

# Sintering and Dielectric Properties of Single-Phase $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$

K. Katayama, M. Abe, T. Akiba

Research & Development Division, Chichibu Cement Co. Ltd, 5310 Mikajiri, Kumagaya-shi, Saitama-ken 360, Japan

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H. Yanagida

Research Center for Advanced Science and Technology, University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

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## Abstract

*Pyrochlore-free  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PMN-PT) (up to 40 mol% PT) perovskite ceramics could be fabricated from molten salt synthesized single-phase PMN-PT powders. The sintering was performed using  $\text{PbZrO}_3$ -based packing powders, and PMN ceramics of 93% density were obtained by firing at 1200°C for 30 min. The density decreased with increasing duration of sintering. Dielectric properties of these ceramics were measured at -50 to 150°C in the 0.1–100 kHz frequency region. Typical ferroelectric relaxor behavior was observed in all the ceramics, and the maximum dielectric constant increased with the increasing PT content. The electrostriction for 0.9 PMN-0.1 PT ceramics was investigated, and more than  $150 \times 10^{-6}$  strain at an electric field of 2.0 kV/cm was achieved. This large strain was attributed to the complete disappearance of the pyrochlore phases.*

*Pyrochlorfreie Perovskitkeramik,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PMN-PT) mit bis zu 40 mol% PT konnte aus einphasigen PMN-PT-Pulvern hergestellt werden. Diese Pulver waren aus den geschmolzenen Salzen synthetisiert worden. Die Sinterung erfolgte in einem  $\text{PbZrO}_3$ -Pulverbett bei 1200°C und 30 Minuten Haltezeit, wobei 93% Dichte erreicht wurden. Mit zunehmender Haltezeit nahm die Sinterdichte ab. Von diesen Keramiken wurden die dielektrischen Eigenschaften bei -50 bis 150°C im Frequenzbereich von*

*0.1 bis 100 kHz gemessen. Ein typisches ferroelektrisches Relaxationsverhalten wurde in allen Keramiken beobachtet, wobei das Maximum der dielektrischen Konstante mit zunehmendem PT-Gehalt anstieg. Die Elektrostriktion für eine 0.9 PMN-0.1 PT-Keramik wurde untersucht und es wurde eine Dehnung von über  $150 \times 10^{-6}$  in einem elektrischen Feld von 2.0 kV/cm erzielt. Diese starke Dehnung wird auf die vollständige Abwesenheit der Pyrochlorphase zurückgeführt.*

*Des perovskites PMN-PT de formule  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PMN-PT) et pouvant contenir jusqu'à 40 mol% de  $\text{PbTiO}_3$  ont été élaborées à partir de poudres monophasées PMN-PT synthétisées en milieu sel fondu. Le frittage a été effectué avec des poudres à base de  $\text{PbZrO}_3$  pour augmenter la compacité, et des céramiques PMN d'une densité de 93% ont été obtenues après cuisson à 1200°C pendant 30 minutes. La densité diminuait lorsque la durée du frittage augmentait. Les propriétés diélectriques de ces céramiques ont été mesurées entre -50°C et 150°C dans la gamme de fréquences 0.1 à 100 kHz. Un comportement typique de relaxation ferroélectrique a été observé pour toutes les céramiques, et la constante diélectrique maximum augmentait lorsque la teneur en PT augmentait. L'électrostriction des céramiques 0.9 PMN-0.1 PT a été étudiée, et une déformation supérieure à  $150 \times 10^{-6}$  a été mesurée à un champ électrique de 2.0 kV/cm. Cette déformation importante a été attribuée à la disparition complète des phases pyrochlores.*

## 1 Introduction

A great deal of attention has been paid to lead magnesium niobate  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) as an important candidate material for multilayer capacitors<sup>1</sup> and electrostrictive strain applications.<sup>2</sup> Therefore, several papers concerning the preparation of PMN powder<sup>3</sup> or ceramics,<sup>4</sup> or the sintering characteristics and dielectric properties of PMN-based ceramics,<sup>5</sup> have been reported. These papers showed that the preparation of single-phase PMN ceramics was difficult because of the inevitable appearance of pyrochlore phases which severely degrade the dielectric properties. Of these unfavorable pyrochlore phases, the cubic pyrochlore was the most stable and was never completely eliminated.<sup>6</sup> Several effective methods for preventing or eliminating the formation of cubic pyrochlore phase have been reported. Among them, the novel columbite precursor method developed by Swartz & Shrouf<sup>7</sup> was quite successful, and has been widely used for the preparation of pyrochlore-free PMN ceramics. However, this method requires many complicated steps such as a high calcination temperature and subsequent milling.

A recent investigation<sup>8</sup> showed that single-phase PMN powder could be prepared by the KCl molten salt method. The purpose of the present investigation was to study the sintering characteristics of PMN powder prepared by the above method and the dielectric properties of the resultant ceramics. Furthermore, the PMN–PT solid solution system was also studied, and the electrostriction of PMN with 10 mol%  $\text{PbTiO}_3$  (0.9 PMN–0.1PT) was evaluated.

## 2 Experimental

The single-phase PMN powder used here was prepared by the KCl molten salt method.<sup>8</sup> Starting materials were commercially available 99.99% purity oxide powders ( $\text{PbO}$ ,  $\text{MgO}$ ,  $\text{Nb}_2\text{O}_5$ ) and analytical grade KCl. Three moles of  $\text{PbO}$ , one-third mole of  $\text{MgO}$  and two-thirds mole of  $\text{Nb}_2\text{O}_5$  were thoroughly mixed in ethanol in an alumina mortar and pestle, and dried at 120°C. Thirty grams of the mixed powder and 20 g of KCl were mixed again, and heated at 900°C for 1 h in a covered alumina crucible. The product was leached in boiling diluted nitric acid (50 wt%) to remove KCl and unreacted  $\text{PbO}$ , simultaneously. The resultant powder was washed and filtered in hot deionized water at least five times. The preparation of single-phase PMN

powder was confirmed by XRD. Furthermore,  $\text{PbO}$  was added to the synthetic PMN powder by a conventional dry process to prepare PMN powders containing various amounts of excess  $\text{PbO}$  (1, 2 or 5 wt%) (hereafter designated as PMN + 1P, PMN + 2P and PMN + 5P).

The preparation of powders in the PMN–PT system was conducted in the same way as that of the PMN powder. A commercial  $\text{TiO}_2$  (99.99%) powder was used as the Ti source. The composition of powders prepared here was 0.95 PMN–0.05 PT, 0.9 PMN–0.1 PT, 0.8 PMN–0.2 PT, 0.7 PMN–0.3 PT and 0.6 PMN–0.4 PT. XRD revealed that the crystal structure of these powders was single-phase perovskite without any traces of other phases. These powders were mixed with 1 wt% stearic acid, pressed into pellets (10 mm  $\phi$   $\times$  1 mm or 5 mm) in a stainless steel die at a pressure of 100 MPa. The pellets were fired in a covered alumina crucible with packing powders at temperatures of 1000–1300°C in air for 15 min to 10 h. Packing powders used in this study were lead zirconate (PZ) or lead zirconate with 1, 2, 5 or 10 wt% lead oxide (PZ + 1P, PZ + 2P, PZ + 5P and PZ + 10P). These packing powders were prepared in the same way as that described by Chiang *et al.*;<sup>9</sup> finer powders sieved through a 100-mesh screen were used. The phases present in the fired pellets were identified using XRD. The density of pellets was measured by the liquid displacement method and toluene was used as the liquid medium. The microstructure was observed using SEM.

The samples for dielectric measurements were prepared from the fired pellets by grinding parallel to 0.5 mm thickness, cleaning ultrasonically and sputtering gold electrodes. Dielectric measurements were conducted at four frequencies (0.1, 1, 10 and 100 kHz) by an Impedance Analyzer with a temperature control box. The electrostrictive strain was measured as a function of the applied electric field (0.002 Hz) at various temperatures in the 0–50°C range. The samples for electrostrictive measurements were cut from fired pellets, and typical dimensions were 3 mm  $\times$  3 mm  $\times$  5 mm. The gold electrode was sputtered on the face of the samples and a polyimide foil strain gauge (Kyowa, KFR-02-C1-11) was bonded with cement (Kyowa, PC-6) on the longitudinal face of samples.<sup>10</sup>

## 3 Results and Discussion

### 3.1 Preparation of single-phase PMN ceramics

The PMN powder prepared by the KCl molten salt method was not stable at elevated temperatures, and

**Table 1.** Stability of PMN powder

Heating temperature (°C)	%PMN (1 - %pyrochlore)
600	100%
700	99
800	92
900	79
1 000	64

Heating duration is 1 h.

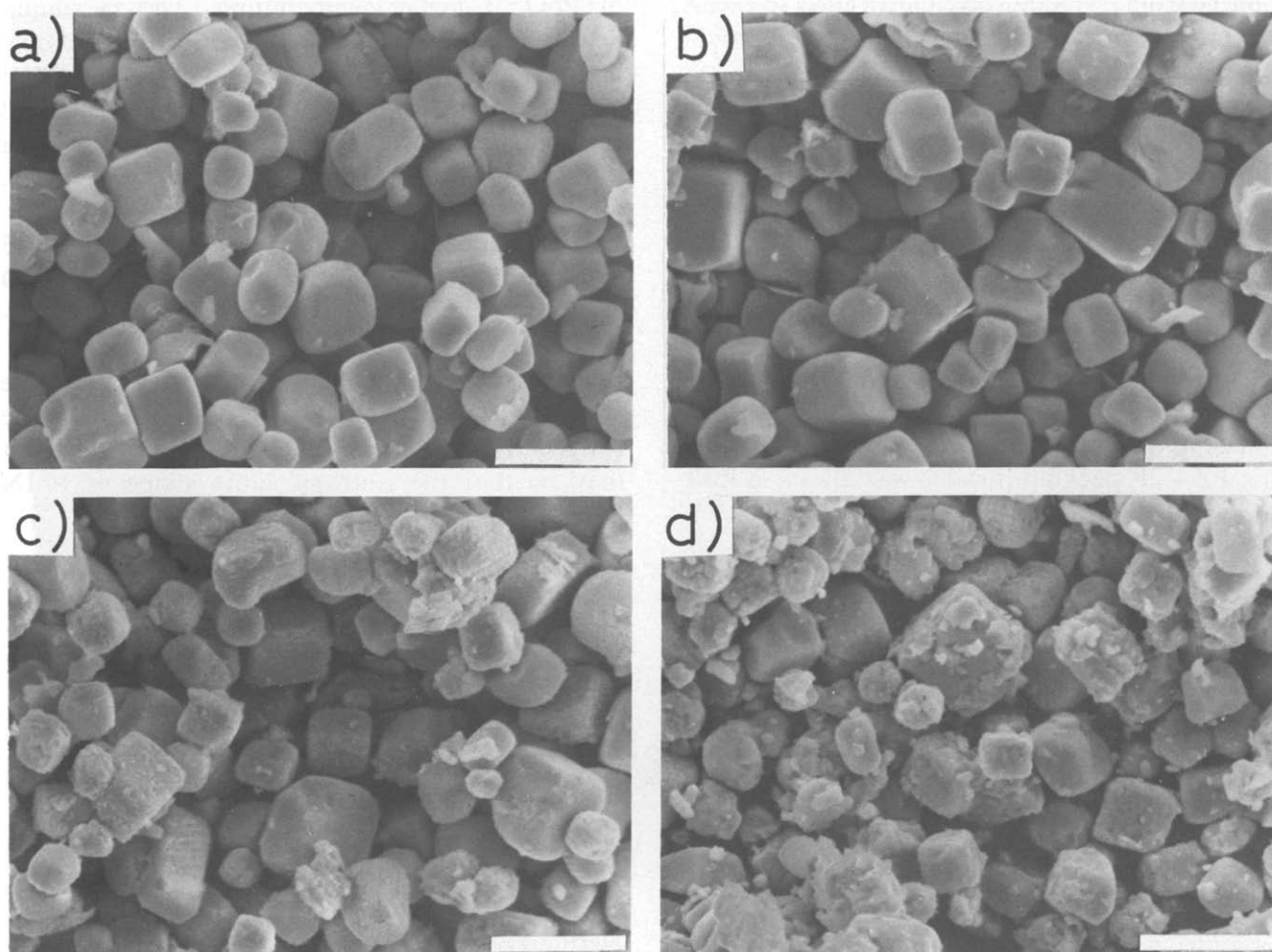
easily transformed into the cubic pyrochlore. Other pyrochlore phases or additional phases could not be detected. The percentage of the cubic pyrochlore in PMN powders heated to several temperatures is shown in Table 1. The relative amounts of pyrochlore were determined by measuring their respective 100% intensity peaks ((110) for perovskite; (222) for pyrochlore) and by calculation using the following equation:

$$\% \text{pyrochlore} = 100 \times \frac{I_{(222) \text{ pyrochlore}}}{(I_{(222) \text{ pyrochlore}} + I_{(110) \text{ perovskite}})}$$

The transformation commenced at 700°C, and the

amount of pyrochlore increased with heating temperature. The morphology of the PMN powders is shown in Fig. 1. The formation of cubic pyrochlore could be confirmed by such visible results as the presence of aggregates on the surface of powders heated at 800°C or above; the amount of cubic pyrochlore increased as the heating temperature increased.

The difficulty in sintering lead containing materials is attributed to the loss of PbO. There have been several papers on the prevention of PbO loss and, in this study, the packing powder method was employed.<sup>9</sup> Pressed pellets made from four kinds of powders (PMN, PMN + 1P, PMN + 2P and PMN + 5P) were fired for 1 h at several temperatures using various packing powders. The phases present in these fired pellets were examined as shown in Table 2. The cubic pyrochlore phase was confirmed in all samples fired using PZ or PZ + 1P packing powders, while single-phase PMN ceramics could be obtained by firing at 1200°C using PZ + 2P, PZ + 5P or PZ + 10P, and at 1300°C with PZ + 2P or PZ + 5P. Trace amounts of MgO were detected in the



**Fig. 1.** PMN powders heated for 1 h at (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C (bar = 5 μm).

**Table 2.** Phases present in ceramics

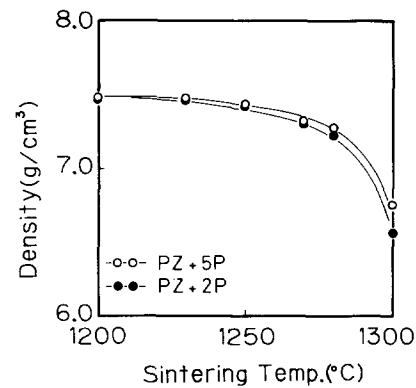
Packing powder	Firing temperature (°C)			
	1000	1100	1200	1300
PZ	PMN, pyro	←	←	←
PZ + 1P	PMN, pyro	←	←	←
PZ + 2P	PMN, (PbO)	←	PMN	←
PZ + 5P	PMN, (PbO)	←	PMN	←
PZ + 10P	PMN, (PbO)	←	PMN	PMN, (MgO)

Parentheses indicates small quantities.

samples fired at 1300°C using PZ + 10P packing powder. The appearance of MgO might be caused by the volatilization of PbO on the formation of the liquid phase,<sup>11</sup> resulting in variations in composition. PbO was detected in samples fired at 1000 and 1100°C using PZ + 2P, PZ + 5P or PZ + 10P. This was probably because excess PbO in the packing powders was incorporated into the samples and could not be released through volatilization at 1000 or 1100°C. The phases present in other samples produced from PMN + 1P, PMN + 2P and PMN + 5P powders were all the same as those in samples produced from PMN powder, and an effect of excess PbO in PMN powder on the phases present could not be confirmed.

The influence of the duration of firing period on the phases present in samples at 1200–1300°C was also investigated. It was found from Table 3 that firing at 1200 or 1250°C with PZ + 2P or PZ + 5P was quite successful in preparing single-phase PMN ceramics. MgO could be detected in some samples, and the amount of MgO increased with increasing excess PbO or duration of firing.

In Fig. 2 is shown the density of PMN ceramics fired at 1200–1300°C for 1 h using PZ + 2P or PZ + 5P packing powders. The density of samples fired using PZ + 2P packing powder was always a little



**Fig. 2.** Density of PMN ceramics fired at 1200–1300°C for 1 h. Packing powders used were PZ + 2P and PZ + 5P.

lower than that of the samples fired using PZ + 5P packing powder, and the density of samples decreased as the firing temperature increased, and fell abruptly at 1300°C. The abrupt decrease in density might be attributed to the liquid formation.<sup>11</sup> The firing duration dependence of the density is shown in Fig. 3. The density of samples fired at 1200°C was a little higher than that of samples fired at 1250°C. This might be attributed to additional vaporization of PbO at higher temperatures. The maximum density of 93% could be observed for the sample fired at 1200°C for 30 min, and the density decreased as the duration increased. Microstructures of several samples are shown in Fig. 4. With the increasing duration of the firing period, the grain size increased, and the edges of grains became much clearer. Ambiguous edges of grains in samples fired for 15 and 30 min were caused by a small amount of PbO existing in the grain boundaries, which was confirmed by XRD and EDX analyses.

The densities obtained in this work were a little lower than those that had been reported earlier. The actual reason for this has not been clarified yet, but it may be that the isotropic grain shape of PMN

**Table 3.** Influence of duration on phases

Firing temperature (°C)	Packing powder	Duration of firing (h)				
		1	2	3	5	10
1200	PZ + 2P	PMN	←	←	←	←
	PZ + 5P	PMN	←	←	←	←
	PZ + 10P	PMN	PMN, (MgO)	←	←	PMN, MgO
1250	PZ + 2P	PMN	←	←	←	←
	PZ + 5P	PMN	←	←	←	←
	PZ + 10P	PMN, (MgO)	←	←	PMN, MgO	←
1300	PZ + 2P	PMN	PMN, (MgO)	←	←	←
	PZ + 5P	PMN	PMN, (MgO)	←	PMN, MgO	←
	PZ + 10P	PMN, (MgO)	←	PMN, MgO	←	←

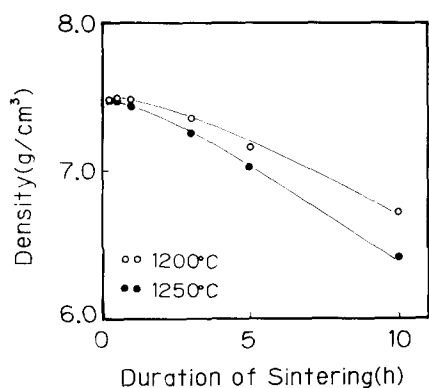


Fig. 3. Density versus duration of firing at 1200 or 1250°C.

powder prepared by the molten salt method was responsible for the lower density.<sup>12</sup> Cho and Biggars<sup>13</sup> obtained similar results in which the densities of lead zirconate-titanate ceramics produced from molten salt synthesized powders were lower than those produced from conventionally calcined powders.

### 3.2 Dielectric properties of PMN ceramics

In Fig. 5 are shown the firing duration dependence of the dielectric constant and the dissipation factor at 1 kHz versus temperature for PMN ceramics fired at 1200°C using PZ + 5P packing powder. The dielectric constant and dissipation factor initially increased as the duration increased, providing a maximum value for samples fired at 3 or 5 h. Lower dielectric constants for samples fired for 15 and 30 min might be attributed to the presence of PbO, and a decrease in the dielectric constant for the sample fired for 10 h might be caused by a decrease in density. It has been said the density affects the dielectric constant and dissipation factor,<sup>14</sup> but the actual relationship between the density and dielectric properties has not yet been clarified. Therefore, these values were not corrected here. The transition range was shifted to a higher temperature as the duration increased, and the temperature of the dielectric constant maximum increased, from -22°C

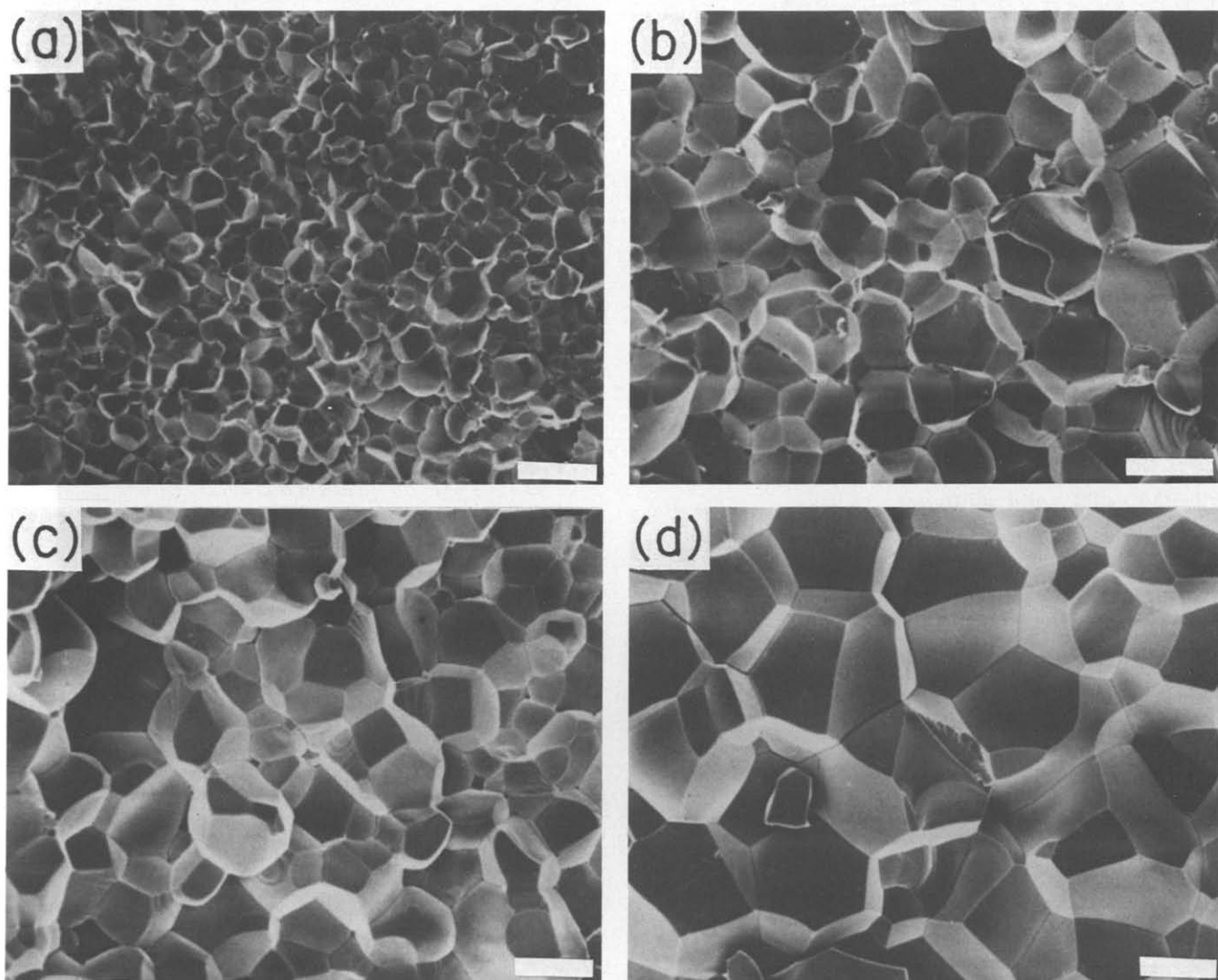
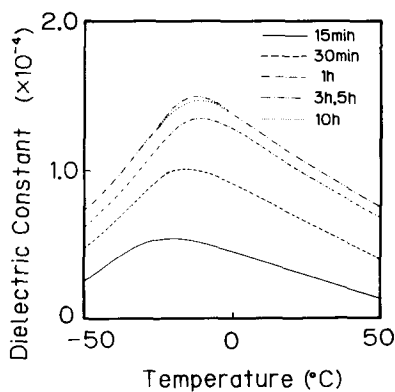
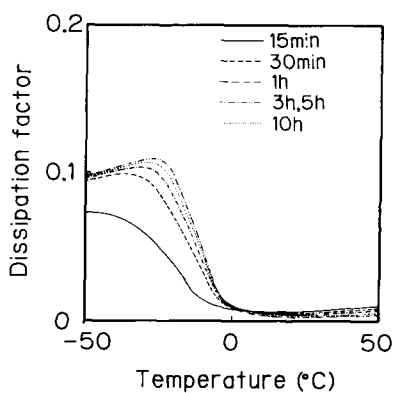


Fig. 4. Microstructures of PMN ceramics fired at 1200°C using PZ + 5P for (a) 15 min, (b) 30 min, (c) 1 h and (d) 5 h (bar = 10 μm).



(a)



(b)

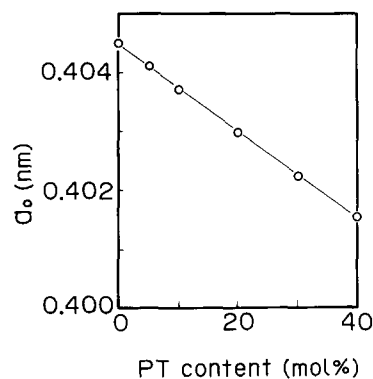
**Fig. 5.** Dielectric constant (a) and dissipation factor (b) versus temperature for PMN ceramics fired at 1200°C for several periods of time (1 kHz).

for the sample fired for 15 min, to  $-10^{\circ}\text{C}$  for that fired for 3 h or more. A maximum magnitude of the dielectric constant of 15 000 at 1 kHz for the sample fired at 1200°C for 3 or 5 h was achieved. The maximum dissipation factor also increased as the duration increased, showing the highest value of 0.11 at around  $-25^{\circ}\text{C}$  for the same sample.

### 3.3 PMN-PT solid solution

Single-phase PMN-PT powders (up to 40 mol%) could be prepared as stated in section 2. The lattice constant of these powders, which decreased monotonically as the PT content increased, is shown in Fig. 6. This result confirms the formation of solid solutions in the PMN-PT system up to 40 mol% PT content. The morphology of these powders was almost identical to that of PMN powder. These powders were pressed and fired at 1200°C for 3 h using PZ + 5P packing powder. The density was almost independent of the PT content, and similar densities were achieved in all PMN-PT ceramics. The lattice constants of these ceramics were exactly the same as those of the powders.

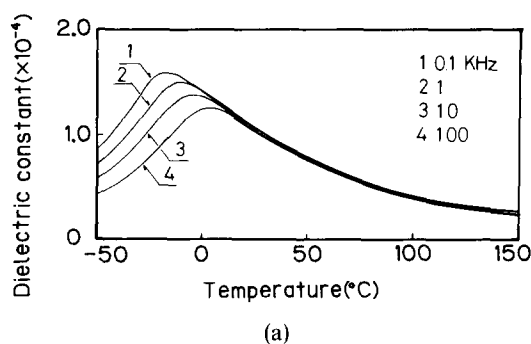
In Figs 7, 8 and 9 are shown the dielectric constant and dissipation factor versus temperature at various



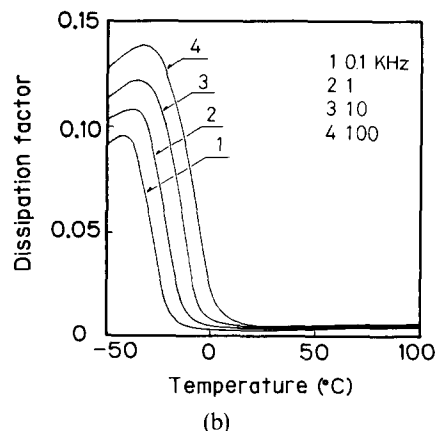
**Fig. 6.** Lattice constants of PMN-PT powders.

frequencies for PMN, 0.9 PMN-0.1 PT and 0.8 PMN-0.2 PT, respectively. The frequency dispersion of the dielectric constant decreased and the magnitude of dielectric constant increased as the PT content increased. Moreover, as is characteristic with all ferroelectric relaxor materials, the temperature of the dielectric constant maximum shifted toward higher temperatures as the frequency increased.

Lanagan *et al.*<sup>15</sup> have also studied the dielectric properties in PMN-PT ceramics. They observed lower and complex dielectric constants in 0.7 PMN-0.3 PT and presumed that a morphotropic phase boundary at around 32 mol% PT content was

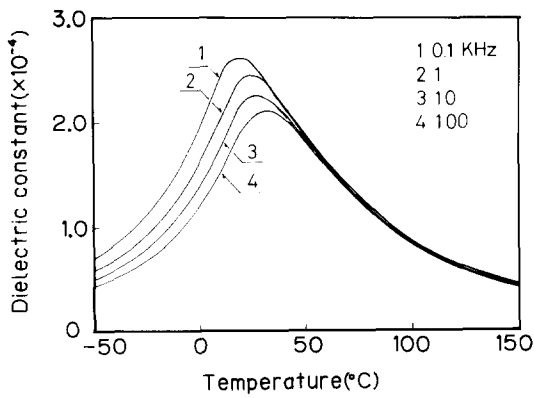


(a)

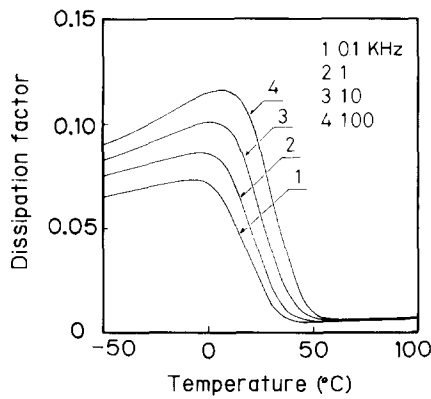


(b)

**Fig. 7.** Dielectric constant (a) and dissipation factor (b) versus temperature for PMN ceramics fired at 1200°C for 3 h using PZ + 5P.

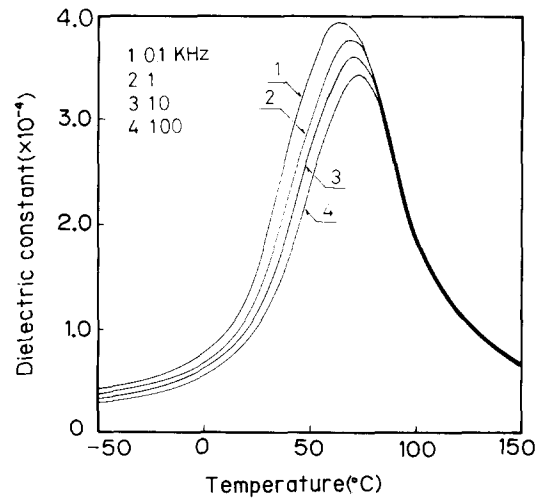


(a)

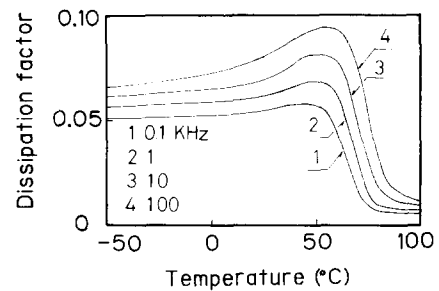


(b)

**Fig. 8.** Dielectric constant (a) and dissipation factor (b) versus temperature for 0.9 PMN-0.1 PT ceramics fired at 1200°C for 3 h using PZ + 5P.



(a)



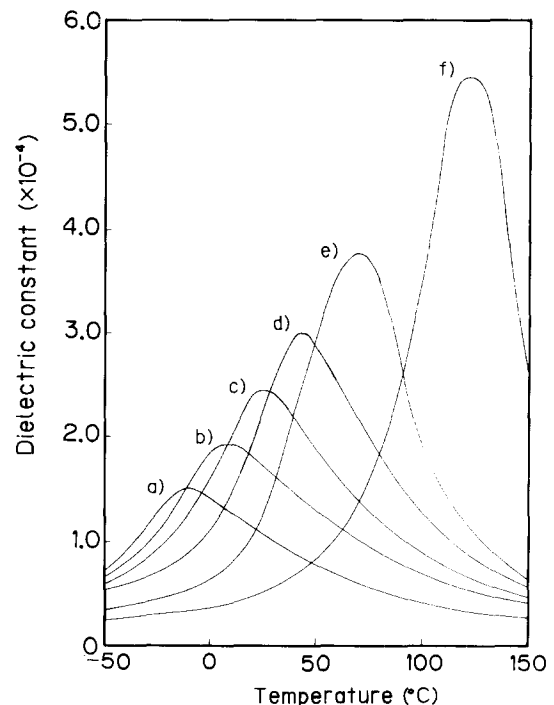
(b)

**Fig. 9.** Dielectric constant (a) and dissipation factor (b) versus temperature for 0.8 PMN-0.2 PT ceramics fired at 1200°C for 3 h using PZ + 5P.

the cause of this phenomenon. On the other hand, Ouchi *et al.*<sup>16</sup> observed that a morphotropic phase boundary exists in the PMN-PT system at around 40 mol%. In Fig. 10 is shown the dielectric constant at 1 kHz as a function of temperature for various PMN-PT solid solution ceramics produced from molten salt synthesized powders. The maximum dielectric constant gradually increased as the PT content increased, and the formation of the solid solution in the system up to 40 mol% was apparently confirmed. In any event, there was no indication of the existence of a morphotropic phase boundary in the PMN-PT system up to 40 mol%.

### 3.4 Electrostriction of PMN-PT

Cross *et al.*<sup>17</sup> found that 0.9 PMN-0.1 PT ceramics exhibited outstanding electrostriction at around room temperature, and this behavior was attributed to the large dielectric constant near the room temperature. In Fig. 11 is shown the longitudinal electrostrictive strain measured at several temperatures for 0.9 PMN-0.1 PT ceramics produced from the molten salt synthesized 0.9 PMN-0.1 PT powder. These strains were proportional to the square of the applied field, which is one of the fundamental



**Fig. 10.** Dielectric constant at 1 kHz versus temperature for PMN-PT solid solution ceramics fired at 1200°C for 3 h. (a) PMN, (b) 0.95 PMN-0.05 PT, (c) 0.9 PMN-0.1 PT, (d) 0.8 PMN-0.2 PT, (e) 0.7 PMN-0.3 PT and (f) 0.6 PMN-0.4 PT.

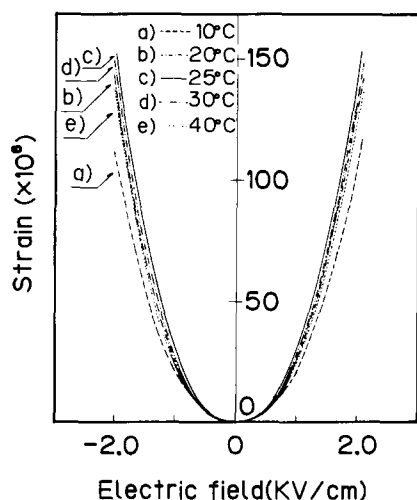


Fig. 11. Electric field dependence of strain for 0.9 PMN-0.1 PT ceramics at various temperatures.

properties of electrostrictive ferroelectrics. The maximum strain which was also achieved at around room temperature was more than  $150 \times 10^{-6}$  at an electric field of 2.0 kV/cm. The strain measured here was much larger than that reported by Jang *et al.*<sup>18</sup> This might be attributed to the complete disappearance of the pyrochlore phases.

In order to investigate how pyrochlore phases affect the electrostriction, samples containing cubic pyrochlore were fabricated as follows: the PMN powder was heated at 800 or 900°C for 1 h and these powders were pressed and fired at 1200°C for 5 h using the PZ + 5P covering powder. The relative amount of cubic pyrochlore in these samples was 25 and 40%, respectively. The strain of these samples, measured at 25°C, is shown in Fig. 12. The strain decreased as the amount of cubic pyrochlore

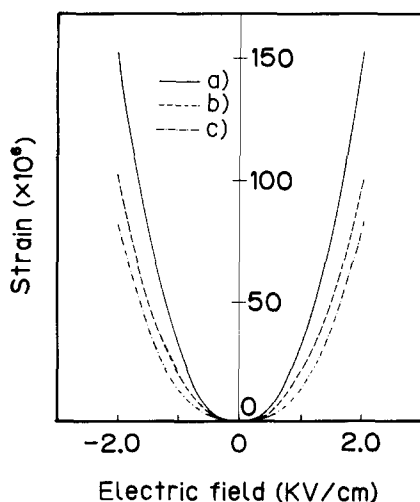


Fig. 12. Effect of cubic pyrochlore phase on strain measured at 25°C: (a) pure PMN; (b) PMN with 25% pyrochlore; and (c) PMN with 40% pyrochlore.

increased, and it was confirmed that the cubic pyrochlore was apparently detrimental to electrostriction.

#### 4 Conclusion

Pyrochlore-free PMN-PT perovskite ceramics could be produced from molten salt synthesized PMN-PT powders. The formation of solid solutions in the PMN-PT system was confirmed up to 40 mol% PT content. The dielectric constant of these ceramics increased with the PT content, and all these ceramics exhibited typical ferroelectric relaxor characteristics. The electrostrictive strain of 0.9 PMN-0.01 PT ceramics measured at room temperature was as large as  $150 \times 10^{-6}$  at 2 kV/cm electric field, and it was found that this large strain was attributed to the complete disappearance of the cubic pyrochlore phase.

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