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Low temperature liquid phase sintering of lead magnesium niobate

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Abstract

It has been observed that PbO (21–5 wt%) is a good sintering aid for low temperature rapid sintering (950°C, 30 min) of lead magnesium niobate (PMN) provided the PMN powder is coarse (average particle size $\sim$ 16 μm or more). For finer PMN powders, along with the same excess of PbO, (1–2 wt%) excess MgO is needed to achieve the same densification. The excess MgO (along with excess PbO) has been found to increase the fluidity of the liquid phase at the sintering temperature leading to liquid penetration inside the finer capillaries of the finer PMN powder with consequent rearrangement and densification. The peak dielectric constant ($\sim$12 000) of MgO added sample was found to be lower than that of the samples containing no excess MgO (K$\sim$13 500) because of the presence of impurity pyrochlore phase in the MgO added samples. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

1. Introduction

Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$, referred to as PMN and related perovskites, otherwise known as relaxor ferroelectrics [1–5], have received much attention in recent times as capacitor and actuator materials because of their high dielectric constant, low electric field dependency, ability to form thin layers, large electrastrictive strain and low firing temperature. However, the preparation of pure perovskite PMN phase without the formation of a pyrochlore phase is difficult by the conventional mixed oxide method [6,7]. The processing problem can be greatly reduced by using the columbite precursor method [6,7] where MgO and Nb_2O_5 are pre-reacted to form $MgNb_2O_6$ followed by its reaction with PbO to get the perovskite PMN. The addition of excess MgO during formation of PMN has been reported to reduce or even eliminate the pyrochlore phase formed [8,9]. In an earlier investigation, the present authors observed that complete conversion to perovskite phase is possible even without adding excess MgO provided $MgNb_2O_6$ (MN) prepared by reacting MgO (from magnesium hydroxycarbonate) and Nb_2O_5 is phase pure which can be obtained by choosing the proper reaction temperature [10].

Since long, the low temperature sintering [3] of PMN has been a sought after process for the reduction of the cost of electrodes for multilayer ceramic capacitors. Excess PbO has been reported [11–13] to lower the sintering temperature of PMN based materials. Van et al. [14] reported that sintered density of PMN increases by increasing the PbO/MgO ratio up to a certain limit. In a previous study [15], we have shown that rapid sintering (30–45 min) of PMN at low temperature (950°C) is possible by using PbO (2-5 wt%) as a sintering aid. Excess MgO (without excess PbO) has been found [7,16,17] to promote grain growth by eliminating the pyrochlore phase from the grain boundary region where the very pyrochlore phase generally acts as a grain growth inhibitor. In the present work, we find that densification in case of PbO aided low temperature sintering of PMN is dependent anomalously on the particle (aggregate) size of the starting powder. We also report the key role of excess MgO (along with excess PbO) in the sintering of PMN powder and provide a possible mechanism for the observed behaviour.

2. Experimental

PMN powders were prepared by reacting PbO (E. Merck, Germany) with MN at 800°C for 10 h and the calcination (reaction) temperatures for the preparation

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of MN were selected to be 1100, 1200 and 1300°C for 20 h. The calcination was done in broad crucibles (unlided) using magnesium hydroxycarbonate ($MgCO_3$, $Mg(OH)_2$, $3H_2O$) & Nb_2O_5 (both of E. Merck, Germany) as raw materials. Particle sizes of the powders were determined by particle size analyser (Sedigraph, Micromeritics no. 5100). The X-ray analysis of the powder samples was done in a Philips PW 1730 diffractometer using CuK_α radiation.

For sintering studies, 0–15 wt% excess PbO with or without 0–5 wt% excess magnesium hydroxycarbonate (equivalent to 0-2 wt% MgO) was added to the PMN powder. The batches were mixed in an agate mortar and pestle under acetone and pellets (~10 mm diameter/3–4 mm thickness) were pressed (pressure ~50 MPa) using 4% PVA binder. The pellets were kept on a platinum base plate and directly introduced into a furnace pre-heated to 950°C. They were kept there for 30 min and were slowly cooled inside the furnace. For isothermal sintering studies, the samples were directly introduced inside the furnace at 950°C and kept there for 5–60 min and finally quenched to room temperature. For electrical measurements, a few samples after sintering were annealed [15] at 800°C for 10 h on a clean alumina plate.

The bulk densities of the samples were measured geometrically and the fracture surfaces of the sintered specimens were viewed in a Cambridge Stereoscan S-250 scanning electron microscope.

The dielectric constant and dissipation factor of some of the sintered pellets with painted silver electrodes were measured in a LCZ meter (Hewlett–Packard 4276A) over a wide range of temperature which was maintained with the help of a constant temperature bath (Haake, Germany). The measurements were made in the frequency range of 500 Hz to 20 KHz and in the temperature range of −20 to 70°C. All the measurements were made in a dry gas (nitrogen or oxygen) atmosphere to avoid any condensation of moisture on the samples at low temperatures.

3. Results and discussion

Fig. 1 depicts the X-ray diffractograms of MN powders calcined at 1100, 1200 and 1300°C. The detailed analysis indicates that the major phase is MN ($MgNb_2O_6$) in all the three cases; however, 1100°C calcined powder and to some extent 1200°C calcined powder contain unwanted phases like Nb_2O_5, $Mg_5Nb_4O_{19}$ and/or $Mg_4Nb_2O_9$. The 1300°C calcined powder is phase pure MN as evident from X-ray analysis. The average particle (aggregate) size of 1100, 1200 and 1300°C calcined powders, as found from sedigraph studies were 5.8, 7.0, 16.8 μm respectively. For our further studies, we chose 1100 and 1300°C calcined powders considering the two extremes of particle sizes and phase purity. The 1100°C calcined powder (batch A) and 1300°C calcined powder (batch B) were reacted with PbO at 800°C for 20 h to form PMN, As reflected from the X-ray studies (Fig. 2) of batch A and batch B PMN, phase pure MN (batch B) produced phase pure perovskite PMN which corroborates with our earlier studies [10], whereas batch A PMN contains unwanted pyrachlore (P_3N_4) and a very small amount of unreacted PbO phase. Intriguingly, as given in Table 1, batch B PMN, which is coarse, can be densified at 950°C (30 min) by using 3–5 wt% excess PbO as a sintering aid, whereas the finer PMN (batch A) powder shows very little

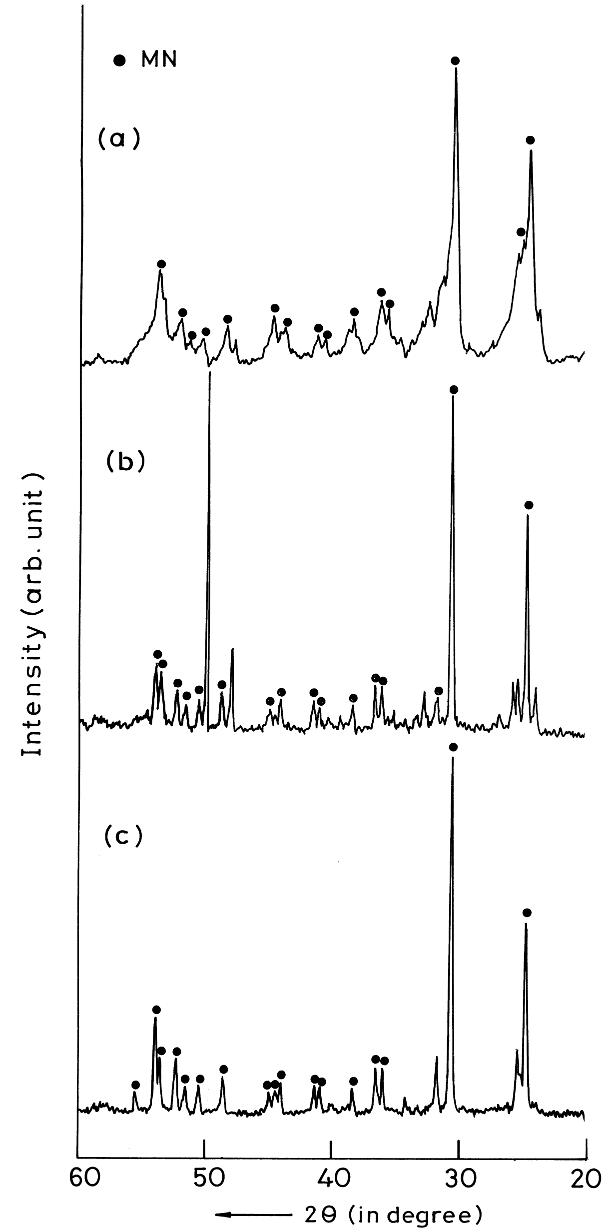


Fig. 1. X-ray diffractograms of MN powders calcined at (a) 1100,(b) 1200 and (c) 1300°C.

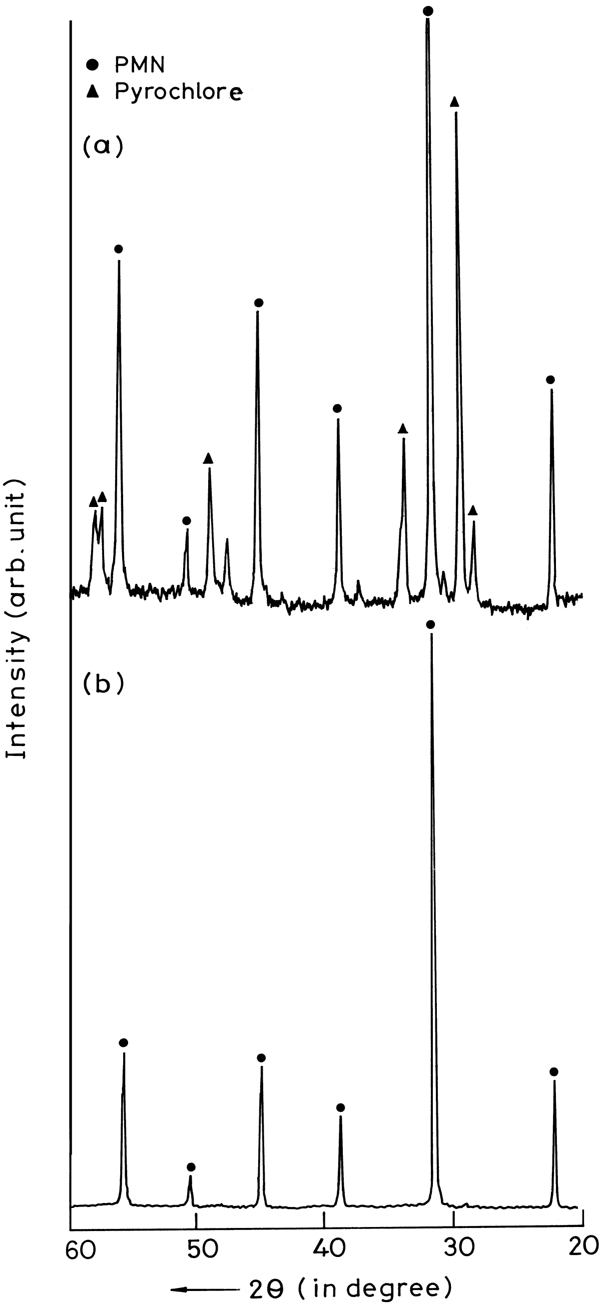


Fig. 2. X-ray diffractograms of PMN powders (a) batch A and (b) batch B, prepared with two different MN powders (refer to text for details).

densification under identical conditions. However batch A powder can be densified by using higher amount of excess PbO (∼10 wt%) as shown in Fig. 3 and such high amounts of excess PbO have been reported to be detrimental [13,17] towards the dielectric properties. Interestingly, as observed by us, the other alternative for batch A PMN powder is to use excess MgO (1–2 wt%) along with the little excess of PbO (3–5 wt%) as a sintering aid to get the desired densification at 950°C (Table 1).

Table 1
Effect of sintering aid on the densification of batch A and B samples (sintering at 950°C/30 min)

Sample no.	Composition	%vol. shrinkage for batch A	%vol. shrinkage for batch B
1.	PMN + 2%PbO	1	17
2.	PMN + 3%PbO	1.5	29
3.	PMN + 5%PbO	2	25
4.	PMN + 2%PbO + 2%MgO	12	—
5.	PMN + 2%PbO + 3%MgO	23	19
6.	PMN + 3%PbO + 2%MgO	21	—
7.	PMN + 3%PbO + 3%MgO	22	29
8.	PMN + 5%PbO + 2%MgO	26	26
9.	PMN + 5%PbO + 3%MgO	32	28
10.	PMN + 5%PbO + 5%MgO	34	27

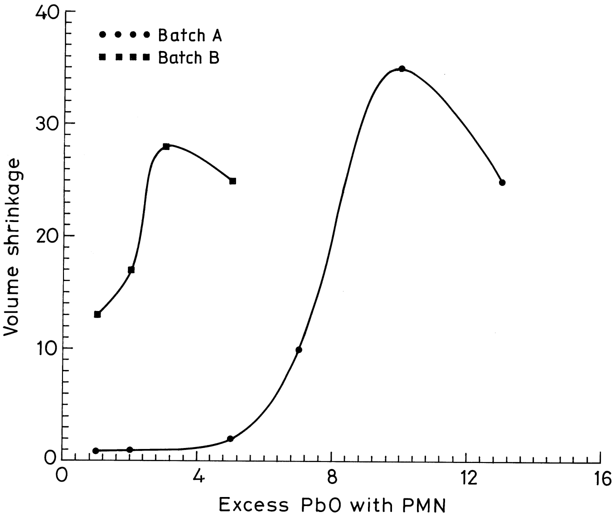


Fig. 3. Variation of volume shrinkage of PMN vs excess PbO during isothermal sintering at 950°C for 30 min.

The effect of excess MgO (along with excess PbO) on the densification behaviour (950°C/30 min followed by furnace cooling) of both batch A and B powders may be seen from the data presented in Table 1. A small amount of excess MgO seems to play a key role in the densification behaviour of batch A powder. For batch B powders the role of excess MgO on densification is trivial (Table 1). To understand the role of excess PbO with or without MgO, we selected two typical compositions for further studies; one from batch A containing both PbO & MgO (composition no. 10 designated A10) and another from batch B containing only PbO (composition no. 2, designated B2) which showed maximum densifications in their respective groups. The selected compositions were subjected to isothermal sintering studies at 950°C for 5 to 60 min. Fig. 4 depicts the logarithmic plot of volume shrinkage vs isothermal sintering time for A10 and B2 compositions. To understand such behaviour (Fig. 4), we have to look into the classic liquid phase sintering which is characterised by three stages [18,19] namely rearrangement, solution-reprecipitation and solid state controlled sintering. The liquid phase formed at high temperature spreads and wets the particles, which cause particle rearrangement through capillary force. Based on the balance between surface tension and an intrinsic frictional force due to viscosity of the liquid, Kingery et al. [19] proposed a model for liquid phase sintering. Huppman [20] considered densification as a function of interparticle force existing between two particles connected by a liquid bridge. Based on this model, rearrangement is significant in systems with small amounts of liquid and low wetting angle. The second stage of liquid phase sintering is characterised by grain growth, dissolution of small grains, grain annealing, densification and development of a rigid solid skeleton. Under complete wetting conditions, Kingery [21] considered contact flattening. However Petzow et al. [22] considered Ostwald ripening with shape accommodation as an important mechanism of second stage liquid phase sintering. During the early stage of liquid phase sintering, the volume shrinkage ($\triangle V/V_o$) is related to time (t) by the following relation [21]:

$$\triangle V/V_o \sim t^y \tag{1}$$

where y is close to unity and generally lies between 1 and 1.5. As evident from Fig. 4, the slope (y) of $\log\triangle V/V_o$ vs $\log t$ curve for both A10 and B2 are very close and are ~1 which corroborates with Eq. (1) and supports the role of molten PbO as a sintering (liquid phase) aid for both the cases. To find out the role of excess MgO (along with excess PbO), we have to appreciate that for rearrangement [23] (either rearrangement 1 or rearrangement II, where the former is the rearrangement of initial particles and the latter is the rearrangement of the grains after particle (aggregate) disintegration), wetting of the solid by the melt is a necessary condition. Even a very small amount (as low as 0.1%) of additive [23] can drastically alter the liquid phase sintering by various mechanisms like modifying the wetting characteristics, forming a second phase, allowing rapid grain growth by decreasing the grain boundary energy by the segregation of the impurities at the grain boundaries, etc. Firstly, the dissolution of some amount of MgO in PbO melt was confirmed by comparing the X-ray diffractograms of powdered PbO + 2 wt%MgO melt (after quenching) and pure PbO powder. We found that the characteristics peaks of PbO have been shifted slightly towards the higher angle (Fig. 5) in case PbO + MgO melt; of course, some amount of unreacted MgO was also present as evident from the X-ray diffractograms. Secondly, the role of dissolved MgO on the surface tension of the melt (and hence wetting) and its consequent effect on sintering, if any, in our case is negligible because the same powder of larger particle size (batch B) can be densified by adding PbO only and there is no exaggerated effect of MgO plus PbO on densification during the liquid phase sintering of such coarse powder (Table 1). At the same time, when the powder of batch B was ground to around the particle size of batch A powder, we observed that the sintering behaviour of such ground powder was similar to that of batch A powder.

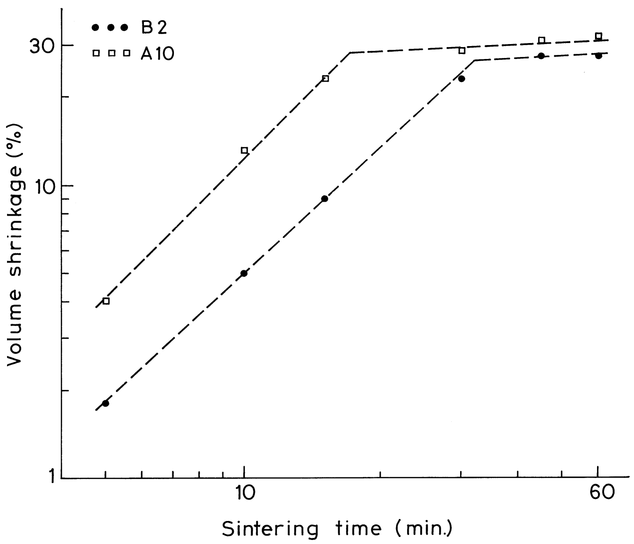


Fig. 4. Logarithmic plot of volume shrinkage vs isothermal sintering time (at 950°C) for A10 and B2 PMN compositions.

To find out the effect of viscosity of the liquid melt (if any) on sintering, we melted powders of pure PbO and PbO plus 1, 1.5 and 2 wt% MgO (assuming very little solubility of MgO in molten PbO at 950°C during the rearrangement period, the latter being quite short) in dense alumina crucibles at 950°C and poured the melts (or melts plus undissolved particles) on a smooth stainless steel plate. We found qualitatively that the fluidity of the PbO plus MgO melts was higher than that of the pure PbO melt. The higher fluidity of PbO plus MgO melts in comparison to pure PbO melt is quite expected [24] as glasses can be made with PbO as a major constituent where PbO acts as a network former; MgO dissolved in PbO melt should act as a network modifier and lower the viscosity. It is to be noted that other than surface tension of the liquid phase the viscosity also plays an important role in the liquid phase sintering because, in an ideal case, the infiltration distance (k) of a melt into a capillary is parabolic with time (t) and can be described by Washburn model [25] as given below:

$$k^2/t = \gamma_{LV} d \cos\theta / 4\eta \tag{2}$$

where γ_{LV} is the surface free energy of the liquid–vapour interface, d is the diameter of the capillary, θ is the wetting angle and η is the viscosity of the melt. Also,

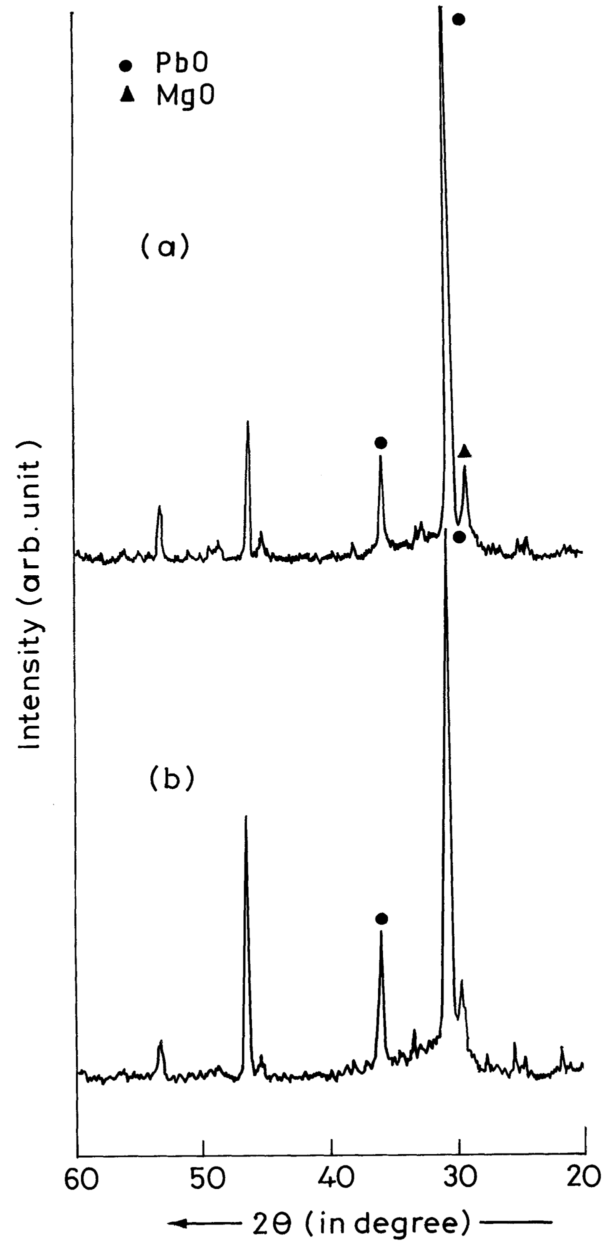


Fig. 5. X-ray diffractograms of powdered (a) PbO + 2 wt% MgO melt and (b) pure PbO melt after quenching.

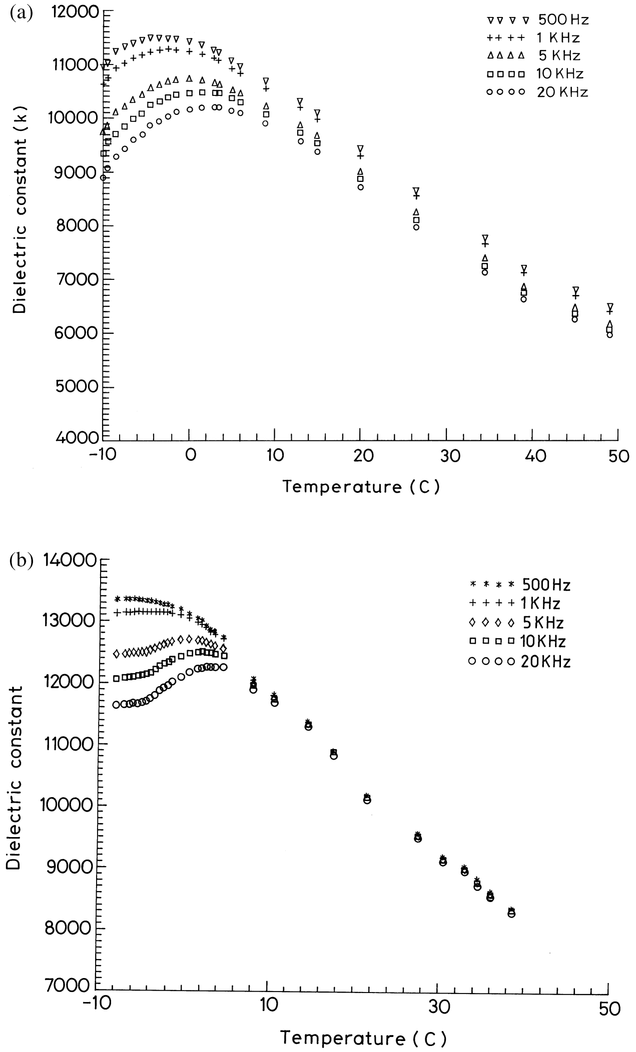
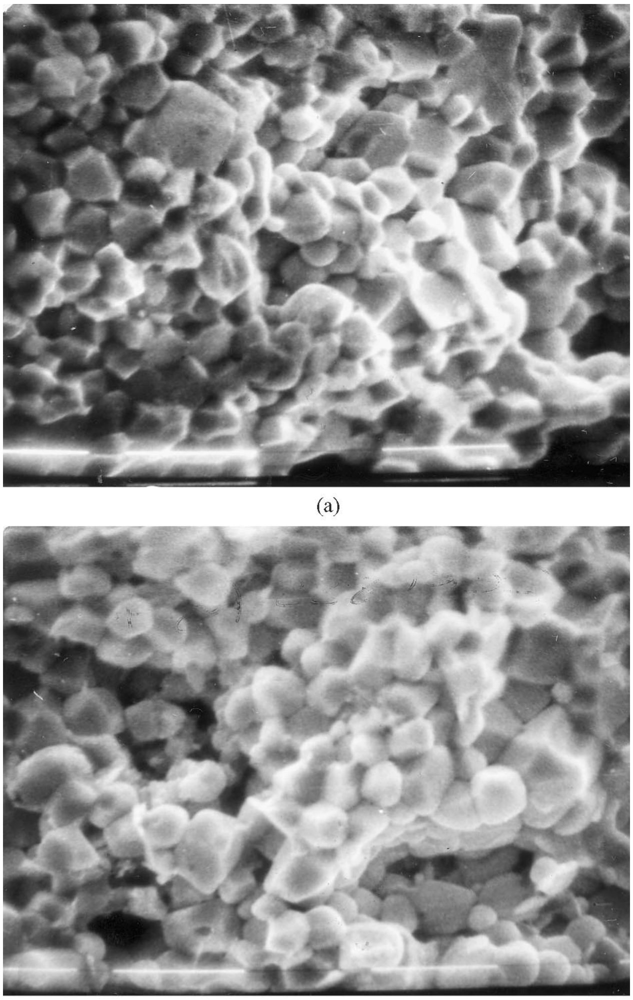


Fig. 6. Temperature dependence of weak field permittivity of (a) A10 and (b) B2 samples for various measuring frequencies.

for a viscous liquid in motion, the liquid near the surface cannot keep up with the advancing front so that a higher dynamic contact angle [26] develops. In our case, for batch B powders, due to larger capillary size (as the particle size is large), the pure PbO melt of relatively lower fluidity can easily penetrate inside the capillaries and exert capillary pressure leading to rearrangement and densification. For finer batch A powders only, the more fluid PbO melt containing some dissolved MgO can penetrate the fine capillaries and lead to rearrangement and densification. The nearly identical slopes of densification curves for A10 and B2 samples (Fig. 4) also indicate that the intrinsic parameters controlling the rearrangement and shrinkage in both the cases are identical. As shown in Fig. 3, batch A powder can also be sintered by adding only PbO provided the latter is quite high (10 wt%) in amount. In this case, along with the capillary suction, the additional fluid pressure due to large amount of molten lead oxide formed at the sintering temperature can be sufficient to force the liquid inside the capillaries leading to densification. However, as expected for liquid phase sintering, there is generally an optimum amount of liquid, as observed by other workers [27,28] too, above which the densification goes down (Fig. 3).

To see the effects of the sintering aids on the final dielectric properties, both A10 and B2 samples after sintering at 950°C for 30 min were annealed at 800°C (10 h) for homogenization [15]. The dielectric behaviour of A10 and B2 samples has been depicted in Fig. 6(a) and (b) (dissipation factor for both the samples were within


(a)

(b)

Fig. 7. The scanning electron micrographs of the fracture surfaces of (a) sintered A10 and (b) sintered B2 samples (sintered at 950°C/30 min).

0.003–0.008 at room temperature). The sample B2 shows higher peak dielectric constant in comparison to sample A10. The scanning electron micrographs of the fracture surfaces of sintered A10 and B2 samples (Fig. 7 (a) and (b)) indicate that the average grain size of both the samples are identical although the initial particle size of B2 powder was much larger than that of A10 powder. Such observation is not unusual if we remember that during rearrangement II [23] (discussed earlier), there is disintegration of the particles. It is to be noted that the apparently large particles of batch B powder (and to some extent batch A powder) are some form of grain aggregates which is evident from the SEM of the fracture surface of a batch B PMN sample (without any excess PbO) fired at 950°C/30 min (Fig. 8); the latter showed practically no shrinkage due to absence of PbO additive and hence the grains in the microstructure reflect the particle morphology of the starting powder. It seems that in our case, the lower dielectric constant of sample A10 is primarily due to the presence of impurity pyrochlore phase (present in the starting powder due to lower calcination temperature of MN (discussed earlier)). However, a little excess PbO was present in all the samples; considering the volatilization loss (for 900°C/30 min schedule), the excess PbO present in the samples was calculated to be in the range of 0.09–0.15 wt%.

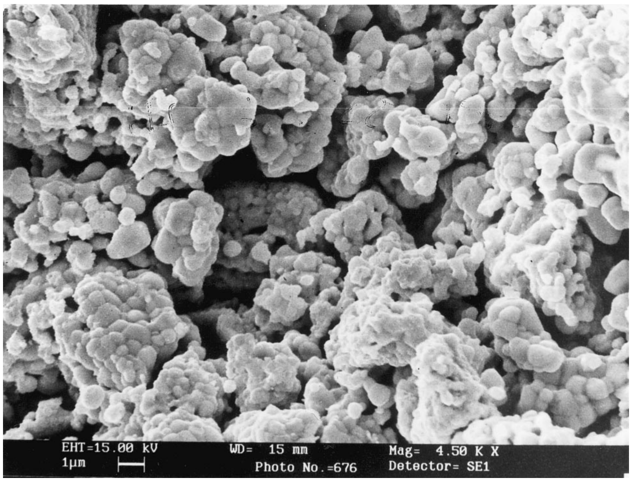


Fig. 8. The scanning electron micrograph of the fracture surface of a batch B PMN sample (without any PbO additive) fired at 950°C/30 min.

4. Conclusion

1. It has been observed thet PbO (2–5 wt%) is a good sintering aid for the low temperature rapid sintering (950°C, 30 min) of PMN provided the initial particle (aggregate) size of the PMN powder is high (around 16–17 μm average size or more).
2. For finer (< 16 μm) PMN powder an excess (1–2 wt%) MgO along with the same amount (2–5 wt%) of excess PbO is needed to achieve the desired densification during low temperature rapid sintering of PMN.
3. The role of excess MgO (along with the excess PbO) is to increase the fluidity of the liquid phase at the sintering temperature so that the liquid can easily penetrate the finer capillaries (for finer powder in contrast with large capillaries for coarse powder) and can exert the capillary pressure leading to rearrangement and densification.
4. The peak dielectric constant of the samples containing excess MgO was found to be lower than that of the samples containing zero excess MgO primarily because of the fact that the MgO added sample contains impurity pyochlore coming from the starting finer powder owing to the low formation (calcination) temperature of $MgNb_2O_6$ from their respective oxides.

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References

[1] L.E. Cross, Relaxor ferroelectrics, Ferroelectrics 76 (1987) 241–267.

[2] G.A. Smolenskii, V.A. Isapov, A.I. Agranovskaya, S.N. Popov, Ferroelectrics, with diffuse phase transition, Sov. Phys.—Solid St., (Engl. transl.) 2 (11) (1961) 2548–2594.

[3] L. Sheppard, Progress continues in capacitor technology, Am. Ceram. Soc. Bull. 72 (3) (1993) 45–57.

[4] L.E. Cross, S.J. Jang, R.E. Newnham, S. Nomura, K. Uchino, Large electrostrictive effects in relaxor ferroelectrics, Ferroelectrics 23 (1990) 187–192.

[5] K. Uchina, Electrostrictive actuators: Materials and applications, Am. Ceram. Soc. Bull. 65 (4) (1986) 647–652.

[6] S.L. Swartz, T.R. Shrout, Fabrication of perovskite lead magnesium niobate, Mat. Res. Bull. 17 (1982) 1245–1250.

[7] T.R. Shrout, A. Halliyal, Preparation of lead based ferroelectric relaxors for capacitors, Am. Ceram. Soc. Bull. 64 (4) (1997) 704–711.

[8] S.L. Swartz, T.R. Shrout, W.A. SchuIze, L.E. Cross, Dielectric properties of lead magnesium niobate ceramics, J. Am. Ceram. Soc. 67 (5) (1994) 311–315.

[9] E. Goo, T. Yamamoto, K. Okazaki, Microstructure of lead magnesium niabate ceramics, J. Am. Ceram. Soc. 69 (9) (1996) C188–C190.

[10] D. Saha, A. Sen, H.S. Maiti, Solid state synthesis of precursor $MgNb_2O_6$ for the preparation of $Pb(Mg_{1/3}Nb_{2/3})O_3$, J. Mat. Sci. Lett. 13 (1994) 723–724.

[11] J.P. Suha, D.J. Hang, H.U. Anderson, Effect of excess PbO on the sintering characteristics and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ based ceramics, J. Am. Ceram. Soc. 71 (3) (1988) C152.

[12] M. Lejeune, J.P. Bailot, Optimization of dielectric properties of lead magnesium niobate ceramics, Am. Ceram. Soc. Bull. 65 (4) (1996) 679–682.

[13] D.H. Kang, K.H. Youn, Dielectric properties due to excess PbO and MgO in lead magnesium niobate ceramics, Ferroelectrics 87 (1988) 255–264.

[14] M.F. Yan, H.C. Ling, W.W. Rodes, Preparation and properties of PbO–MgO–Nb_2O_5 ceramics near the$Pb(Mg_{1/3}Nb_{2/3})O_3$ composition, J. Mat. Res. 4 (4) (1989) 930–944.

[15] D. Saha, A. Sen, H.S. Maiti, Fast firing of lead magnesium niobate at low temperature, J. Mat. Res. 11 (4) (1996) 932–937.

[16] M. Lejeune, J.P. Boilot, Low firing dielectrics based on lead magnesium niabate, Mat. Res. Bull. 20 (1985) 493–499.

[17] H. Wang, W.A. Schulze, The role of excess magnesium oxide or lead oxide in determining the microstructure and properties of lead magnesium niabate, J. Am. Ceram. Soc. 73 (4) (1990) 825–832.

[18] W.D. Kingery, Densification during sintering in the presence of a liquid phase, J. Appl. Phys. 30 (3) (1959) 301–306.

[19] W.D. Kingery, E. Niki, M.D. Narashimhan, Sintering of oxide and carbide-metal compositions in presence of a liquid phase, J. Am. Ceram. Soc. 44 (1961) 29–35.

[20] W.J. Huppman, Sintering in the presence of liquid phase, in: G.C. Kuczynkiz, (Ed.) Materials Science Research, Vol.10, Sintering and Catalysis, Plenum, New York, 1995, pp. 359–378.

[21] W.D. Kingery, Sintering in the presence of a liquid phase, in: W.D. Kingery (Ed.), Kinetics of High Temperature Process. M.I.T., John Wiley & Sons, and Chapman and Hall, Massachusetts, 1959, pp. 187–192.

[22] G. Petzow, W.A. Kaysser, M. Aoterbrink, Liquid phase and activated sintering in: D. Kolar, S. Pejovink, M. M. Ristic (Eds.), Sintering–Theory and practice, Elsevier, Amsterdam, 1982, pp. 27–36.

[23] M. Sprissler, W.A. Kayser, W.J. Huppman, G. Petzow, Influence of MgO and liquid phase sintering and solid phase sintering of $A1_2O_3$, in: H. Hausner (Ed.) Science of Ceramics, Vol. 10, Dentsche Keramische Gesellschaft, 1980, pp. 321–323.

[24] W.A. Weyl, E.C. Marboe, The Constitution of Glasses—A Dynamic Interpretation, vol. II, part I, John Wiley Interscience, New York, 1964, p. 606.

[25] E.O. Einset, Capillary infiltration rates into porous media with applications to silcomp processing, J. Am. Ceram. Soc. 79 (1996) 333–338.

[26] A.J. Kinloch, Adhesion: Fundamental principles, in: M. B. Beven (Ed.), Encyclopedia of Materials Science and Engineering, vol. I, Pergamon, Oxford, 1996, p. 67.

[27] E.M. Kostic, Sintering of $MgAl_2O_4$ in the presence of liquid phase, in: G.C. Kuczynski (Ed.), Materials Science, Research, vol.10, Sintering and Catalysis, Plenum, New York, 1995, 379–383.

[28] K.H. Yoon, Y.S. Cho, D.H. Lee, D.H. Kang, Interfacial phenomenon and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with excess PbO, in: L. M. Levinson and S. Hirano (Eds.), Grain Boundaries and Interfacial Phenomena in Electronic Cerainics, American Ceramic Society, Westerville, OH, 1994, pp. 371–378.