

Relaxor ceramics for multilayer capacitor application

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Abstract. Relaxor ferroelectrics, lead magnesium niobate (PMN) and lead zinc niobate (PZN) and their solid solution with lead titanate (PT) and barium titanate (BT) were studied. Unlike lead magnesium niobate, the pyrochlore-free material for lead zinc niobate could not be prepared by reaction between lead niobate and ZnO below 1000°C. However, some improved composition was obtained when lead zinc niobate (85%) and a mixture of lead titanate (10%) and barium titanate (5%) sintered at 950°C. XRD examination of the samples revealed that lead magnesium niobate prepared by us contained 9.9% pyrochlore phase, whereas the solid solution between 90% lead magnesium niobate and 10% lead titanate was completely free from the same phase. The dielectric constant for PZN–PT–BT (85:10:5) ternary system was 4000, whereas the same for lead magnesium niobate and its solid solution with 10% lead titanate was 4100 and 6000 respectively. The comparatively low value obtained for PZN–PT–BT solid solution was probably due to the presence of appreciable amount of pyrochlore phase. The grain diameter for PMN and PMN–PT (90:10) solid solution was 1.37 μm and 2.34 μm respectively.

Keywords. Relaxor ceramics; solid solution; multilayer capacitor; perovskite transducer.

1. Introduction

Relaxor ferroelectrics has been developed because the BaTiO_3 -based capacitors, which are still being used in the capacitor industry, require expensive and precious metal (Pd) for electroding. Replacing these with the highly fluxed compositions which densify at temperature ($< 1000^\circ\text{C}$) with less expensive high silver-palladium alloy electrode is desirable. Relaxor ferroelectrics exhibit a frequency dispersion of dielectric medium i.e. the maximum dielectric constant increases and shifts to lower temperature as frequency is increased. This is because the statistical inhomogeneity in the distribution of B-site cations creates microregions of varying transition temperature T_c (Shrout *et al* 1964). It may be pointed out here that besides low firing temperature capability, the promising dielectrics should have a high dielectric constant (> 5000), low dielectric loss, good insulation resistance and good life performance. The relaxor ceramics of the type $\text{Pb}(\text{B}'_{1/3}\text{Nb}_{2/3})\text{O}_3$, where $\text{B}' = \text{Mg, Zn, Ni, Fe, etc.}$ and their solid solution with lead titanate or barium titanate near the morphotropic phase boundary exhibit very high dielectric constant and considerably large electrostrictional strains. This paper reports our preliminary results on the study of relaxor ferroelectrics, lead magnesium niobate and lead zinc niobate and their solid solution with lead titanate/barium titanate for possible capacitor application. Relaxor ceramics are advantageous over normal perovskite transducers in that they require no poling, show excellent positional reproducibility, have electrostrictive strains comparable to the best piezoelectric ceramics and also have low thermal coefficient. It is pertinent to mention here that the series of products made using multilayer ceramic technology started with three-layer quartz crystal package. It was followed sequentially by packages for diodes, transistors and multichip arrays. IBM used up to 123 chips/33 layer packages for the 3081 computer. Schwartz (1984) recently reviewed the technology used for making these substrates.

2. Experimental

To avoid pyrochlore phase which develops during preparation, lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) was synthesized by reaction between lead niobate, $\text{Pb}_3\text{Nb}_2\text{O}_8$ (PN) and MgO (1% excess) (Guha and Anderson 1986) instead of using the conventional method (Swartz and Shrout 1982; Swartz *et al* 1984) where magnesium niobate MgNb_2O_6 was used to react with PbO. Lead niobate was prepared by sintering PbO and Nb_2O_5 mixture in equimolar proportion for 9 h at 820°C. Lead niobate and MgO were sintered in two steps for preparation of lead magnesium niobate. After sintering at 800°C in the first step, the disks were crushed into powder and new disks (2.54 cm diam) prepared under 154.5 MPa inch pressure by hydraulic press and sintered finally at 900°C for 6 h. The solid solution between 90% lead magnesium niobate (PMN) and 10% lead titanate (PT) was similarly prepared by sintering the mixture (PN, MgO and PT in appropriate proportion) of the components in two separate steps, at 800°C and 950°C in the first and final steps respectively.

Unlike lead magnesium niobate, the preparation of pyrochlore-free material for lead zinc niobate, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) by reaction between lead niobate and ZnO at 900°C was not possible. However, some improved composition was obtained by sintering between 85% lead zinc niobate (a mixture of PN and ZnO in appropriate proportion), and a mixture of 10% lead titanate and 5% barium titanate at 950°C for 6 h. Since firing temperature of less than 1000°C was used, no atmospheric source of PbO was made use of.

X-ray diffraction of the compositions was examined using crushed ceramic disks. Lattice constants were determined using a Philips X-ray diffractometer (model PW 1730) with nickel-filtered CuK_α radiation at a 2θ scanning rate 1° per min. The angular range of 2θ covered was 20 to 80°. The peak angles were carefully indexed. The (001) and (200)/(004) peaks of the perovskite phase were chosen to determine the lattice constants.

Scanning electron photomicrographs of the test samples were taken using a scanning electron microscope (Cambridge Stereoscan 150, Cambridge, England). As-fired samples were used for recording the photomicrographs.

3. Results and discussion

Figure 1A shows the XRD pattern of lead niobate prepared by sintering PbO and Nb_2O_5 mixture (disks) in equimolar proportion at 820°C. Complete solid solution with tetragonal symmetry (a_0 and c_0 as 0.7557 nm and 1.087 nm respectively) comparable with the data ($a_0 = 0.753$ nm and $c_0 = 1.082$ nm) given for PN, $\text{Pb}_3\text{Nb}_2\text{O}_8$ in JCPDS card No 30-712 was observed. PMN obtained by us contained some pyrochlore ($\text{Pb}_2\text{Nb}_3\text{O}_7$) phase which was revealed by XRD examination of the product (figure 1B). The volume fraction of the pyrochlore phase in the composition was estimated by the relation (Swartz and Shrout 1982; Goo *et al* 1986) given below

$$\text{volume fraction of pyrochlore} = \frac{I_{PY} \times 100}{I_{PE} + I_{PY}}$$

and was found to be 9.9%. Here I_{PY} is the intensity of the (222) pyrochlore X-ray peak and I_{PE} the intensity of the (110) perovskite peak. However, the solid solution between

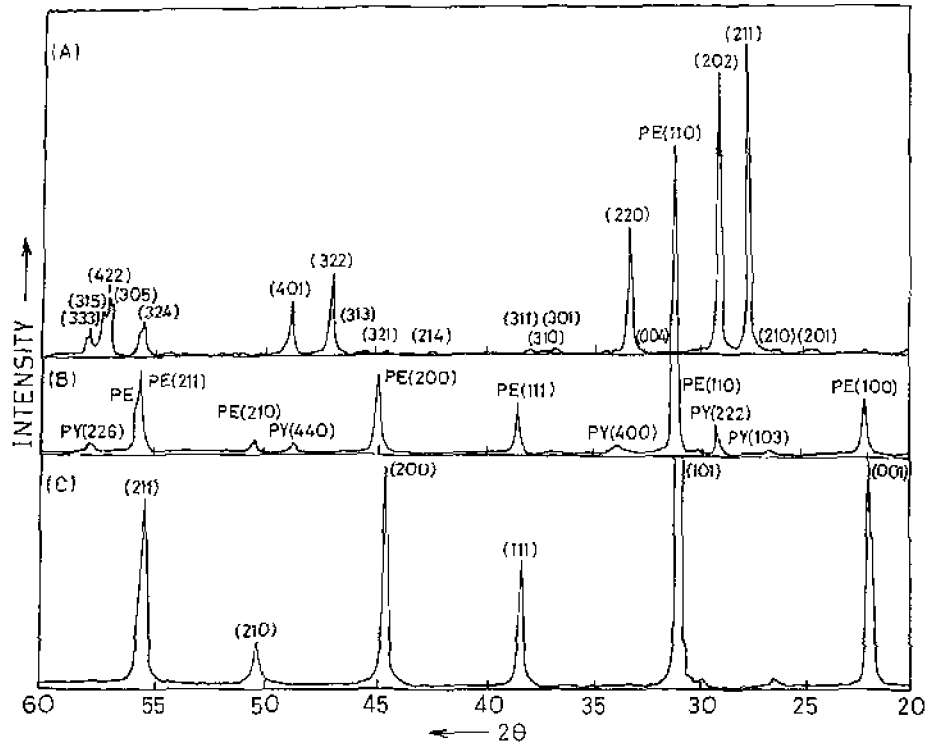


Figure 1. X-ray powder diffraction pattern of (A) lead niobate (PN), (B) lead magnesium niobate (PMN) and (C) solid solution of 90% lead magnesium niobate and 10% lead titanate (PMN-PT).

Table 1. Lattice parameters for PN, PMN and PMN-PT (90:10) ceramics.

Material	$a_0(\text{nm})$	$c_0(\text{nm})$	c_0/a_0	Structure	Symmetry
$\text{Pb}_3\text{Nb}_2\text{O}_8(\text{PN})$	0.7557	1.0876	1.459	Perovskite	Tetragonal
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3(\text{PMN})$	0.40324	—	—	Perovskite	Cubic
	1.0548	—	—	Pyrochlore	Cubic
$90[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3] - 10[\text{PbTiO}_3](\text{PMN-PT})$	0.4036	0.4050	1.003 ₄	Perovskite	Tetragonal

90% PMN and 10% PT was found to be free from any pyrochlore phase (figure 1C). Complete solid solution with tetragonal symmetry ($a_0 = 0.4036 \text{ nm}$ and $c_0 = 0.4050 \text{ nm}$) was observed. Our results of lattice parameters are summarized in table 1. The Curie temperature T_c of the solid solution PMN-PT was measured as 53°C which was above the room temperature. The T_c of PMN was much below the room temperature. As expected, since the Curie temperature for PMN lay below the room temperature, the XRD measurement taken at room temperature indicated that the symmetry was cubic, whereas in the case of the solid solution PMN-PT, where T_c was above room temperature, the symmetry was tetragonal (table 1). The structural analysis results of the solid solution PZN-PT-BT (85:10:5) will be communicated elsewhere.

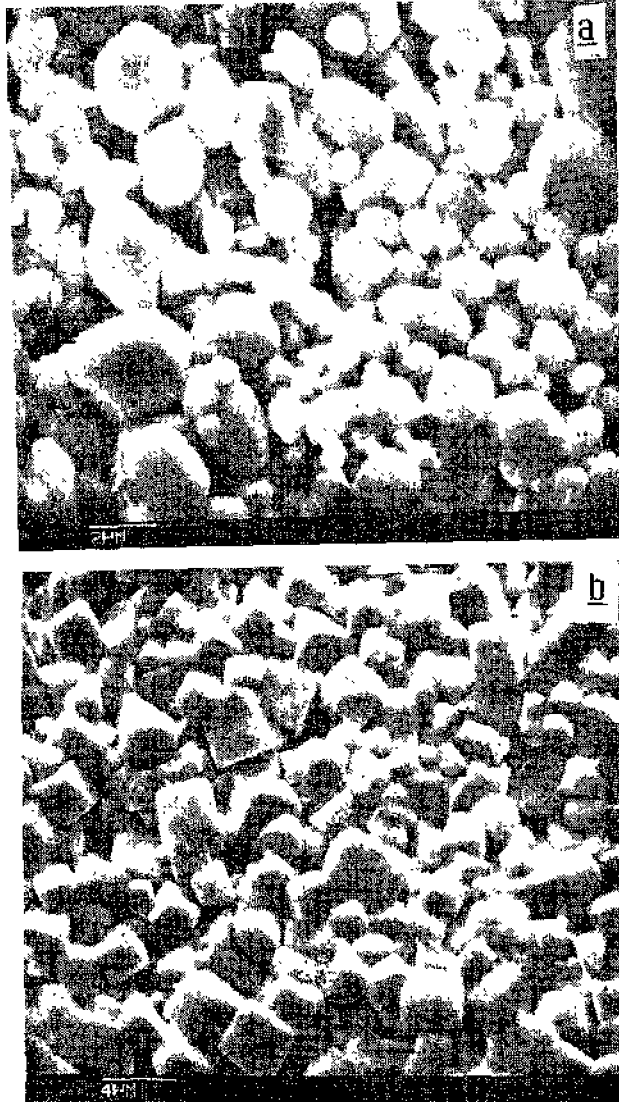


Figure 2. Scanning electron micrographs of the as-fired surfaces of (a) Lead magnesium niobate (PMN) and (b) solid solution of 90% lead magnesium niobate and 10% of lead titanate (PMN-PT).

The value of ϵ_T of PMN measured at 1 kHz was 4100 (reported value ~ 5000) which was somewhat lower because of the presence of pyrochlore phase. ϵ_T of the materials was reduced drastically due to the presence of pyrochlore phase which developed during preparation. In the case of the solid solution PMN-PT, the dielectric constant was found to increase to 6000 (reported value being 7000 (Uchino *et al* 1981)). Further in the case of PZN-PT-BT (85:10:5) ternary system, the dielectric constant was 4000 which was very low compared to the reported value (15000) (Halliyal *et al* 1987).

The typical photomicrographs of the as-fired surfaces for PMN and its solid solution with 10% PT are shown in figure 2 (A and B). There was a wide distribution of grain

sizes in both cases. The average grain diameter was determined by the linear intercept method (Fullman 1953) which was $1.37 \mu\text{m}$ and $2.34 \mu\text{m}$ for PMN and PMN-PT solid solution respectively. A two-fold increase of grain size was observed in the case of PMN-PT solution.

4. Conclusion

The relaxor ceramic PMN prepared by the reaction between lead niobate and MgO below 1000°C showed promise for use in multilayer capacitors with high silver-palladium electrodes. The solid solution between 90% PMN and 10% PT showed further improvement of dielectric constant (from 4100 to 6000). The Curie temperature of PMN-PT solid solution was 53°C , whereas the same for PMN was much below the room temperature. The preparation of pyrochlore-free material for PZN by reaction between lead niobate and ZnO was not achieved, but the stabilization of the perovskite phase to some extent was done with the addition of 10% lead titanate and 5% barium titanate. The dielectric constant of the composition obtained was 4000. The symmetry for PMN and its solid solution with 10% PT measured at room temperature was cubic and tetragonal as the Curie temperature for the two compositions was below and above the room temperature respectively.

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