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Piezoelectric properties, hysteresis behaviour and dielectric properties of PMN–PZT ceramics

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Abstract. Ferroelectric and piezoelectric properties of $x\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$(1-x)\mathrm{Pb}(\mathrm{Zr}_{0\cdot55}\mathrm{Ti}_{0\cdot45})\mathrm{O}_3$ system have been investigated. X-ray diffraction patterns indicate rhombohedral and cubic structures. Maximum dielectric constant and piezoelectric properties are exhibited by 0·5–0·5 PMN–PZT composition. P_r is high in 0·6–0·4 PMN–PZT composition.

Keywords. Piezoelectricity; PMN; dielectric constant.

1. Introduction

This paper highlights the structure, hysteresis behaviour and piezoelectric properties of $\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$\mathrm{Pb}(\mathrm{Zr}_{0\cdot55}\mathrm{Ti}_{0\cdot45})\mathrm{O}_3$ composition and the effect of lanthanum doping on selected compositions. Previous work on PMN–PZT (Ouchi *et al* 1965) has shown that the system exhibits high values of dielectric constant and planar coupling coefficient at morphotropic phase boundary. Hysteresis behaviour and d_{33} measurements have not been reported for this potentially important system. In this work we used the columbite precursor method (Swartz and Shrout 1982) to eliminate the pyrochlore structure. The dielectric, piezoelectric and hysteresis behaviour of $x\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$(1-x)\mathrm{Pb}(\mathrm{Zr}_{0\cdot55}\mathrm{Ti}_{0\cdot45})\mathrm{O}_3$ for $x = 0{\cdot}4$, 0·5, 0·6, 0·7 and 0·8 are reported.

2. Experimental

The ceramics were prepared by conventional sintering of relevant oxides. To avoid pyrochlore phase formation, columbite precursor of $\mathrm{MgNb}_2\mathrm{O}_3$ was prepared first and then mixed with PbO to prepare PMN. The calcination and sintering temperatures for preparing PMN–PZT ceramics were 950°C for 3 h and 1225–1250°C for 4 h, respectively. For piezoelectric measurements and hysteresis behaviour the sintered pellets were poled by applying a d.c. electric field of 20 kV/cm for 1 h at elevated temperatures in silicon oil. The samples were cooled to room temperature for 1 h with field maintained.

Powder X-ray diffraction studies were carried out on Philips X-ray diffractometer (PW-1710) using CuK_α radiation with Ni filter at room temperature. The diffraction patterns were recorded at a slow scan of 1°/min.

Dielectric constant and dissipation factor were measured with Hewlett-Packard LF impedance analyser model 1492 A. Planar and thickness coupling coefficients were also investigated using the same instrument. The coefficient d_{33} is measured on Berlincourt d_{33} meter. For the observation of hysteresis loops modified Sawyer and Tower circuit (Sinha 1965) was used.

3. Results and discussion

All the compositions lie in the pseudocubic region of PMN–PZT phase diagram (Ouchi *et al* 1965). X-ray diffraction patterns of calcined powders are shown in figure 1. Pyrochloro phase remained in the calcined powders as shown in figure 1. In sintered powders, pyrochloro phase is absent. But to emphasize the effect of lanthanum doping X-ray patterns of calcined powders âre only shown. 0·5–0·5 PMN–PZT exhibits rhombohedral structure. Lanthanum doping leads to strong cubic character as is evident from the intensities of labelled peaks which match those of cubic PMN (JCPDS 27–1119). La doping leads to ordering of the structure. Same conclusion was reached in a previous work on lanthanum doped PMN–PZT (Kim *et al* 1989). Pyrochlore phase decreases with lanthanum doping. In 0·6–0·4 PMN–PZT which is rhombohedral, lanthanum doping leads to decrease in intensity of 100, 111, 200 and 211 lines. In 0·7–0·3 lanthanum doping causes decrease of intensity of 211 line. Smaller peaks may correspond to scattering effects of interstitial ions or diffusion of larger amount of ions into grain. Pyrochloro phase is maximum in 0·8–0·2 PMN–PZT as PMN content is maximum.

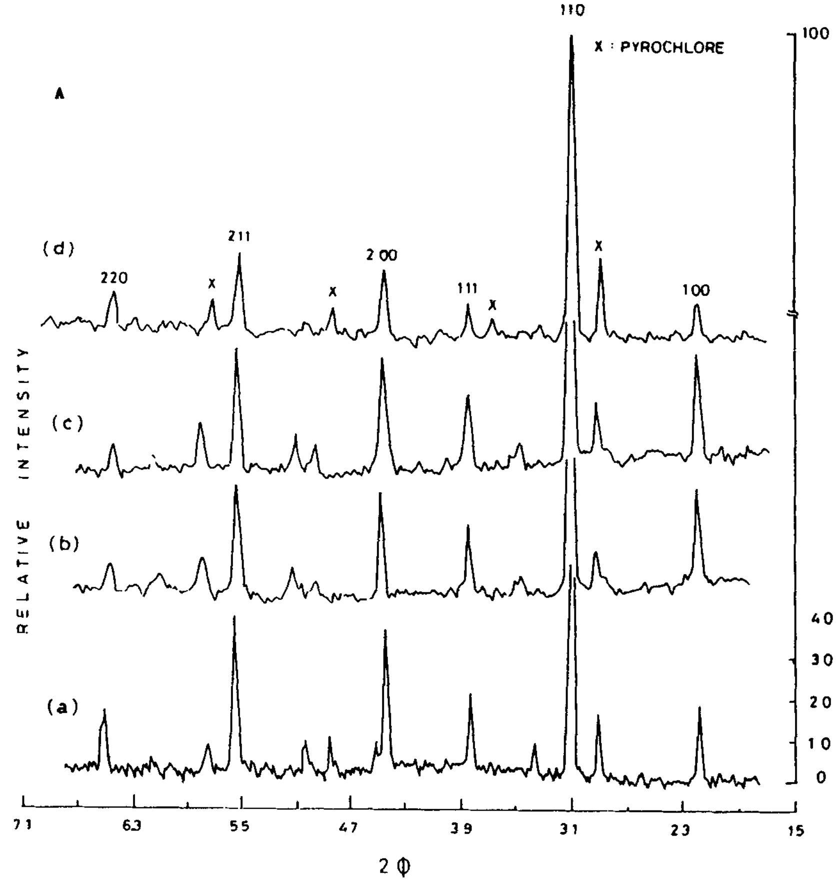

Figure 1. A.

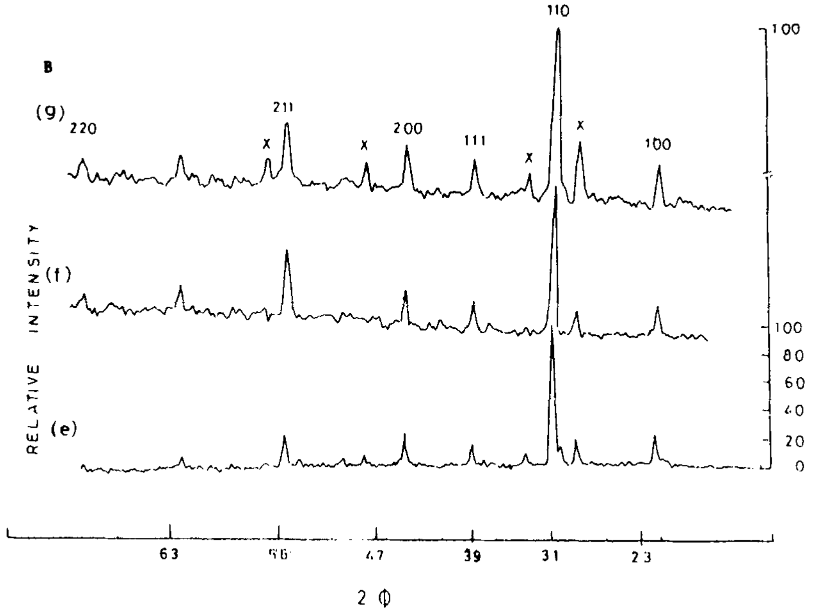

Figure 1. A. X-ray diffraction patterns of (a) 0·5–0·5, (b) 0·5–0·5 (La), (c) 0·6–0·4 and (d) 0·6–0·4 (La) PMN-PZT compositions and **B**. X-ray diffraction patterns of (e) 0·7–0·3 (La), (f) 0·7–0·3 and (g) 0·8–0·2 PMN-PZT compositions.

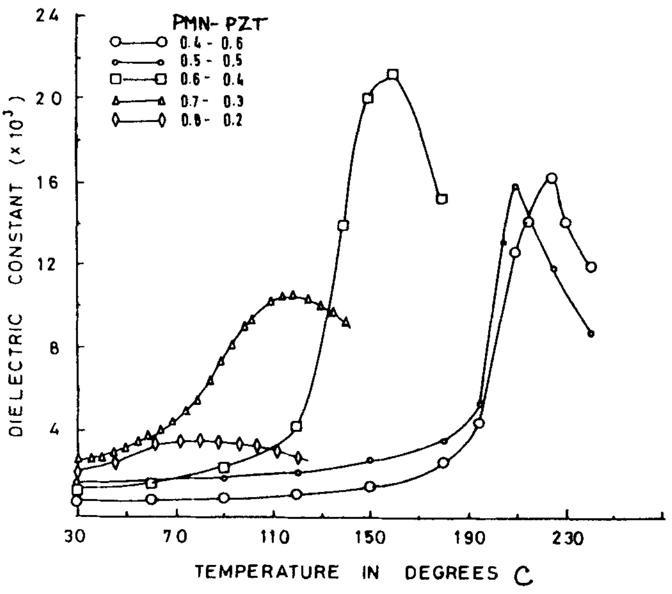

Figure 2. Dielectric constant variation with temperature.

Variation of dielectric constant with temperature is shown in figure 2. Maximum in dielectric constant is found to increase with increasing PZT up to 22 mole % PZ (0·6–0·4) composition. T_c increases with the increase of PZT. Variation of T_c for different compositions are shown in table 1. All compositions exhibit typical relaxor

Table 1. Lattice parameters and dielectric data of modified PMN–PZT ceramics.

Composition PMN–PZT	Density	Lattice constant	ε_{RT}	T_c(°C)	Tan δ	$\varepsilon_{\max}$
0·4–0·6	7·55	4·041	633	222	0·06	16375
0·5–0·5	7·56	4·08	1586	210	0·08	15965
0·6–0·4	7·51	4·083	1096	157	0·03	20753
0·6–0·4 (0.01 La)	7·53	4·074	4260	102	0·06	12637
0·7–0·3	7·55	4·085	2616	118	0·09	10580
0·7–0·3 (0.01 La)	7·58	4·056	7243	60	0·09	9380
0·8–0·2	7·60	4·055	2181	78	0·03	3573

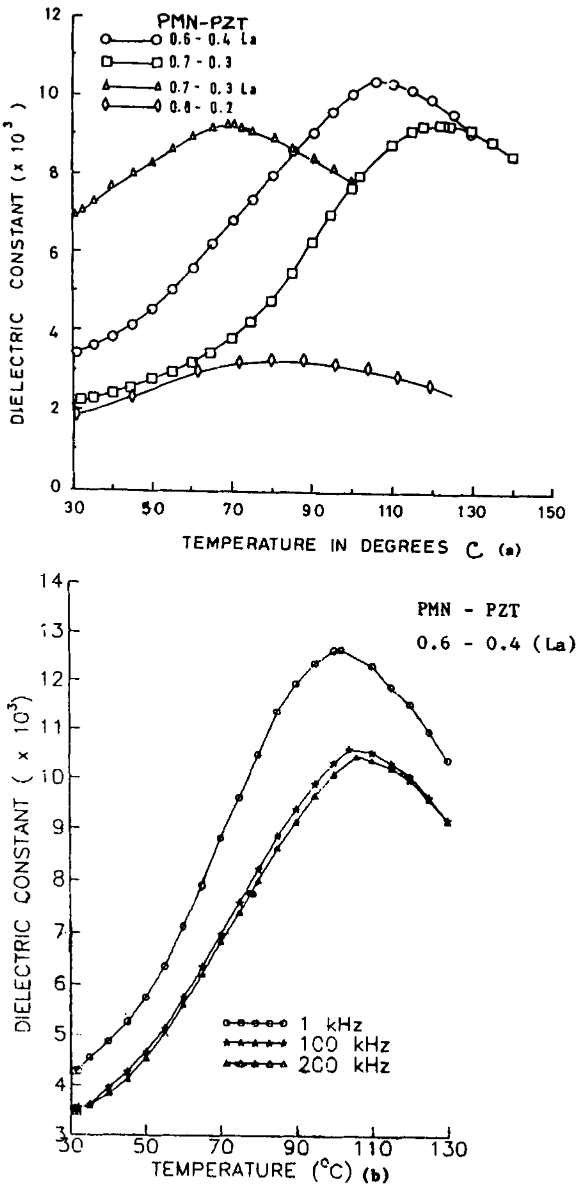

Figure 3. a–b.

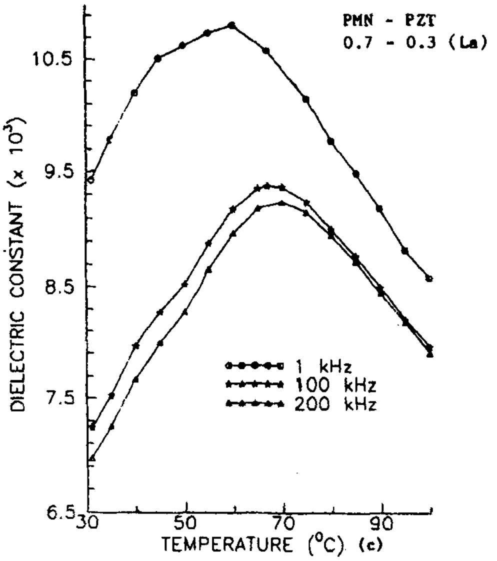

Figure 3. a–c. Relaxor behaviour of PMN–PZT compositions.

Table 2. Hysteresis data and piezoelectric properties of PMN–PZT ceramics at room temperature.

PMN–PZT	P_r (μc/cm^2)	P_s (μc/cm^2)	E_c (Kv/cm)	K_p	K_t	d_{33} (Pc/N)
A	13·63	18·54	2·28	26·3	10·5	116
B	19·56	25·48	3·14	38·2	11·9	262
C	30·48	43·55	1·81	28·6	14·1	132

Composition: A, 0·4 PMN–0·6 PZT; B, 0·5 PMN–0·5 PZT; C, 0·6 PMN–0·4 PZT.

behaviour as evidenced by decrease of dielectric maximum and shift of Curie temperature upwards with increasing frequency as shown in figure 3. Lanthanum doping of 1 mole% in selected composition leads to a remarkable increase in room temperature dielectric constant. Dielectric constant variation with temperature is nearly flat for 0·8–0·2 composition. This composition may have application in multilayer capacitors. This result is supported by the fact that already more than ten PMN based capacitors have been patented (Goodman *et al* 1991). It is significant that one of them is PMN–PLZT. For standard MLC (Takahashi and Ochi 1992) room temperature capacitance is 1 μF and change in capacitance for 10°C is 380 PF. In our work for 0·8–0·2 PMN–PZT the change in capacitance for 10°C is 383 PF and room temperature capacitance is 1838 PF.

Piezoelectric measurements were done on 0·4–0·6, 0·5–0·5 and 0·6–0·4 PMN–PZT compositions. Piezoelectric properties and hysteresis behaviour are given in table 2. K_p value of 0·38 obtained in 0·5–0·5 composition is slightly lower than the K_p value of 0·46 in PZT (55/45) (Landolt-Bornstein 1981). Low E_c values in these compositions indicate dominance of rhombohedral structure. While in PMN–PZT (Kim 1989) ceramics maximum remanent polarization is of the order of 20 μc/cm^2 at approximately

-110°C, P_r value of $30\,\mu$c/cm^2 obtained in 0·6–0·4 PMN–PZT composition in the present work is high.

PZT (55/45) (Landolt-Bornstein 1981) exhibits a d_{33} value of $150 \times 10^{-12}\,\mathrm{CN}^{-1}$. In PMN (Nomura and Uchino 1982) electric field induced d_{33} is $240 \times 10^{-12}\,\mathrm{CN}^{-1}$ with an electric field of 12×10^5 V/m. The d_{33} value of $262 \times 10^{-12}\,\mathrm{CN}^{-1}$ obtained in 0·6–0·4 PMN–PZT composition is certainly greater than either of the end members. Hence it can be concluded that the d_{33} value is enhanced in 0·5–0·5 PMN–PZT when compared with either of the end members.

4. Conclusions

(i) X-ray diffraction results indicate rhombohedral structure in 0·5–0·5, 0·7–0·3 and 0·8–0·2 PMN–PZT compositions. It is found that lanthanum doping leads to ordering of the structure.
(ii) Variation of dielectric constant with temperature at different frequencies exhibits relaxor characteristics. 0·8–0·2 shows flat dielectric response with temperature indicating applications in multilayer capacitors.
(iii) Piezoelectric measurements indicate high d_{33} value in 0·5–0·5 PMN–PZT composition. Low E_c values are obtained in all compositions consistent with rhombohedral structure.

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