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

Part II *The ternary system PbO-MgO-Nb_2O_5*

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Subsolidus compatibility relations in the lead-based relaxor system PbO-MgO-Nb_2O_5 were investigated by the solid-state reaction technique and the various phase assemblages that occur at 825°C in this system established. The existence of two previously reported ternary compounds, i.e. a cubic perovskite $Pb_3MgNb_2O_9$ [$Pb(Mg_{1/3}Nb_{2/3})O_3$] and an oxygen-deficient cubic pyrochlore $Pb_6MgNb_6O_{22}$ [$Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$] was confirmed. A minor amount of PbO enters into the pyrochlore lattice and forms a narrow homogeneity range within the ternary system PbO-MgO-Nb_2O_5 which corresponds to a general formula $Pb_{2-x}(Mg_{0.286}Nb_{1.714})O_{6.571-x}$, where $0 > x > 0.286$. At subsolidus temperatures (<825°C), the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ is compatible with the ternary pyrochlore solid solution and together they form a biphasic area within the system in which the perovskite and the pyrochlore phases coexist with one another. Both PbO and MgO are compatible with the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ and these phases constitute a compatibility triangle with one another in the ternary system. However, the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ is not compatible with Nb_2O_5 and these two phases react with one another to yield the pyrochlore $Pb_6MgNb_6O_{22}$ and MgO. The ternary pyrochlore solid solution is compatible with several binary lead niobates, i.e. $Pb_3Nb_2O_8$, $Pb_5Nb_4O_{15}$, $Pb_2Nb_2O_7$ and $Pb_3Nb_4O_{13}$ and forms pseudobinary tie-lines with these compounds in the ternary system PbO-MgO-Nb_2O_5. The pyrochlores $Pb_3Nb_4O_{13}$ [$Pb_{1.5}Nb_2O_{6.5}$] and $Pb_6MgNb_6O_{22}$ [$Pb_{1.714}(Mg_{0.286}$ $Nb_{1.714})O_{6.286}$] are isostructural compounds and a series of continuous solid solution is formed between them.

1. Introduction

During the last several years, numerous studies related to the processing of perovskite solid solutions involving the lead-based relaxor compound $Pb_3MgNb_2O_9$ [$Pb(Mg_{1/3}Nb_{2/3})O_3$] have been reported and sintering characteristics and microstructure development of several of these solid solution compositions were evaluated for potential use as materials for dielectric [1–8], piezoelectric [9–12] and pyroelectric [13] applications. In practice, superior performance of these materials for various electronic applications, especially, for multilayer ceramic capacitors has been achieved mostly through compositional modifications and microstructure development that require a careful control throughout the successive stages of processing steps starting from powder synthesis to consolidation of the final products. Despite the usefulness of these materials for various electronic devices, several problems related to the processing of a phase-pure product and sintering the same to high densities have been recognized.

In the synthesis of the perovskite compound $Pb_3MgNb_2O_9$ by the conventional solid-state reaction techniques, an undesirable pyrochlore phase is known to appear at an early stage of the reaction process. The pyrochlore phase, once formed, remains stable with the perovskite solid solutions at elevated temperatures and its presence in the ceramics, even in small quantities, has been associated with inferior dielectric properties [2, 3, 14, 15]. Several attempts were made so far to eliminate the unwanted pyrochlore phase during the synthesis of the perovskite $Pb_3MgNb_2O_9$ by introducing alternate processing techniques in which different sets of reactants have been frequently used as precursor materials [16–18]. Of these processing techniques, the most common and widely used technique that has attracted considerable attention at the present time is the Columbite process first reported by Swartz and Shrout [16]. In this technique, magnocolumbite, $MgNb_2O_6$, from which the name of the process was originally derived, is first prepared by the solid-state reaction between equimolar proportions of MgO and Nb_2O_5. $MgNb_2O_6$ thus obtained was then reacted with an appropriate proportion of PbO to form $Pb_3MgNb_2O_9$. However, in this particular process, a slight deficiency of MgO in the final product and volatilization of PbO from the specimens inevitably lead to the formation of an undesirable pyrochlore phase. Thus, the initial stoichiometry of the precursor oxides and optimization of the reaction temperature at which $MgNb_2O_6$ interacts with PbO to yield perovskite $Pb_3MgNb_2O_9$ are very critical. Additionally, volatilization of PbO from the materials during the subsequent sintering process, which increases with increasing temperature, results in a compositional change, thereby, leading to the formation of the undesirable pyrochlore phase. Evidently, minor additions of excess PbO [2–4, 15, 19–23] and/or MgO [2–4, 15, 20, 23–27] to the stoichiometric composition of $Pb_3MgNb_2O_9$ have been found to be effective in enhancing the reaction process, thereby, leading to a substantial increase in the proportion of the perovskite phase in the final product.

In Part I of this study [28], the reaction mechanisms involved in the formation of a pyrochlore phase with a chemical composition $Pb_6MgNb_6O_{22}$ [$Pb_{1.714}$ $(Mg_{0.286}Nb_{1.714})O_{6.286}$] and perovskite $Pb_3MgNb_2O_9$ [$Pb(Mg_{1/3}Nb_{2/3})O_3$] phases have been presented. It was reported in this study that both PbO and MgO are compatible with the perovskite $Pb_3MgNb_2O_9$ and, as such, these oxides remain as stable phases in the sintered ceramics. However, at elevated temperatures, PbO and MgO readily combine with $Pb_3MgNb_2O_9$ to yield a low-melting PbO-rich liquid phase which predominantly remains in the grain boundaries of the sintered ceramics and adversely affects the dielectric properties of the resulting products. As a result, widespread use of excess PbO and/or MgO as additives in the processing of $Pb_3MgNb_2O_9$-based perovskite materials for capacitor applications remains somewhat limited.

From the above-mentioned studies, it has become abundantly clear that in the processing of phase-pure $Pb_3MgNb_2O_9$-based solid solutions and for optimization of the sintering process, an understanding of the compatibility relations existing between the various phases in the system PbO-MgO-Nb_2O_s is very important. The study reported herein, which forms Part II of a continuing investigation related to the development of Pb-based relaxor materials for electronic applications, deals with subsolidus equilibria in the ternary system PbO-MgO-Nb_2O_5. The nature and characteristics of various phase assemblages that form at different heat-treatment temperatures and the subsolidus compatibility relations between the ternary compounds and the various binary Pb- and Mg-niobates that occur in this system were established.

2. Experimental

The precursor oxides used in this study for the preparation of various compositions were high-purity reagent-grade PbO, MgO and Nb_2O_5. The oxides in the form of fine powder were dried in an oven and stored in a dessicator before use. Compositions containing various proportions of the oxides were mixed under alcohol using an agate mortar and pestle. The mixtures were then dried, cold pressed into cylindrical pellets and heat-treated at temperatures between 800° and 950°C for periods ranging from 3 to 6 h. For heat-treatment of the compositions, specimens were placed on sacrificial discs made from the same composition and stacked inside an alumina crucible covered with a tightly fitted lid. The crucible containing the pellets was embedded in coarse-grained calcined $PbZrO_3$ powder inside a covered crucible and then heat-treated at different temperatures for various time periods until equilibrium was attained. This arrangement was found to be very effective in sustaining a PbO-rich atmosphere surrounding the specimens and, as a result, the PbO loss during the heat-treatment process was substantially reduced.

During equilibration of the compositions, it was observed that a number of secondary phases, especially an unwanted pyrochlore phase, remain as stable products even after prolonged heat-treatment of the specimens. To overcome these difficulties and to yield a phase-pure product, the starting materials and the heat-treatment procedure i.e. temperature and time used for the equilibration of the various specimens were carefully controlled. For several compositions, prefabricated binary Pb-niobates and Mg- niobates, prepared by the solid-state reaction technique, were used as starting materials. Thus, the perovskite $Pb_3MgNb_2O_9$ was prepared by heat-treating a mixture containing appropriate proportions of prefabricated $MgNb_2O_6$ and PbO at 825°C for 3 hrs. Whereas, the ternary pyrochlore $Pb_6MgNb_6O_{22}$ was obtained by solid-state reaction between appropriate proportions of PbO, MgO and Nb_2O_5 at 800°C for 3 hrs.

Several compositions, especially those containing a high proportion of PbO, were found to undergo partial melting when heat-treated at temperatures below the melting point of PbO (886°C). The melt formation was attributed to eutectic melting near the PbO-rich region of the system PbO-MgO-Nb_2O_5. In most cases, the melting was accompanied by volatilization of PbO from the specimens, the rate of which increased rapidly with increasing temperature. Consequently, the equilibration temperatures used for these compositions were varied from one set of specimens to the other, depending on the PbO content of the compositions. Furthermore, on prolonged heating at temperatures above 850°C, PbO loss from the specimens led to a compositional change, thereby, allowing the formation of the pyrochlore phase. Thus, the compositions with a high PbO content (>60 mol% PbO) were heat-treated for a relatively shorter time period up to a maximum temperature of 825°C to achieve equilibrium. Considerable difficulties have been encountered with equilibration of specimens contained a high proportion of MgO. For these specimens, repeated heat-treatments at temperatures higher than 900°C for time periods ranging from 3 to 8 hrs were found necessary to achieve complete equilibrium. At the end of the equilibration process, the specimens were quenched and/or rapidly cooled in air and the crystalline phases formed at different temperatures were identified by x-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

The XRD patterns were obtained using Ni-filtered Cu K_α radiation at diffraction angles ranging from 10° to 75° at a scanning rate of $1^\circ\ 2\,\theta$/min. The patterns were compared with the standard x-ray diffraction patterns for various known compounds as listed in the Powder Diffraction File [29]. Both polished sections and fracture surfaces of the heat treated specimens were examined by SEM (JEOL, JCM-35F, Tokyo, Japan). An energy dispersive x-ray analyzer (EDX) (Tracor Northern,

TABLE I Chemical composition, crystal structure and melting behaviour of various compounds in the binary system $PbO-Nb_2O_5$

Compound	PbO (mole %)	Nb_2O_5 (mole %)	Crystal structure	Unit-cell parameters (Å)	Density (gm/cm^3)	Melting point (°C)	JCPDS card no.
$Pb_3Nb_2O_8$	75	25	Tetragonal	$a = 7.536$, $c = 10.829$	7.595	985°, cong.	83-1959
$Pb_5Nb_4O_{15}$	71.43	28.57	Monoclinic	$a = 12.944$, $b = 7.420$, $c = 33.618$, $\beta = 108.68$	7.100	1220°, incong.	46-0638
$Pb_2Nb_2O_7$	66.67	33.33	Hexagonal	$a = 7.472$, $c = 28.351$	7.333	1233°, incong.	43-0960
$Pb_3Nb_4O_{13}$	60	40	Cubic	$a = 10.56$	6.766	1233°, cong.	25-0433
$PbNb_2O_6$	50	50	Rhombohedral	$a = 10.501$, $c = 11.555$	6.623	1150°, transformation temperature	73-2298
			Orthorhombic	$a = 17.65$, $b = 17.92$, $c = 3.87$	6.634	1343°, cong.	70-1388
$PbNb_4O_{11}$	20	80	Orthorhombic	$a = 34.87$, $b = 17.608$, $c = 7.914$	5.159	1337°, cong.	25-0442

cong. = Congruent melting and incong. = Incongruent melting.

TABLE II Chemical composition, crystal structure and melting behaviour of various compounds in the binary system $MgO-Nb_2O_5$

Compound	PbO (mole %)	Nb_2O_5 (mole %)	Crystal structure	Unit-cell parameters (Å)	Density (gm/cm^3)	Melting point (°C)	JCPDS card no.
$Mg_5Nb_4O_{15}$	83.33	16.67	Orthorhombic	$a = 11.427$, $b = 10.058$, $c = 10.26$	4.285	stable above 1420°, melts at 1550°C, incong.	20-0681
$Mg_4Nb_2O_9$	80	20	Hexagonal	$a = 5.162$, $c = 14.024$	4.328	1550°, incong.	38-1459
$MgNb_2O_6$	50	50	Orthorhombic	$a = 5.700$, $b = 14.193$, $c = 5.032$	4.995	1630°, cong.	33-0875
$Mg_{0.666}Nb_{11.333}O_{29}$	10.526	89.474	Orthorhombic	$a = 28.74$, $b = 3.832$ $c = 20.65$	4.476	1445°, incong.	26-1218

cong. = Congruent melting and incong. = Incongruent melting.

Wisconsin, USA) was used in conjunction with the SEM to identify the nature of the phases present in the specimens. Differential thermal analysis (DTA) combined with thermogravimetric analysis (TGA) (STA-409, Netzsch Thermal Analyzer, Selb, Germany) have been carried out on selected compositions with a view to obtain an indication of the first sign of melt formation in this system. The DTA/TGA experiments were carried out at a heating rate of 10°C/min in air using Pt-crucibles as specimen holder and α-Al_2O_3 as a reference material. For compositions with a high PbO-content (>60 mol% PbO), the DTA/TGA runs were restricted up to a maximum temperature of 875°C due to the reaction of the specimens with the Pt-holder as well as for rapid volatilization of PbO from the specimens above the melting point of PbO (886°C). The commencement of an endothermic peak in the DTA trace, which is characteristic of the onset of melting for a given composition, provided an indication of melt formation in various phase-field areas in this system.

3. Results and discussion

3.1. The binary system $PbO-Nb_2O_5$

The phase equilibrium relations in the binary system $PbO-Nb_2O_5$ and crystal chemistry of various Pb-niobates occurring in this system have been reported by Roth [30]. To the author's knowledge, no other phase diagram of this system has since been reported although numerous studies on crystal structures of several Pb-niobates have been published in the literature. In all, six binary compounds are known to exist in the system $PbO-Nb_2O_5$. These are $Pb_3Nb_2O_8$, $Pb_5Nb_4O_{15}$, $Pb_2Nb_2O_7$, $Pb_3Nb_4O_{13}$, $PbNb_2O_6$ and $PbNb_4O_{11}$. The data on the crystal structure, unit-cell parameters, density and melting behaviour of these compounds, as compiled from different sources, are listed in Table I. According to the existing $PbO-Nb_2O_5$ phase diagram [30], the compounds $Pb_5Nb_4O_{15}$, $Pb_2Nb_2O_7$, $PbNb_2O_6$ and $PbNb_4O_{11}$ melt congruently at 1220°, 1233°, 1343° and 1337°C, respectively, whereas, $Pb_3Nb_2O_8$, and $Pb_3Nb_4O_{13}$ melt incongruently at 985° and 1233°C, respectively. The compound $PbNb_2O_6$ was found to undergo a reversible phase transformation from a low-temperature rhombohedral form to a high-temperature orthorhombic form at 1150°C. The lowest melting point in this system has been established at 835°C, which is attributed to a eutectic between PbO and $Pb_3Nb_2O_8$ at a composition of 94 mol% PbO.

3.2. The binary system $MgO-Nb_2O_5$

The phase diagram of the binary system $MgO-Nb_2O_5$ showing the solid-liquid equilibrium relationships between the various Mg-niobates has been reported by Abbattista *et al.* [31]. In this phase diagram, four binary compounds are shown to occur. These are $Mg_4Nb_2O_9$, $Mg_5Nb_4O_{15}$, $MgNb_2O_6$ and a Nb_2O_5-rich compound with a chemical composition $Mg_{0.666}Nb_{11.333}O_{29}$ ($2MgO{:}17Nb_2O_5$). The Mg-niobates, $Mg_4Nb_2O_9$ and $MgNb_2O_6$ were found to be stable at room temperature, whereas, $Mg_5Nb_4O_{15}$ and $Mg_{0.666}Nb_{11.333}O_{29}$ exist only at temperatures above 1200°C. The various data on the crystal structure, unit-cell parameters, density and melting behaviour for these compounds are listed in Table II. The compound $Mg_4Nb_2O_9$ melts incongruently at 1730°C to yield MgO and a liquid. The compound $Mg_5Nb_4O_{15}$, which is stable only at temperatures above 1200°C, melts incongruently at 1580°C to yield $Mg_4Nb_2O_9$ and a liquid. The compound $MgNb_2O_6$ melts congruently at 1570°C and forms a eutectic with $Mg_5Nb_4O_{15}$ at 37 mol% Nb_2O_5 with a melting point at 1530°C. Also shown in the phase diagram [31], the compound $Mg_{0.666}Nb_{11.333}O_{29}$, which is stable above 1245°C, melts incongruently to yield Nb_2O_5. A eutectic is formed between $Mg_{0.666}Nb_{11.333}O_{29}$ and $MgNb_2O_6$ at 73 mol% Nb_2O_5 which melts at 1430°C.

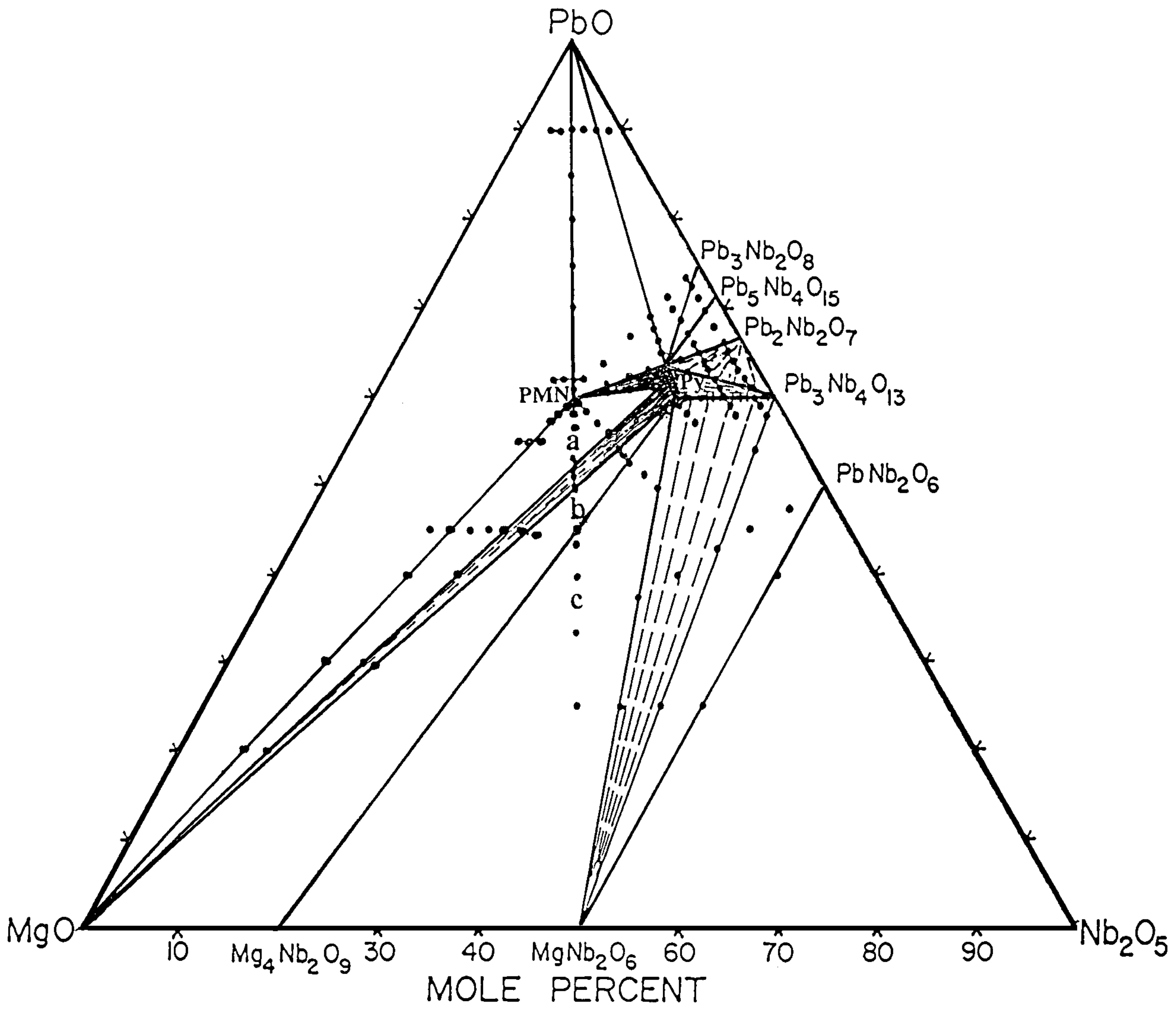

Figure 1 Subsolidus phase diagram of the ternary system PbO-MgO-Nb_2O_5 showing the compatibility relations between the various phases at 825°C (PMN = $Pb_3MgNb_2O_9$ and Py = pyrochlore solid solution).

3.3. Subsolidus compatibility relations in the system PbO-MgO-Nb_2O_5

3.3.1. Formation and characteristics of equilibrium phase assemblages

The subsolidus phase diagram of the ternary system PbO-MgO-Nb_2O_5 as established in the present study is shown in Fig. 1. The system is characterized by the existence of two previously known ternary compounds, namely, a perovskite $Pb_3MgNb_2O_9$ that corresponds to a composition $Pb(Mg_{1/3}Nb_{2/3})O_3$ and a pyrochlore $Pb_6MgNb_6O_{22}$ that corresponds to an oxygen-deficient ternary composition $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$. A small amount of PbO enters into the pyrochlore lattice and forms a narrow homogeneity range which is represented by the general formula $Pb_{2-x}(Mg_{0.286}Nb_{1.714})O_{6.571-x}$, where $0 > x > 0.286$. With a minor amount of PbO entering into the cubic pyrochlore lattice, the homogeneity range extends from the composition $Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$ to a composition $Pb_7MgNb_6O_{23}$ $[Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}]$ with a corresponding increase in the cubic cell parameter from $a = 10.5867$ Å to 10.6012 Å. The interplanar spacings with corresponding intensities for the pyrochlore $Pb_6MgNb_6O_{22}$ $[Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}]$ and the characteristics of the pyrochlore solid solution have been presented earlier in the Part I of this study [28] and, therefore, are not discussed here. However, it is worthy of mention that the end members of the pyrochlore solid solution can be readily obtained by the interaction between appropriate proportions of prefabricated $Pb_3MgNb_2O_9$ and several lead-niobates. Thus, solid state reaction between equimolar proportions of the ternary perovskite $Pb_3MgNb_2O_9$ and the binary compound $Pb_3Nb_4O_{13}$ at 825°C gave rise to the formation of the pyrochlore $Pb_6MgNb_6O_{22}$ $[Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}]$ according to the equation:

$$\underset{\text{Perovskite } Pb(Mg_{1/3}Nb_{2/3})O_3}{Pb_3MgNb_2O_9} + Pb_3Nb_4O_{13} \longrightarrow \underset{\text{Pyrochlore } Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}}{Pb_6MgNb_6O_{22}} \qquad (1)$$

Whereas, a mixture containing appropriate proportions of the perovskite $Pb_3MgNb_2O_9$ and the binary compound $Pb_2Nb_2O_7$, on heat treating at the same temperature, resulted in the formation of the pyrochlore $Pb_7MgNb_6O_{23}$ $[Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}]$ according

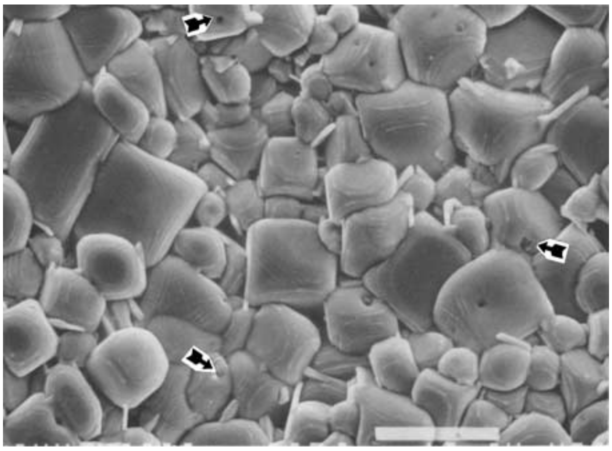

Figure 2 SEM micrograph of a perovskite $Pb_3MgNb_2O_9$-rich composition located in the compatibility triangle PbO-$Pb_3MgNb_2O_9$-MgO, heat treated at 900°C for 3 h showing large grains of $Pb_3MgNb_2O_9$ coexisting with MgO (small dark particles) and PbO (white flakes in the grain boundaries).

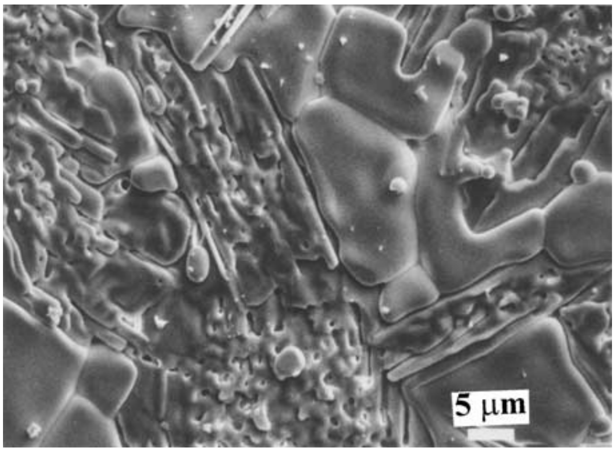

Figure 3 SEM micrograph of a PbO-rich composition located in the compatibility triangle PbO-$Pb_3MgNb_2O_9$-MgO, heat treated at 900°C for 3 h showing partially melted grains of $Pb_3MgNb_2O_9$ coexisting with a liquid.

to the reaction:

$$\underset{\text{Perovskite } Pb(Mg_{1/3}Nb_{2/3})O_3}{Pb_3MgNb_2O_9} + 2Pb_2Nb_2O_7 \longrightarrow \underset{\text{Pyrochlore } Pb_2(Mg_{0.286}Nb_{1.714})O_{6.571}}{Pb_7MgNb_6O_{23}} \qquad (2)$$

As is evident from the phase diagram (Fig. 1), both PbO and MgO are compatible with perovskite $Pb_3MgNb_2O_9$, and they constitute a phase assemblage in which these three phases coexist with one another. Several compositions located in the PbO-corner of the compatibility triangle PbO-$Pb_3MgNb_2O_9$-MgO, when heat treated at temperatures above 850°C, were found to undergo partial melting. The amount of liquid formed increased with increasing temperature as well as with increasing PbO content of the specimens. An SEM micrograph of a specimen with composition located in the compatibility triangle PbO-$Pb_3MgNb_2O_9$-MgO, which has been heat treated at 900°C and then slowly cooled to room temperature, is exhibited in Fig. 2. The micrograph essentially represents a well-sintered body consisting of numerous equiaxed grains of $Pb_3MgNb_2O_9$ as the major phase which coexist with small amounts of several other phases. Seemingly, the overall grain morphology has a close resemblance to that of a material that has been sintered in presence of a liquid phase. As visible in this microstructure, numerous small spherical particles, randomly distributed in the matrix of the sintered ceramics, are present. These were identified as MgO by SEM/EDX analysis. Another phase, appearing in the form of white flakes at the grain boundary region, has been identified as PbO. The characteristic morphology of PbO as appeared herein suggests that these flakes must have formed in the grain boundaries by crystallizing from the liquid during cooling. It is to be noted that the characteristic microstructural feature as observed in the heat-treated specimens are consistent with those reported earlier by Gupta and Kulkarni [32], who also found the flake-like PbO phase in the grain boundaries of $Pb_3MgNb_2O_9$. In contrast to this specimen, another compositions located in the same phase-field area but containing a high proportion of PbO, when heat-treated at 900°C, was found to undergo extensive melting. The SEM micrograph of this specimen is exhibited in Fig. 3 which shows the presence of several massive grains of $Pb_3MgNb_2O_9$ that seem to have partially melted and appear to be coexisting in equilibrium with a liquid phase that resembles to a eutectic liquid. Further evidence obtained from the DTA/TGA experiments indicated that melt formation within the compatibility triangle PbO-$Pb_3MgNb_2O_9$-MgO commences at about 830°C. Evidently, this is the lowest temperature at which a liquid phase first appears in the ternary system PbO-MgO-Nb_2O_5. Thus, the various tie-lines and the compatibility triangles between the ternary phases (perovskite $Pb_3MgNb_2O_9$ and pyrochlore solid solution) and several binary Pb-and Mg-niobates as exhibited in the subsolidus phase diagram (Fig. 1) are considered valid at temperatures up to 825°C.

Although perovskite $Pb_3MgNb_2O_9$ coexists in equilibrium with both PbO and MgO in the ternary system PbO-MgO-Nb_2O_5, XRD analysis of the heat-treated specimens revealed that the perovskite $Pb_3MgNb_2O_9$ is not compatible with Nb_2O_5. Thus, at subsolidus temperatures, $Pb_3MgNb_2O_9$ reacts with Nb_2O_5 to yield the pyrochlore phase and MgO. As evident from the phase diagram (Fig. 1), an interaction between these two compounds causes the stoichiometric $Pb_3MgNb_2O_9$ composition to shift to a compatibility triangle (marked as "a" in the phase diagram in Fig. 1) in which the perovskite $Pb_3MgNb_2O_9$ coexists in equilibrium with the pyrochlore solid solution and MgO. This observation is consistent with the findings of several earlier reported studies [33–35] in which it has been reported that an addition of excess Nb_2O_5 to the perovskite $Pb_3MgNb_2O_9$ gives rise to the formation of the pyrochlore phase.

3.3.2. Compatibility relations between perovskite $Pb_3MgNb_2O_9$ and pyrochlore compounds

It is evident from the phase diagram (Fig. 1) that the perovskite $Pb_3MgNb_2O_9$ coexists in equilibrium with the pyrochlore solid solution. An SEM micrograph showing the presence of the perovskite $Pb_3MgNb_2O_9$ and the pyrochlore phase is exhibited Fig. 4. This is typical of

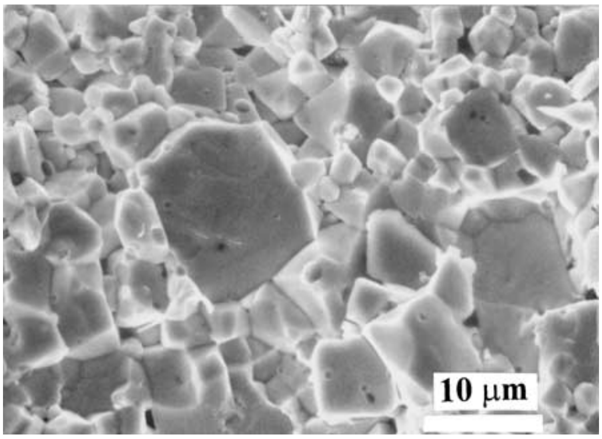

Figure 4 SEM micrograph of a composition located in the diphasic area consisting of perovskite $Pb_3MgNb_2O_9$ and pyrochlore solid solution, heat treated at 900°C for 3 h showing large rectangular grains of the pyrochlore phase dispersed in a matrix comprised of perovskite $Pb_3MgNb_2O_9$.

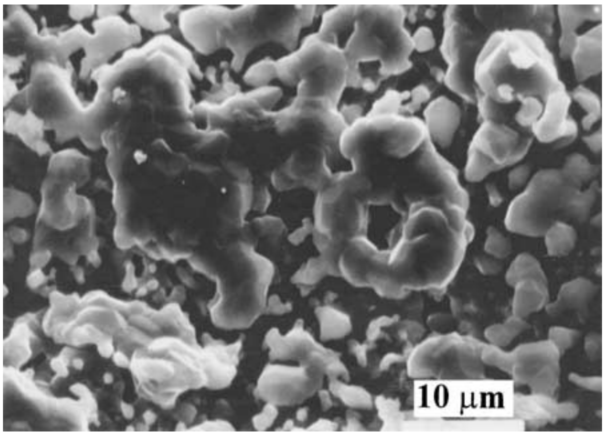

Figure 5 SEM micrograph of a stoichiometric pyrochlore $Pb_3MgNb_2O_9$, heat treated at 1240°C for 3 h exhibiting the morphology of a near melted specimen.

the microstructures in which the pyrochlore phase frequently appeared in the form of large rectangular grains randomly dispersed in a matrix comprised of numerous small grains of perovskite $Pb_3MgNb_2O_9$. Evidence obtained in this study also indicated that MgO, which is compatible with the pyrochlore solid solution, forms a narrow biphasic area in which MgO coexists in equilibrium with the pyrochlore phase. As can be seen from the phase diagram (Fig. 1), the perovskite $Pb_3MgNb_2O_9$ and the pyrochlore solid solution are compatible with MgO and together they constitute a compatibility triangle in the ternary system $PbO\text{-}MgO\text{-}Nb_2O_5$. Likewise, the perovskite $Pb_3MgNb_2O_9$ and the pyrochlore solid solution are compatible with PbO and together these phases constitute a compatibility triangle in this system.

An important finding that has emerged from this study is that unlike the perovskite $Pb_3MgNb_2O_9$, the ternary pyrochlore phase does not constitute a compatibility triangle with PbO and MgO. Instead, an interaction between the pyrochlore phase and these oxides leads to the formation of the perovskite $Pb_3MgNb_2O_9$. The chemical reaction is expressed by the equation:

$$\underset{\substack{Pb_6MgNb_6O_{22}\\ \text{Pyrochlore } [Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}]}}{Pb_6MgNb_6O_{22}} + 3PbO + 2MgO \longrightarrow \underset{\text{Perovskite } [Pb(Mg_{1/3}Nb_{2/3})O_3]}{3Pb_3MgNb_2O_9} \tag{3}$$

The chemical reaction as shown above implies that simultaneous additions of excess PbO and MgO to a pyrochlore solid solution result in the formation of the perovskite $Pb_3MgNb_2O_9$.

SEM and XRD data obtained from several specimens indicated that the ternary pyrochlore $Pb_6MgNb_6O_{22}$ $[Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}]$ is stable up to a temperature near 1220°C and melts incongruently above this temperature to yield $Mg_4Nb_2O_9$ and a liquid. The XRD pattern of the melted specimen, which revealed the presence of $Mg_4Nb_2O_9$ along with the pyrochlore phase, has been presented in Part I of this study [28]. However, because of the incongruent nature of melting of the pyrochlore phase, only a small amount of liquid was formed at the onset of melting of this compound at 1220°C. Nevertheless, melting of the pyrochlore phase was readily detectable by SEM when the specimen was heat-treated at slightly higher temperatures (>1220°C). Fig. 5 shows a SEM micrograph of a specimen that has been heat-treated at 1240°C exhibiting the characteristic morphology of partially melted pyrochlore phase.

3.3.3. Compatibilty relations between the ternary pyrochlore phase and binary Pb- and Mg-niobates

It was observed from the various XRD and SEM data obtained in the present investigation that the pyrochlore solid solution is compatible with the binary Pb-niobates, i.e. $Pb_3Nb_2O_8$, $Pb_5Nb_4O_{15}$, $Pb_2Nb_2O_7$, $Pb_3Nb_4O_{13}$ and forms binary tie-lines with these compounds in the ternary system $PbO\text{-}MgO\text{-}Nb_2O_5$. Among the various Pb-niobates encountered in this study, the binary compound $Pb_3Nb_4O_{13}$, which corresponds to an oxygen-deficient pyrochlore formula $Pb_{1.5}Nb_2O_{6.5}$ was found to be isostructural with the ternary pyrochlore $Pb_6MgNb_6O_{22}$ $[Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}]$. Evidence obtained by XRD analysis of several heat-treated specimens revealed that these two compounds form a series of complete solid solution with one another. The change in the unit-cell parameter for the various solid solution compositions is shown in Fig. 6. The characteristic linear relationship derived from the decreasing lattice parameter values from $a = 10.587$ Å to 10.561 Å is consistent with the Vegard's law applicable to the systems exhibiting complete solid solutions. It is further evident from the phase diagram (Fig. 1) that the binary pyrochlore $Pb_3Nb_4O_{13}$ $[Pb_{1.5}Nb_2O_{6.5}]$ forms solid solutions with the entire range of the ternary pyrochlore solid solution and thus, a single phase-field area comprised of a cubic pyrochlore phase occurs within the ternary system.

As shown in the phase diagram (Fig. 1), the ternary pyrochlore solid solution is compatible with the Mg-niobates, i.e. $Mg_4Nb_2O_9$ and $MgNb_2O_6$. Thus, at subsolidus temperatures, the pyrochlore $Pb_6MgNb_6O_{22}$ coexists with $Mg_4Nb_2O_9$ and MgO (marked as "b"

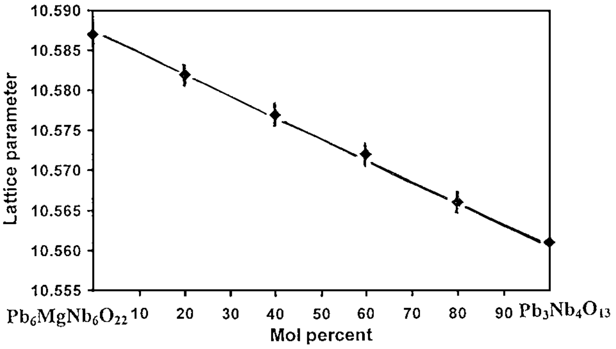

Figure 6 Linear relationship of the lattice parameters obeying Vegards law for the various solid solution compositions formed between the ternary pyrochlore $Pb_3MgNb_2O_9$ and $Pb_3Nb_4O_{13}$.

in Fig.1) and together they constitute a three-phase assemblage in the ternary system PbO-MgO-Nb_2O_5. Also, the pyrochlore $Pb_6MgNb_6O_{22}$ is compatible with $MgNb_2O_6$. Thus $Pb_6MgNb_6O_{22}$, $Mg_4Nb_2O_9$ and $MgNb_2O_6$ form a three-phase assemblage in the ternary system PbO-MgO-Nb_2O_5 (marked as "c" in Fig.1).

3.4. The implications of the formation and stability of equilibrium phase assemblages in the system PbO-MgO-Nb_2O_5

3.4.1. Formation and stability of perovskite $Pb_3MgNb_2O_9$

A closer examination of the tie-lines depicting the compatibility relationships between the various phases which occur in the ternary system PbO-MgO-Nb_2O_5 provides additional information on the formation and stability of the perovskite $Pb_3MgNb_2O_9$ and the pyrochlore solid solution. For instance, it can be seen from the various tie-lines shown in Fig.1 that at subsolidus temperatures, the perovskite $Pb_3MgNb_2O_9$ coexists in equilibrium with the pyrochlore solid solution. This is why the unwanted pyrochlore phase, once formed at the initial stage of the reaction process for the synthesis of perovskite $Pb_3MgNb_2O_9$, is difficult to eliminate completely from the resulting products, even after prolonged heating at elevated temperatures. However, the phase diagram (Fig. 1) also reveals that an addition of excess MgO to the starting mixture causes a shift of the overall composition from the pyrochlore phase towards the perovskite $Pb_3MgNb_2O_9$ composition. As a result, the fraction of the pyrochlore phase, which mostly appears at the initial stages of the reaction process, is significantly decreased in the presence of excess MgO at the end of the reaction process. It is important to note that in the Columbite processing technique [16], the perovskite $Pb_3MgNb_2O_9$ [$Pb(Mg_{1/3}Nb_{2/3})O_3$] is obtained by the solid-state reaction between appropriate proportions of PbO and prefabricated $MgNbO_6$ according to the reaction:

$$3PbO + MgNb_2O_6 \xrightarrow{} \underset{\text{Perovskite } Pb(Mg_{1/3}Nb_{2/3})O_3}{Pb_3MgNb_2O_9} \qquad (4)$$

It is recognized that a small amount of pyrochlore phase (∼2%) is also formed in this reaction process along with the perovskite $Pb_3MgNb_2O_9$. In an earlier reported study, Joy and Sreedhar [27] have observed that an addition of excess MgO to the stoichiometric $Pb_3MgNb_2O_9$ mixture results in the formation of $Mg_4Nb_2O_9$. This is consistent with the compatibility relations shown in the phase diagram (Fig. 1) which indicates that an excess MgO reacts with $MgNb_2O_6$ to yield $Mg_4Nb_2O_9$. The phase diagram indicates that the $Mg_4Nb_2O_9$ thus formed further combines with PbO to yield the undesirable pyrochlore phase. Notwithstanding, the Columbite processing technique has a certain advantage over the other solid-state processing techniques. Namely, there is no 'free Nb_2O_5' involved in this reaction process and as such the possibility of a reaction between Nb_2O_5 and PbO leading to the formation of several pyrochlore-based binary Pb-niobates, i.e., $Pb_3Nb_2O_8$, $Pb_2Nb_2O_7$ and $Pb_3Nb_4O_{13}$ as observed by several earlier workers [1–3, 16, 17, 19] is eliminated. Nevertheless, as PbO is a major constituent in the Columbite reaction process, volatilization loss of PbO from the specimens causes a compositional change. According to the compatibility relations shown in the phase diagram (Fig. 1), such a change inevitably leads to the formation of the pyrochlore phase. Thus, it is apparent that the use of prefabricated precursors in the Columbite processing technique does not necessarily ensure the formation of a phase-pure perovskite $Pb_3MgNb_2O_9$. In an alternative approach, Guha and Anderson [18] have used a different set of reactants to facilitate the formation of a phase-pure perovskite $Pb_3MgNb_2O_9$ without incurring any significant PbO loss during the reaction process. In this processing technique, equimolar proportions of $Pb_3Nb_2O_8$ and MgO have been reacted with one another to yield a phase-pure perovskite $Pb_3MgNb_2O_9$ according to the reaction:

$$Pb_3Nb_2O_8 + MgO \xrightarrow{} \underset{\text{Perovskite } Pb(Mg_{1/3}Nb_{2/3})O_3}{Pb_3MgNb_2O_9} \qquad (5)$$

Since 'free-PbO' is not involved in this reaction process, volatilization of PbO from the specimens does not appear to be a major problem. Furthermore, in the absence of any 'free PbO' in the starting mixture, the reaction between $Pb_3Nb_2O_8$ and MgO to yield the perovskite $Pb_3MgNb_2O_9$ can be carried out at temperatures much higher than that of the melting point of PbO (886°C). Thus, in this reaction process the possibility of any compositional change due mainly to the PbO loss from the specimens leading to the formation of an undesirable pyrochlore phase as a reaction product is largely eliminated.

4. Conclusions

Subsolidus compatibility relationships between the various phases occurring in the ternary system PbO-MgO-Nb_2O_5 as established in this investigation reveal that a cubic perovskite $Pb_3MgNb_2O_9$ [$Pb(Mg_{1/3}Nb_{2/3})O_3$] and an oxygen-deficient cubic pyrochlore $Pb_6MgNb_6O_{22}$ [$Pb_{1.714}(Mg_{0.286}Nb_{1.714})O_{6.286}$] are the only two ternary phases that occur in this system. A small amount of PbO enters into the cubic pyrochlore lattice and forms a narrow homogeneity range in the ternary system. The perovskite $Pb_3MgNb_2O_9$ is compatible with the pyrochlore $Pb_6MgNb_6O_{22}$ and together these two phases form a biphasic area in the ternary system. The perovskite $Pb_3MgNb_2O_9$ coexists in equilibrium with PbO and MgO, and these phases constitute a compatibility triangle in the ternary system. The pyrochlore phase reacts with appropriate amounts of PbO and MgO to yield perovskite $Pb_3MgNb_2O_9$. Thus, simultaneous addition of PbO and MgO to the ternary pyrochlore solid solution causes a compositional shift towards the perovskite $Pb_3MgNb_2O_9$. The perovskite $Pb_3MgNb_2O_9$ is not compatible with Nb_2O_5 and a reaction between these two phases leads to the formation of pyrochlore $Pb_6MgNb_6O_{22}$ and MgO. The ternary pyrochlore solid solution coexists in equilibrium with several binary Pb-niobates, i.e. $Pb_3Nb_2O_8$, $Pb_5Nb_4O_{15}$, $Pb_2Nb_2O_7$, $Pb_3Nb_4O_{13}$, and the binary Mg-niobates, $Mg_4Nb_2O_9$ and $MgNb_2O_6$. Among the various Pb-niobates, the binary pyrochlore $Pb_3Nb_4O_{13}$ [$Pb_{1.5}Nb_2O_{6.5}$] is isostructural with the ternary pyrochlore solid solution. As a result, a single-phase pyrochlore solid solution region formed between these phases occurs in the ternary system $PbO\text{-}MgO\text{-}Nb_2O_5$.

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