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A Modified Two-Stage Mixed Oxide Synthetic Route to Lead Magnesium Niobate and Lead Iron Niobate

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Abstract

A modified mixed oxide synthetic route has been developed for the synthesis of lead magnesium niobate [$Pb(Mg_{1/3}Nb_{2/3})O_3$; PMN] and lead iron niobate [$Pb(Fe_{1/2}Nb_{1/2})O_3$; PFN] powders. The formation of perovskite and pyrochlore phases in the calcined PMN and PFN powders has been investigated as a function of calcination temperature and time by XRD and DTA techniques. The particle size distribution of calcined powders was determined by laser diffraction, with the morphology, phase composition and crystal structure determined via SEM, TEM and EDX techniques. In both cases it has been found that cubic pyrochlore phases in the $PbO–Nb_2O_5$ system tend to form, as well as the perovskite phase. However, pyrochlore-free PMN and PFN powders were successfully obtained for a calcination temperature of 800°C for 4 and 3 h, respectively, without the introduction of excess PbO and/or MgO. © 1998 Elsevier Science Limited. All rights reserved

Keywords: powders: solid state reaction, niobates, perovskites, pyrochlore, calcination.

1 Introduction

The mixed oxide synthesis of lead magnesium niobate (PMN) in the perovskite phase has been a subject of considerable interest over the past decade.[1–6] This is a reflection both of the status of PMN as a prominent relaxor material and of the difficulty in obtaining a single-phase perovskite product. The initial work of Lejeune and Boilot[1] considered the many parameters which influence the synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ from PbO, MgO and Nb_2O_5 precursors, concluding that the formation of a lead niobate pyrochlore phase could not be completely eliminated. Moreover, it was proposed that the reactivity of magnesium oxide with lead and niobium oxides was the definitive factor governing products of the reaction. This was demonstrated by comparison with the synthesis of $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), using Fe_2O_3 in place of MgO, where the higher reactivity of iron oxide compared to magnesium oxide could give rise to perovskite PFN with 100% yield.

These authors later proposed two modifications, i.e. the use of $MgCO_3$ in place of MgO, and milling in acetone instead of water.[2] These were found to increase the yield of perovskite PMN. Swartz and Shrout[3] sought to simplify the synthesis of perovskite PMN by the introduction of a two-step process. In essence, reaction of MgO and Nb_2O_5 at 1000°C was carried out, to form $MgNb_2O_6$ (columbite). This compound was then reacted at 800°C with PbO to form PMN, the lower reaction temperature reducing the amount of lead volatilisation. This approach yielded perovskite as the dominant phase, with pyrochlore impurities of less than five per cent. It was also claimed that the concentrations of pyrochlore phases could be reduced to zero in the presence of excess MgO.

Butcher and Daglish[5] subsequently combined the approach of Lejeune and Boilot with that of Swartz and Shrout by investigating a two-stage synthesis with hydrated magnesium carbonate–magnesium hydroxide, $(MgCO_3)_4.Mg(OH)_2.5H_2O$ as a precursor. The essentially pyrochlore-free powders obtained could be attributed to its high reactivity with Nb_2O_5. Recent work[6] has confirmed the superiority of the two-stage synthesis, also highlighting the importance of excess PbO and/or MgO in determining the yield of perovskite product.

Whereas some workers have been prompted to investigate synthetic routes different from the

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mixed oxide approach, e.g. sol-gel,[7] combustion[8] and coprecipitation,[9] the overall aim of the work described here is to refine the two-stage mixed oxide method further. The following elements are investigated in this connection:

1. development of a faster synthetic route;
2. reproducibility of the synthetic route;
3. the ability to use laboratory grade chemicals.

The generality of the conclusions drawn for the synthesis of PMN is subsequently demonstrated by applying the same principles to the synthesis of lead iron niobate (PFN), where the reaction in the first stage is:

$$Fe_2O_3 + Nb_2O_5 \rightarrow 2FeNbO_4 \qquad (1)$$

2 Method

2.1 Synthesis of PMN powder

The two-stage mixed oxide synthetic route employed is shown in Figs 1 and 2 where a McCrone mill was used for the vibro-milling.[10] Precursors were as follows: PbO (Aldrich, 99·9+ purity); $(MgCO_3)_4.Mg(OH)_2.5H_2O$ (Aldrich, 99% purity); Nb_2O_5 [Alfa (Johnson Matthey), 99·9;+% purity]. Five calcination temperatures were monitored as alternatives for the reaction of $MgNb_2O_6$ and PbO to form the perovskite phase of PMN: 600, 700, 750, 800 and 850°C for 4 h, with the products obtained at each temperature compared by XRD. Having established the optimum temperature, alternative calcination times of 2, 3 and 5 h were applied at this temperature. In order to frame the study, calcination times of 5 h at a temperature 25°C below and 3 h at 25°C above the optimum temperature were also investigated.

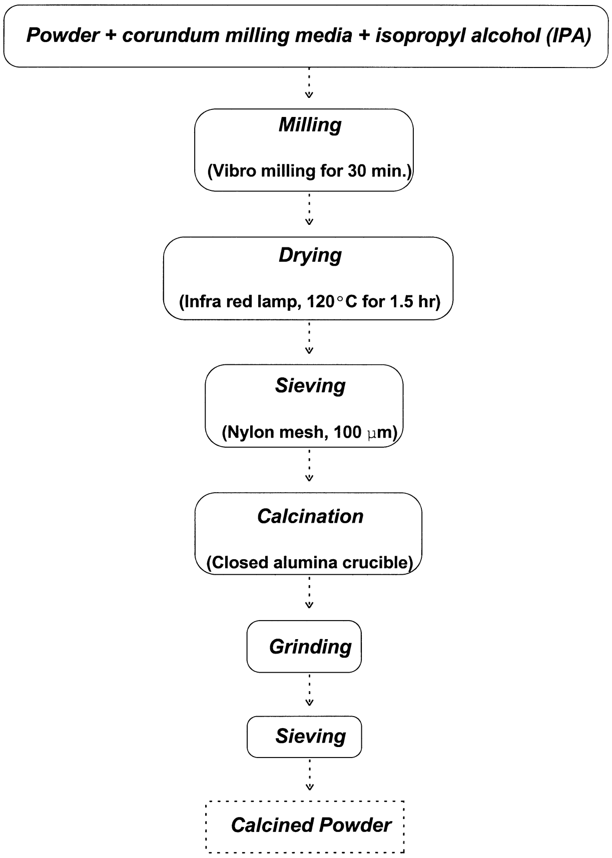


Fig. 1. Mixing process for powder preparation.

2.2 Synthesis of PFN powder

In order to synthesize lead iron niobate, Fe_2O_3 [Alfa (Johnson Matthey), 99·5% purity] was used in place of $(MgCO_3)_4.Mg(OH)_2.5H_2O$. First, the intermediate phase of iron niobate, $FeNbO_4$ was synthesised by according to the method previously reported,[11] employing an optimized calcination temperature of 1150°C for 4 h. A similar methodology was adopted for the reaction of $FeNbO_4$ and PbO to form the perovskite phase PFN (Fig. 3). Alternative calcination temperatures and times were investigated as described for PMN in Section 2.1. However all times were reduced by one hour compared to those in the PMN study.

2.3 Powder characterisation

Changes of the uncalcined PMN and PFN powders during heat treatment were investigated by differential thermal analysis (DTA) (Perkin–Elmer, 7 Series Thermal Analysis System) using a heating rate of 10°C min^{-1} in the temperature range from

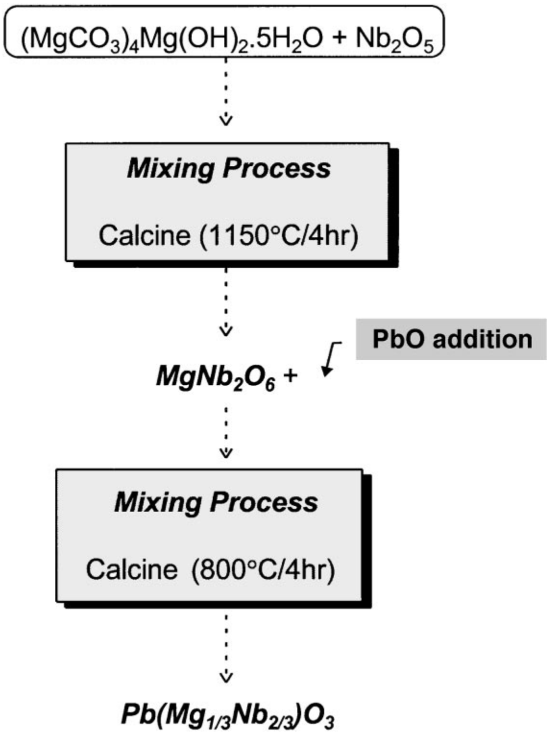


Fig. 2. Two-stage processing route for perovskite PMN powders.

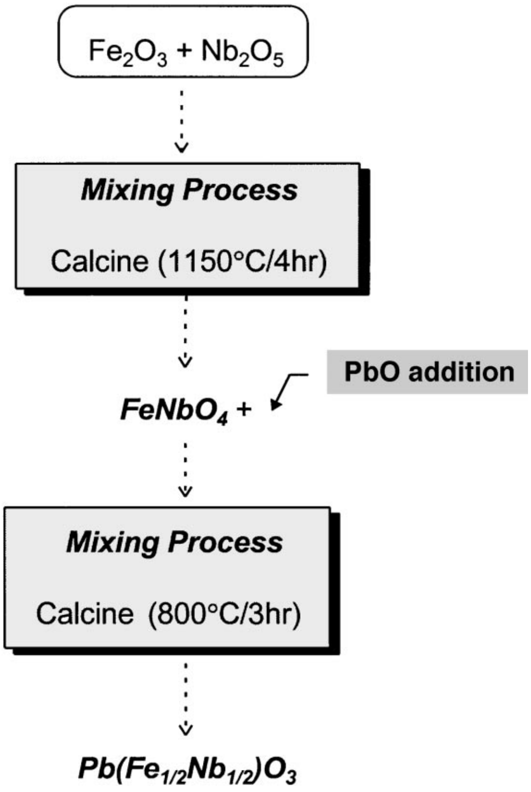


Fig. 3. Two-stage processing route for perovskite PFN powders.

25 to 900°C. Calcined powders were subsequently examined by X-ray diffraction (CuK_α radiation) to identify the phases formed along with optimum calcination temperatures and times.

Particle size distributions of powders were determined by laser diffraction techniques (MasterSizer, Malvern, UK), with the grain sizes and morphologies of powders observed by SEM. The chemical compositions and structures of the phases formed were elucidated by transmission electron microscopy (CM20 TEM/STEM operated at 200 keV) and an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. Powder samples were dispersed in solvent and deposited by pipette on to 3 mm holey carbon grids for observation by TEM.

3 Results and Discussion

3.1 Identification of optimum calcination temperatures for the formation of lead magnesium niobate and lead iron niobate

DTA curves for the PMN and PFN powders are compared in Fig. 4. Whereas the trace for PMN exhibits a single exothermic peak at 717°C, PFN gives rise to both an exothermic peak at 687°C and an endothermic peak at 732°C. These data were used to define the range of temperatures for XRD investigation to between 600 and 800°C. It is to be noted that there is no obvious interpretation of the endothermic peak for PFN, although it is likely to correspond to a phase transition.

Powder XRD patterns of the calcined PMN powders are given in Figs 5 and 6. The strongest reflections in the majority of the XRD patterns indicate the formation of the perovskite phase lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$, which could be matched with JCPDS file 27-1199 (Fig. 9) To a first approximation, this major phase has cubic perovskite-type structure, space group *Pm3m*

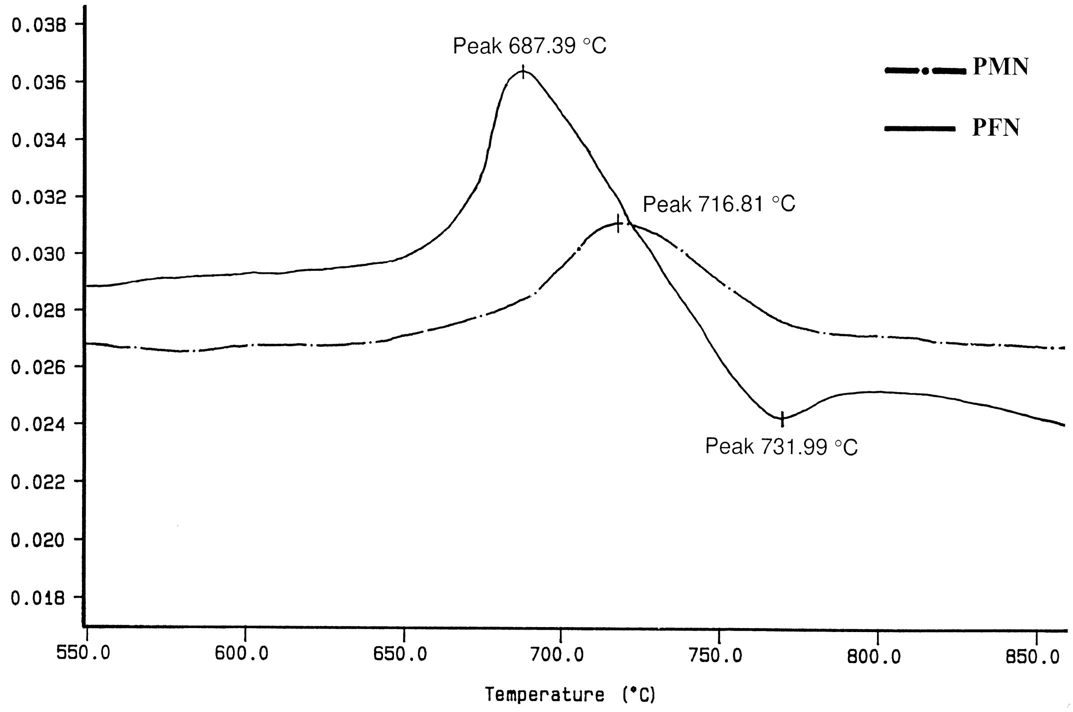


Fig. 4. DTA curves for lead-based complex perovskite PMN and PFN powders.

(no. 221), with cell parameter $a=405$ pm. The additional reflections (marked by ●) correlate with a pyrochlore phase of lead niobium oxide, $Pb_2Nb_2O_7$ (JCPDS file no. 40-828). This phase has a cubic structure with cell parameter $a=1{\cdot}051$ nm.

Powder XRD patterns of the calcined PFN powders are shown in Figs 7 and 8. The strongest reflections indicate formation of the perovskite phase, lead iron niobate, $Pb(Fe_{1/2}Nb_{1/2})O_3$ which can be matched with JCPDS file 32-522 (Fig. 10). To a good approximation, this major phase also has cubic symmetry with cell parameter $a=401$ pm. Additional reflections (marked by ▼) correlate with another type of pyrochlore phase of lead niobium oxide, $Pb_3Nb_4O_{13}$ (JCPDS file no. 25-443). This phase also has a cubic structure with cell parameter $a=1{\cdot}056$ nm in space group *Fd3m* (no. 227).

The amount of perovskite phase present in each calcined powder may, in principle, be calculated from the intensities of the major X-ray reflections for the perovskite and pyrochlore phases. In this connection, Swart and Shrout[3] have proposed the use of the following equation:

$$\text{wt\% perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{pyro}}}\right) \times 100 \tag{2}$$

This equation should be seen as a first approximation, since its applicability requires comparable

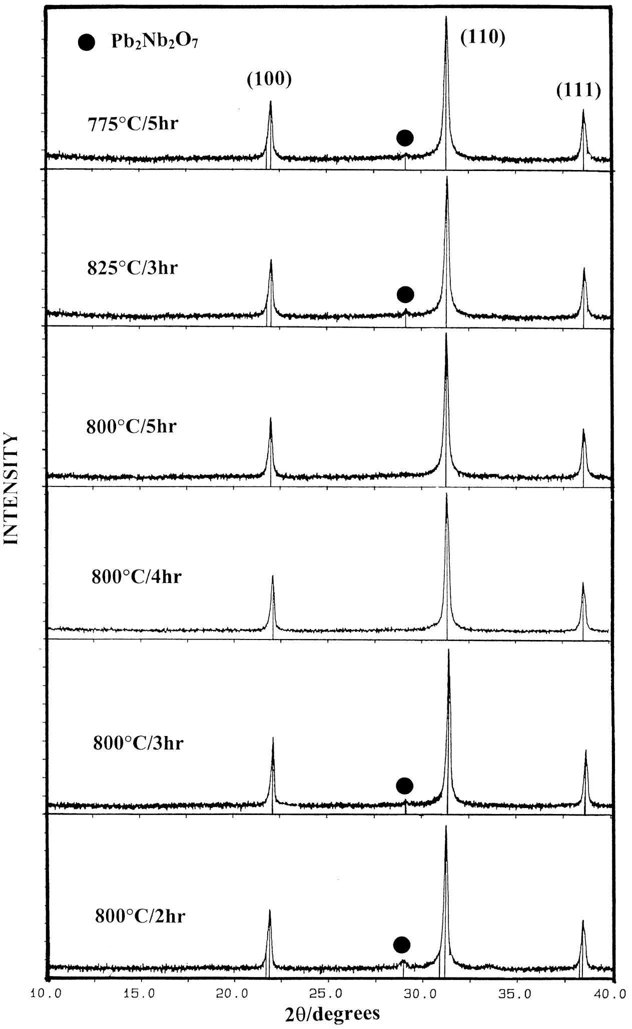


Fig. 6. Powder XRD patterns of the calcined PMN powders at various calcination temperatures and times.

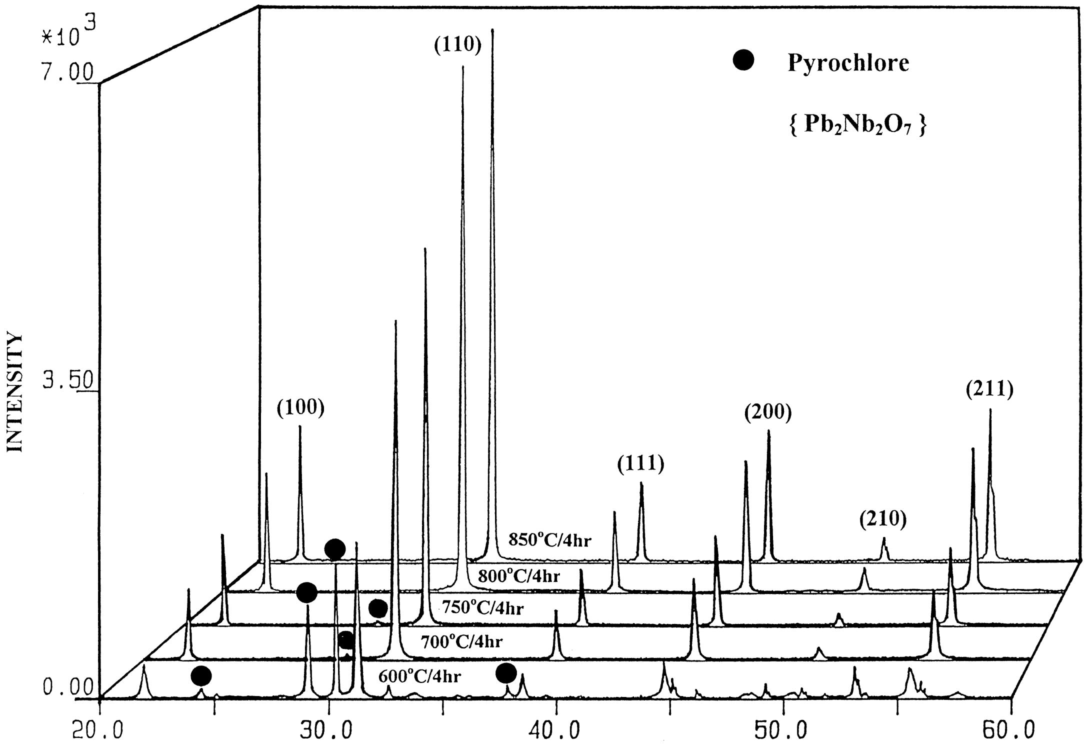


Fig. 5. Powder XRD patterns of the calcined PMN powders at various calcination temperatures at constant time.

maximum absolute intensities of the pair of perovskite and pyrochlore peaks being used. Here I_{perov} refers to the intensity of the {110} perovskite peak and I_{pyro} to the intensity of the {222} pyrochlore ($Pb_2Nb_{1.87}Mg_{0.32}O_7$) peak, these being the most intense reflections in the XRD patterns of both phases. This equation has been widely employed in connection with the fabrication of PMN and other lead-based complex perovskite materials.[4,6,8]

However, in the work reported here, the cubic pyrochlore phases of $Pb_2Nb_2O_7$ (JCPDS file 40-828) and $Pb_3Nb_4O_{13}$ (JCPDS file 25-443) have been found in PMN and PFN, respectively, instead of $Pb_2Nb_{1.87}Mg_{0.32}O_7$. For the purposes of estimating the concentrations of pyrochlore phase present, eqn (2) has been applied to the diffraction patterns obtained (Tables 1 and 2). It should be noted that, despite the composition of the pyrochlore changing, the peaks of maximum intensity still correspond to {222} reflections.

Moreover, no evidence of pyrochlore phases $Pb_3Nb_2O_8$ and $Pb_5Nb_4O_{15}$[12,13] has been found here. In connection with the $Pb_2Nb_2O_7$ phase, where both rhombohedral and cubic phases have been reported in the temperature range 550 to 800°C (JCPDS files 40-829 and 40-828, respectively),[12] only the cubic phase has been found here, in agreement with other work.[8,14] By increasing the calcination temperature, the yield of perovskite phases in both PMN and PFN systems

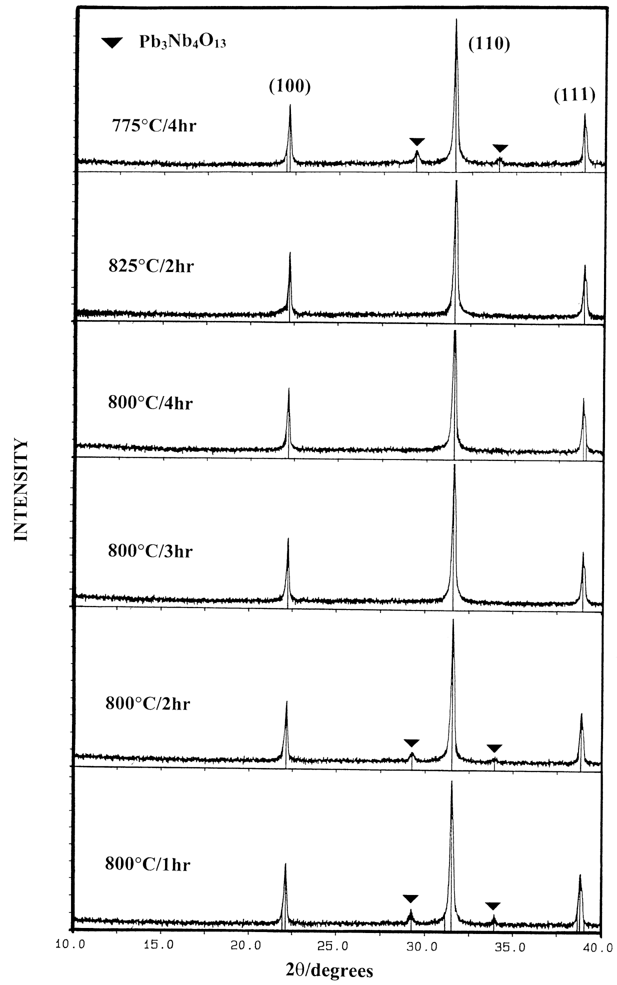


Fig. 8. Powder XRD patterns of the calcined PFN powders at various calcination temperatures and times.

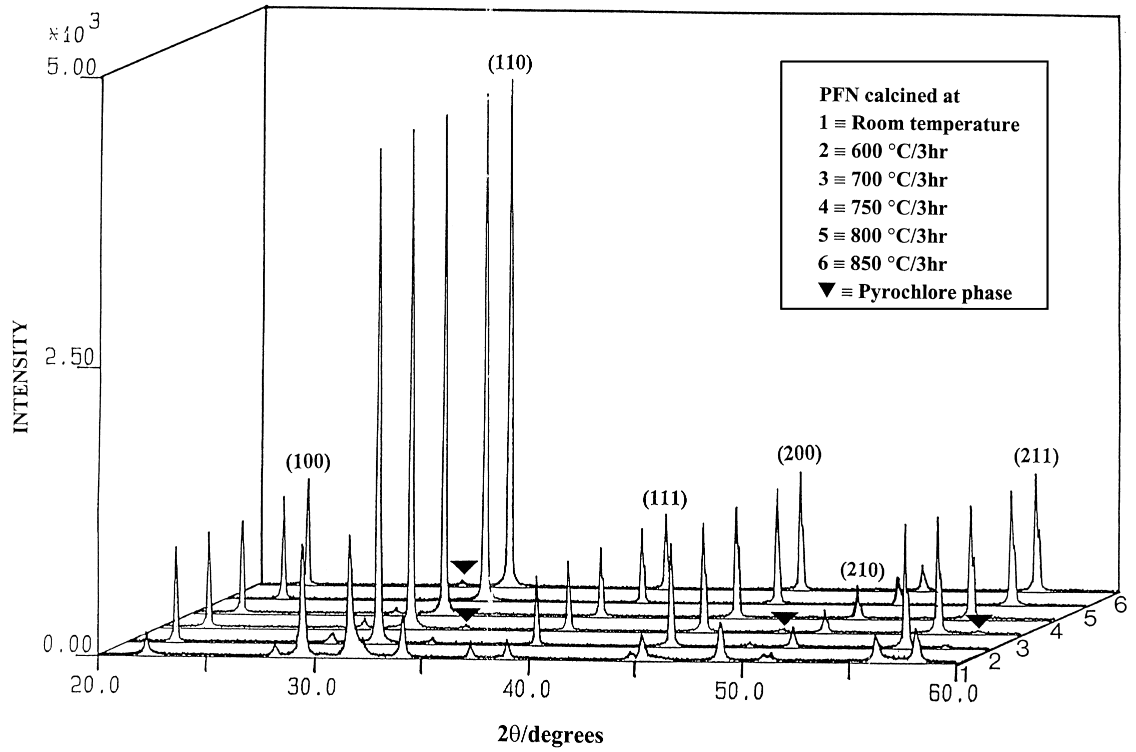


Fig. 7. Powder XRD patterns of the calcined PFN powders at various calcination temperatures at constant time.

increases significantly until 800°C, whereafter higher temperatures and different dwell times do not enhance the yield. No evidence of precursor phases PbO, MgO, Fe_2O_3 and Nb_2O_5 was detected by XRD. From Tables 1 and 2, it is clear that the optimal calcination conditions for single phase PMN and PFN are 800°C/4 h and 800°C/3 h, respectively. The observation that shorter calcination

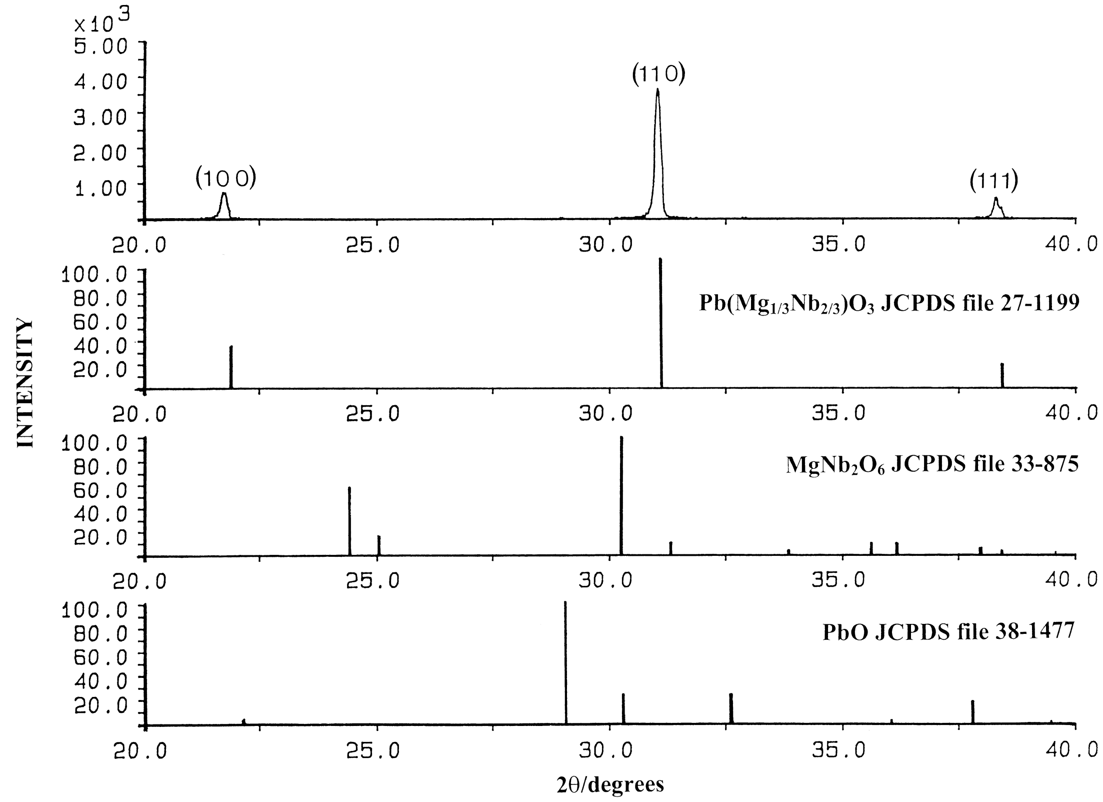


Fig. 9. Computerised JCPDS data-matching (file 27-1199) confirms formation of the perovskite phase $Pb(Mg_{1/3}Nb_{2/3})O_3$.

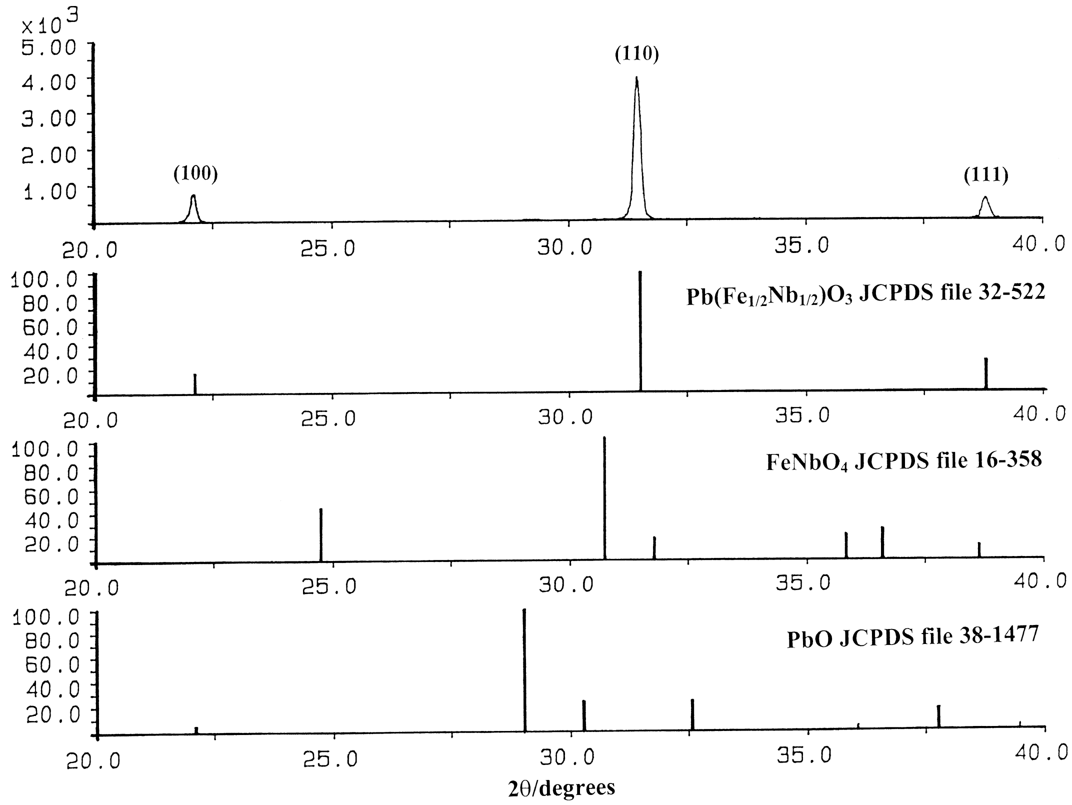


Fig. 10. Computerised JCPDS data-matching (file 32-522) confirms formation of the perovskite phase $Pb(Fe_{1/2}Nb_{1/2})O_3$.

times are required for PFN compared to PMN is also consistent with earlier work.[4,5,8,15]

3.2 Particle size analysis of PMN and PFN powders

Figure 11 shows the particle size distribution curves of calcined PMN and PFN powders, which indicate appreciable size fractions at approximately 4·5 μm diameter within the range of $\approx$1·3 to 19·0 μm and $\approx$1·3 to 25·0 μm, respectively.

3.3 Microstructural analysis

SEM micrographs of the calcined PMN (800°C/4 h) and PFN (800°C/3 h) powders are shown in Figs 12 and 13, respectively. The particles are irregular in shape and agglomerated, particularly in the PFN powder. Observed diameters range from 1·3 to 3·1 μm and 1·0 to 3·9 μm for PMN and PFN, respectively, in good agreement with the particle size distribution previously determined (Fig. 11). TEM bright field images of agglomerated and discrete particles of PMN and PFN powders, which provide better resolution for particle size determination are shown in Figs 14 and 15 The particle diameters range from 0·07 to 1·40 μm

Table 1. Phase analysis for calcined PMN powders

Sample	*Calcination conditions*		*Qualitative concentrations of phases*	
	Temperature (°C)	*Time (h)*	*Perovskite (wt%)*	*Pyrochlore (wt%)*
PMN1	600	4	52·6	47·4
PMN2	700	5	99·1	0·9
PMN3	750	3	99·1	0·9
PMN4	775	4	99·4	0·6
PMN5	800	2	99·6	0·4
PMN6	800	3	99·6	0·4
PMN7	800	4	100·0	0·0
PMN8	800	5	100·0	0·0
PMN9	825	3	99·7	0·3
PMN10	850	4	100·0	0·0

Table 2. Phase analysis for calcined PFN powders

Sample	*Calcination conditions*		*Qualitative concentrations of phases*	
	Temperature (°C)	*Time (h)*	*Perovskite (wt%)*	*Pyrochlore (wt%)*
PFN1	600	3	98.5	1·5
PFN2	700	3	98·6	1·4
PFN3	750	3	99·3	0·7
PFN4	775	4	99·4	0·6
PFN5	800	1	99·4	0·6
PFN6	800	2	99·5	0·5
PFN7	800	3	100·0	0·0
PFN8	800	4	100·0	0·0
PFN9	825	2	99·7	0·3
PFN10	850	3	100·0	0·0

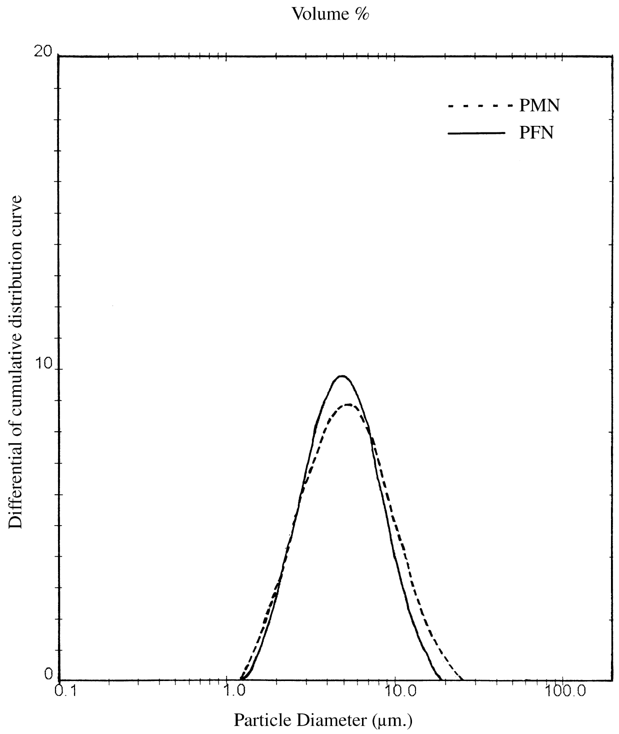


Fig. 11. Particle size distribution curves of calcined PMN and PFN powders.

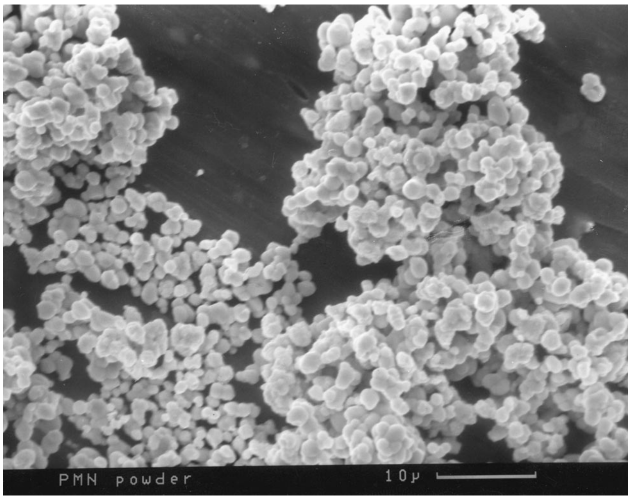


Fig. 12. SEM micrograph of the calcined PMN powder.

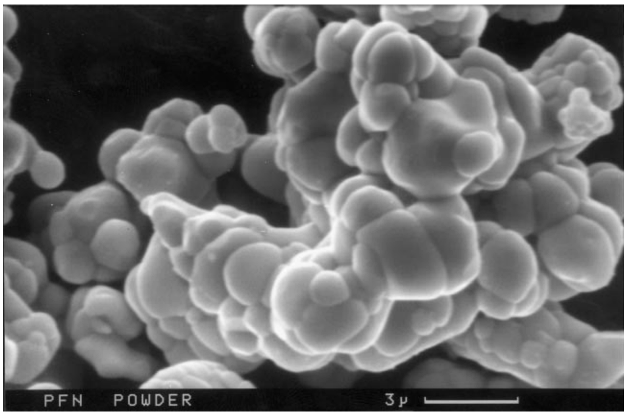
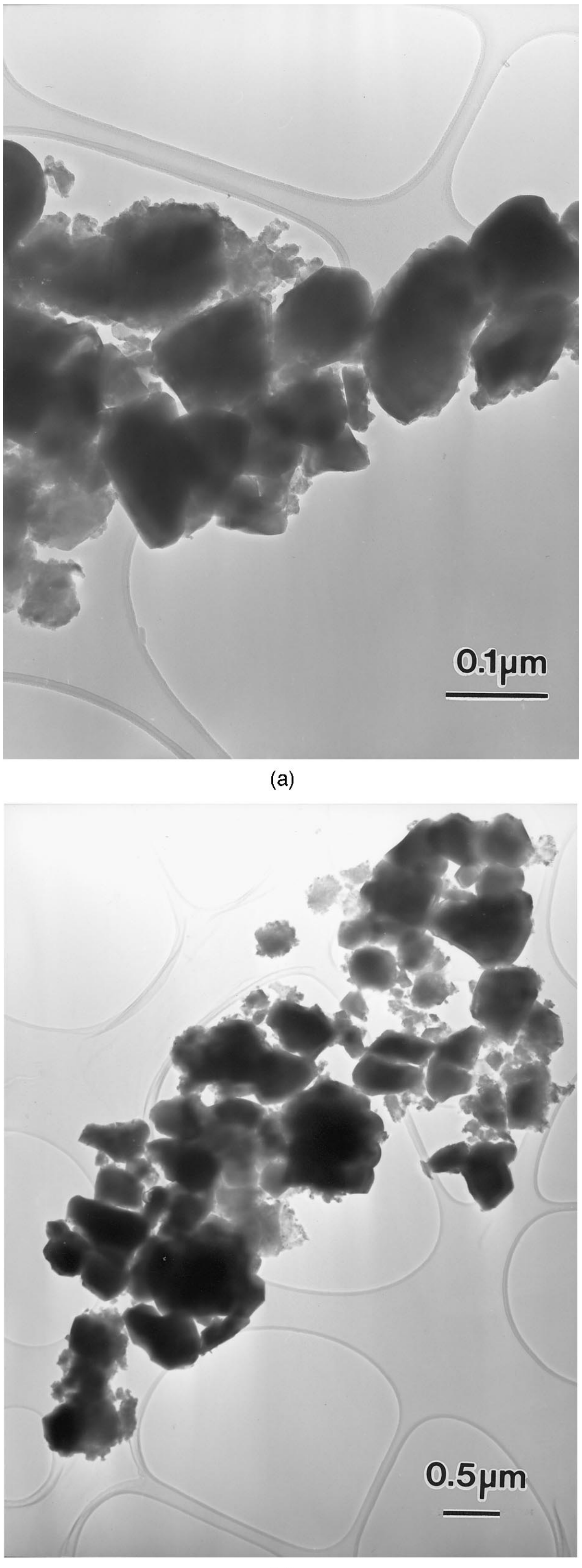


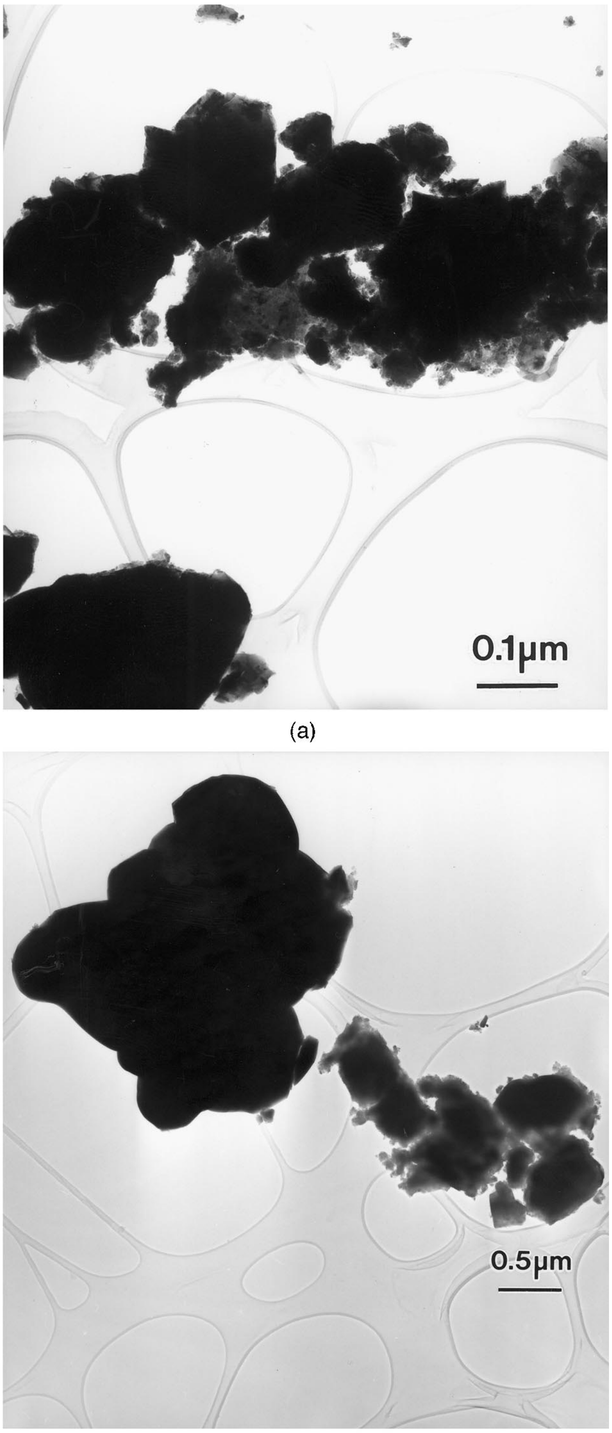
Fig. 13. SEM micrograph of the calcined PFN powder.



(a)

(b)

Fig. 14. TEM micrographs of the calcined PMN powder.



(a)

(b)

Fig. 15. TEM micrographs of the calcined PFN powder.

in PMN powders and 0·03 to 2·80 μm in PFN powders.

In general, EDX analysis using a 20 nm probe from a large number of particles of both calcined PMN and PFN powders confirms the existence of single phase perovskite (Figs 16 and 17), in good agreement with XRD results. One of the great attractions of the mixed oxide approach towards synthesizing complex perovskites is its simplicity. Furthermore, solid-state reactions of this kind lend themselves to straightforward diagnosis by several physical techniques, e.g. DTA, XRD, EDX, TEM. The synthesis used here for PMN and PFN powders represents a considerable advance, in terms of simplicity, time and cost, over a molten salt synthesis recently advocated.[14] Furthermore, the reproducibility of the synthetic route has been demonstrated in earlier work.[10,11]

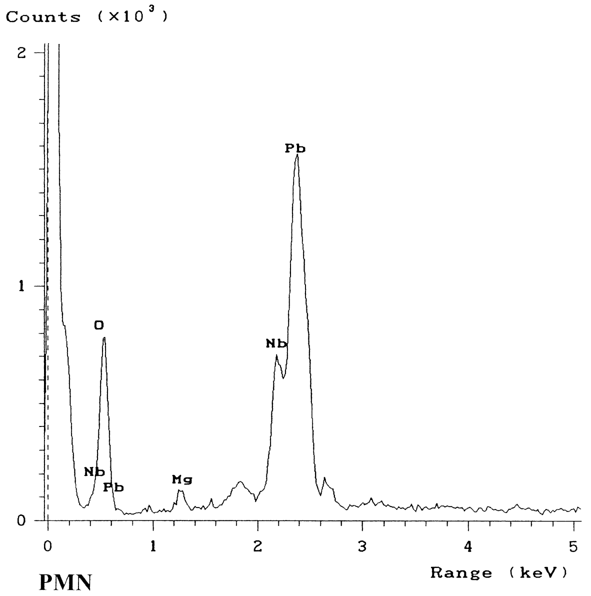


Fig. 16. EDX analysis of the calcined PMN powder.

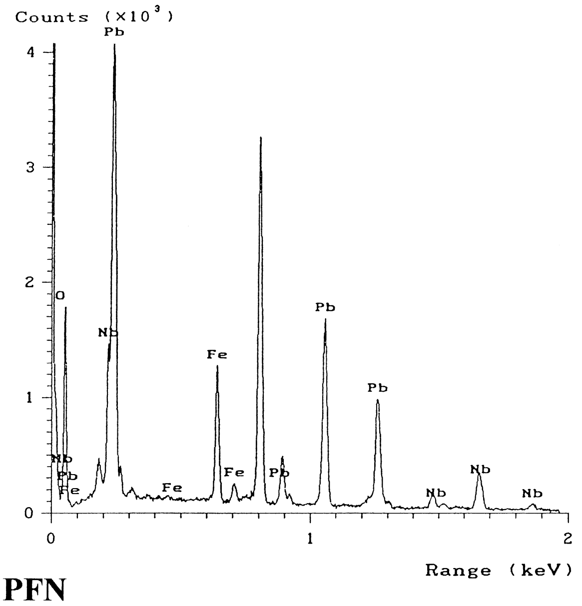


Fig. 17. EDX analysis of the calcined PFN powder.

4 Conclusion

Two-stage mixed oxide synthetic routes to single phases of lead-based complex perovskite PMN and PFN compounds have been developed, which show a high level of reproducibility. These involve the use of laboratory-grade precursors, low milling and drying times of powders, together with moderately low calcination temperatures (at 800°C) and times (3–4 h) without the introduction of excess amounts of PbO and/or MgO. These represent significant time-savings compared to currently advocated synthetic procedures and require only relative impure laboratory-grade precursors.

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