Journal of the European Ceramic Society **19** (1999) 629–635
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00253-2
0955-2219/99/$—see front matter

Relationships between Sintering Conditions, Microstructure and Dielectric Properties of Lead Magnesium Niobate

Supon Ananta and Noel W. Thomas*

Department of Materials, University of Leeds, Leeds, LS2 9JT, UK

(Received 6 July 1998; accepted 30 September 1998)

Abstract

Lead magnesium niobate, ($Pb(Mg_{1/3}Nb_{2/3})O_3$; PMN) ceramics have been produced by sintering PMN powders synthesized from lead oxide (PbO) and magnesium niobate ($MgNb_2O_6$). As these PMN powders could be prepared in a reproducible manner, attention has been focused on relationships between sintering conditions, phase formation, density, microstructural development and dielectric properties. A method has been developed whereby volatilisation of PbO can be minimised, thereby avoiding the formation of pyrochlore phases and maximising the perovskite yield. The optimum sintering conditions have been identified as 1275°C for 2h. © 1999 Elsevier Science Limited. All rights reserved

Keywords: sintering, microstructure-final, dielectric properties, niobates, lead magnesium niobate.

1 Introduction

A great deal of effort has recently been dedicated to the manufacturing and engineering of lead-containing relaxor perovskite compounds. Amongst this type of material, lead magnesium niobate (PMN) has been extensively investigated both for academic science and for technological applications. Owing to its broad, high permittivity Curie maximum, high electrostrictive strain coefficient and relatively low sintering temperature compared to barium titanate, ceramics based on PMN have become strong candidates for many dielectric and electrostrictive applications.[1–4]

However, the formation of lead magnesium niobate perovskite is often accompanied by the occurrence of a secondary pyrochlore-type phase.[3–5] In general, the latter is undesirable, since it is one of the many factors which may affect properties, such as the electromechanical coupling factor and relative permittivity of the ceramic adversely. Several innovative techniques, for example the columbite mixed oxide, coprecipitation and partial oxalate synthetic routes, have been applied to this.[2–8] Whereas most of these have enabled the synthesis of pyrochlore-free, perovskite PMN, the dielectric properties vary considerably between methods.

There is evidence that a high purity single phase perovskite powder of composition $Pb(Mg_{1/3}Nb_{2/3})O_3$ will not, by itself, give rise to pyrochlore-free PMN ceramics. This is due to high sintering temperatures required, typically above 1000°C, where the degree of PbO volatilisation affects the stoichiometry of the product by forming a pyrochlore, as well as a perovskite phase.[2–5] This article deals with the sintering stage of forming PMN ceramics, utilising starting powders which have been synthesized optimally to produce single phase perovskite PMN.[9] As the objective of the work is to produce sintered PMN ceramics with maximum density and relative permittivity, the suppression of PbO loss during sintering is a major objective. Thus consideration is given here to the phases formed, densification, microstructural development and dielectric properties in PMN ceramics sintered at various temperatures.

2 Methods

PMN powders were synthesized by a modified two-stage mixed oxide route, as reported earlier.[9] Ceramic fabrication was achieved by adding 3 wt%

---

*To whom correspondence should be addressed at present address: WBB Technology Ltd., Watts Blake Bearne & Co plc, Park house, Courtenay Park, Newton Abbot, TQ12 4PS, UK. Fax: +44-(0)1626-322386; e-mail: nthomas@wbb.co.uk

polyvinyl alcohol (PVA) binder, prior to pressing as pellets in a pseudo-uniaxial die press at 100 MPa. Using an arrangement of green pellets as shown in Fig. 1, four sets of sintering experiments were carried out: (*i*) in air, (*ii*) inside a closed alumina crucible, (*iii*) inside a closed alumina crucible containing a PMN atmosphere powder; and (*iv*) inside a platinum foil and closed alumina crucible with PMN atmosphere powder. Green pellets were placed between PMN setters, with the binder burnt out at 500 °C for 4 h. The PMN pellets were extracted for weighing, to verify that all the binder had been removed. The dimensions of the green pellets were also measured and the surfaces of the setter pellets repolished before reinserting into the alumina crucible, together with PMN atmosphere powder. The use of setter pellets was in order to avoid a chemical reaction with the alumina crucibles, along with pellet distortions arising from one-sided contacts with the crucibles. The latter is important in obtaining pellets with parallel faces for dielectric measurements.

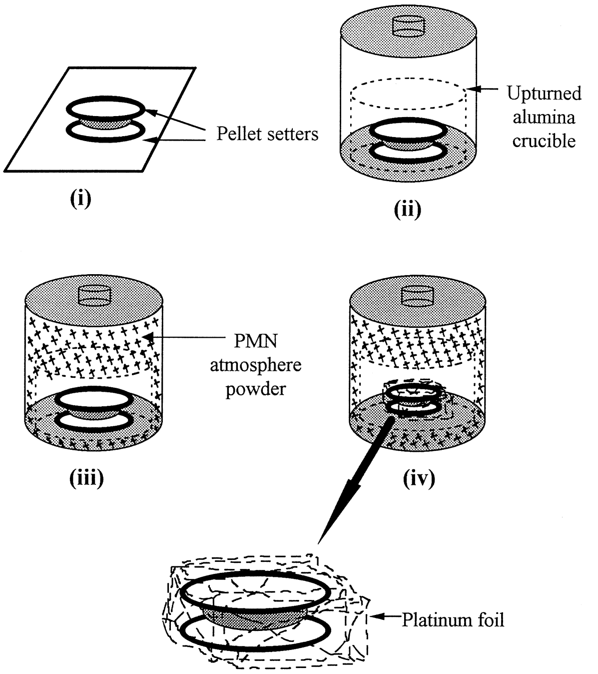

Fig. 1. Schematic representations of the experimental set-up for four sintering conditions: (*i*) in air; (*ii*) inside a closed alumina crucible, (*iii*) inside a closed alumina crucible containing a PMN atmosphere powder; and (*iv*) inside a platinum foil and closed alumina crucible with atmosphere powder.

Sintering was carried out at temperatures from 1200 to 1300 °C for 2 h, with constant heating rates of 10 °C min^{-1} applied. Densities of the sintered pellets were determined by using the Archimedes principle. XRD was used to identify the crystalline phases formed, with the microstructural development examined by scanning electron microscopy (SEM). The dielectric properties of the final products were measured for signal voltages at various frequencies between 100 Hz and 100 kHz in the temperature range from −60 to 60 °C, using an HP4284A precision LCR meter in conjunction with a Delta Design 9023 temperature chamber.

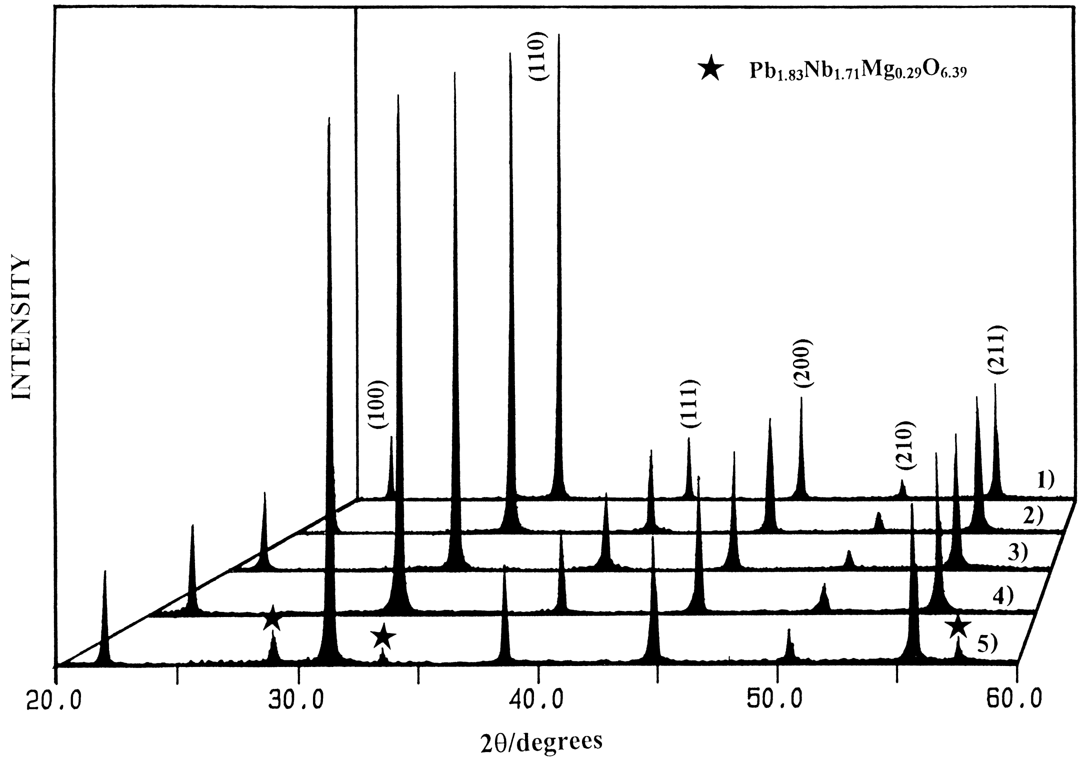

Fig. 2. XRD patterns of PMN ceramics sintered at various temperatures according to procedure (*iv*): 1. 1200 °C; 2. 1225 °C; 3. 1250 °C; 4. 1275 °C and 5. 1300 °C.

3 Results and Discussion

3.1 Analysis of phases formed

XRD patterns of the PMN ceramics formed at various sintering temperatures are given in Fig. 2. The strongest reflections in the majority of the XRD patterns indicate formation of the perovskite phase of PMN, which could be matched with JCPDS file 27-1199. To a first approximation, this phase has a cubic perovskite-type structure in space group *Pm3m* (no. 221), with cell parameter $a = 405$ pm. However, some additional reflections (marked by ⋆), which correlate with a pyrochlore phase of composition $Pb_{1{\cdot}83}Nb_{1{\cdot}71}Mg_{0{\cdot}29}O_{6{\cdot}39}$ (JCPDS file 37-71), are found in some XRD patterns. This phase has a cubic structure with cell parameter $a = 1.059$ nm in space group *Fd3m* (no. 227).

The relative amounts of perovskite and pyrochlore phases present in each sintered ceramic may be calculated from the intensities of the major X-ray reflections for the perovskite and pyrochlore phases. In this connection, the following approximation proposed by Swartz and Shrout[3] was employed:

$$\text{wt\% perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{pyro}}}\right) \times 100 \tag{1}$$

Here I_{Perov} and I_{pyro} refer to the intensities of the {110} perovskite and {222} pyrochlore peaks, respectively, these being the most intense reflections in the XRD patterns of both phases. Consequently, in order to estimate the concentrations of pyrochlore phase present in the different samples, eqn (1) has been applied to the diffraction patterns obtained, as given in Table 1.

The effect of sintering temperature in the range from 1200 to 1275 °C on phase formation was found to be insignificant, with a single phase of perovskite PMN (yield of 100% within the limitations of the XRD technique) obtained in all cases. This is probably due to a combination of effective vibro-milling, the carefully optimised reaction to form single-phase precursor powders[9] and the sintering procedure adopted (method (*iv*); Fig. 1). The sintering procedure leads to low lead losses and consequently avoids the formation of pyrochlore. As shown in Table 1, pyrochlore phase (~0·5%) was found to coexist with the perovksite phase in PMN sintered at 1200 °C, to be suppressed at the sintering temperatures from 1225 to 1275 °C and then to reappear with a significant amount of ca 24 wt% in PMN sintered at 1300 °C. The small amount of pyrochlore formed in PMN ceramics sintered at 1200 °C could be attributed to many factors, including inhomogeneity of the mixture,[6] whilst at 1300 °C pyrochlore formation is most likely to be due solely to PbO evaporation.

Table 1. Effect of sintering temperature on phase formation and densification for PMN ceramics sintered under procedure (*iv*)

Sintering temperature (°C)/2 h	*Perovskite (wt%)*	*Pyrochlore (wt%)*	*Density*[a] *(%)*
1200	99·5	0·5	90
1225	100·0	0·0	92
1250	100·0	0·0	95
1275	100·0	0·0	96
1300	76·1	23·9	93

[a]The maximum density value of PMN is ~8·136 g cm^{-3}, this being larger than the maximum density of the pyrochlore phase. Thus all %-densities are expressed relative to the maximum density value of PMN, in order to provide a uniform comparative scale.

3.2 Densification analysis

Weight losses occurring during the sintering of PMN samples are due to PbO volatilisation. Thus, by recording the weights of the pellets before and after sintering, the level of PbO loss may be calculated for each sample. Weight loss data of all samples sintered at temperatures from 1200 to 1300 °C for 2 h are shown in Fig. 3. Whereas, in general, the

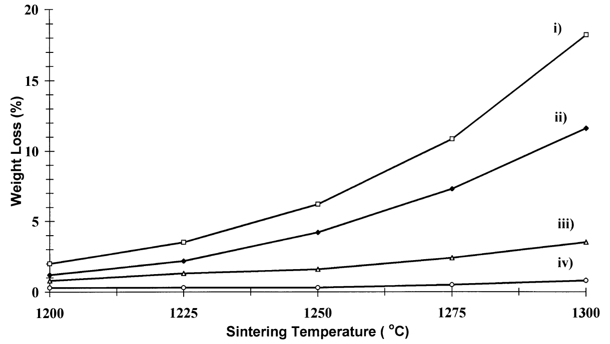

Fig. 3. Weight loss as a function of the sintering temperature for PMN ceramics sintered: (*i*) in air; (*ii*) inside a closed alumina crucible, (*iii*) inside a closed alumina crucible containing a PMN atmosphere powder; and (*iv*) inside a platinum foil and closed alumina crucible with atmosphere powder.

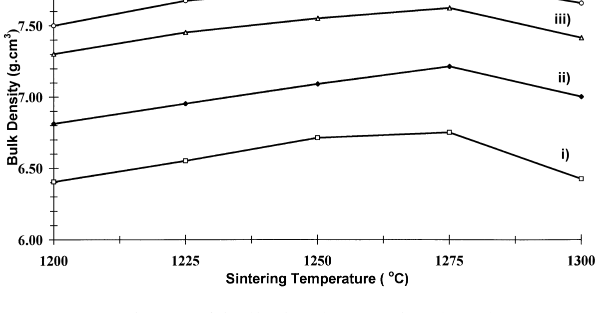

Fig. 4. Dependence of bulk density on the sintering temperature in PMN ceramics sintered: (*i*) in air; (*ii*) inside a closed alumina crucible, (*iii*) inside a closed alumina crucible containing a PMN atmosphere powder; and (*iv*) inside a platinum foil and closed alumina crucible with atmosphere powder.

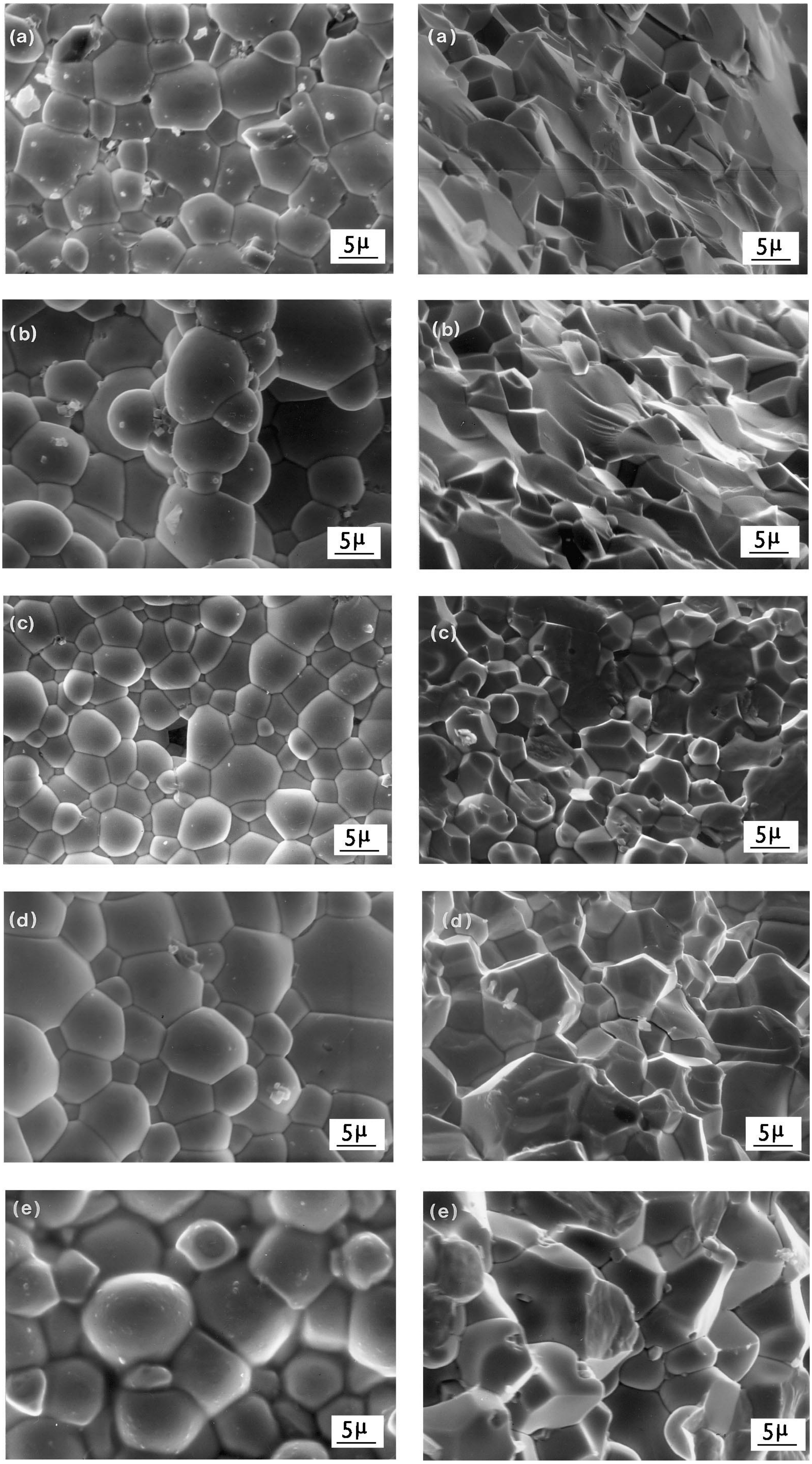

Fig. 5. SEM micrographs of free and fracture surfaces of PMN ceramics sintered under procedure (*iv*) at (a) 1200 °C, (b) 1225 °C, (c) 1250 °C, (d) 1275 °C and (e) 1300 °C.

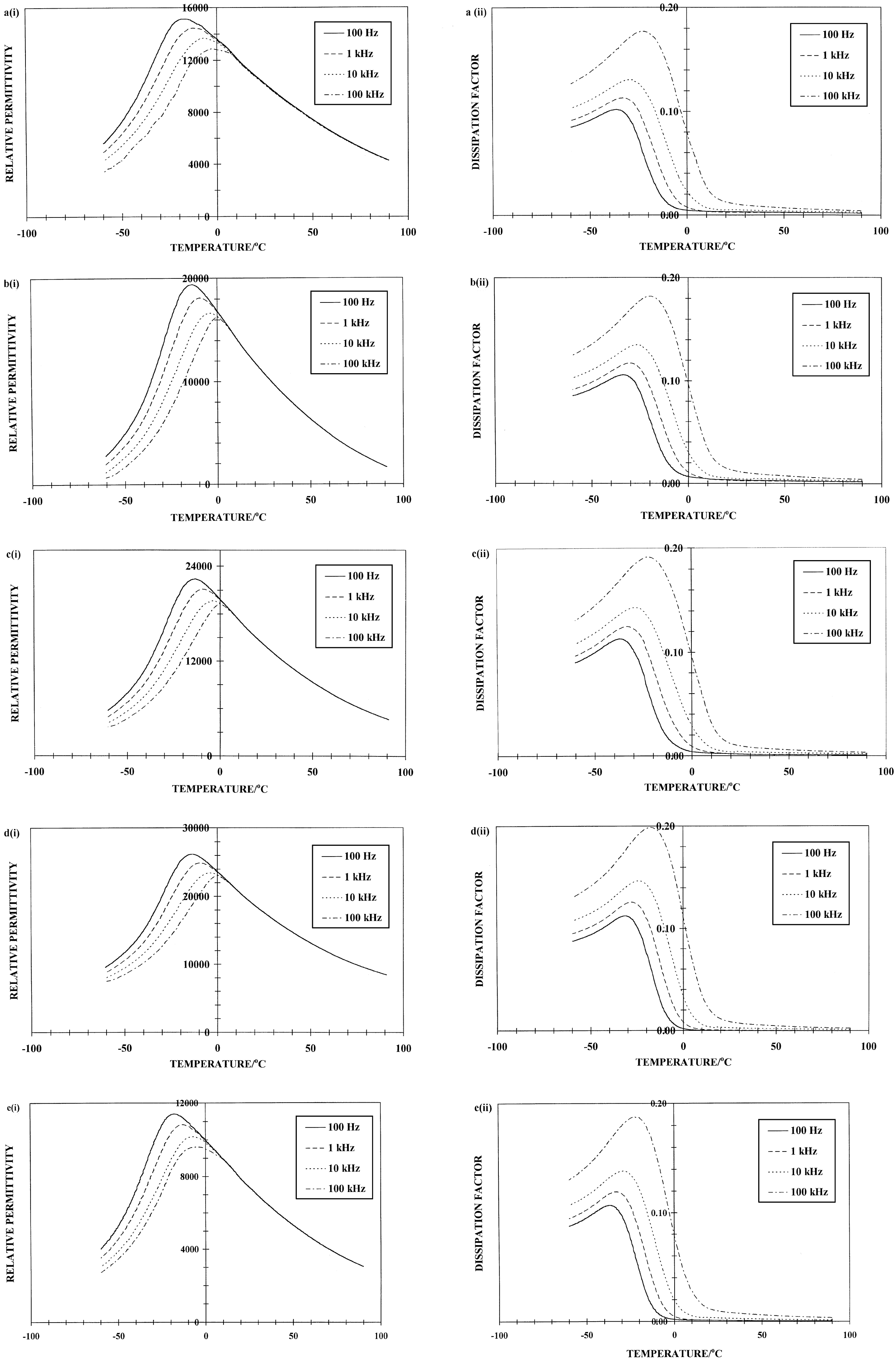

Fig. 6. Variation of (*i*) relative permittivity and (*ii*) tan δ for PMN ceramics sintered under procedure (*iv*) at (a) 1200 °C, (b) 1225 °C, (c) 1250 °C, (d) 1275 °C and (e) 1300 °C.

weight loss increases with sintering temperature, it is interesting to note that the level of lead loss can be effectively minimised by the use of platinum foil and PMN atmosphere powder. A density of about 92–96% of the maximum value for PMN can be achieved in this way (Table 1; Fig. 4). The maximum density was obtained by sintering method (*iv*) at 1275 °C. The observed fall-off in density at 1300 °C is due both to PbO volatilisation impeding the sintering process and the lower density of the pyrochlore phase, which is present with a concentration of 24 wt%.

3.3 Microstructural analysis

Microstructural development during sintering was investigated by scanning electron microscopy (SEM). Free and fracture surface micrographs of PMN ceramics sintered at various temperatures from 1200 to 1300 °C are shown in Fig. 5. The results indicate that grain size tends to increase with sintering temperature, in agreement with other work.[6,8] The microstructure becomes denser as the sintering temperature increases up to 1275 °C, as indicated by the grain packing and increases in grain boundary thickness.

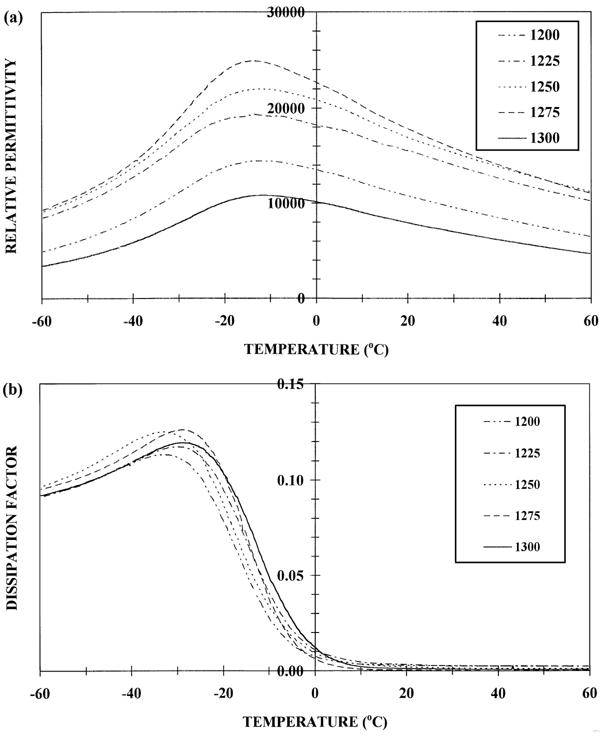

Fig. 7. Comparison of dielectric response at 1 kHz for different sintering temperatures using procedure (*iv*): (a) relative permittivity (b) dissipation factor. The legend indicates the sintering temperatures (in °C).

3.4 Dielectric response of the ceramics

The temperature dependence of relative permittivity and dissipation factor for the samples sintered at the five temperatures are shown in Fig. 6. As the sintering temperature is increased to 1275 °C, both the relative permittivity and dissipation factor increase for a given frequency, as shown for 1 kHz in Fig. 7. Values at 1300 °C are lower then those obtained at 1200 °C, reflecting the observed trends in phase formation and densification. The temperatures of maximum relative permittivity and maximum dissipation factor are summarised in Tables 2 and 3. A straightforward assessment of

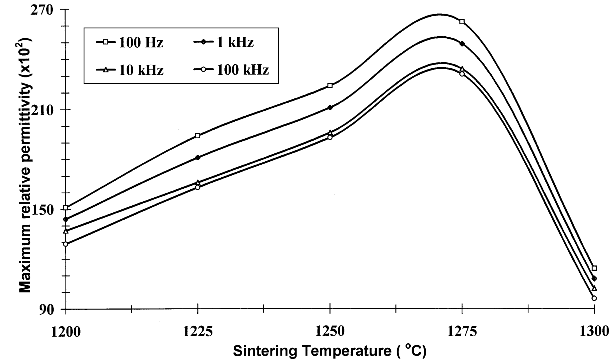

Fig. 8. Variation of the temperature of maximum relative permittivity of PMN ceramics with sintering temperature [procedure (*iv*)].

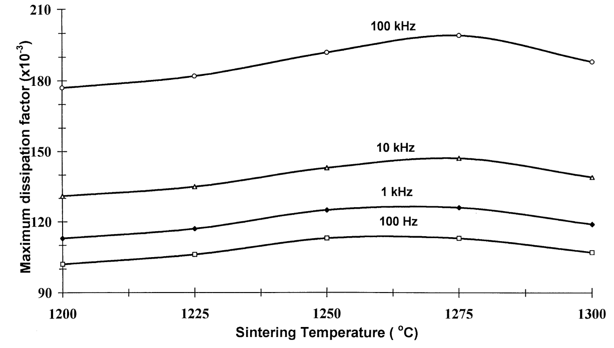

Fig. 9. Variation of the temperature of maximum dissipation factor of PMN ceramics with sintering temperature [procedure (*iv*)].

Table 2. Variation in temperatures of maximum relative permittivity $T(\varepsilon_{r,\max})$ with the sintering temperature and frequency measurements

Sintering temperature (°C)	$T(\varepsilon_{r,\max})$				ΔT
	100 Hz	*1 kHz*	*10 kHz*	*100 kHz*	
1200	−20·1 to −13·6	−15·1 to −7·7	−8·8 to −5·2	−3·5 to −0·9	13–17
1225	−18·2 to −13·4	−10·8 to −7·6	−6·0 to −1·8	−0·6 to −0·6	14–18
1250	−16·7 to −12·7	−10·4 to −7·6	−5·4 to −2·2	−0·9 to −0·4	13–16
1275	−17·4 to −12·7	−10·8 to −7·6	−5·6 to −1·8	−0·6 to −0·6	13–17
1300	−20·1 to −15·5	−15·7 to −9·9	−9·1 to −5·7	−6·3 to −3·1	12–14

Table 3. Variation in temperatures of maximum relative dissipation factor $T(\varepsilon''_{r,\max})$ with the sintering temperature and frequency measurements

Sintering temperature (°C)	*100 Hz*	$T(\varepsilon''_{r,max})$			ΔT
		1 kHz	*10 kHz*	*100 kHz*	
1200	−38·4 to −34·2	−35·6 to −30·8	−30·8 to −27·5	−24·8 to −20·5	14
1225	−35·2 to −32·3	−32·8 to −27·9	−28·3 to −24·3	−21·8 to −18·1	13–14
1250	−38·8 to −35·2	−34·9 to −31·5	−31·5 to −26·8	−23·1 to −21·6	14–16
1275	−32·1 to −30·6	−29·6 to −26·2	−25·4 to −22·8	−18·1 to −16·5	14
1300	−38·4 to −35·4	−35·8 to −30·9	−29·4 to −28·1	−23·4 to −21·7	14–15

the level of frequency dispersion is provided by the parameter $\Delta T = T(\varepsilon_{\mathrm{r,max}})_{100\,\mathrm{kHz}} - T(\varepsilon_{\mathrm{r,max}})_{100\,\mathrm{Hz}}$, as previously employed.[10,11] The variation of maximum relative permittivity and dissipation factor with sintering temperature is given in Figs 8 and 9, for all frequencies.

Since lead volatilisation is a more significant problem at the sintering stage compared to calcination, use of an atmosphere powder is essential. However, there are other significant factors such as impurities, heating rate, sintering time, grain size, grain boundary structure, stoichiometry of the perovskite phase and pyrochlore distribution, which share responsibility in determining the dielectric response of the final sintered products.

4 Conclusion

PMN ceramics of high density and optimised dielectric properties may be produced by use of a sintering method employing platinum foil and a PMN atmosphere powder. Furthermore, straightforward sintering conditions are appropriate, i.e. a temperature of 1275 °C for 2 h. Also required is the use of pyrochlore-free PMN starting powders, which may be derived from industrial grade precursors.[9] Evidence has been gained from XRD that the formation of pyrochlore phases may be avoided by adopting these procedures, leading to very good dielectric properties of the PMN ceramics.

Acknowledgements

Thanks are due to Dr D. Hind and Mr J. Harrington for experimental assistance and helpful discussions. One of the authors (S.A.) wishes to express his gratitude to the DPST project and to the Thai Government for financial support.

References

1. Uchino, K., Electrostrictive actuators: materials and applications. *Am. Ceram. Soc. Bull.*, 1986, **65**, 647–652.
2. Swartz, S. L., Shrout, T. R., Schulze, W. A. and Cross, L. E., Dielectric properties of lead magnesium niobate ceramics. *J. Am. Ceram. Soc.*, 1984, **67**, 311–315.
3. Swartz, S. L. and Shrout, T. R., Fabrication of perovskite lead magnesium niobate. *Mat. Res. Bull.*, 1982, **17**, 1245–1250.
4. Shrout, T. R. and Halliyal, A., Preparation of lead-based ferroelectric relaxors for capacitors. *Am. Ceram. Soc. Bull.*, 1987, **66**, 704–711.
5. Lejeune, M. and Boilot, J. P., Low firing dielectric based on lead magnesium niobate. *Mat. Res. Bull.*, 1985, **20**, 493–499.
6. Watanabe, A., Haneda, H., Moriyoshi, Y., Shirasaki, S., Kuramoto, S. and Yamamura, H., Preparation of lead magnesium niobate by a coprecipitation method. *J. Mater. Sci.*, 1992, **27**, 1245–1249.
7. Sekar, M. M. A. and Halliyal, A., Low-temperature synthesis, characterization, and properties of lead-based ferroelectric niobates. *J. Am. Ceram. Soc.*, 1998, **81**, 380–388.
8. Gupta, S. M. and Kulkarni, A. R., Dielectric and microstructure studies of lead magnesium niobate prepared by partial oxalate route. *J. Eur. Ceram. Soc.*, 1996, **16**, 473–480.
9. Ananta, S. and Thomas, N. W., A modified two-stage mixed oxide synthetic route to lead magnesium niobate and lead iron niobate. *J. Eur. Ceram. Soc.*, 1999, **19**(2), 155–163.
10. Belsick, J. R., Halliyal, A., Kumar, U. and Newnham, R. E., Phase relations and dielectric properties of ceramics in the system $Pb(Zn_{1/3}Nb_{2/3})O_3$–$SrTiO_3$–$PbTiO_3$. *Am. Ceram. Soc. Bull.*, 1987, **66**, 664–667.
11. Halliyal, A., Kumar, U., Newnham, R. E. and Cross, L. E., Stabilization of the perovskite phase and dielectric properties of ceramics in the $Pb(Zn_{1/3}Nb_{2/3})O_3$–$BaTiO_3$ System. *Am. Ceram. Soc. Bull.*, 1987, **66**, 671–676.