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Reaction chemistry and subsolidus phase equilibria in lead-based relaxor systems:

Part I *Formation and stability of the perovskite and pyrochlore compounds in the system PbO-MgO-Nb_2O_5*

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The reaction chemistry involved in the synthesis of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ $[Pb_3MgNb_2O_9]$ was studied by the solid state reaction technique using precursor oxides as reactants. At the initial stage of the reaction process, a large fraction of PbO present in the mixtures combined with Nb_2O_5 and a small amount of MgO to form an oxygen-deficient pyrochlore phase with a composition $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ $[Pb_6MgNb_6O_{22}]$. The pyrochlore phase thus formed further reacted with the remaining PbO and MgO to yield the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. The pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ accomodates a small amount of PbO into its lattice and forms a narrow homogeneity range which extends from the composition $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ $[Pb_6MgNb_6O_{22}]$ to a composition $Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}$ $[Pb_7MgNb_6O_{23}]$ with a corresponding increase in the lattice constant value from $a = 10.586$ to 10.601 Å. The pyrochlore phase melts incongruently at a temperature near 1230 °C to yield $Mg_4Nb_2O_9$ and a liquid. Below this temperature, the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ coexists with the pyrochlore solid solutions. However, the compound $Pb(Mg_{1/3}Nb_{2/3})O_3$ is not compatible with Nb_2O_5 and these two phases react with one another to form the pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ and MgO.

1. Introduction

Perovskite solid solutions in the lead-based relaxor systems exhibit excellent dielectric and electrostrictive properties, and are currently of considerable interest as materials for electronic applications. Among the more common solid solutions in the various relaxor systems, the most vigorously explored as well as widely published system is $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$. During the last several years, numerous studies [1–8] related to solid state processing, microstructure development and dielectric properties of various compositions in this particular system have been carried out with a view to develop suitable materials for use as multilayer capacitors. In these studies, it has been generally recognized that solid state reactions between the precursor oxides proceed in several steps during which the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ solid solution appears as the major phase along with a number of intermediate compounds formed as reaction products. As often is the case, an undesirable pyrochlore phase is formed at an early stage of the reaction process which, once formed, is extremely difficult to eliminate, even after repeated heat treatment for a prolonged period. Seemingly, the pyrochlore phase coexists with the perovskite solid solution at elevated temperatures and its presence in the ceramics is detrimental to the dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$. As a result of the inevitable formation of this unwanted pyrochlore phase during synthesis of phase-pure perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, the widespread use of the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ solid solutions as materials for capacitor applications has been somewhat limited.

Numerous attempts have been made so far to develop processing techniques by which perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$-based solid solutions were obtained without the formation of an appreciable amount of the pyrochlore phase. Among the relevant studies, repeated heat treatments of the stoichiometric $Pb(Mg_{1/3}Nb_{2/3})O_3$ compositions [9], minor additions of an excess MgO [3, 10–13] and/or PbO [3, 4, 12–16] to the solid solutions, and reactions between prefabricated $MgNb_2O_6$ and PbO [17] as well as between $Pb_3Nb_2O_8$ and MgO [18] were found to be useful for suppressing the pyrochlore phase formation, thereby, allowing an increase in the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ content of the final product. Also, minor substitutions of Ba in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ solid solutions were found to be effective for obtaining a fine-grained, single-phase perovskite material [19].

Although synthesis of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and its solid solutions with other oxides has been extensively reported in the literature, many ambiguities still persist regarding the nature of the reactions involved in the formation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ using different sets of reactants. Also, the identity of the various reaction products which form at different stages of the reaction process and the compatibility relations between them at different temperatures are not clearly resolved. Numerous studies [2–4, 9, 20–23] reported on the solid state synthesis of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and its solid solutions with $PbTiO_3$ using different sets of reactants have observed that the PbO present in the initial mixtures first reacts with Nb_2O_5 to form several binary lead-niobates. These lead niobates, once formed, further combine with unreacted MgO present in the mixture to yield the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. Although the reaction sequences involved in the formation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ as proposed in these studies are generally acknowledged, their acceptance is by no means universal. For instance, a number of studies aimed at identification and characterization of the various phases formed during the synthesis of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ have identified the pyrochlore phase as a Pb-Mg-niobate ternary phase. Adrianova *et al.* [24] have grown single crystals of a ternary pyrochlore compound and assigned a composition $Pb_2Mg_{0.32}Nb_{1.87}O_7$ to this compound. In a study on solid state synthesis and characterisation of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, Swartz and Shrout [17] have observed that a small amount of MgO was incorporated into the lead niobate pyrochlore lattice and allowed the formation of a ternary pyrochlore phase having a composition similar to that reported by Andrianova *et al.* [24]. In another study, Shrout and Swartz [25] successfully prepared a ternary pyrochlore compound by the solid state reaction technique using precursor oxides and assigned a composition $Pb_{1.83}(Mg_{0.29}Nb_{1.71})O_{6.39}$ to this compound. These workers have indexed the X-ray powder diffraction pattern of this compound on the basis of a cubic unit-cell with $a = 10.5988$ Å. Wakiya *et al.* [26] have grown single crystals of a ternary pyrochlore compound having a composition $Pb_{1.86}Mg_{0.24}Nb_{1.76}O_6$ and assigned a lattice constant value $a = 10.6029$ Å to this compound. In a study related to microstructural characterisation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ using energy dispersive X-ray analysis, Goo *et al.* [27] have identified a ternary pyrochlore compound with a composition $Pb_{2.25}(Mg_{0.27}Nb_{1.79})O_7$. In a similar study, Chen *et al.* [28] have used wavelength dispersive X-ray spectroscopy to determine the composition of the ternary pyrochlore phase and assigned a formula $Pb_2(Mg_{0.25}Nb_{1.75})O_{6.62}$ to this compound. Also, in an attempt to prepare the perovskite compound $Pb(Mg_{1/3}Nb_{2/3})O_3$ by the sol-gel technique using alkoxide precursors, Chaput *et al.* [29] have obtained a ternary pyrochlore phase at a relatively low temperature (250 °C) and proposed a general formula $Pb_2(Mg_xNb_{1.33})O_{5.33+x}$, where $0 < x < 0.66$ for the compound.

Several attempts have been made to stabilize the ternary pyrochlore phase by simultaneously altering the Mg and Nb concentration in diphasic mixtures containing various proportions of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore phase. Thus, Chen and Harmer [30] have successfully produced diphasic mixtures by increasing the Nb concentration and simultaneously decreasing the Mg concentration in a perovskite composition with a general formula $Pb_3(Mg_{1-x}Nb_{2+x})O_{9+3x/2}$, where x varied from 0 to 0.625. These workers have observed that increasing additions of Nb to the B-site of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ lattice led to an increase in the pyrochlore phase content. On the other hand, Wakiya *et al.* [31] have examined the extent of solid solubility of Mg^{2+} in an oxygen-deficient pyrochlore-based compound $Pb_3Nb_4O_7$ ($Pb_{1.5}Nb_2O_{6.5}$) along the composition $Pb_{(3+3x)/2}(Mg_xNb_{2-x})O_{6.5}$, where $0 < x < 0.5$. These workers have observed that with $x = 0.24$, a ternary pyrochlore phase with a composition $Pb_{1.86}Mg_{0.24}Nb_{1.76}O_{6.5}$ was formed. Recently, Mergen *et al.* [32] have examined the microstructures of several diphasic compositions containing various proportions of the pyrochlore and perovskite phases by varying the Mg content in the composition $Pb_{1.83}Mg_{0.29+x}Nb_{1.71-x}O_{6.39-1.5x}$, where $x = 0.1 < x < 0.522$ and obtained a near phase-pure ternary perovskite compound with the Mg concentration $x = 0.522$. It is apparent from the above studies that an oxygen-deficient ternary pyrochlore compound with a substantial compositional variability does exist in the PbO-MgO-Nb_2O_5 system. Nevertheless, considerable disagreements still persist among the aforementioned studies regarding the nature of the pyrochlore phase and its interactions with the other phases leading to the formation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$.

The purpose of the present investigation was to obtain a better understanding of the reaction chemistry involved in the formation of various phases in the Pb-based relaxor system PbO-MgO-Nb_2O_5 and to establish the compatibility relations between them. In Part I of this study, attention was mainly focused on the identification of various phases, especially, the ternary pyrochlore phase which formed at an early stage of the reaction process. The nature and characteristics of the pyrochlore phase were studied and its compatibility relations with $Pb(Mg_{1/3}Nb_{2/3})O_3$, PbO and MgO established. Various data evolved from this study were used to derive the possible reaction mechanisms leading to the formation of a single-phase perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$.

2. Experimental

2.1. Sample preparation and processing technique

A series of compositions containing appropriate proportions of the precursor oxides were prepared from analytical reagent-grade PbO (99.99%), MgO (Electronic grade) and Nb_2O_5 (99.9%) powders. Mixtures representing the ternary compositions were mixed under ethanol, dried in an oven and pressed into pellets. The pellets were then stacked on prefabricated $Pb(Mg_{1/3}Nb_{2/3})O_3$ setters inside a covered alumina crucible filled with $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder to avoid

PbO loss during heat-treatment. The specimens were heat treated in air at various predetermined temperatures between 700 and 1250 °C for periods ranging from 2 to 8 h at a heating rate of 10 °C/min. At the end of the heat treatment process, the specimens were cooled to room temperature inside the furnace and then subjected to various analyses for phase identification.

During preliminary heat-treatment runs, it was observed that several mixtures, especially those containing large proportions of PbO, incurred a weight-loss due mainly to the volatilization of PbO from the specimens. The amounts of the PbO loss incurred at various heat treatment temperatures were determined by the differences in weight of the specimens before and after heat-treatment. To prevent an excessive PbO loss, the crucible containing the specimens was embedded in precalcined $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder inside a second crucible having a slightly larger diameter. The crucible was then covered with a tightly-fitted lid and the whole assembly was placed inside the furnace ready for heat-treatment. By this arrangement, the vapour pressure of PbO surrounding the specimens during heat-treatment was substantially increased and, as a result, the amount of the PbO loss was significantly reduced. Nevertheless, a complete elimination of PbO volatilization could not be achieved, especially when the specimens were heat treated at elevated temperatures (>850 °C) regardless of the precautions adopted in this study.

2.2. Phase identification and characterization

2.2.1. *X-ray diffraction analysis*

In order to obtain an understanding of the reaction sequences involved in this system and to identify different intermediate reaction products that formed at various stages of the reaction process, the X-ray powder diffraction technique (XRD) was extensively used and the data thus obtained were carefully examined. The crystalline phases present in the heat treated specimens were identified by XRD (Scintag, Model-PAD V, Santa Clara, CA, USA) using Ni-filtered CuK_α radiation. The XRD patterns were compared with the standard patterns available in the JCPDS card file. A ternary pyrochlore compound, which was found to appear in almost all the specimens examined in this study, was distinguished from other phases by discerning the three intense peaks occurring at $d_{222} = 3.06$ Å, $d_{400} = 2.65$ Å and $d_{440} = 1.87$ Å. The unit-cell parameters for the single-phase pyrochlore compound were derived from the powder data using a computerized least-square refinement program. Powder patterns were obtained at diffraction angles ranging from 10° to 130° using high-purity silicon powder as an internal standard. The extent of the pyrochlore solid solution was determined by XRD analysis of the selected specimens which were first equilibrated at 900 °C and then rapidly cooled to room temperature. Prior to analyzing the various data, the XRD profiles were corrected for background and stripped off $K\alpha_2$ peaks with a pattern processing software package.

2.2.2. *Microstructural analysis*

Both polished sections and fracture surfaces of the heat treated specimens were examined by scanning electron microscopy (SEM) (JEOL, Model JCM-35CF, Tokyo) using both secondary emission and backscatterd electron imaging. The various phases present in the specimens were identified by energy dispersive X-ray analysis (EDX) (Tracor Northern, Wisconsin, USA) using representative areas exhibiting homogeneous microstructures. Many of the reaction products that formed during the synthesis of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore-based solid solutions had compositional ranges sufficiently narrow so that a semiquantitative point analysis employing EDX was found to be very reliable. Nevertheless, wavelength dispersive spectroscopy (WDS) (JEOL, Model JSM-5800, Tokyo) was employed periodically for quantitative analysis of selected compositions using polished surfaces. High-purity $PbTiO_3$, MgO and Nb_2O_5 powders sintered to high densities were employed as standards for the WDS analysis. The various EDS and WDS data thus obtained were used in conjunction with the XRD data to determine the composition of the reaction products and the extent of the pyrochlore solid solutions which occur in this system.

3. Results and discussion

3.1. Interactions between the precursor oxides

3.1.1. *Melt formation and PbO loss during heat-treatment process*

Preliminary heat treatments of the compositions containing variable proportions of the precursor oxides PbO, MgO and Nb_2O_5 revealed that the reaction products which formed at temperatures between 700 °C and 900 °C consisted of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and a pyrochlore phase as major phases. At temperatures between 700° and 800 °C, these two phases appeared with some unreacted PbO and a small amount of MgO; however, no trace of Nb_2O_5 was detected in these specimens. At temperatures near 850 °C, small amounts of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore phases combined with the unreacted PbO to form a ternary eutectic liquid phase. The evidence obtained in this study indicated that the eutectic composition is located very close to the PbO-rich region of the ternary system PbO-MgO-Nb_2O_5. However, attempts to determine the exact composition of the eutectic and its melting temperature using different experimental techniques met with only limited success. For instance, specimens containing a high proportion of PbO, when melted in a Pt-crucible at temperatures above 850 °C, resulted in an excessive weight loss due to volatilization of PbO from the melt which led to a compositional change. Whereas, during preliminary DTA runs, PbO present in the mixtures reacted with the Pt-holder at temperatures near 850 °C. This coupled with PbO volatilization from the specimens led to erroneous results. Inevitably, none of these experimental procedures was found to be suitable for the determination of the composition and melting temperature of the eutectic.

Nevertheless, the presence of the PbO-rich eutectic liquid at grain junctions and grain boundary regions at a temperature near 850 °C was detected by SEM/EDX. From the data thus obtained, it was apparent that the products which formed at an early stage of the reaction process combined with the PbO present in the mixtures to yield a PbO-rich liquid phase at a temperature just below 850 °C.

An important finding which has clearly emerged from the microstructural characterisation and weight loss measurement data was the gradual increase in the rate of PbO volatilization at temperatures above 800 °C regardless of the experimental precautions used. In general, it was observed that the weight loss due to PbO volatilization was closely associated with the melt formation in this system. For instance, when specimens containing 5 g material were heat treated at temperatures of 750° and 800 °C for a period of 3 h at a heating rate of 10 °C/min did not incur any appreciable changes in weight. On the other hand, the same specimens when heat treated at temperatures between 850° and 950 °C under the same experimental conditions showed weight loss values ranging from 1 to 1.5%. Seemingly, at the heating rate of 10 °C/min, the weight loss due to the PbO volatilization commenced with the formation of the liquid phase near 850 °C and gradually increased with increasing heat treatment temperatures reaching a maximum at 950 °C. Evidently, the PbO loss allowed the compositions to shift to a phase-field area in which the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ was found to coexist with several other phases, especially, the pyrochlore phase. The observed changes in the phase assemblage led to a significant change in the microstructure of the ceramics which are elaborated in the following section.

3.1.2. Characterization of reaction products

The XRD pattern of a specimen heat treated at 750 °C is exhibited in Fig. 1A which reveals the presence of substantial amounts of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore phase as major reaction products. However, a small amount of unreacted PbO and, probably, some MgO are also present in this specimen. It was recognized that the XRD data alone could neither confirm nor rule out the presence of MgO in the heat treated specimens because the high intensity XRD peak of MgO at $d_{200} = 2.106$ Å is overlapped by the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ peak at $d_{200} = 2.03$ Å. Nevertheless, the presence of MgO in the specimens was confirmed by SEM/EDX analysis. The SEM micrograph of this specimen is shown in Fig. 2 which reveals the presence of a large fraction of the pyrochlore phase appearing in the form of rectangular particles in a fine grained matrix consisting mostly of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ grains. A few dark particles which appeared as a discrete phase dispersed within the matrix have been identified as MgO. At temperatures above 750 °C, no significant change in the phase assemblages was observed except that a substantial increase in the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ with a corresponding decrease in the amount of the pyrochlore phase ensued with increasing heat treatment temperatures.

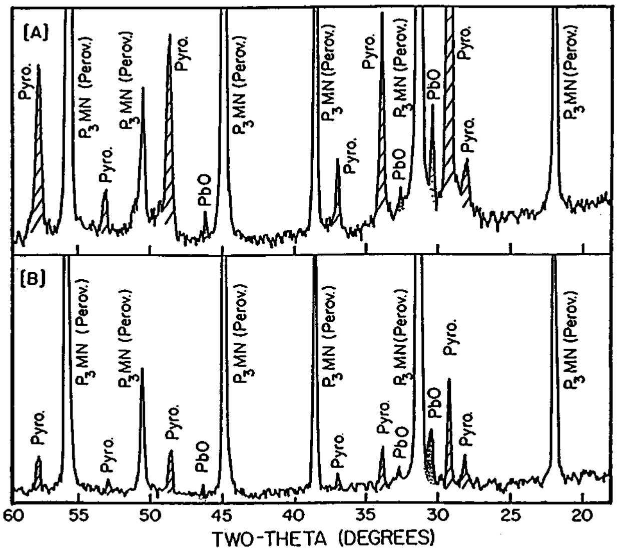

Figure 1 X-ray powder diffraction patterns of a stoichiometric composition of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ heat treated for 3 h at (A) 750 °C and (B) 800 °C.

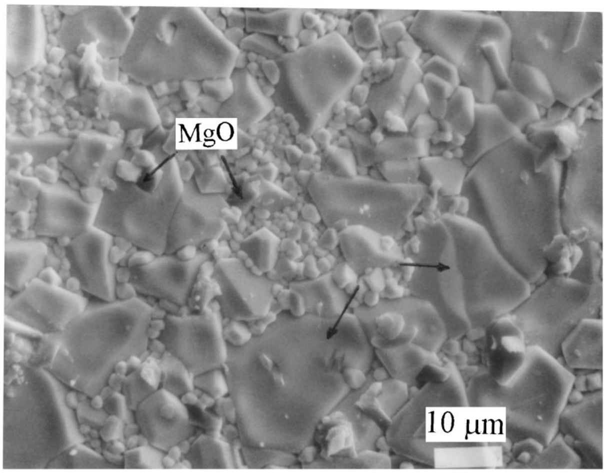

Figure 2 SEM micrograph of a stoichiometric composition of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ heat treated at 750 °C for 3 h showing the distribution of various reaction products.

The XRD pattern of a specimen heat treated at 800 °C is exhibited in Fig. 1B showing the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ as the major phase along with a small amount of the pyrochlore phase. Seemingly, a small amount of PbO and perhaps traces of MgO remained unreacted at this temperature. No significant microstructural changes were found to occur at this temperature except that the fraction of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase had substantially increased. However, on heat treating the specimens at temperatures above 800 °C, a change in the phase assemblages due mainly to the formation of a liquid phase led to a drastic change in the microstructure. The SEM micrograph of a specimen heat treated at 850 °C is shown in Fig. 3. This is typical of the microstructures in which the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, pyrochlore phase and a small amount of MgO were found to coexist with a PbO-rich liquid phase. As can be seen in this micrograph, the liquid phase that has been solidified on cooling predominantly appears in the grain junctions and grain boundaries of $Pb(Mg_{1/3}Nb_{2/3})O_3$. Also visible in

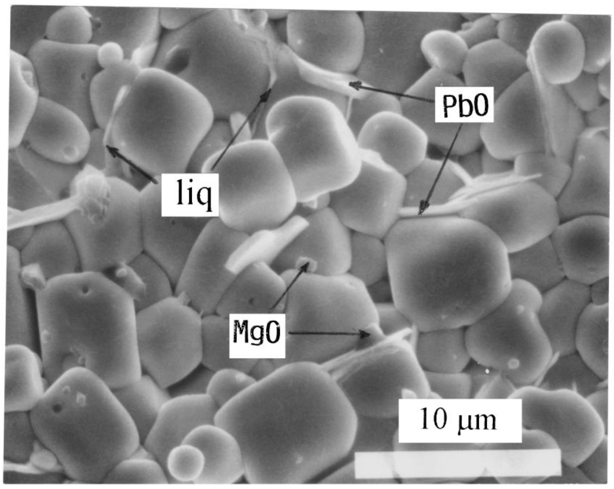

Figure 3 SEM micrograph of a stoichiometric composition of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ heat treated at 850 °C for 3 h showing melt formation and crystallization of PbO in the grain boundaries.

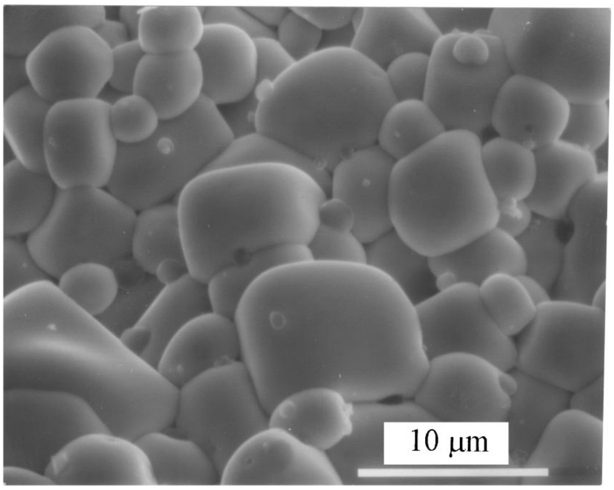

Figure 4 SEM micrograph of a stoichiometric composition of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ heat treated at 900 °C for 3 h showing a near single-phase microstructure.

the grain boundary region, a white phase appearing in the form of elongated platelets and/or as long needles was identified as PbO. The characteristic morphology of the platelets and needles suggests that these have probably formed during cooling by crystallizing from the melt.

XRD analysis of several specimens which were heat treated at temperatures above 850 °C revealed that a near-single-phase perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ material was formed along with a small amount of the pyrochlore phase; however, no trace of PbO could be detected in these specimens. A SEM micrograph of the specimen heat treated at 900 °C is shown in Fig. 4 and resembles that of a single-phase material. The large rounded grains of $Pb(Mg_{1/3}Nb_{2/3})O_3$ with grain-size varying from 2 to 10 μm suggest that significant grain growth has occurred, probably due to the formation of a PbO-rich liquid phase at this temperature. Presumably, during the heat treatment process, the liquid phase undergoing rapid PbO volatilization had led to the development of a dense but inhomogeneous microstructure and thus caused a wide grain-size variation in the specimen. EDS analysis revealed the presence of a small fraction of the pyrochlore phase in isolated areas within the $Pb(Mg_{1/3}Nb_{2/3})O_3$ matrix. Also, a small amount of MgO, appearing mostly in the form of spherical particles, can be found randomly distributed within the matrix. Seemingly, rapid volatilization of PbO at this temperature had led to a depletion of the liquid present in the grain boundaries and caused a significant change in the microstructure. This probably explains why PbO was not detected in the XRD patterns and why a residual PbO-rich liquid could not be observed in the grain boundary region.

3.2. Formation and stability of ternary pyrochlore phase

3.2.1. Characterization of the pyrochlore phase

In an earlier published study performed by Shrout and Swartz [25], the existence of an anion-deficient ternary pyrochlore phase with a composition $Pb_{1.83}(Mg_{0.29}Nb_{1.71})O_{6.39}$ was confirmed. In this study, the X-ray d-spacings for the pyrochlore phase, which were derived from a lattice constant $a = 10.5988$ Å and a pycnometric density of 7.2 g/cm^3, have been reported. In the present investigation, this and several other compositions lying close to the pyrochlore phase were equilibrated at different temperatures and then characterised by XRD, SEM/EDS and WDS. It was evident from these results that the ternary pyrochlore phase occurs at a composition with a $PbO:MgO:Nb_2O_5$ molar ratio of $6:1:3$ which corresponds to a formula $Pb_6MgNb_6O_{22}$. In terms of the $A_2B_2O_7$ pyrochlore structural form, this formula corresponds to an oxygen-deficient pyrochlore composition of $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$. The XRD pattern of this ternary pyrochlore phase was indexed on the basis of a cubic unitcell with $a = 10.5867$ Å. The interplanar spacings with the corresponding intensities for the pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ are given in Table I. It is to be noted that currently there are two X-ray index cards available in the JCPDS file for the pyrochlore compound with a chemical composition $Pb_{1.83}Nb_{1.71}Mg_{0.029}O_{6.39}$ [33, 34]. As is apparent from the various data presented in these cards, they belong to a pyrochlore compound having the same chemical formula that has been prepared by the same group of researchers showing exactly the same set of d-spacings having the identical hkl values which are indexed on the basis of a cubic-unit-cell with $a = 10.5988$ Å and a space group Fd3m.

From the various XRD and WDS data obtained in this study, it was apparent that a small amount of PbO enters into the pyrochlore lattice of $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$, thereby, allowing the formation of a narrow homogeneity range in the ternary system $PbO\text{-}MgO\text{-}Nb_2O_5$. It was observed that with the incorporation of PbO, the homogeneity range of the pyrochlore phase extends from the composition $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ [$Pb_6MgNb_6O_{22}$] to a composition $Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}$ [$Pb_7MgNb_6O_{23}$] with a corresponding increase in the lattice parameter

TABLE I X-ray powder diffraction data for the ternary pyrochlore compound $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$

I/I_o	d_{obs}	d_{calc}	$h\,k\,l$
15	6.11	6.1122	1 1 1
1	3.743	3.7430	2 2 0
12	3.192	3.1920	3 1 1
100	3.056	3.0561	2 2 2
50	2.646	2.6467	4 0 0
15	2.429	2.4288	3 3 1
2	2.161	2.1610	4 2 2
5	2.037	2.0374	3 3 3/5 1 1
60	1.871	1.8715	4 4 0
2	1.790	1.7895	5 3 1
2	1.674	1.6739	6 2 0
2	1.614	1.6145	5 3 3
45	1.596	1.5960	6 2 2
10	1.528	1.5280	4 4 4
1	1.482	1.4824	5 5 1/7 1 1
2	1.378	1.3783	5 5 3/7 3 1
4	1.323	1.3233	8 0 0
2	1.293	1.2934	7 3 3
2	1.222	1.2224	5 5 5/7 5 1
12	1.214	1.2144	6 6 2
10	1.183	1.1836	8 4 0
2	1.162	1.1620	9 1 1/7 5 3
2	1.128	1.1285	6 6 4
3	1.080	1.0805	8 4 4
1	1.064	1.0640	9 3 3/7 7 1
8	1.023	1.0235	9 5 1/7 7 3
1	0.9546	0.9546	11 1 1/7 7 5
2	0.9357	0.9357	8 8 0
1	0.9250	0.9250	9 7 1/11 3 1
1	0.8980	0.8980	9 7 3/11 3 3
2	0.8947	0.8947	10 6 2
2	0.8822	0.8822	8 8 4/0 12 0
2	0.8292	0.8292	9 9 1

Indexed on the basis of a cubic unit-cell with $a = 10.5867$ Å.

value from $a = 10.5867$ to 10.6012 Å. Seemingly, the compositions represented by the formulae $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ [$6PbO{\cdot}MgO{\cdot}3Nb_2O_5$] and $Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}$ [$7PbO{\cdot}MgO{\cdot}3Nb_2O_5$] are the two end members of an oxygen-deficient pyrochlore-based solid solution with a general formula $Pb_{2-x}(Mg_{0.286}Nb_{1.714})O_{6.571-x}$, where $x > 0 > 0.286$. Beyond the PbO-rich end composition of this homogeneity range i.e., $Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}$, traces of PbO were found to appear in the XRD patterns along with the pyrochlore phase indicating that these two phases are compatible with one another. It is interesting to note that the various compositions which have been proposed for the ternary pyrochlore phase in the earlier published studies [24–29] lie either within this homogeneity range or correspond to the compositions which are located very near to it. Thus, the pyrochlore compound $Pb_{1.83}(Mg_{0.29}Nb_{1.71})O_{6.39}$ originally proposed by Shrout and Swartz (25) actually represents a composition which lies near to the middle of the homogeneity range.

3.2.2. Melting behaviour and stability of the pyrochlore phase

From the various XRD and SEM/EDX analyses performed in the present investigation, it was evident that the ternary pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ [$6PbO{\cdot}MgO{\cdot}3Nb_2O_5$] melts incongruently at a temperature just below 1250 °C to yield $Mg_4Nb_2O_9$ and liquid. It is to be noted that due to the incongruent nature of melting, only a limited amount of liquid was formed at the onset of melting of this compound. Thus, the exact melting temperature of the pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ was difficult to determine from a phase-pure composition. Nevertheless, the melting characteristics of this compound was clearly demonstrated when a diphasic mixture containing the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore compound was heat treated at various temperatures and then subjected to XRD and SEM/EDX examinations. The XRD pattern of a specimen that has been partially melted at 1250 °C and then rapidly cooled to room temperature is shown in Fig. 5. The pattern shows the presence of a large fraction of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ phases along with a small amount of $Mg_4Nb_2O_9$. This is consitent with a recently published study by Lu and Wen (35) who observed that the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ dissociates at temperatures between 1250 and 1300 °C

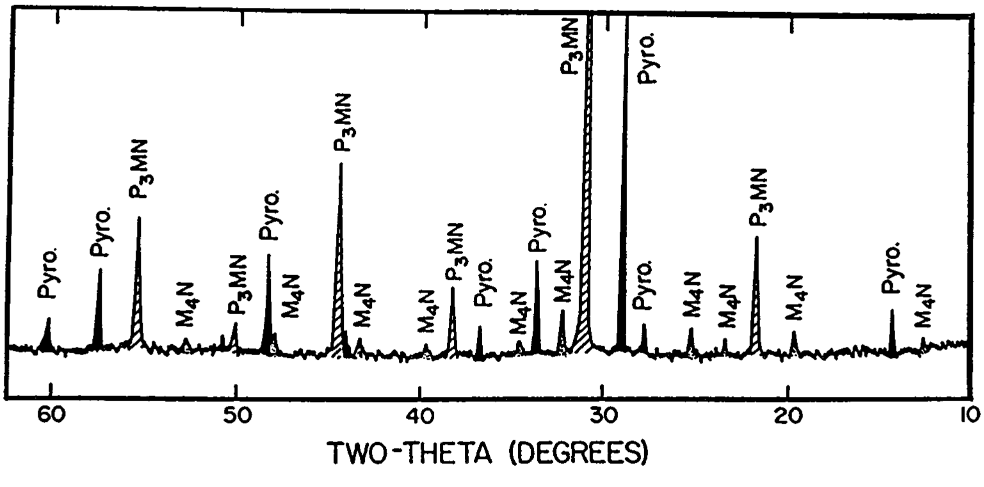

Figure 5 X-ray powder diffraction pattern of a diphasic mixture containing perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore phase which was partially melted at 1250 °C showing the formation of $Mg_4Nb_2O_9$ (P_3MN = Perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, Pyro = Pyrochlore phase, and $M_4N = Mg_4Nb_2O_9$).

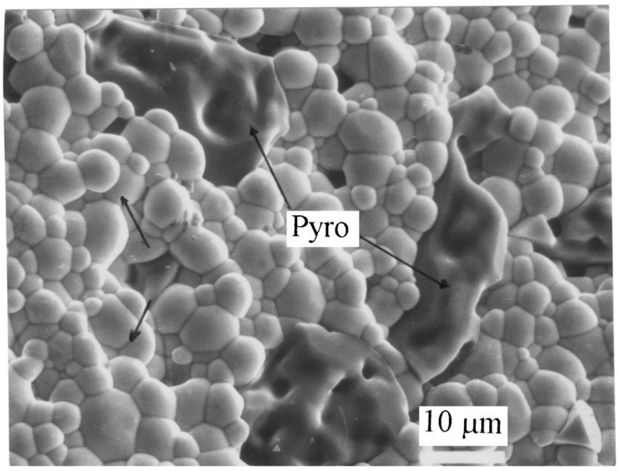

Figure 6 SEM micrograph of a diphasic mixture containing perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the ternary pyrochlore phase showing the onset of melting of the pyrochlore phase at 1250 °C.

with the evaporation of PbO and results in the formation of the pyrochlore phase with a small amount of $Mg_4Nb_2O_9$. A SEM micrograph exhibiting the onset of melting of the ternary pyrochlore phase at 1250 °C is shown in Fig. 6. As evident from the micrograph, the phase assemblage present herein essentially consists of a fine-grained matrix of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ with several large and partially melted particles of the pyrochlore phase. The EDX spectra of a sintered and unmelted pyrochlore grain is exhibited in Fig. 7a which reveals the characteristic peaks of Pb, Mg and Nb. By comparison, the EDX pattern exhibited in Fig. 7b, which was obtained from the solid grain that had formed after partial melting of the specimen, shows the presence of only the Mg and Nb peaks. The Mg/Nb ratio as derived from the EDX analysis indicated that the composition of this solid phase corresponds to that of the compound $Mg_4Nb_2O_9$.

3.3. Compatibility relations between the phases

To obtain a clear understanding of the reaction chemistry involved in the formation of various reaction products and their stability at different temperatures, subsolidus compatibility relations between the phases occurring in the system $PbO\text{-}MgO\text{-}Nb_2O_5$ were examined. Based on the data obtained in this study, a partial phase diagram is constructed and shown in Fig. 8. The phase diagram essentially consists of several pseudobinary joins which the ternary phases, namely, the perovskite and the pyrochlore compounds, form with PbO and MgO. Since liquid formation in this system occurs at a temperature just below 850 °C, the various pseudobinary joins as depicted herein represent the subsolidus compatibility relations at temperatures up to 825 °C. As is evident from the phase diagram, PbO and MgO are compatible with each other as well as with the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. Thus, the tie-lines which these phases form with one another constitute a compatibility triangle within the system $PbO\text{-}MgO\text{-}Nb_2O_5$ in which both PbO and MgO coexist with $Pb(Mg_{1/3}Nb_{2/3})O_3$. Also, PbO and MgO are compatible with the pyrochlore solid solutions and thus, several tie-lines occur between these phases in the phase diagram as shown in Fig. 8. Among these, the one which occurs between the ternary pyrochlore and PbO shows the presence of a narrow homogeneity range representing the pyrochlore solid solutions. The various compositions located within this homogeneity range were found to be compatible with the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. As a result, a diphasic area occurs within the ternary system in which the complete range of the pyrochlore solid solutions and the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ coexist with one another.

An important consequence of the compatibility relations as evolved from this study is that simultaneous additions of PbO and MgO to the pyrochlore phase result in a compositional shift and lead to the formation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. This is consistent witht the earlier findings [28–32] in which a variation in the Mg/Nb ratio of either the ternary perovskite or the pyrochlore phase was found to cause a compositional shift from the pyrochlore to the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and vice versa. It is further evident from the phase diagram that a PbO loss from the stoichiometric $Pb(Mg_{1/3}Nb_{2/3})O_3$ mixture results in a compositional shift to a phase-field area in which both the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the pyrochlore

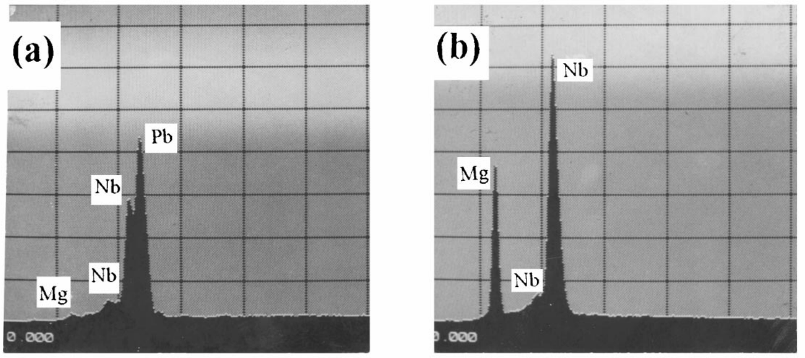

Figure 7 EDX patterns of different grains of the ternary pyrochlore composition (a) sintered grain of phase-pure pyrochlore phase, (b) solid grain that formed after partial melting at 1250 °C.

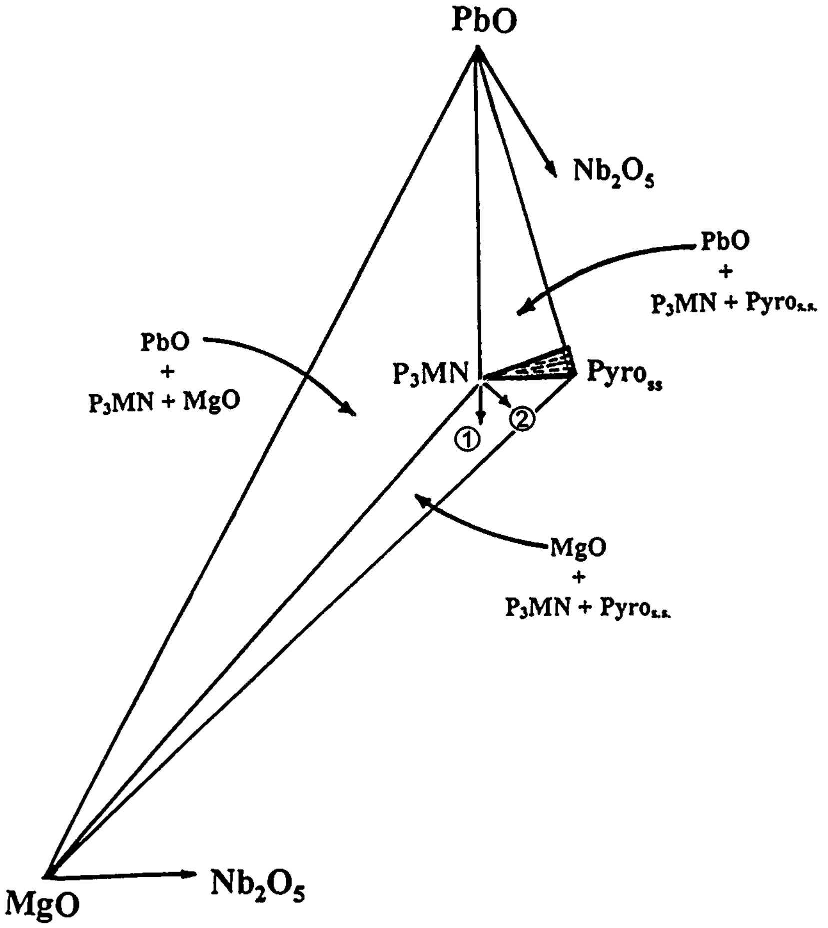

Figure 8 Partial phase diagram of the ternary system PbO-MgO-Nb$_2$O$_5$ showing the subsolidus compatibility relations between the various phases at 800 °C (P$_3$MN = perovskite Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and Pyro$_{s.s.}$ = Pyrochlore solid solutions).

phase coexist with MgO. This area is depicted by the arrow marked ① in the phase diagram shown in Fig. 8.

Another important feature which has emerged from the present study is the incompatibility between the compounds Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and Nb$_2$O$_5$. XRD patterns of several heat treated specimens indicated that the perovskite Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ reacts with Nb$_2$O$_5$ to yield the ternary pyrochlore phase and MgO. In the phase diagram (Fig. 8), the phase-field area to which the stoichiometric Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ composition shifts with additions of an excess Nb$_2$O$_5$ is indicated by the arrow marked ②. Thus, it is clear that minor additions of excess Nb$_2$O$_5$ to the stoichiometric perovskite Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ lead to the formation of the pyrochlore phase.

3.4. Reaction chemistry in the formation of perovskite Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$

Interactions between the precursor oxides and reaction sequences in the formation of the perovskite Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ have long been the subject of much controversy. In a number of earlier published studies related to the synthesis of perovskite Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ [2, 4, 9, 11–13, 20–23], a pyrochlore phase which mostly appeared at the early stages of the reaction process has been identified as Pb$_3$Nb$_4$O$_{13}$. In these studies, it has been reported that the pyrochlore Pb$_3$Nb$_4$O$_{13}$, which was formed by the solid state reaction between PbO and Nb$_2$O$_5$, subsequently combined with the unreacted MgO present in the mixture to yield the perovskite Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. In the present study, no experimental evidence was obtained to corroborate these findings. Nevertheless, the possibility of the formation of the pyrochlore Pb$_3$Nb$_4$O$_{13}$ and other binary Pb-niobates by preferential reaction between PbO and Nb$_2$O$_5$ at an initial stage of the reaction process cannot be completely overruled. It is recognized that the formation of Pb$_3$Nb$_4$O$_{13}$ or any other intermediate phases in this system largely depends on several variables, such as the nature of the starting materials, particle-size of the reactants, time-temperature variations, rate of heating, and the amount of PbO loss that incurs during the heat treatment process. However, from the evidence obtained in the present investigation, it has become apparent that the correct identity of the pyrochlore phase that appears in this particular system cannot be satisfactorily resolved by the XRD analysis alone. The difficulty in the identification of this phase lies in the fact that the binary compound Pb$_3$Nb$_4$O$_{13}$, which can also be represented by an oxygen-deficient pyrochlore formula Pb$_{1.5}$Nb$_2$O$_{6.5}$, is isostructural with the ternary pyrochlore Pb$_{1.714}$(Mg$_{0.286}$Nb$_{1.714}$)O$_{6.286}$. Thus, these two compounds when subjected to XRD analysis yield essentially identical XRD patterns which are virtually impossible to distinguish from one another. However, the characteristic microstructural features as observed by the SEM examinations together with the EDX and

WDS elemental analysis of the individual phases which appeared at various stages of the reaction process were found to be very useful in obtaining reasonably accurate and consistent results. Thus, microstructural analysis of the heat treated specimens has been considered to be a more reliable means for phase identification in this particular system.

In accordance with the various data obtained in this study, it seems reasonable to believe that the solid state reactions between the precursor oxides leading to the formation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ proceed in two stages. At the intial stages of the reaction process, a large fraction of PbO present in the stoichiometric $Pb(Mg_{1/3}Nb_{2/3})O_3$ composition combines with all of the Nb_2O_5 and a small amount of MgO to yield the ternary pyrochlore phase according to the equation:

$$\begin{aligned} &6PbO + MgO + 3Nb_2O_5 \\ &\quad \rightarrow 3.5Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286} \\ &\qquad Pb_6MgNb_6O_{22}(\text{Pyrochlore}) \end{aligned} \tag{1}$$

The validity of the above reaction is further corroborated by the XRD and thermal analysis data reported in several earlier studies dealing with the formation mechanisms of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (20, 36) and the ternary pyrochlore phase (37). The data obtained in the present investigation indicated that at the initial stages of the reaction process, interactions between the precursor oxides led to the formation of the ternary pyrochlore phase as a major reaction product while small proportions of unreacted MgO and PbO remained in the specimen. With increasing reaction temperatures and time, the pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ further combined with the remaining PbO and MgO to yield the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ according to the equation:

$$\begin{aligned} &3.5Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286} + 3PbO + 2MgO \\ &\quad Pb_6MgNb_6O_{22}(\text{pyrochlore}) \\ &\quad \rightarrow 9Pb(Mg_{1/3}Nb_{2/3})O_3 \\ &\quad Pb_3MgNb_2O_9(\text{Perovskite}) \end{aligned} \tag{2}$$

Combining Equations 1 and 2, the reaction between the precursor oxides leading to the formation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ can be summarized as follows:

$$\begin{aligned} 3PbO + MgO + Nb_2O_5 \rightarrow 3&Pb(Mg_{1/3}Nb_{2/3})O_3 \\ &Pb_3MgNb_2O_9(\text{Perovskite}) \end{aligned} \tag{3}$$

It is to be noted that the reaction sequences involved in the formation of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, and the appearance and disappearance of the ternary pyrochlore phase as outlined above are consistent with the compatibility relationships shown in the phase diagram (Fig. 8). However, it should also be noted that regardless of the various precautions taken during the synthesis of a phase-pure perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, the resulting products inevitably contained a small amount of the pyrochlore phase. As described earlier, the formation of the pyrochlore phase was attributed mainly to the volatilization of PbO from the specimens at temperatures above 800 °C. Since PbO predominantly volatilized off from the surface, a large fraction of the pyrochlore phase was found near the top along with the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ present at the interior of the specimens.

An interesting point worth mentioning here is that in recent years, an alternate method, commonly referred to as the Columbite method [25], has been extensively used with considerable success. In this method, solid-state reaction between appropriate proportions of pre-reacted $MgNb_2O_6$ and PbO allows the formation of a near pyrochlore-free perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ material. It was observed that in this method, the reaction proceeds to completion at a much faster rate with very little PbO losses and, as a result, a near single-phase perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ was readily obtained. However, subsequent studies [3, 23, 38] have revealed that if proper precautions are not taken for suppressing the PbO volatilization during the reaction process, it is equally difficult to obtain a pyrochlore-free perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ as an end product. Thus, as in the case of the conventional processing technique in which the precursor oxides are used as reactants, the initial reaction temperature in the Columbite method must also be restricted to 830 °C to obtain a phase-pure material. The reaction chemistry involved in the solid state synthesis of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ by mixed-oxide processing techniques using prereacted compounds and their compatibility relations with the pyrochlore phase and various Mg- and Pb- niobates in the ternary system $PbO\text{-}MgO\text{-}Nb_2O_5$ will be reported in Part II of this investigation.

4. Conclusions

In the solid state synthesis of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ $[Pb_3MgNb_2O_9]$ using precursor oxides, interactions between the constituent oxides allow the formation of an oxygen-deficient ternary pyrochlore phase with a composition $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ $[Pb_6MgNb_6O_{22}]$. The pyrochlore phase thus formed further reacts with appropriate proportions of PbO and MgO to yield the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. The pyrochlore phase accomodates a small amount of PbO into its lattice and forms a narrow homogeneity range which extends from the composition $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ to the composition $Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}$ $[Pb_7MgNb_6O_{23}]$ with a slight increase in the cubic unit-cell parameter from $a = 10.586$ to 10.601 Å.

The formation of a phase-pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ is difficult to accomplish by the conventional solid state processing technique due mainly to the volatilization of PbO from the specimens. During the reaction process, a PbO loss from the stoichiometric $Pb(Mg_{1/3}Nb_{2/3})O_3$ mixture results in a compositional change and leads to the formation of a ternary pyrochlore phase. This pyrochlore phase, once formed, combines with a part of the pervoskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and unreacted PbO that remained in the mixture to yield a ternary eutectic liquid at a temperature near 850 °C. The melt formation accompanied by an enhancement of the PbO volatilization from the specimen results in a change in the composition which leads to an increase in the pyrochlore phase content of the end product.

The pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ melts incongruently at a temperature near 1250 °C to yield $Mg_4Nb_2O_9$ and a liquid. Below this temperature, the pyrochlore phase is compatible with the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and thus, once formed, these two phases coexist with one another.

The perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ is not compatible with Nb_2O_5 and a reaction between these phases results in the formation of the pyrochlore $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ and MgO. Thus, a minor addition of excess Nb_2O_5 to the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ leads to the formation of the pyrochlore phase and MgO.

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