Phase analysis and dielectric properties of ceramics in PbO–MgO–ZnO–Nb$_2$O$_5$ system: A comparative study of materials obtained by ceramic and molten salt synthesis routes

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Abstract. Compositions of the type 3PbO–MgO/ZnO–Nb$_2$O$_5$ were synthesized by the ceramic route at 1000°C and sintered at 1200°C. Powder X-ray diffraction studies of the 1000°C heated products show the presence of the cubic pyrochlore and the columbite (Mg/ZnNb$_2$O$_6$) type phase in the ratio of 3 : 1 for all possible combinations of MgO and ZnO. Further heating at 1200°C led to a decrease in the cubic pyrochlore phase and an increase in the columbite phase by around 10%. Compacted pellets sintered further showed the appearance of the perovskite phase. Similar compositions synthesized using the KCl–NaCl molten salt method at 900°C for 6 h gave a significant amount of the cubic perovskite related phase of the type Pb(Mg/Zn)$_{1/3}$Nb$_{2/3}$O$_3$ for all compositions containing MgO. The amount of the perovskite phase was nearly 55% for the Mg rich compositions and decreased with increase in Zn content, the pure Zn composition yielding mainly the cubic pyrochlore phase. On sintering these phases at 1000°C the perovskite phase content decreased. The dielectric constant of the composite materials formed by the ceramic route was in the region of 14 to 20 and varied little with frequency. The composites obtained by the molten salt method, however, showed much larger dielectric constants in the region 40–150 at 500 kHz for various compositions. The dielectric loss tangent of these composites were lower by an order (0·005–0·03 at 500 kHz) compared to the ceramic route.

Keywords. Ceramics; dielectrics; X-ray diffraction.

1. Introduction

Lead based niobates containing Mg and Zn are known to give rise to important ferroelectric materials and have several features which are much more promising in multi-layer ceramic capacitor (MLCC) applications compared to the normally utilized BaTiO$_3$ (Yamashita 1994). However, it is very difficult to prepare pure Pb$_3$ZnNb$_2$O$_9$ (PZN) or Pb$_3$MgNb$_2$O$_9$ (PMN) by conventional processing by the ceramic route due to the formation of a pyrochlore phase (Pb$_3$Nb$_4$O$_{13}$) and several novel methods were explored to realize the pure phases.

Pure PMN was synthesized by the columbite route, where MgNb$_2$O$_6$ was first prepared and then reacted with PbO to give the desired phase (Swartz *et al* 1984; Lejeune and Boilot 1986; Saha *et al* 1994). Pb$_3$Nb$_2$O$_8$ precursors were known to react with various Mg sources like MgO (Guha and Anderson 1986) or Mg(OH)$_2$ (Sreedhar and Mitra 1997) to yield the PMN phase. Single phase PMN was also synthesized by direct reaction of oxides and carbonates by using a simple and novel mixing and calcining procedure (Yan *et al* 1989) with a final sintering at relatively low temperatures of 980°C in flow-ing oxygen for 4 h. Similar procedures for preparing the pure PZN phase are not yet reported. Several lead based ceramics were also synthesized by the molten salt route using chlorides, sulphates, etc as the salt. For example, Pb$_3$MgNb$_2$O$_9$ (PMN) was synthesized (Yoon *et al* 1995) at 750°C for 1 h using Li$_2$SO$_4$–Na$_2$SO$_4$ flux and was nearly phase pure (98%) while with other salts the phase purity was lower. The synthesis of PZN by the molten salt route has so far yielded the perovskite related phase in very small amount (10 to 15%), the rest being the pyrochlore phase (Yoon *et al* 1995).

In all the above syntheses the pure phase was obtained as a powder (usually at low temperatures of 700 to 800°C) and had to be ultimately sintered at higher temperatures to obtain disks for obtaining the dielectric materials for characterization. Sintering temperatures > 900°C tend to give the pyrochlore phase. For example, a pure phase of PMN obtained by the sol-gel method using alkoxide precursors on sintering at 1000°C destabilizes the perovskite phase and leads to a pyrochlore phase (Chaput *et al* 1989). Several methods were tried to enhance the ratio of the perovskite phase to the pyrochlore phase at high temperatures (1000–1100°C); these involved addition of stable perovskite phases like BaTiO$_3$, PbTiO$_3$, PZT, etc (Belsick *et al* 1987; Halliyal *et al* 1987; Villegas *et al* 2000).

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We have investigated in detail by powder X-ray diffraction studies the phases obtained in the 3PbO–MgO/ZnO–Nb_2O_5 system by both the ceramic route and molten salt (NaCl–KCl) synthesis route. The emphasis here is to characterize and compare the composite materials obtained by sintering at high temperatures (1000–1200°C). In our studies we have not added any extra additives like $BaTiO_3$ normally used during high temperature sintering of the PZN or PMN phases. We report our studies using powder X-ray diffraction on the phase analysis (before and after sintering), microstructures and dielectric properties of the materials in the 3PbO–MgO/ZnO–Nb_2O_5 system. These studies are aimed at understanding the nature of the secondary phases that normally occur in the synthesis of PMN or PZN phase and to characterize the dielectric properties of these composites.

2. Experimental

Stoichiometric amounts of yellow PbO, ZnO, MgO and Nb_2O_5 were taken for ceramic synthesis. The mixed powders were calcined in air at 1000°C for 45 h with intermittent grindings and then at 1200°C for 10 h. These were then pelletized after mixing with 5% PVA solution and then sintered at 1000°C for 12 h.

Molten salt synthesis was carried out with stoichiometric amounts of yellow PbO, ZnO and Nb_2O_5 along with a 1 : 1 KCl–NaCl mixture. These were heated at 900°C for 6 h in an open crucible and also in a closed crucible (not sealed, the crucible was covered with a lid).

The crucibles were quenched to room temperature (for the molten salt method) after heating. The product was washed with distilled water till the filtrate gave no precipitate with $AgNO_3$ solution. The resulting mass was dried in an oven at 100°C. They were then pelletized after adding few drops of PVA solution and sintered at 1000°C for 12 h. Powder X-ray diffraction studies were carried out on the powders obtained prior to sintering as well as after sintering using a Siemens or a Phillips X-ray diffractometer. The phase analysis was carried out by powder X-ray diffraction after every processing step and the percentage of the phases was calculated by following the most intense peak of each phase. For example, the formula,

$$\text{\% perovskite} = (I_{110})_{per} \times 100/[(I_{110})_{per} + (I_{222})_{pyr}],$$

will give the percentage of the perovskite phase in a biphasic mixture of perovskite and pyrochlore phases. Scanning electron microscopy studies were carried out using a Cambridge Stereoscan 360 electron microscope. For dielectric measurements, the sintered disks were coated with aluminium (99·999%) in a vacuum coating unit. The variable frequency dielectric measurements were carried out using a HP 4284L LCR meter in the frequency range 40 Hz–500 kHz. The density of the sintered samples was obtained by the Archimedes method and was found to be around 92% of the theoretical density.

3. Results and discussion

In table 1 we show the details of the loaded composition and the phases obtained by the ceramic route before and
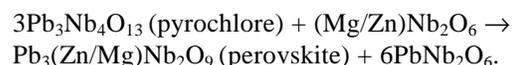
Table 1. Details of synthetic condition and phases obtained by the ceramic route in 3PbO–(1–x)MgO–(x)ZnO–Nb_2O_5.

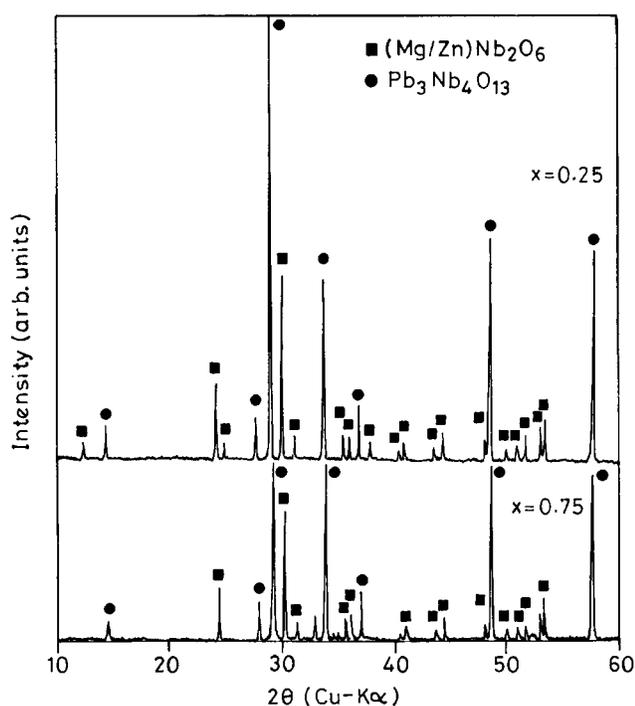|	Phases obtained		Phases obtained after sintering[C]
x	A	B	
0	$Pb_3Nb_4O_{13}$ 70% $MgNb_2O_6$ 30%	$Pb_3Nb_4O_{13}$ 60% $MgNb_2O_6$ 40%	Perovskite 7% $MgNb_2O_6$ 33% $Pb_3Nb_4O_{13}$ 25% $PbNb_2O_6$ 35%
0·25	$Pb_3Nb_4O_{13}$ 70% $(Mg/Zn)Nb_2O_6$ 30%	$Pb_3Nb_4O_{13}$ 60% $(Mg/Zn)Nb_2O_6$ 40%	Perovskite 11% $MgNb_2O_6$ 17% $PbNb_2O_6$ 29% ZnO 28%
0·5	$Pb_3Nb_4O_{13}$ 70% $(Mg/Zn)Nb_2O_6$ 30%	$Pb_3Nb_4O_{13}$ 65% $(Mg/Zn)Nb_2O_6$ 35%	Perovskite 20% $PbNb_2O_6$ 75% ZnO 5%
0·75	$Pb_3Nb_4O_{13}$ 75% $(Mg/Zn)Nb_2O_6$ 25%	$Pb_3Nb_4O_{13}$ 65% $(Mg/Zn)Nb_2O_6$ 35%	Perovskite 18% $PbNb_2O_6$ 64% ZnO 18%
1	$Pb_3Nb_4O_{13}$ 75% $ZnNb_2O_6$ 25%	$Pb_3Nb_4O_{13}$ 55% $ZnNb_2O_6$ 45%	Perovskite 17% $PbNb_2O_6$ 57% ZnO 26%

A. 1000°C for 30 h; B. samples heated like condition A and then further heated at 1000°C for 5 h and then at 1200°C for 10 h and C. compacted pellets after condition B sintered at 1000°C for 12 h.

after sintering. We find that after the first heating at 1000°C for 30 h two phases are present, the cubic pyrochlore phase (75%) and an ANb_2O_6 (25%) type of columbite phase (figure 1). Here A is either Mg or Zn or mixture of both. Since the lattice parameters of $MgNb_2O_6$ and $ZnNb_2O_6$ are nearly identical it is not possible to differentiate between the two or their solid solutions. The perovskite phase (PMN–PZN) is absent in the powder patterns. The pyrochlore phase, normally considered to be of the formula $Pb_3Nb_4O_{13}$ has been found earlier (Shrout and Swartz 1983; Goo *et al* 1986) to have some magnesium substituted in the Nb sites ($Pb_{1.8}Mg_{0.3}Nb_{1.7}O_{6.5}$ or $Pb_{2.25}Mg_{0.27}Nb_{1.79}O_{6.4}$) during the synthesis of PMN phase. However, we find that our powder X-ray diffraction pattern shows lines which correspond more closely to the reported diffraction pattern of $Pb_3Nb_4O_{13}$ cubic pyrochlore phase (JCPDS # 25–443). After further heating at 1000°C/45 h and 1200°C/10 h, the cubic pyrochlore phase decreases to around 60% to 65% while the ANb_2O_6 phase increases slightly to 35–45%. This is true for all the compositions studied. Since we do not see any unreacted MgO lines in the powder patterns, it is possible that MgO is probably present in amorphous form which reacts at the high temperatures with the Nb_2O_5 released from the decomposed cubic pyrochlore. This would lead to an increase in the columbite phase. Powder X-ray diffraction studies on the sintered pellets show a dramatic decrease in the cubic pyrochlore phase and the appearance of the cubic perovskite phase along with $PbNb_2O_6$ (figure 2). If we look carefully at the phase analysis after sintering (table 1), we see that the columbite phase (Mg/Zn) Nb_2O_6 decreases and the perovskite phase increases with increase in Zn concentration and the maximum perovskite phase obtained (20%) is at $x = 0.5$, where no columbite phase is present after sintering. This indicates that the reactivity of the columbite phase is crucially dependent on Zn-doping. Note that a slight amount of ZnO starts coming out at this point ($x = 0.5$). At higher Zn concentrations, the amount of ZnO increases. Figure 3 shows clearly the relative changes of the phases as described above. At $x = 0.5$ note the maximum in the perovskite phase content, the minimum of ZnO phase content and absence of the columbite phase. This indicates that the reactivity of the columbite phase can be suitably modified for an optimum ratio of Mg/Zn which has improved reactivity compared to pure $MgNb_2O_6$ and has much less volatility compared to pure $ZnNb_2O_6$. However these reactions seem to be facilitated by the compaction of powder into disks (free powders at similar or higher temperatures did not lead to any perovskite phase formation). The balanced chemical reaction at the optimum composition ($x = 0.5$) can be written as follows (neglecting the 5% ZnO formed)

$$3Pb_3Nb_4O_{13} \text{ (pyrochlore)} + (Mg/Zn)Nb_2O_6 \rightarrow$$
$$Pb_3(Zn/Mg)Nb_2O_9 \text{ (perovskite)} + 6PbNb_2O_6.$$

The ratio of the perovskite : $PbNb_2O_6$ is 1 : 6 from the above reaction. Our X-ray diffraction studies give nearly

**Figure 1.** Powder X-ray diffraction patterns of the phases obtained by the ceramic route in the $3PbO–(1–x)MgO–xZnO–Nb_2O_5$ system after 1000°C heating.
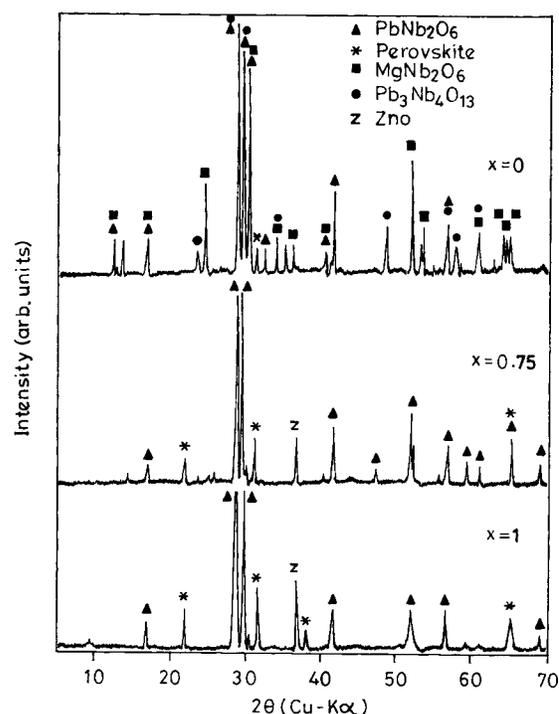
Figure 2. Powder X-ray diffraction patterns of the phases obtained by the ceramic method in the $(1–x)MgO–xZnO–Nb_2O_5$ system after sintering at 1200°C.

similar ratios (1 : 5) for all the compositions studied (table 1).

In table 2 we show the details of the phases obtained by the molten salt synthesis of compositions heated in an open crucible. After the 900°C/6 h initial heating, we do find an appreciable amount of the perovskite phase of the type $Pb(Mg/Zn)_{1/3}Nb_{2/3}O_3$ in the X-ray powder diffraction patterns (figure 4). The amount of Mg and Zn is difficult to ascertain since the $Pb(Mg/Zn)_{1/3}Nb_{2/3}O_3$ lattice parameters are nearly same for the pure Mg and Zn phases. The maximum amount of cubic perovskite phase (nearly 55%) is found for the pure Mg composition. In Zn rich compositions, the cubic perovskite phase content decreases drastically; the pure Zn composition showing no perovskite phase (figure 4). On further sintering the compositions at 1000°C/12 h, we see a decrease of the perovskite phase content and a concomitant increase in the cubic pyrochlore phase content.
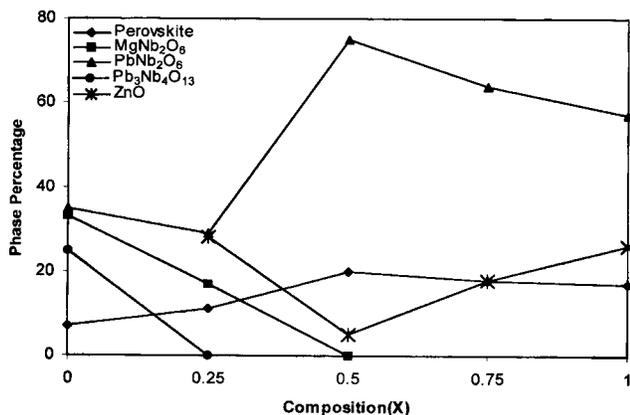
Figure 3. Evolution of phases obtained by the ceramic route with initial ZnO content (x) in $3PbO–(1–x)MgO–xZnO–Nb_2O_5$ after sintering the compacted pellets at 1200°C.

Similar molten salt reactions when carried out in a closed (not sealed) crucible results in a mixture of phases (see table 2) which are not significantly different from the above open crucible method. After the initial heating at 900°C/6 h, the Mg rich compositions have nearly 55% of perovskite phase which decreases for the Zn rich compositions and there is no perovskite phase present in the pure Zn composition (figure 5). There is some ZnO present in the Zn rich compositions. On further sintering these phases at 1000°C/12 h the perovskite phase content decreases like in the open crucible method and has nearly similar phase compositions as obtained by the open crucible method.

From the above studies we see that there is not much difference to the product compositions in the open and closed crucible reactions. The above synthesis leads to around 60% of the perovskite phase for Mg rich samples. The pure Zn composition does not yield any perovskite phase by the molten salt method under our conditions.

Scanning electron microscopic (SEM) studies were carried out on various samples after sintering. Figure 6 shows the SEM micrographs of composites obtained by the ceramic route for the pure Mg containing composition. It shows grains of size 2–4 µm. Similar composition synthesized by the molten salt route show two types of grains (figure 7), one poorly crystalline, irregular, small and agglomerated grain of size less than 1 µm and the other larger more non agglomerated grain of 2–3 µm size. The larger more well-faceted grains are probably of the pyrochlore phase and are best observed in the case of pure Zn composition (figure 8) prepared in a closed crucible (X-ray diffraction studies show nearly 97% pyrochlore phase content in this sample, table 2). It has been shown earlier (Goo *et al* 1986) using microdiffraction that the pyrochlore phase has such well faceted grains. However, we also observe very different microstructure (figure 9) for a

Table 2. Details of synthetic condition and phases obtained by the NaCl–KCl flux route in $3PbO–(1–x)MgO–(x)ZnO–Nb_2O_5$.

|	Phases obtained in open crucible method		Phases obtained in closed crucible method	
x	900/6 h	Sintered 1000°C/12 h	900/6 h	Sintered 1000°C/12 h
0	$Pb_3Nb_4O_{13}$ 45% Perovskite 55%	$Pb_3Nb_4O_{13}$ 65% Perovskite 35%	$Pb_3Nb_4O_{13}$ 45% Perovskite 55%	$Pb_3Nb_4O_{13}$ 65% Perovskite 35%
0·25	$Pb_3Nb_4O_{13}$ 40% Perovskite 45% Unidentified 15%	$Pb_3Nb_4O_{13}$ 65% Perovskite 35%	$Pb_3Nb_4O_{13}$ 40% Perovskite 60%	$Pb_3Nb_4O_{13}$ 65% Perovskite 35%
0·5	$Pb_3Nb_4O_{13}$ 45% Perovskite 55%	$Pb_3Nb_4O_{13}$ 70% Perovskite 30%	$Pb_3Nb_4O_{13}$ 60% Perovskite 40%	$Pb_3Nb_4O_{13}$ 85% Perovskite 15%
0·75	$Pb_3Nb_4O_{13}$ 85% Perovskite 15%	$Pb_3Nb_4O_{13}$	$Pb_3Nb_4O_{13}$ 61% Perovskite 13% ZnO 11% Unidentified 15%	$Pb_3Nb_4O_{13}$ 98% ZnO 2%
1	$Pb_3Nb_4O_{13}$ 97% 3% (ZnO)	$Pb_3Nb_4O_{13}$ 97% ZnO 3%	$Pb_3Nb_4O_{13}$ 70% ZnO 13% Unidentified 17%	$Pb_3Nb_4O_{13}$ 97% ZnO 3%

sample of the same composition but synthesized in an open crucible. In the SEM photographs (figures 8 and 9) we also see some secondary phases which are highly agglomerated and of irregular size and shapes. We believe that this secondary phase is amorphous in nature (and hence not observed in powder X-ray diffraction) and might be of PbO which got redeposited on the surface of the major pyrochlore phase after getting volatilized. However, an electron microprobe study would be ideal to confirm these secondary phases.

We have also studied the dielectric properties of the resulting composite materials produced by the ceramic route and the molten salt method at high temperatures and longer heating times. In figure 10 we show typical plots of the variation of the dielectric constant (E) and dielectric loss tangent (D) as a function of frequency for the composites prepared by the ceramic route. We find that the dielectric constants for all the compositions studied are very low—of the order of 14 to 18 in the range of 100 Hz to 100 kHz. The change in the dielectric constant with frequency is within 5 to 7%. From the dielectric studies on the composite obtained from the pure Mg composition, we find that the dielectric constant varies between 19 at 100 Hz to 17·8 at 100 kHz and for the pure Zn composition (which has the cubic pyrochlore phase content of nearly 97%) varies in the region of 16 (at 100 Hz) to about 14·5 (at 100 kHz). The dielectric loss tangent observed in these composites lie in the region of 0·01 to 0·05 over a large frequency range.
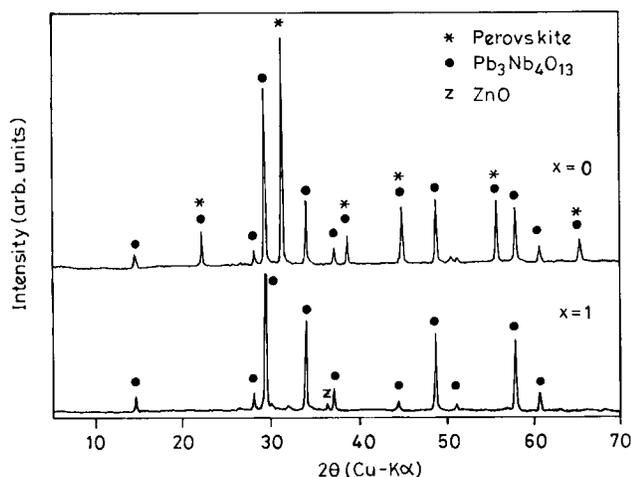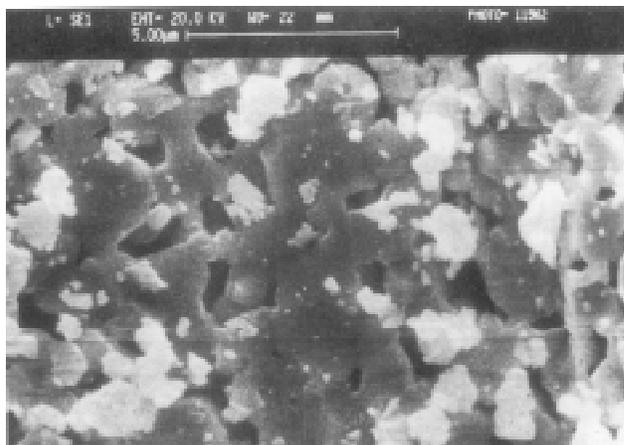

Figure 4. Powder X-ray diffraction patterns obtained by the molten salt method in an open crucible.
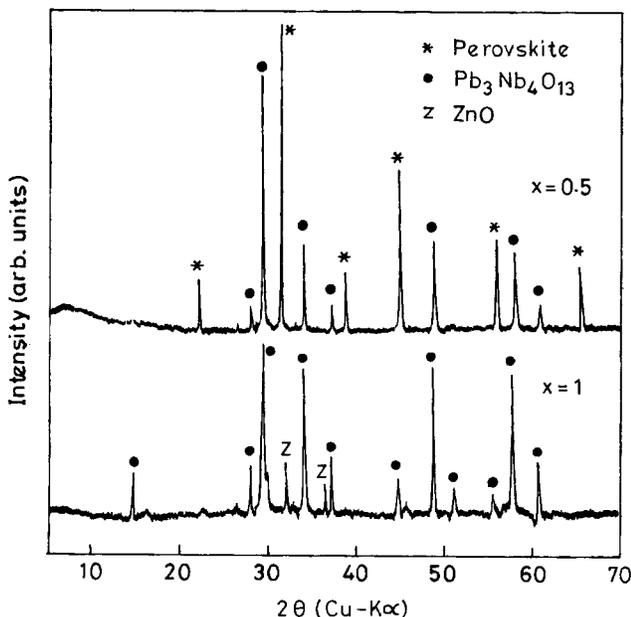
Figure 5. Powder X-ray diffraction patterns obtained by the molten salt method in a closed crucible.
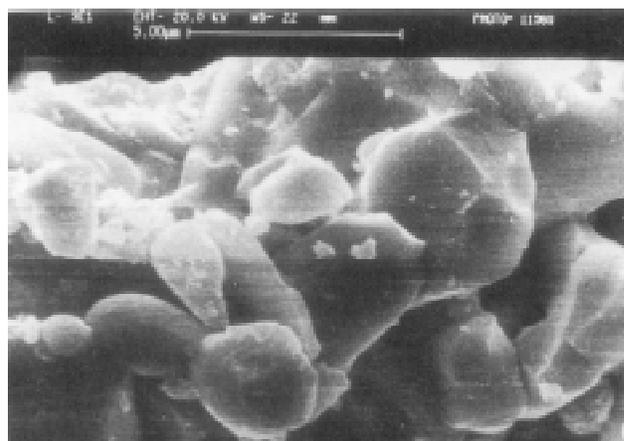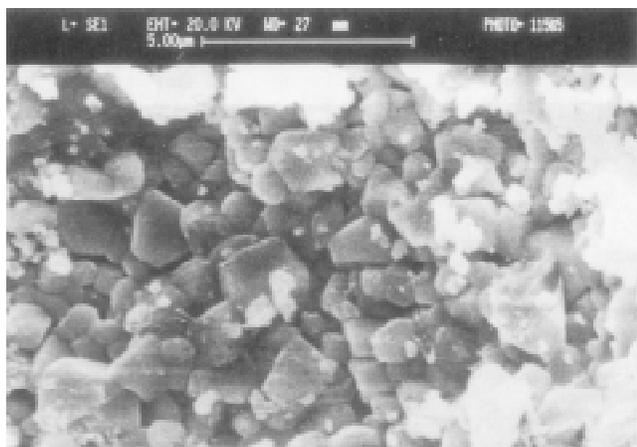

Figure 6. Scanning electron micrograph of the pure Mg composition obtained by the ceramic route (after sintering).
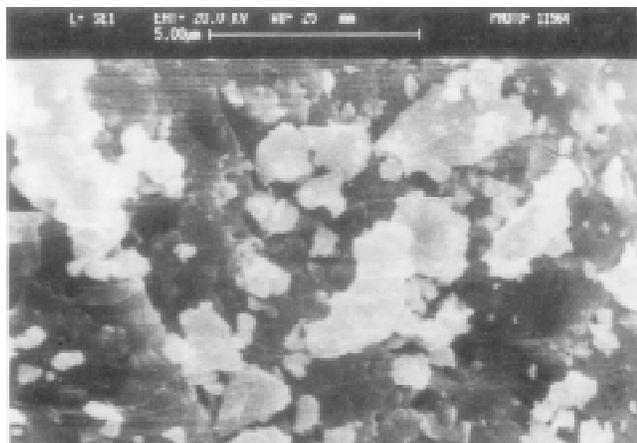

Figure 7. Scanning electron micrograph of the pure Mg composition obtained by the molten salt method (after sintering).

The dielectric properties of the above compositions synthesized by the molten salt synthesis method (in open crucible) are shown in figure 11. The pure Mg composition shows dielectric constant varying from 270 at 100 Hz to 150 at 100 kHz, while for pure Zn composition these values are much lower being 43 at 100 Hz to 38 at 100 kHz. The intermediate compositions have the dielectric constants in between these values. It must be noted that these mixed phases have the perovskite phase (PMN) in the Mg rich compositions which is a known ferroelectric with a high dielectric constant (Uchino 1986). Though the PMN phase is present to nearly 35% in the above Mg-rich compositions the dielectric constants are two orders

of magnitude lower than in pure PMN. In the pure Zn composition where there is no perovskite phase, the dielectric constant is much lower (~ 40). In most of the above cases the dielectric loss tangent lies in the region 0·005 to 0·05 in the frequency range of 1 kHz to 100 kHz.

4. Conclusions

The phases obtained in our study are highly dependent on the synthetic route. Reactions in the $3PbO-MgO/ZnO-Nb_2O_5$ system at high temperatures by the ceramic method in open crucibles lead to a mixture of two phases, the cubic pyrochlore $Pb_3Nb_4O_{13}$ and the columbite $(Mg/Zn)Nb_2O_6$ by the ceramic route. Sintering of compacted pellets at high temperatures leads to a decrease in the pyrochlore phase and an increase in the cubic perovskite phase and $PbNb_2O_6$ which shows that there is

Figure 8. Scanning electron micrograph of the pure Zn composition obtained by the molten salt method in a closed crucible (after sintering).
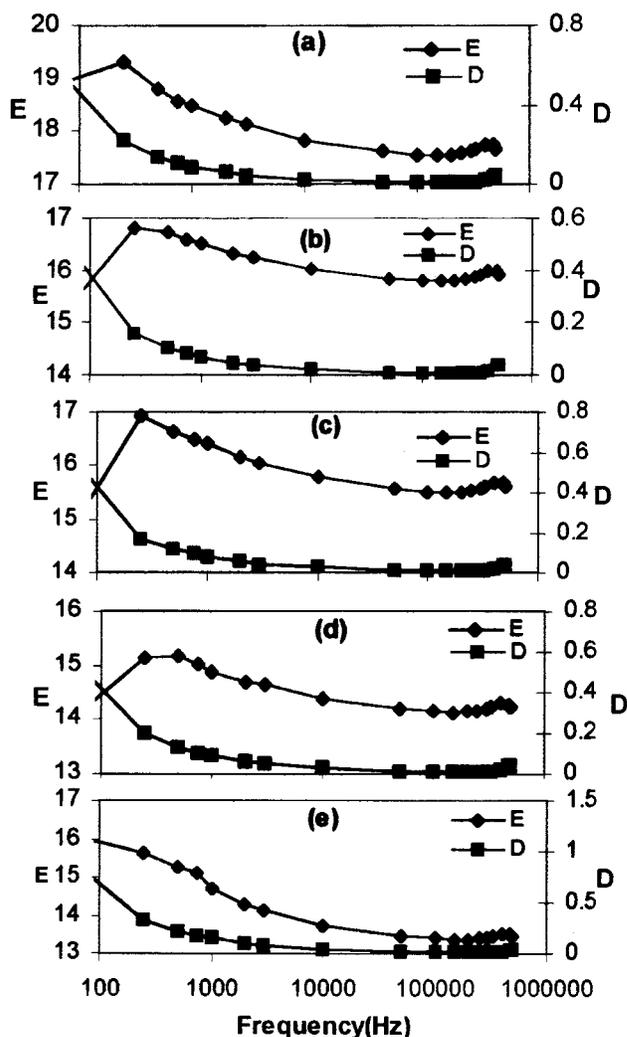

Figure 9. Scanning electron micrograph of the pure Zn composition obtained by the molten salt method in a open crucible (after sintering).
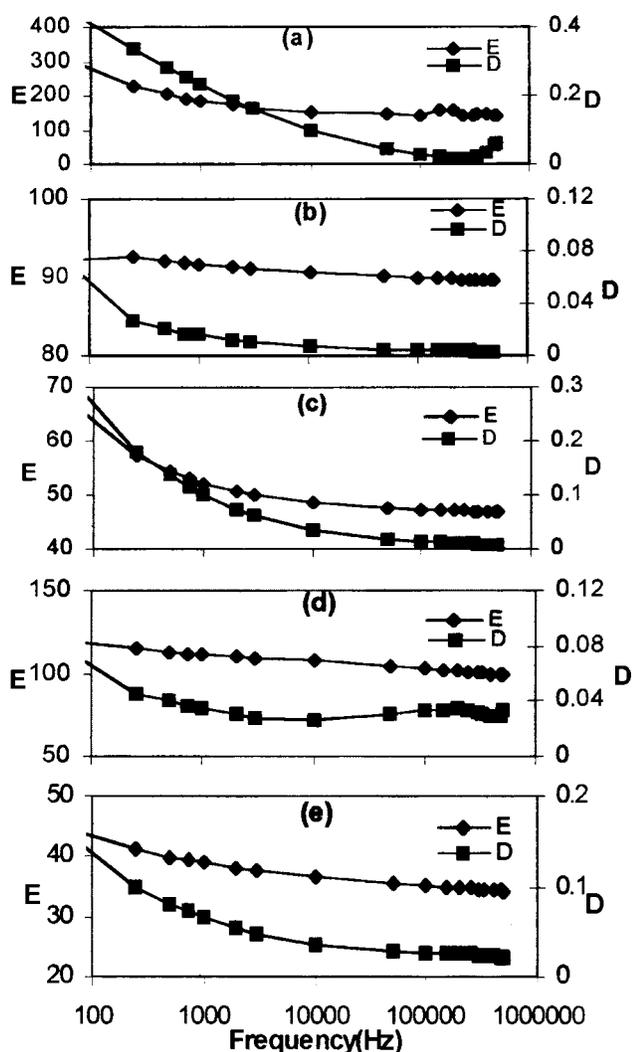

Figure 10. Variation of the dielectric constant and dielectric loss of composites obtained by the ceramic route, in the $3PbO-(1-x)MgO-(x)ZnO-Nb_2O_5$ system. (**a**) $x = 0$, (**b**) $x = 0·25$, (**c**) $x = 0·50$, (**d**) $x = 0·75$ and (**e**) $x = 1·0$.

Figure 11. Variation of the dielectric constant and dielectric loss of composites obtained by the molten salt (open crucible) route, in the 3PbO–(1–x)MgO–(x)ZnO–Nb$_2$O$_5$ system. (**a**) $x = 0$, (**b**) $x = 0.25$, (**c**) $x = 0.50$, (**d**) $x = 0.75$ and (**e**) $x = 1.0$.

Molten salt synthesis of similar compositions in NaCl–KCl (at 900°C/6 h) leads to a biphasic mixture with a significant increase in the perovskite Pb(Mg/Zn)$_{1/3}$Nb$_{2/3}$O$_3$ phase content for Mg-rich compositions. This procedure is of little use for Zn-rich compositions. The perovskite phase content decreases with an increase in the pyrochlore phase content on further sintering for all compositions. There is very little difference in the phase contents obtained whether the molten salt reactions are carried out in open crucibles or crucibles covered with a lid (not sealed). The dielectric constant is quite low (14 to 18) for the composites prepared by the ceramic route whereas the composites (pyrochlore + perovskite) obtained by the molten salt method have much larger dielectric constant which increases with the perovskite content. However, composites obtained by both the above methods have much lower (two orders or more) dielectric constant compared to the pure PMN or PZN phases.

Acknowledgements

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reaction of the pyrochlore phase and the columbite phase (MgNb$_2$O$_6$) to yield the cubic perovskite phase. The reactivity of the columbite phase depends crucially on an optimum Mg : Zn ratio. The maximum perovskite phase obtained is about 20% which may be increased by increasing the reactivity of the columbite phase (may be use small particles, nanoparticles, etc) at the same time keeping the volatility to a minimum.