JOURNAL OF MATERIALS SCIENCE **28** (1993) 3335–3340

Piezoelectric properties of hot-pressed 18PMN–41PZ–41PT ceramics

JIN-CHEN SHAW, KUO-SHUNG LIU, I-NAN LIN*
*Department of Materials Science and Engineering, and *Materials Science Centre, National Tsing Hua University, Hsin-Chu, Taiwan*

Piezoelectric ceramics of 18PMN–41PZ–41PT were sintered by hot-pressing and normal sintering methods. The microstructure, density, *P–E* curve and *S–E* curve were also compared. The best hot-pressing condition for 18PMN–41PZ–41PT material was obtained at a temperature of 1000 °C and a pressure of 700 kg cm^{-2}; it could achieve 99.66% theoretical density and a fine, uniform microstructure as a result of a 200–300 °C decrease in the sintering temperature. A higher coercivity was attained with the density increase. The fine, uniform microstructure also enhanced the increase in polarization and strain.

1. Introduction

The grain size and bulk density is well known to be influenced by the electrical characteristics of sintered piezoelectric ceramics. The grain growth and densification process could be controlled by use of the hot-pressing technique. This method can yield ≈ 100% dense ceramics with a controlled grain size.

The uniaxial hot-pressing of PLZT ceramics for electro-optic application has been studied by numerous investigators [1–5]. The same technique has been applied to different PZT compositions [6, 7]. Research into hot-pressed sintering, at a high temperature (> 1200 °C) and at long times has, however, been sparse. While increasing the density of the sample, hot-pressing sintering, however, can simultaneously coarsen the grains. It has a much more positive effect on the piezoelectric properties.

In the present work, the best piezoelectric properties component 18PMN–41PZ–41PT (which is closed to the MPB) was chosen in PMN–PZ–PT ceramics system. The process of hot-pressing, which can be used as a faster method (increasing both pressure and the rate of temperature) to attain a high density and fine microstructure sample, has been investigated. The effect of the density and microstructure on the piezoelectric properties was also studied.

2. Experimental procedure

2.1. Composition selection

A ceramic of composition 18PMN–41PZ–41PT was taken as the base composition. The plain material was composed of the rhombohedral ferroelectric phase and showed maximum piezoelectric activity in the PMN–PZ–PT solid solution. Three samples, A, B and C, existed in this area. The composition of Samples A and C was 18PMN–41PZ–41PT, and that of Sample B was 18PMN–41PZ–41PT + 0.1 mol % Nb ion.

2.2. Ceramic sample preparation

The ceramic samples of PMN–PZ–PT composition were prepared by the mixed oxides methods. The starting materials consisted of high-purity PbO, ZrO_2, TiO_2, MgO and Nb_2O_5 of correct composition. The fine oxides were weighed by the molar composition and were then wet ball-milled in ethanol for 8 h. The mixed powder was then dried and calcined at 850 °C in covered alumina crucibles for 6 h. The calcined powders were then wet ball-milled in ethanol with the addition of 0.5 wt % PVA for 8 h. They were then dried and pulverized. The fine powders were pressed into 12 mm diameter and 1–2 mm thickness pellets at a pressure of 1000 kg cm^{-2}. The same process was used for the hot-pressed and normal sintering powder.

The pellets were then sintered at 1250 °C (Sample B) and 1220 °C (Sample C) for 1 h in sealed alumina crucibles. A PbO-rich atmosphere was maintained by placing $PbZrO_3$ inside the crucible in order to compensate for the PbO weight loss. Fired-on silver paint was applied to the fine polished surfaces of the sintered pellets and fired at 580 °C for 1 h. All the sintered samples were then poled in silicon oil at 120 °C for 20 min under a d.c. field of 3 kV cm^{-1}. Poled samples were aged for 24 h prior to property measurement.

2.3. Measurement

2.3.1. Structure measurement

All the sintered samples were analysed by using CuK_α radiation with an X-ray diffractometer (Rigaku DMAX-II) for identifying their phases at room temperature.

2.3.2. Field-induced polarization

The polarization versus electric-field hysteresis loop was studied at room temperature, with various field

0022–2461 © *1993 Chapman & Hall*

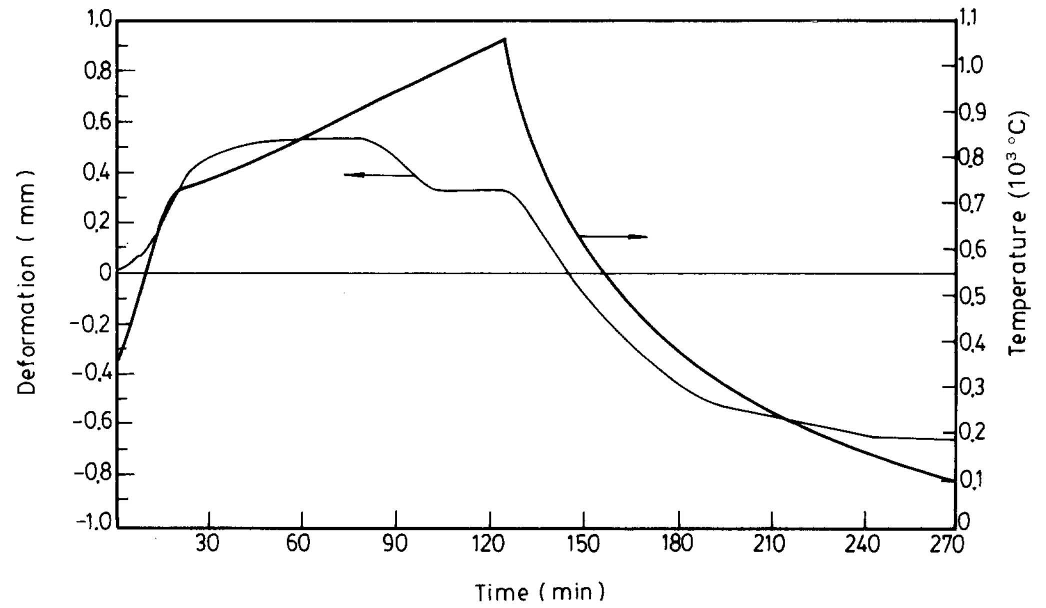

Figure 1 The relationship between temperature and deformation versus time under constant pressure (1000 kg cm^{-2}).

levels at 60 Hz, using a modified Sawyer–Tower circuit [8, 9].

2.3.3. Field-induced strain

The strain versus electric field curve was measured under a low frequency, for a cycle time of 6 min, using a Michelson interferometer; the wavelength of the laser was 632.8 nm [10, 11].

2.3.4. Density measurement

The specimens were first finely polished, and immersed in pumped water for 30 min. The bulk density of the sintered chips was measured by Archimedes' method and calculated using the following equation

$$\text{Bulk density} = \frac{W_d}{W_w - W_s} \quad (1)$$

where W_d is the dry weight, W_w the wet weight in air, and W_s the wet weight suspended in water.

3. Results and discussion

3.1. Hot-pressed condition

The 18PMN–41PZ–41PT ceramic powders were pressed into a pellet 10 mm diameter and 5 mm thick and placed in an alumina mould. MgO powder was interlayered between pellet and mould to avoid reactions between 18PMN–41PZ–41PT and the alumina.

The pellet was heated in the hot-pressing sintering process at a rate of 20 °C min^{-1} up to 700 °C, then at 2.5 °C min^{-1} up to 1050 °C, and air-cooled to room temperature. The pressure was maintained at 1000 kg cm^{-2} during the hot-pressing process, but was lowered after the temperature was raised to 1050 °C. The relationship between temperature, strain and time is shown in Fig. 1.

The temperature and strain versus time curves have shown that the pellet had a thermal expansion below 800 °C, began plastic deformation and reduction above 800 °C, and this was finished at 1000 °C. The quantity of reduction was nearly zero from 1000–1050 °C, indicating that the 18PMN–41PZ–41PT was fully densified at 1000 °C. The relationship between pressure and deformation at constant temperature (1000 °C) is shown in Fig. 2. With the pressure below 700 kg cm^{-2}, the reduction increased with increasing applied pressure. The degree of reduction increase was almost zero when the pressure rose above 700 kg cm^{-2}.

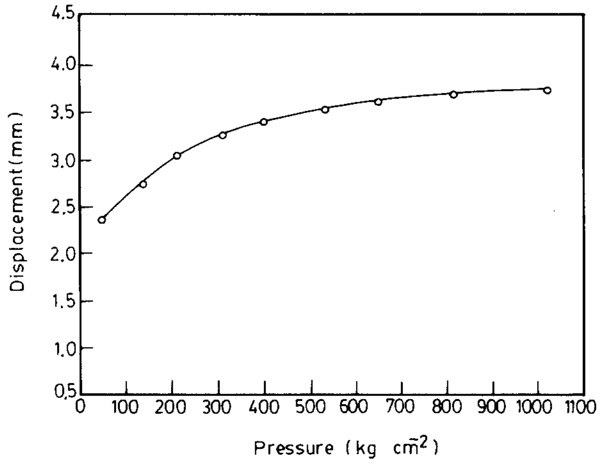

Figure 2 The relationship between displacement and pressure under constant temperature (1000 °C).

The densities which were obtained by different sintering methods for 18PMN–41PZ–41PT materials are listed in Table I. The highest density obtained by the hot-pressing method was 99.66% theoretical density. The theoretical density, calculated from the X-ray diffraction pattern, was 8.039 g cm^{-3}. This demonstrated that the best sintering conditions for 18PMN–41PZ–41PT were a temperature of 1000 °C and a pressure of 700 kg cm^{-2}. This also shows that the hot-pressing sintering method, compared with the normal sintering method, could produce a density increase of 4%–6%.

TABLE I The density and density ratio of three different sintering conditions

Sample condition	Density ($g\,cm^{-3}$)	Density ratio (%)
18PMN–41PZ–41PT hot-pressed	8.012	99.66
18PMN–41PZ–41PT + 0.1 mol % Nb 1250 °C sintering	7.673	95.45
18PMN–41PZ–41PT 1220 °C sintering	7.516	93.49

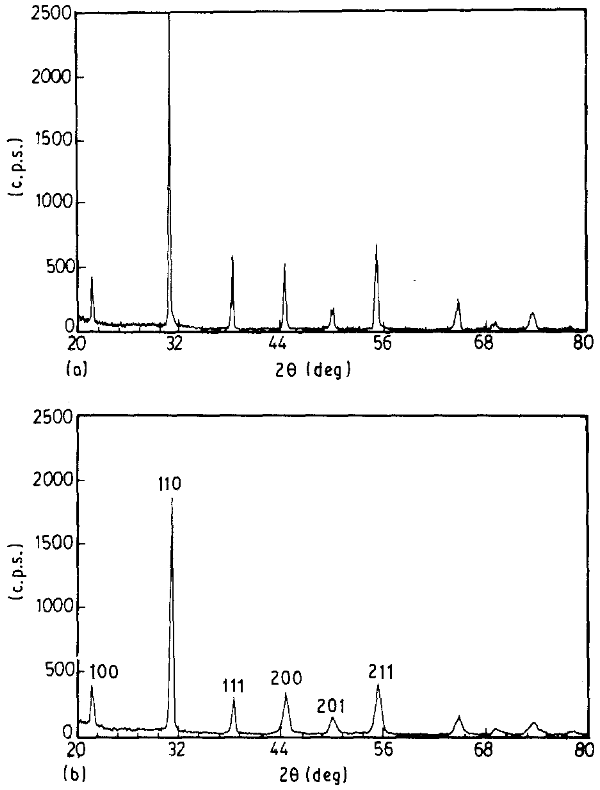

Figure 3 The X-ray diffraction pattern for (a) normal unpressed sintered, (b) hot-pressed sintered samples of 18PMN–41PZ–41PT material.

3.2. Crystal structure analysis

The 18PMN–41PZ–41PT is a three-component piezoelectric ceramic. A solid-solution structure is therefore necessary in order to obtain good piezoelectric property.

The X-ray diffraction (XRD) patterns, obtained under different sintering conditions for 18PMN–41PZ–41PT, are shown in Fig. 3. The XRD pattern of the normal unpressed sintering at 1220 °C is shown in Fig. 3a; that of the hot-pressed sintered specimen is shown in Fig. 3b.

Both sintering processes are indicated, from these results, to be able to achieve the single phase of the solid solution. The crystal structure of 18PMN–41PZ–41PT was a rhombohedral phase with a theoretical density of 8.039 $g\,cm^{-3}$. The difference between Fig. 3a and b is that the peak in Fig. 3b is lower and broader than that in Fig. 3a.

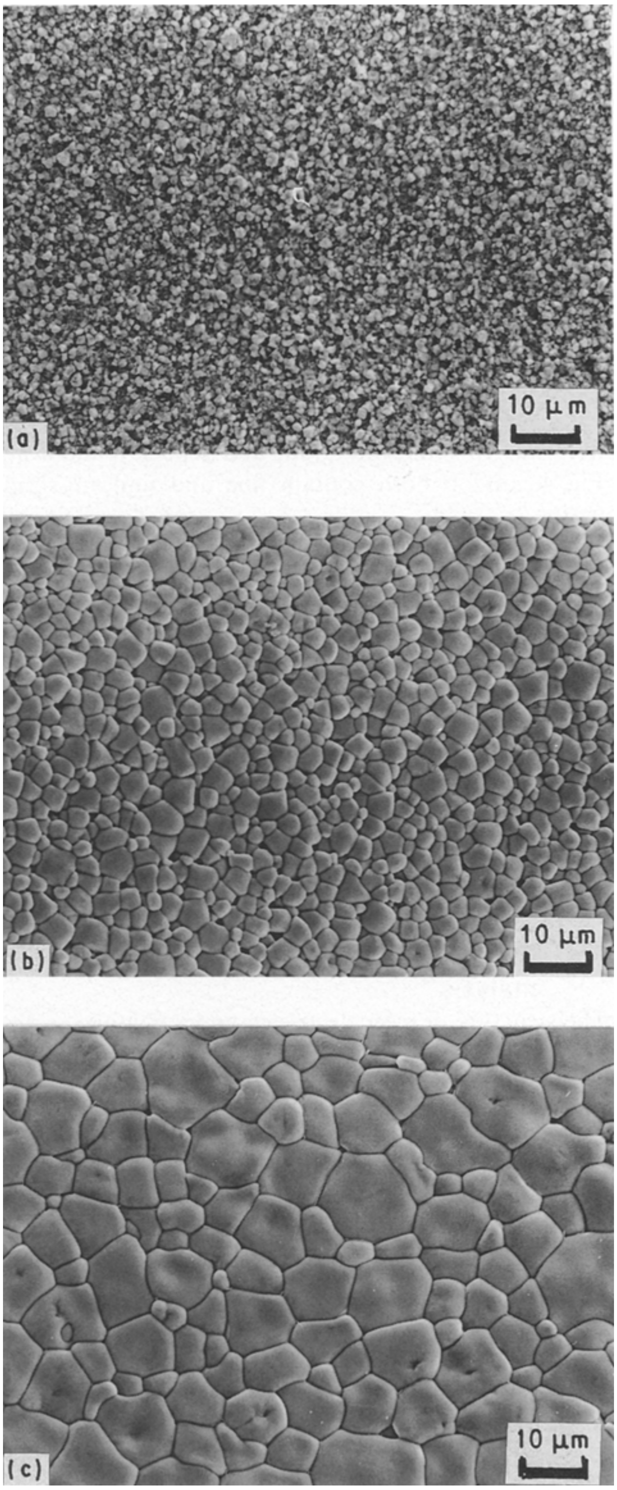

Figure 4 The microstructure produced by the three different sintering conditions: (a) 18PMN–41PZ–41PT, hot-pressed; (b) 18PMN–41PZ–41PT + 0.1 mol % Nb ions, 1250 °C, sintered; (c) 18PMN–41PZ–41PT, 1220 °C, sintered.

3.3. Microstructure analysis

In addition to the crystal structure, the microstructure also has a great influence on piezoelectric properties. Three kinds of microstructure exist for the three differently processed samples, as shown in Fig. 4. The microstructure of the hot-pressed sintered samples is given in Fig. 4a. The average grain size was approximately 1–2 µm. The grain size of the sample doped with 0.1 mol % Nb ions and sintered at 1250 °C for 1 h, was 3–4 µm (Fig. 4b). The object of the additional niobium

TABLE II The properties of samples subjected to three different sintering conditions

Sample condition	Density ratio (%)	Grain size (μm)	E_c (kV cm^{-2})	P_r (μC cm^{-2})	P_s (μC cm^{-2})	S_r ($\times 10^{-3}$)	S_s ($\times 10^{-3}$)
18PMN-41PZ-41PT hot-pressed	99.66	1-2	11.43	24.73	31.20	2.87	5.28
18PMN-41PZ-41PT + 0.1 mol % Nb 1250 °C sintering	95.45	3-4	7.71	29.62	34.52	5.33	8.93
18PMN-41PZ-41PT 1220 °C sintering	93.49	8-10	6.31	25.34	29.38	2.10	3.15

ions was to refine the grain and render it uniform. Fig. 4a and b both contain fine and uniform-sized grains.

The microstructure of 18PMN-41PZ-41PT is shown in Fig. 4c after normal sintering at 1220 °C for 1 h; the average grain size was 8–10 μm but it was, however, significantly non-uniform. The hot-pressed 18PMN-41PZ-41PT sample doped with a small amount of niobium ions may, therefore, attain a uniform and fine grain size. The sintering temperature of the hot-pressing process was, however, 250 °C lower than the normal sintering process. The hot-pressed method could thus achieve a finer and more uniform microstructure.

3.4. Piezoelectric properties analysis

The structure of piezoelectric ceramics belongs to the perovskite (ABO_3) group. This structure has an asymmetrical centre B cation and it has a dipole moment in the unit cell. The dipole moment can line up when being subjected to an electric field. This arrangement of dipole moments could produce a polarization, differing with different electrical fields. This could be observed from polarization–electrical field curves (*P–E* curve). The three *P–E* curves for different sintering conditions are illustrated in Fig. 5. The detailed data are listed in Table II.

Crystal structure, tetragonality, doping ion, . . ., etc. are the factors which affect the coercivity of piezoelectric ceramics. Coercivity could also be affected by density ratio, with which it exhibits a linear relationship as shown in Fig. 6.

With an applied electric field, the dipole moment becomes lined up within the piezoelectric material resulting in a strain. The curve revealing the relationship between strain and applied electric field is called an *S–E* curve. The *S–E* curves for three different sintering conditions are shown in Fig. 7.

The largest magnitude of strain was obtained from the sample doped with 0.1 mol % Nb ions, and the second largest was from the hot-pressed sample. We assume this to result from the residual stress in the sample which was caused by the hot-pressing process, because the hot-pressed sample was produced by applying a force to the powders, allowing it to develop plastic deformation. This could decrease the sintering temperature and increase the density of the sample.

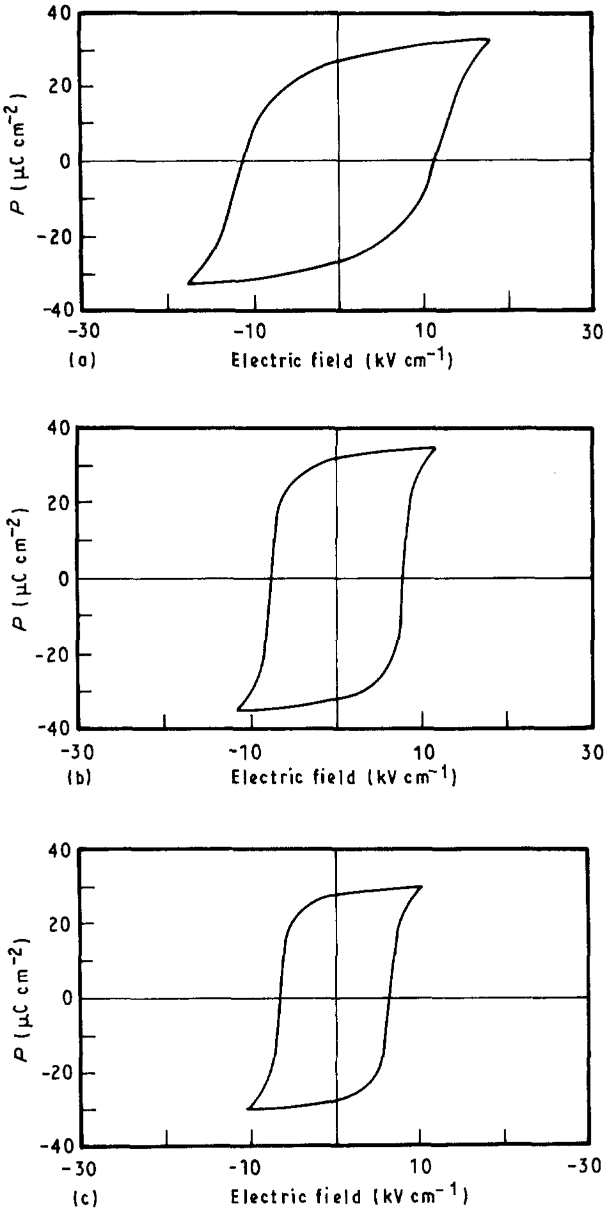

Figure 5 The polarization versus electric field curve for the three different sintering conditions: (a) 18PMN–41PZ–41PT, hot pressed; (b) 18PMN-41PZ-41PT + 0.1 mol % Nb ions, 1250 °C, sintered; (c) 18PMN–41PZ–41PT, 1220 °C, sintered.

This assumption is evident from Fig. 3. The X-ray peaks of the hot-pressed sample were broader than in the normal sintered sample, because the hot-pressed sample contained some residual stress which allowed the crystal structure to become distorted. The X-ray

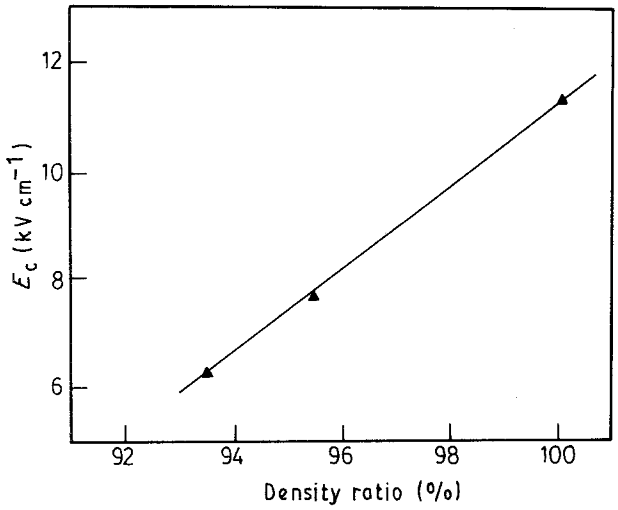

Figure 6 The relationship between coercivity and density ratio.

peaks were therefore broader than in the normal sintered sample.

It is necessary for the electric field to overcome the residual stress by causing a strain when the electric field was being applied to the sample. The saturation strain was therefore less than that in the niobium ions-doped sample. The residual stress not only affected the saturation strain, but also affected the dipole moment reorientation. More stress is required for dipole moment reorientation, so the saturation polarization of the hot-pressed sample was again lower than that of the 0.1 mol% Nb ion-doped sample [12, 13].

The reasons for the small strain in the samples sintered at 1220 °C are probably (1) the large grain and grain-size deviation, and (2) the internal defects and the pores, which eliminate the strain. An increase in grain size and dipole moment reorientation requires more stress when being applied to the electric field. The saturation polarization would, therefore, decrease when grain growth occurred.

The 18PMN–41PZ–41PT piezoelectric ceramics with a fine, uniform microstructure and good piezoelectric characteristics have been obtained by using the rapid hot-pressing technique. This is, therefore, a good technique for producing high-quality piezoelectric ceramics.

4. Conclusions

1. The best hot-pressing conditions for obtaining an 18PMN–41PZ–41PT piezoelectric ceramic material were a temperature of 1000 °C and a pressure of 700 kg cm^{-2}. Under these conditions a high density (99.66 % theoretical density) and good quality piezoelectric ceramics could be achieved.

2. The sintering temperature of the hot-pressing method was approximately 200–300 °C lower than that of the normal sintering method; a smaller and finer microstructure could, therefore, be achieved.

3. The hot-pressed sintering enhanced the density which had a linear relationship with E_c. The porosity and defects were reduced; therefore, coercivity was further enhanced.

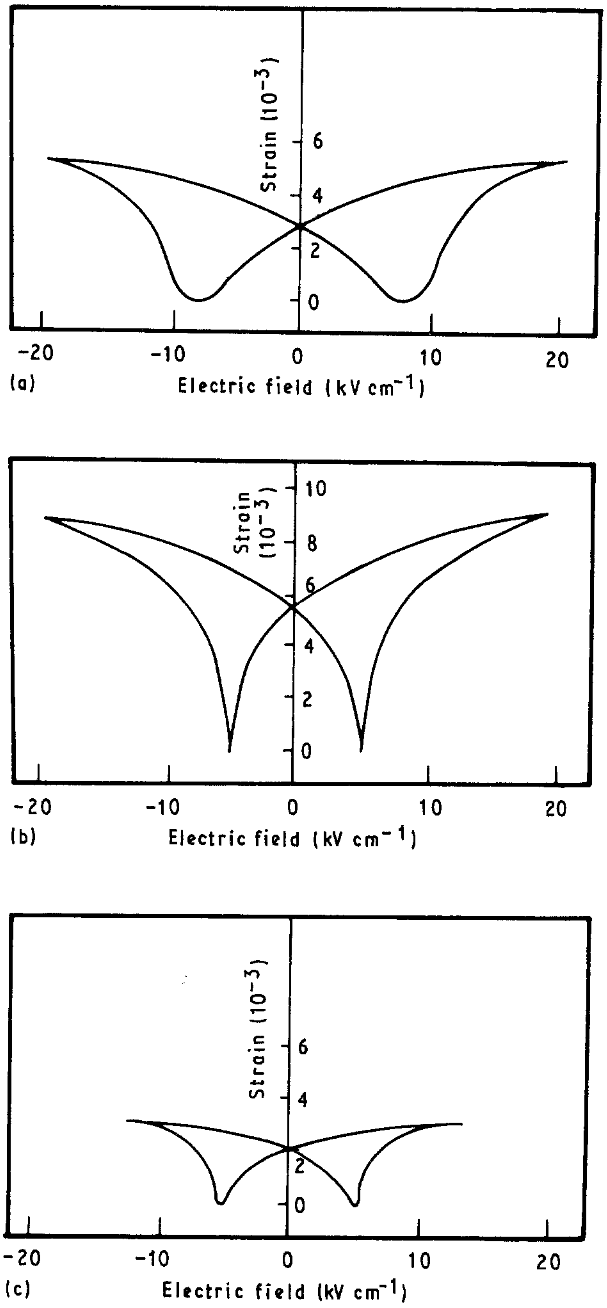

Figure 7 The strain versus electric field curve for the three different sintering conditions: (a) 18PMN–41PZ–41PT, hot-pressed; (b) 18PMN–41PZ–41PT + 0.1 mol % Nb ions, 1250 °C, sintered; (c) 18PMN–41PZ–41PT, 1220 °C, sintered.

4. The fine uniform microstructure was favourable for enhancing the polarization and strain, while a higher density would enhance the coercivity.

Acknowledgement

We thank the National Science Council, Taiwan, for financial support for this research under Grant NSC81-0404-E007-103.

References

1. R. H. DUNGAN and G. S. SNOW, *J. Amer. Ceram. Soc.* **56** (1977) 781.
2. G. H. HEARTLING and C. E. LAND, *ibid.* **54** (1971) 1.
3. J. T. CUTCHEN, J. O. HARRIS and G. R. LAGUNA, *Appl. Opt.* **14** (1976) 1866.

4. G. H. HEARTLING and C. E. LAND, *Ferroelectrics* **3** (1972) 267.
5. W. Y. PAN, Q. M. ZHANG, Q. Y. JIANG and L. E. CROSS, *ibid.* **88** (1988) 1.
6. V. L. BALKEVICH and G. M. FLIDLIDER, *Ceram. Int.* **2** (1976) 81.
7. NARENDA D. PATEL and PATRICK S. NICHOLSON, *J. Amer. Ceram. Soc. Bull.* **65** (1986) 783.
8. HIROMU OUCHI, *ibid.* **51** (1968) 169.
9. I. K. SINHA, *J. Sci. Instrum.* **42** (1965) 696.
10. W. Y. PAN, Q. M. ZHANG, Q. Y. JIANG and L. E. CROSS, *Ferroelectrics* **88** (1988) 1.
11. Q. M. ZHANG, W. Y. PAN and L. E. CROSS, *J. Appl. Phys.* **63** (1988) 2492.
12. M. J. HAUN, E. FURMAN, S. J. JANG and L. E. CROSS, *Ferroelectrics* **99** (1989) 13.
13. YA. KVAPULIN'SKI, Z. SUROV'YAK, M. F. KUPRIYANOV, S. M. ZAITSEV, A. YA. DANTSIGER and E. G. FESENKO, *Sov. Phys. Tech. Phys.* **24** (1979) 621.

Received 14 September
and accepted 19 November 1992