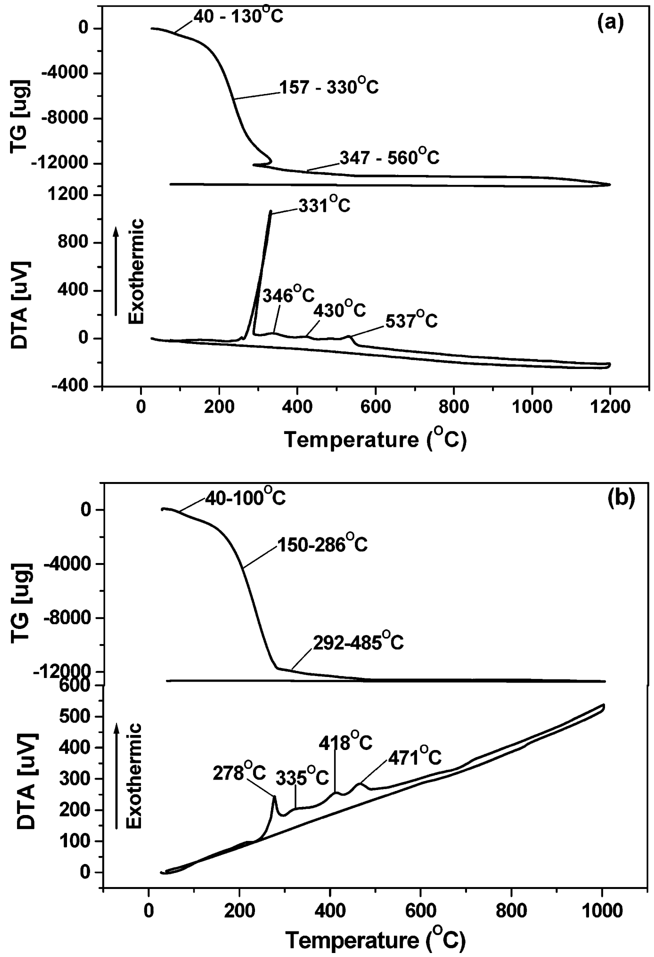

Figure 3. TG/DTA curves from room temperature to 1000 °C at a heating rate of 5 °C/min for (a) PEG(S)T and (b) PEG(S) precursor solutions

treatment at 1040 °C for 8 h. As a result, the ceramics are not 100% pure perovskite although the density also reaches ~96%.

IV. Mechanisms of the Reactions

IV. (a) Thermogravimetric/Differential Thermal Analysis. To determine the best conditions for the pyrolysis of the precursor solutions and the sintering of the precursor powders and to study the mechanisms of the reactions, thermal analyses were performed. Figure 3 a and 3b shows the thermogravimetric analysis/differential thermal analysis (TGA/TGA) curves of the PEG(S)T and PEG(S) precursor solutions, respectively, measured from room temperature up to 1000 °C at a heating rate of 5 °C/min. On the TGA curve of the PEG(S)T solution (Figure 3a), three different weight loss regions are identified. The initial weight loss in the region of 46−130 °C corresponds to the volatilization of solvent or moisture still present in the precursor solution. A second weight loss in the region of 157−330 °C results from the decomposition of the PEG chains as well as of THOME molecules and the acetate groups present in the sol. The strong and sharp exothermic peak at 331 °C arises from the decomposition of the PEG chains and the THOME molecules that were bound to the cations in the precursor solution, in the form of a self-combustion reaction. In separate DTA experiments on a sample of PEG200 (not shown), oxidation and decomposition peaks were observed below 300 °C. The endothermic peaks that appeared on the DTA curve of pure THOME at 197 °C, and 261.5 °C and 273.8 °C (not shown), corresponding to the melting and decomposition of the molecule, are absent on the DTA curve of the PEG(S)T sol. This indicates that THOME has also taken part in the precursor solution formation by binding to the metal centers. Therefore, the strong exothermic peak at 331 °C on the DTA of the PEG(S)T sol must result from the decompositions of the PEG chains and of the THOME molecules which interacted with the cations. The fact that they were bound to the metal ions in the precursor solution increased their molecular weights and thereby shifted their decomposition points to a higher temperature than for the free chains or molecules. The final weight loss observed between 347 and 560 °C refers to the decomposition of more complex metal−organic moieties or oligomers that could form in the solution through the linking of chains during the condensation reactions. This process is accompanied by the weak exothermic peaks observed at 346 °C and 430 °C. The other exothermic peak that appears at 537 °C can be attributed to the formation of a crystalline mixed oxide phase.[21] This crystallization process is also confirmed by X-ray diffraction patterns that show the formation of a pyrochlore phase in a powder heat-treated at 500 °C (see Section III(b)). These observations lead to the conclusion that all the organic components of the precursor solution are burnt out at temperatures below ~450 °C, above which the resulting matter crystallizes into the pyrochlore phase through rearrangement of the random M−O−M networks present.

The thermal analyses on the PEG(S) precursor solution are given in Figure 3b. The only difference in this solution as compared to PEG(S)T is the absence of THOME as one of the starting materials in the sol−gel process. The results are similar: three different weight loss regions are found on the TGA curve in the temperature ranges of 40−100 °C, 150−286 °C, and 292−485 °C, corresponding to the evaporation of solvent or moisture from the precursor solution, the decompositions of the PEG−cation complexes and more complex PEG−cation structures, and the formation of crystalline mixed oxide phase, respectively. The exothermic peaks observed on the DTA curve at 278 °C, and at 335 °C and 418 °C, result from the thermal events associated with the second and third weight losses, respectively. The exothermic peak at 471 °C is attributed to the crystallization of the pyrochlore phase, which is confirmed by X-ray diffraction (see Section III(b)). The presence of this phase was detected in a powder synthesized at 500 °C, that is, lower than that of the PEG(S)T sample. It can be seen that the presence of THOME in the PEG(S)T precursor solution increases the temperature of formation of the pyrochlore phase, from 471 °C in PEG(S) to 536 °C. This is attributed to the fact that THOME was also bound to the cations in the presence of PEG in the PEG(S)T solution. As a result, the mechanisms of decomposition of the metal−organic complexes in PEG(S)T and PEG(S) during the high-temperature heat treatment become different, thereby making the rearrangements of the metal−

---

[21] Thomas, R.; Mochizuki, S.; Mihara, T.; Ishida, T. *J. Mater. Res.* **2002**, *17* (10), 2652.

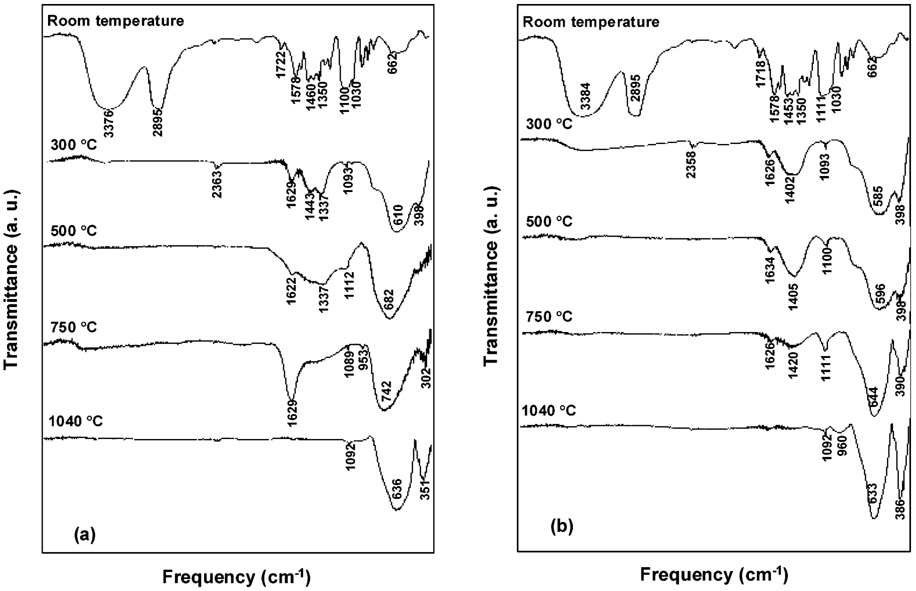

Figure 4. FTIR spectra of the (a) PEG(S)T and (b) PEG(S) precursor solutions at room temperature and of the resulting products after thermal treatments at various temperatures.

oxygen−metal network also proceed through different pathways. This may be the main reason pure perovskite phase has been obtained in PMN−PT ceramics made from the PEG(S)T precursor solution, while some pyrochlore still exists in the ceramics synthesized from the PEG(S) solution. Therefore, THOME is shown to play a key role in the formation of the pure PMNT ceramics.

IV. (b) Fourier Transform Infrared Spectroscopy. Figure 4 shows the spectra of Fourier transform infrared spectroscopy (FTIR) of the initial PEG(S)T and PEG(S) precursor solutions at room temperature, and the resulting products after these solutions were treated at different temperatures of 300, 500, 750, and 1040 °C for a period of 2 h. The frequency region of the spectra is from 4000 to 200 cm^{-1}. The spectra clearly show the decomposition of the organometallic species present in the precursor solutions as well as their rearrangements into the inorganic crystalline phases. The room-temperature spectra for the PEG(S)T and PEG(S) solutions are very similar. The peaks in the region of 1100−1000 cm^{-1} and 700−300 cm^{-1} are due to the C−O and the M−O vibrations, respectively.[22] These peaks appear at 1100, 1030, and 662 cm^{-1} in PEG(S)T and 1111, 1030, and 662 cm^{-1} in PEG(S). The absorption peaks in the region of 3200−2800 cm^{-1} are assigned to the O−H and the C−H vibrations coming from the excess solvent present.[23] These two spectra also contain peaks from other organic moieties such as carbonyl (~1722 cm^{-1}), acetate (1578 cm^{-1}), and acetylacetonate (1460 and 1350 cm^{-1}) groups which come from the starting materials. After the heat treatment of these precursor solutions at 300 °C, most of the peaks from the organic moieties (O−H: 3376 cm^{-1}, C−H: 2895 cm^{-1}, C=O: 1722 cm^{-1}, C−O: 1100 cm^{-1}, conjugated C=C: 1578 cm^{-1})[22,23] disappear, indicating the breaking down of the bonds and the decomposition of these species. The peaks that show up at 2363 and 1629 cm^{-1} for the PEG(S)T sample treated at 300 °C can be assigned to the C=O and C≡O stretching of carbon dioxide and carbon monoxide molecules trapped in the pores of the powder, respectively. Similar results were obtained for the PEG(S) sample treated under the same conditions.

As the treatment temperature is increased to 500 °C, some differences appear between the PEG(S)T and PEG(S)T spectra. The peaks at 1622, 1337, and 1112 cm^{-1} practically merge together into a broad peak on the PEG(S)T spectrum, while they remain distinct on the PEG(S) spectrum. The other remarkable difference is the intense broad peak at 682 cm^{-1} for the PEG(S)T sample, which is assigned to metal−metal and metal−oxygen bonds formed as the organic components burned out and the M−M and M−O networks rearranged themselves toward a more ordered crystalline structure. On the PEG(S) spectrum, the two peaks at 596 and 398 cm^{-1} almost merge into a broad one. This clearly points to the existence of different arrangements of metal−oxygen−metal networks in these two samples, resulting from the effect of THOME present in the synthesis of the PEG(S)T sol. After the treatments at 750 and 1040 °C, all the organic moieties have completely been eliminated and the absorption peaks are solely from the M−M and M−O bonds both for PEG(S)T and PEG(S).

At 750 °C, both samples still contain some pyrochlore phase as shown by the XRD patterns in Figure 2a and b. However, the FTIR spectra of the PEG(S)T and PEG(S) samples treated at this temperature show difference in the peak positions, indicating different arrangements of the metals and oxygen ions in these two powders. After the treatment at 1040 °C, the sharp peak at 1629 cm^{-1} completely disappears and the 742 cm^{-1} peak shifts to 636 cm^{-1} on the PEG(S)T spectra (Figure 4a), which is associated with the disappearance of the pyrochlore phase and the formation of the pure perovskite phase, as confirmed by the XRD spectra (Figure 2a). On the other hand, the FTIR spectra of the PEG(S) powder treated at 750 and 1040 °C (Figure 4b) do not

---

(22) Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy,* 2nd ed.; Harcourt Brace College Publishers: Fort Worth, TX, 1996.

(23) Zhang, L. Synthesis and Characterization of Relaxor-Based Piezo- and Ferroelectric (1-x)Pb($\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3}$)$\mathrm{O}_3$-xPbTiO$_3$ [PZN−PT] and (1-x)Pb($\mathrm{M}_{1/3}\mathrm{Nb}_{2/3}$)$\mathrm{O}_3$-xPbTiO$_3$ [PMN−PT]. Masters Thesis, Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A 1S6, 2000.

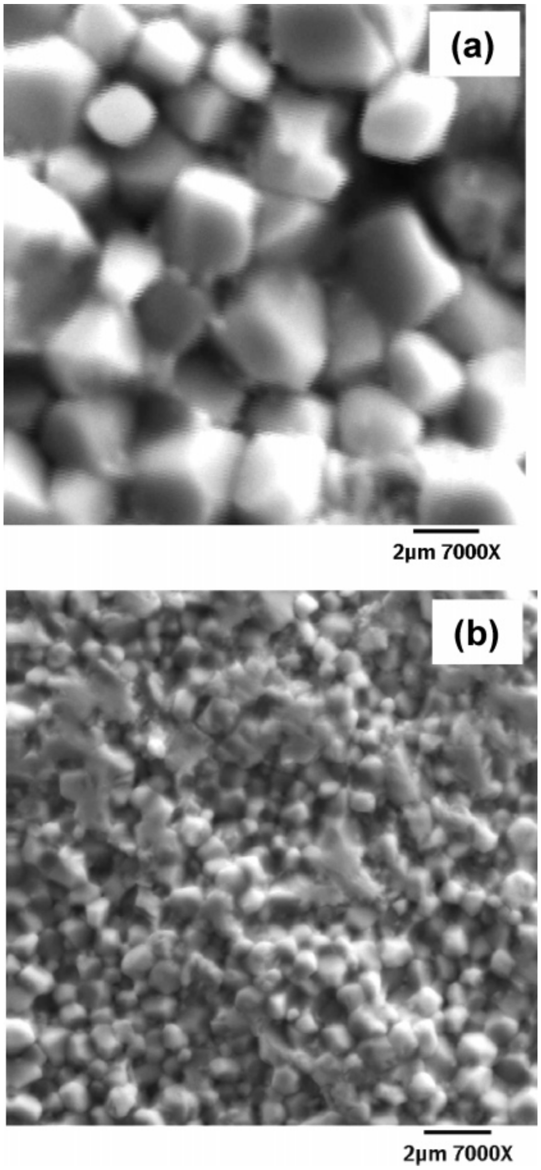

Figure 5. Scanning electron microscopic images of (a) PEG(S)T and (b) PEG(S) ceramics sintered at 1140 °C for 8 h.

show significant difference, because they exhibit the same phase components with some pyrochlore phase retained, as can be seen from the XRD patterns (Figure 2b). Therefore, the FTIR results are consistent with the XRD data, supporting the fact that pure perovskite phase is obtained at 1040 °C in ceramics synthesized from precursor solutions containing THOME.

V. Characterization

V. (a) Microstructures by Scanning Electron Microscopy (SEM). The SEM images of microstructure and grain morphology of the PEG(S)T and PEG(S) ceramics sintered at 1140 °C are given in Figure 5a and 5b, respectively. As can be seen from these photographs, both samples show a relatively uniform grain size distribution but they differ remarkably from each other in their average grain sizes. While the PEG(S)T ceramic shows an average particle size of >2 μm, that of PEG(S) ceramic is ~0.8 μm only. The ceramics prepared by this soft chemistry technique exhibit much finer grain size than for those derived from the conventional solid-state synthesis where grain size is usually >10 μm.[23] Our results also point out that the use of THOME in the synthesis of the ceramic precursor solution gives rise to a larger particle size as compared to the ceramic obtained from the THOME-free reaction.

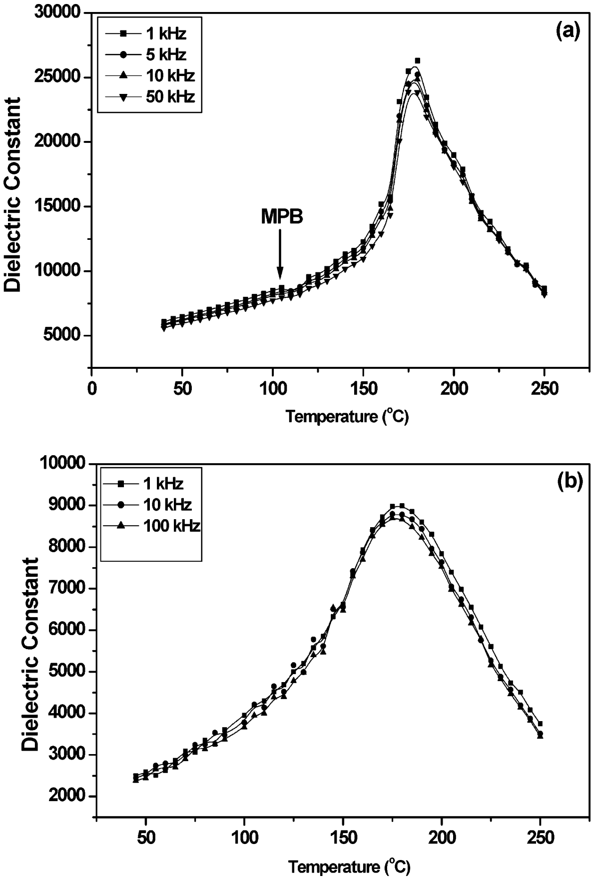

Figure 6. Impedance spectroscopic data showing the dependence of dielectric constant as a function of temperature and frequency for (a) PEG(S)T and (b) PEG(S) ceramics sintered at 1140 °C for 8 h.

V. (b) Dielectric Properties. Figure 6a and 6b illustrates the temperature and frequency dependences of the real part of dielectric permittivity (ϵ') of the PEG(S)T and PEG(S) ceramics, respectively, sintered at 1140 °C. The peak at ~175 °C in both figures indicates the Curie temperature (T_C) of the ferroelectric to paraelectric phase transition upon heating, in agreement with the PMN–PT phase diagram reported in ref 3. For the PEG(S)T ceramic, the dielectric constant reaches above 5000 at room temperature, which is significantly higher than the values of 2000–3000 usually obtained for the PMN–PT ceramics prepared via solid-state reactions.[23] A maximum value of the dielectric constant (ϵ'_{max}) of ~27 000 is attained at the T_C at a frequency of 1 kHz. The weak anomaly observed around 100 °C corresponds to the morphotropic phase transition between the rhombohedral and the tetragonal phases.[3] The dielectric constant increases sharply just before it peaks at the T_C, indicating a first-order phase transition. The PEG(S) ceramic, however, shows a much lower dielectric constant of ~2500 at room temperature, with an ϵ'_{max} of ~9000 only at the same T_C of ~175 °C. As discussed earlier in Section III.b, after sintering at 1140 °C for 8 h, the PEG(S)T ceramic shows the pure perovskite phase. The PEG(S) sample, however, con-

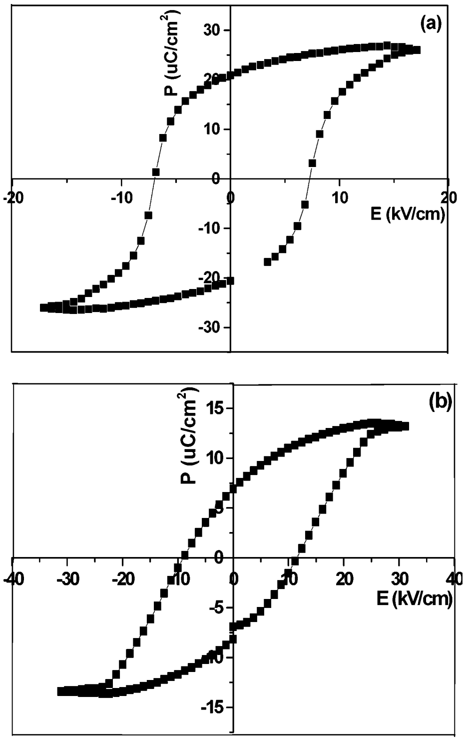

Figure 7. Variation of electrical polarization as a function of applied bipolar electric field for (a) PEG(S)T and (b) PEG(S) ceramics sintered at 1140 °C for 8 h, showing ferroelectric hysteresis loops.

tains ~5% of the undesired pyrochlore phase which significantly deteriorates the dielectric properties in it, even though both ceramics have a high relative density of ~96%. In addition, the dielectric peak for the PEG(S) ceramic becomes much broadened, which can be explained by the particle sizes of the respective ceramics. It was shown by Chattopadhyay et al.[24] that a decrease in the particle size of nanocrystalline ferroelectric lead titanate, prepared by coprecipitation, leads to a broadening of the peak in the dielectric constant versus temperature curve and lowers the value of the $\epsilon'_{\max}$. The same explanation could apply here: since the grain size is much smaller in the PEG(S) sample (Figure 5), its dielectric peak becomes broadened with a low $\epsilon'_{\max}$. This observation leads to the conclusion that THOME used in the synthesis of the precursor solution plays an important role not only in favoring the formation of the pure perovskite phase, but also in substantially improving the dielectric properties of the PMN−PT ceramics.

V. (c) Ferroelectricity. The polarization versus electric field relations of both the PEG(S)T and PEG(S) ceramics sintered at 1140 °C exhibit hysteresis loops as displayed in Figure 7a and 7b, indicating a typical ferroelectric behavior. The PEG(S)T ceramic shows excellent ferroelectric properties with a well-defined and saturated hysteresis loop, a high remnant polarization of $P_r = 21\ \mu C/cm^2$, and a coercive field of $E_c = 7.5$ kV/cm. The PEG(S) ceramic, on the other hand, displays a much smaller remnant polarization of 7.5 $\mu C/cm^2$ and a slightly larger E_c of about 10 kV/cm, and the polarization is still unsaturated even at a field up to ±30 kV/cm. The improved ferroelectricity in PEG(S)T ceramics can be attributed to the effect of the THOME. As discussed above, the triol molecule favors the formation of pure perovskite phase in the PEG(S)T ceramic, hence bringing about better dielectric and ferroelectric properties than the PEG(S) sample.

VI. Conclusions

A new solution method for the synthesis of the relaxor ferroelectric $0.65Pb(Mg_{1/3}Nb_{2/3})O_3{-}0.35PbTiO_3$ ceramics has been developed in this study. By using poly(ethylene glycol) and methanol as solvent, a sol that is very stable to air can be obtained at room temperature. The formation of this sol does not require refluxing and distillation steps that are usually required in conventional sol−gel reactions. More interestingly, the sol−gel reaction is carried out using a stoichiometric amount of the lead starting material, which gives rise to pure and high-density ceramics after sintering, with very good dielectric and ferroelectric properties. The positive effects of the triol molecule, 1,1,1-tris(hydroxymethyl)ethane (THOME), on the synthesis and performance of the perovskite PMN−PT ceramic, have been demonstrated in this work, which are related to its nature as a very good metal complexing agent. With three hydroxyl groups in its structure, the THOME molecule can bind to up to three metal centers at a time, thereby forming linear oligomeric species in solution. This has an influence on the arrangement of the M−O−M networks in the precursor powder. Evidence of the presence of different M−O−M arrays in the precursor powder when THOME was used or not in the sol−gel process has been revealed by the FTIR spectroscopy. The presence of THOME in the system during the precursor solution synthesis has not only led to the formation of a pure perovskite phase but also greatly improved the dielectric and ferroelectric properties of the PMN−PT ceramics with a room-temperature dielectric constant $\epsilon'_{rt} = 5000$, a maximum dielectric constant (at $T_C = 175$ °C) $\epsilon'_{\max} = 27\,000$, and a remnent polarization $P_r = 21\ \mu C/cm^2$, as compared to $\epsilon'_{rt} = 2500$, $\epsilon'_{\max} = 9000$, and $P_r = 7.5\ \mu C/cm^2$ for the ceramics prepared without THOME. The higher maximum dielectric constant with a sharp peak in the ϵ' versus temperature curve is associated with a larger grain size (>2 μm) in the ceramic prepared with THOME, as revealed by SEM. On the other hand, the ceramics prepared without THOME showed a finer particle size (<1 μm) and a broad maximum in the dielectric peak. The excellent ferroelectric properties of PEG(S)T ceramics make the material a very promising candidate for applications in advanced electromechanical devices.

Acknowledgment. This work was supported by Natural Science and Engineering Research Council of Canada (NSERC).

CM049134S

---

(24) Chattopadhyay, S.; Ayyub, P.; Palkar, V. R.; Multani, M. *Phys. Rev. B* **1995**, *52* (18), 13177.