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The formation and phase stability of lead magnesium niobate in the presence of a molten flux

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The formation of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) by the molten salt synthesis method using sulphate flux has been investigated as a function of calcination temperature and mole ratio between Li_2SO_4 and Na_2SO_4. A 97% perovskite phase was synthesized at 750° C for 30 min with $0.635Li_2SO_4$–$0.365Na_2SO_4$ flux without any sub-products affecting the formation reaction of the PMN phase. The percentage of the perovskite phase was influenced by changes in the Li_2SO_4/Na_2SO_4 mole ratio at a given temperature. The pyrochlore phase present was identified as $Pb_3Nb_4O_{13}$ (P_3N_2) when $0.635Li_2SO_4$–$0.365Na_2SO_4$ flux was used. The results for other lead-based ferroelectrics are also discussed.

1. Introduction

Lead-containing relaxor ferroelectrics based on the perovskite structure are of current interest for multilayer capacitors and actuators owing to their excellent dielectric and electrostrictive properties [1, 2]. Many approaches have been taken as an attempt to form a pure perovskite phase, but the formation of a pyrochlore phase by the calcining of mixed oxides has posed difficulties [3, 4]. The molten salt synthesis (MSS) method is one of the simplest methods for obtaining a pure perovskite phase at a relatively low temperature for a shorter soaking time, in which the molten salts are used as a reaction aid [5]. Requirements for selecting the salt in MSS are as follows:

(i) the melting point of any given salt must be appropriately low compared to the formation temperature of the main phase;

(ii) the solubility of a salt must be sufficient to be eliminated by a simple washing step;

(iii) there must be no undesirable reactions between salt and constituent oxides.

Various ferroelectric materials such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) have been prepared by MSS using KCl or 0.5NaCl–0.5KCl salts [6, 7]. However, there has been no systematic study of the formation of the perovskite phase by MSS using Li_2SO_4 and Na_2SO_4 mixtures. This paper deals with the formation reaction of various perovskite phases in the presence of sulphate or chloride flux, as well as a comparison of the characteristics of powders obtained by sulphate or chloride MSS. The stability of the PMN phase in the salts and the effect of different Li_2SO_4 to Na_2SO_4 molar ratios on the reaction are investigated to understand the role of the salts during the reaction. Also, the reaction routes of the PMN phase in MSS using sulphates are discussed.

2. Experimental procedure

Reagent-grade oxides, PbO, MgO and Nb_2O_5, were mixed with Li_2SO_4–Na_2SO_4 or NaCl–KCl to prepare the $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase. The ratio of the total weight of salts to total weight of oxides was 0.5. The mole fraction of Li_2SO_4 was varied from 0.14–0.635 to study the effects on the formation of the perovskite phase. The $0.635Li_2SO_4$–$0.365Na_2SO_4$ composition (mol %) corresponds to the eutectic composition of Li_2SO_4–Na_2SO_4 system. The mole fractions of NaCl and KCl were equal. Reagent-grade oxides, Fe_2O_3, ZnO, CoO and NiO were also used to synthesize the other ferroelectrics, $Pb(Fe_{1/2}Nb_{1/2})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$, $Pb(Ni_{1/3}Nb_{2/3})O_3$ and $Pb(Co_{1/3}Nb_{2/3})O_3$, respectively. After mixing in ethanol with zirconia balls, the dried powders were investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA, STA 1500, Stanton Co.) at a heating rate of 5 °C min^{-1}. The powders were fired at various temperatures in covered alumina crucibles, then washed several times with deionized water. The phases present both before and after washing were determined by XRD (290612 A14, Rigaku Co.) analysis with CuK_α radiation [6]. The relative amount of the perovskite phase of the powders after washing was calculated from the relative intensities of the (1 1 0) perovskite peak and the (2 2 2) pyrochlore peak, respectively [8].

3. Results and discussion

3.1 Effect of variation in molar ratio between sulphate salts

TGA and DTA curves for the PMN system prepared in eutectic composition, $0.635Li_2SO_4$–$0.365Na_2SO_4$ (T_m = 594 °C), are illustrated in Fig. 1. The endothermic peak (1) around 100 °C in the DTA curve is due to

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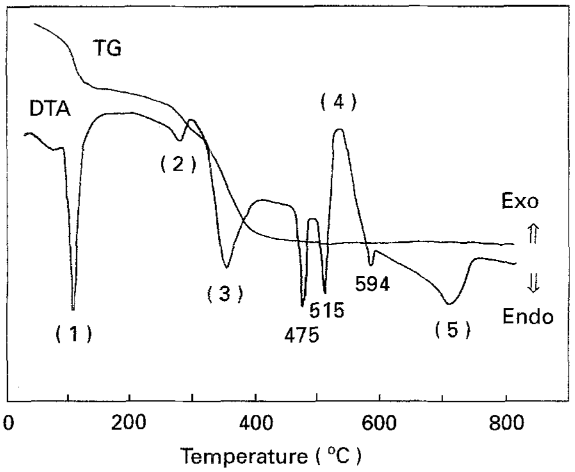

Figure 1 TGA and DTA curves for $0.635Li_2SO_4$–$0.365Na_2SO_4$ in the PMN system.

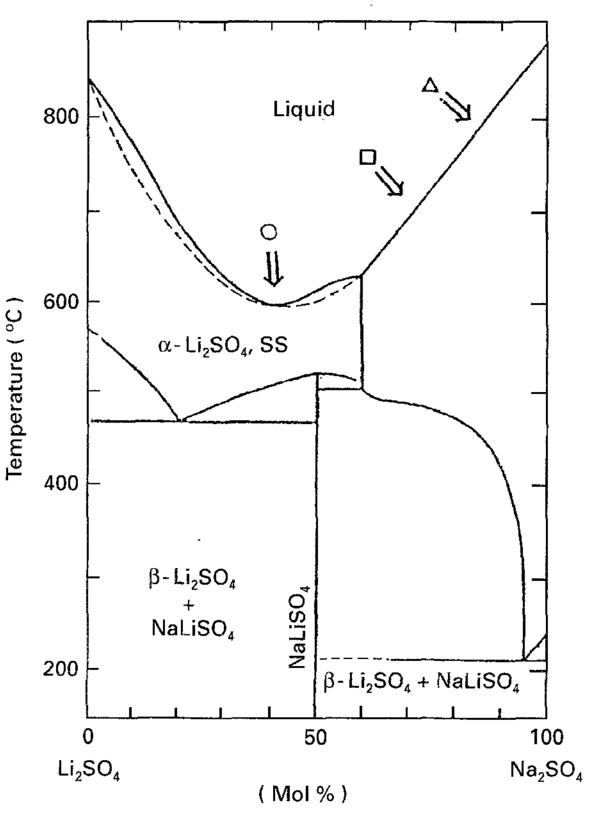

Figure 2 Phase diagram of the Li_2SO_4–Na_2SO_4 system [10]. (○) 0.635/0.365, □ 0.29/0.71, (△) 0.14/0.86.

the evaporation of water from $Li_2SO_4{\cdot}H_2O$ with the resulting weight loss, as indicated by the TG curve. Peaks 2 (around 270 °C) and 3 (around 350 °C) are caused by the decomposition of carbon dioxide and water from $Pb_3(CO_3)_2(OH)_2$, which was formed during the milling process using ethanol, and by the polymorphic change of Pb_3O_4 to PbO, respectively [9]. The exothermic peak (4) at about 550 °C can be attributed to the formation of pyrochlore phase, and peak 5 is due to the formation of perovskite phase. The endothermic peaks around 475 and 515 °C correspond to the phase transition in the Li_2SO_4–Na_2SO_4 system, as indicated by the phase boundaries at about 475 and 515 °C for 0.635/0.365 composition in the phase diagram of Li_2SO_4–Na_2SO_4 as shown in Fig. 2.

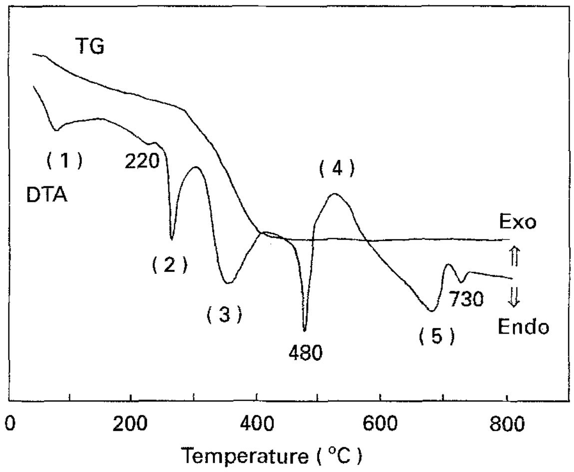

Figure 3 TGA and DTA curves for the $0.29Li_2SO_4$ –$0.71\,Na_2SO_4$–PMN system.

The peak at 594 °C is also due to the phase transition to liquid phase.

The TGA and DTA curves for $0.29Li_2SO_4$–$0.71\,Na_2SO_4$ in the PMN system, as shown in Fig. 3, illustrate the effect of Li_2SO_4/Na_2SO_4 ratio on the reaction of perovskite phase. Peaks 1–5 correspond to peaks with the same number in Fig.1. At this compositional ratio, the Li_2SO_4–Na_2SO_4 has a melting point of about 730 °C according to the phase diagram. In the 0.29/0.71 PMN system, the endothermic peaks at 220, 480 and 730 °C were also observed, in agreement with phase boundaries in the phase diagram.

Table I shows the effect of the variation of ratio (Li_2SO_4/Na_2SO_4) on the amount of PMN phase with respect to firing temperature. As the mole fraction of Li_2SO_4 decreases from 0.635 to 0.14, the formation temperature of the flux due to the melting of the salts should increase, as expected from the phase diagram of Fig. 2. The melting temperature of each composition is about 594, 730 and 800°C, respectively. The perovskite phase (97%) was obtained at 750 °C in the 0.635/0.365 composition which has the lowest melting point of 594 °C, whereas, for the 0.29/0.71 and 0.14/0.86 compositions, a temperature of 850 °C was necessary to reduce the pyrochlore phase down to about 2%. For the first two compositions, the perovskite phase began to form at 700 °C simultaneously, which suggests that calcination temperatures above 700 °C, in the case of PMN by MSS under these experimental conditions, are required to form the perovskite phase. However, it is apparent that the lower the melting temperature of the given salts, the higher is

TABLE I Percentage of PMN phase for each salt composition with firing temperature

Composition	PMN phase (%)				
$Li_2SO_4:Na_2SO_4$	650° C	700° C	750° C	800° C	850° C
0.635:0.365	0	37	97	98	98
0.29:0.71	0	27	91	96	98
0.14:0.86	0	0	55	88	98

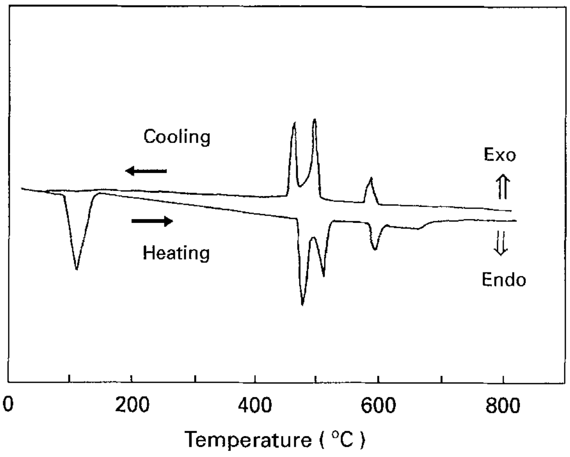

Figure 4 DTA curves on heating and cooling for $0.635Li_2SO_4$–$0.365Na_2SO_4$.

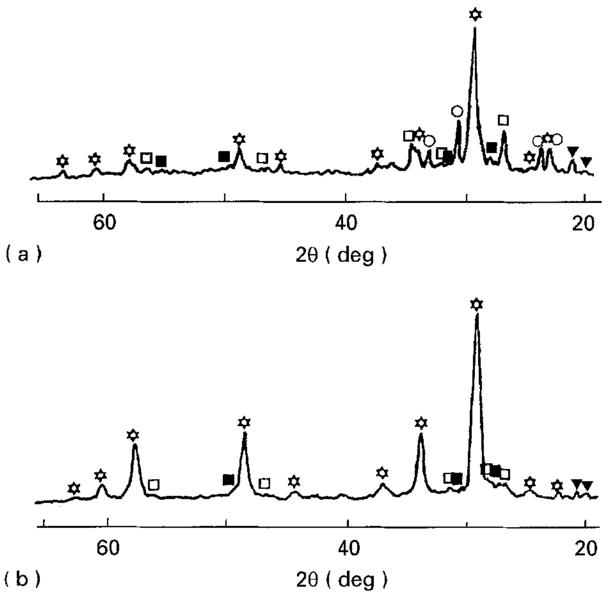

Figure 5 XRD patterns of reaction products at 550°C for 5 min (a) before and (b) after washing. (○) $LiNaSO_4$, (□) Pb_3O_4, (✡) pyrochlore phase, (■) PbO, (▼) Nb_2O_5.

the percentage of PMN phase for each firing temperature. Also, as similarly reported in the ferrite system and PMN by chloride MSS [6], the formation reaction of PMN phase was accelerated before the complete transition of salts to liquid phase in the binary sulphate system.

3.2 Stability of the perovskite phase in molten salts

The $0.635Li_2SO_4$-$0.365Na_2SO_4$ PMN composition, having the highest perovskite phase of 97% at 750°C for 30 min, was selected for study of the phase stability in the flux. Fig. 4 shows the DTA curves only for $0.635Li_2SO_4$–$0.365Na_2SO_4$ during heating and cooling. As discussed previously, all endothermic peaks during heating matched well with the phase boundaries in the Li_2SO_4–Na_2SO_4 phase diagram (Fig. 2). This seems to indicate the PMN–sulphate salts system has no side reactions which affect the formation reaction of PMN phase. However, this result contradicts the results of Chiu *et al.* [7] on the $Pb(Fe_{1/2}Nb_{1/2})O_3$ synthesis by NaCl–KCl. Namely, PFN formation in the chloride salts was thought to be related to a side reaction of $PbCl_2$ formation, and a significant loss of PbO by the formation of $PbCl_2$ was expected. However, in this case, there was no loss of PbO by the formation of a lead–salt anion compound.

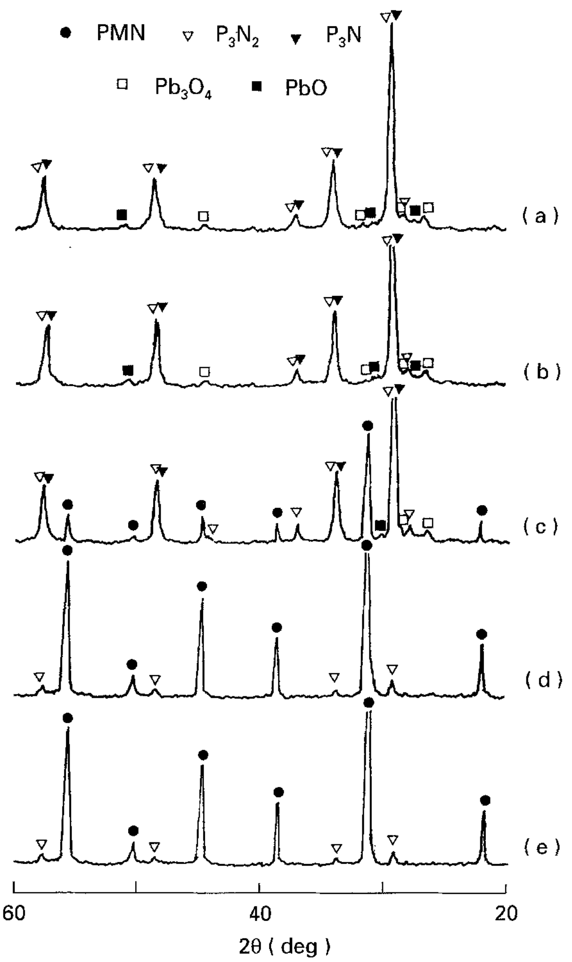

Figure 6 XRD patterns of reaction products as a function of firing temperature after washing for $0.635Li_2SO_4$–$0.365Na_2SO_4$–PMN: (a) 600 °C, (b) 650 °C, (c) 700 °C, (d) 750 °C, and (e) 800 °C.

To determine phases responsible for these endothermic peaks by sulphate salts, reaction products quenched at a given temperature were analysed by X-ray diffractometry for 0.635/0.365 composition. Fig. 5 shows the XRD results of reaction products before and after the washing step after calcining at 550°C for 5 min. Both $LiNaSO_4$ phase and pyrochlore phase were detected before the washing step. However, after washing, the $LiNaSO_4$ phase disappeared due to the dissolution of the salts in the deionized water during washing. Also, before washing, after calcining at 450 and 500 °C, both the same phases were observed by XRD analysis. However, the phase outlined by the 475 and 515 °C peaks in the DTA curve was not observed in the XRD spectra. Fig. 6 shows a series of XRD spectra for the PMN powders prepared by 0.635/0.365 sulphates at various temperatures. The pyrochlore phases (P_3N, P_3N_2), PbO and Pb_3O_4 existed at 600 °C. Above 650 °C, these pyrochlore phases progressively react with PbO and MgO to form perovskite PMN. Upon heating, the formation rate of PMN phase was greatly enhanced by the aid of the molten sulphates, and only a small amount of P_3N_2 was

TABLE II Analysis of phases present in various lead-based ferroelectrics synthesized at 750° C for 30 min

Composition	Salt species	Melting point (° C)	Perovskite phase (%)[a]
$Pb(Mg_{1/3}Nb_{2/3})O_3$	KCl	769	73(93)
	NaCl-KCl	650	86(96)
	Li_2SO_4-Na_2SO_4	594	97(98)
$Pb(Fe_{1/2}Nb_{1/2})O_3$	NaCl-KCl	650	93(95)
	Li_2SO_4-Na_2SO_4	594	91(95)
$Pb(Zn_{1/3}Nb_{2/3})O_3$	NaCl-KCl	650	9(13)
	Li_2SO_4-Na_2SO_4	594	6(18)
$Pb(Ni_{1/3}Nb_{2/3})O_3$	NaCl-KCl	650	11(78)
	Li_2SO_4-Na_2SO_4	594	21(84)
$Pb(Co_{1/3}Nb_{2/3})O_3$	NaCl-KCl	650	25(81)
	Li_2SO_4-Na_2SO_4	594	33(86)

[a] The amount of perovskite phase formed at 800°C for 30 min is shown in parentheses.

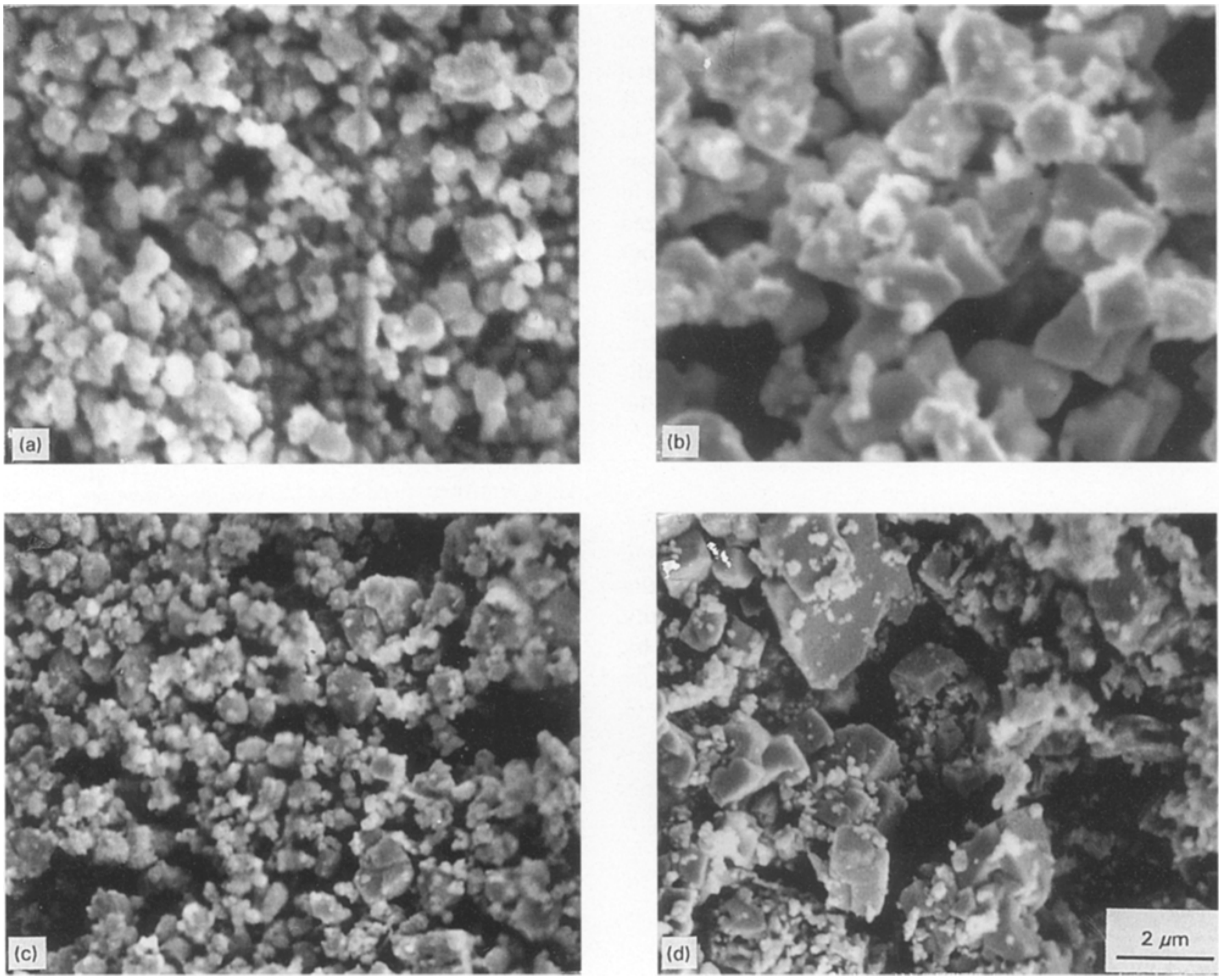

Figure 7 Scanning electron micrographs of powders synthesized at 750 °C for 30 min for (a) 0.5KCl-0.5NaCl-PMN, (b) $0.635Li_2SO_4$-$0.365Na_2SO_4$-PMN, (c) 0.5 KCl-0.5 NaCl-PFN, and (d) $0.635Li_2SO_4$-$0.365Na_2SO_4$-PFN.

unaltered. These reaction sequences are very similar to the results of PMN formation using KCl salt [6] except for the trace of Pb_3O_4 at lower firing temperatures, possibly due to the short soaking time.

3.3 Synthesis of various lead-based ferroelectrics in molten salts

Table II shows the results of phase analysis in lead-based relaxors synthesized at 750 and 800 °C for 30 min, respectively. All compositions were observed to consist of perovskite phase and pyrochlore phase. In the case of PMN, chloride flux was less effective than sulphate flux in respect to perovskite phase formation at 750 °C. This is mainly due to the variations in melting point for each salt used, as shown in Figs. 1 and 3. KCl and 0.5 NaCl-0.5KCl have melting points of about 769 and 650 °C, respectively. The PFN phase also was effectively synthesized at 750 °C. However, no significant difference in PFN phase content was observed for either salt. For PNN and PCN, low contents of perovskite phase at 750 °C apparently increased with increasing calcination temperature, while the MSS method was not effective in the formation of PZN, probably due to the insufficient ionic character of zinc oxide, as discussed elsewhere [11]. A PZN phase content above 20% could not be synthesized despite the increased temperature and time.

Fig. 7 shows scanning electron micrographs of powders synthesized at 750 °C for 30 min for the PMN and PFN by chloride or sulphate flux. Relatively small-sized particles with a relatively uniform distribution were obtained in a less agglomerated state, possibly due to the fast reaction rate in the molten salt. Generally, characteristics of powders obtained by MSS are affected by the variations in firing condition, salt species and salt amount [8, 12]. This figure shows the effect of salt species. In both cases, the sulphate MSS powder has relatively larger particle size than chloride MSS powder. The average particle size is about 0.8 μm in chloride flux and about 1.4 μm in sulphate flux for both PMN and PFN. The morphological difference caused by the salt species in PFN can be explained mainly by the different-sized anions of Cl^- or SO_4^{2-} with the difference in PbO solubility in both salts, as discussed in the PMN study [8]. When PMN specimens using chloride or sulphate flux were sintered at 1200 °C, the maximum dielectric constant was 14 000–15 000. Also, the maximum dielectric constant above 20 000 was obtained for the PFN specimen by MSS sintered at 1000 °C.

4. Conclusions

The perovskite phase as PMN or PFN was effectively synthesized at a relatively low temperature in the presence of chloride or sulphate salts without any detrimental reaction by the salts, as confirmed by thermal analysis. However, PZN phase could not be obtained by the MSS method. In the case of $0.635Li_2SO_4$–$0.365Na_2SO_4$ with a eutectic temperature of 594 °C, PMN containing 97% perovskite phase was obtained at 750 °C for 30 min. The pyrochlore phase identified as P_3N_2 remained up to 850 °C. The variations in Li_2SO_4/Na_2SO_4 mole ratio influenced the formation reaction of perovskite phase, mainly due to the differences in the melting temperatures of the salts.

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