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Stabilization of the perovskite phase and dielectric properties in the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$BaTiO_3$ system

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The stability of the perovskite phase of PMN ceramics was investigated as a function of $BaTiO_3$ content and the dielectric properties of various compositions in the PMN–$BaTiO_3$ system are presented.

The pyrochlore phase in PMN was completely eliminated by the addition of 4 to 5 m/o $BaTiO_3$. The dielectric constant increased slightly with $BaTiO_3$ up to the composition in which the pyrochlore phase was eliminated but decreased with further addition of $BaTiO_3$. The addition of $BaTiO_3$ lowered the transition temperature and decreased the lattice constant. PMN–$BaTiO_3$–$PbTiO_3$ compositions useful for capacitors are identified.

1. Introduction

There has been much interest in lead-based perovskite ferroelectric compounds such as $Pb(Mg_{1/3}Nb_{2/3})O_3$(PMN), $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$(PZN), because of their high dielectric constants and their potential for low firing temperatures [1].

In these materials, however, the major problem is that the ferroelectric perovskite phase is often associated with a pyrochlore phase that can be detrimental to the dielectric properties. Recently, some improved techniques using preformed $MgNb_2O_6$ and adding excess PbO or MgO have been developed for forming monophase PMN [2]. A previous paper from this laboratory reported the effect of excess PbO and MgO on the dielectric properties of PMN ceramics [3]. From these studies, it has been shown that to fabricate 100% perovskite PMN, excess MgO (at least 5 m/o) should be added as stated by Shrout *et al.* [1]. On the other hand, it has been reported by Furukawa *et al.* [4] and Halliyal *et al.* [5, 6] that the formation of the pyrochlore phase in PZN could possibly be suppressed by the addition of more ionic compounds such as $BaTiO_3$, $SrTiO_3$ or $PbTiO_3$.

The present work, therefore, was undertaken to stabilize the perovskite phase in PMN ceramics by adding $BaTiO_3$ and to investigate the sinterability and dielectric properties of several PMN–$BaTiO_3$ (PMN–BT) ceramic compositions.

2. Experimental details

The compositions in the PMN–BT system were prepared as shown in Table I and were synthesized from reagent-grade PbO, MgO, Nb_2O_5 and $BaTiO_3$ powders. The PMN powders calcined at 800 °C for 4 h were mixed with $BaTiO_3$ in appropriate proportions and an excess of PbO (5 w/o) was added to all compositions in order to aid the firing process. The mixtures were ball milled and then cold-pressed into discs using polyvinyl alcohol as a binder. Following binder burn-out at 500 °C, the pellets were sintered in a closed alumina crucible at temperatures ranging from 900 to 1200 °C using a heating rate of 300 °C h^{-1} in an SiC resistance furnace. PbO loss was limited by the use of a sintered PMN source powder.

For selected compositions of PMN–$PbTiO_3$–$BaTiO_3$(PMN–PT–BT) ceramics, calcined PMN–PT

TABLE I Sintering condition, Perovskite phase percentage, bulk density and lattice constant as a function of the amount of $BaTiO_3$ addition, x, in $(1-x)$PMN–$x$$BaTiO_3$

Composition x		Sintering temperature (° C)	Time (h)	Percentage perovskite phase (%)	Bulk density ($g\,cm^{-3}$)	$\frac{d_{cal} \times 100}{d_{theo}}$ (%)	Lattice constant (nm)
PB-0	0	900	4	92	7.78	95	0.4046
PB-1	0.03	950	4	98	7.62	94	0.4044
PB-2	0.05	1000	2	100	7.65	95	0.4043
PB-3	0.1	1050	2	100	7.47	94	0.4040
PB-4	0.2	1100	2	100	7.19	93	0.4034
PB-5	0.3	1100	2	100	7.0	93	0.4029
PB-6	0.5	1200	2	100	6.54	93	0.4020

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powder at 800 °C and $BaTiO_3$ powder were mixed and then ball milled. The rest of the procedure for preparing ceramics was the same as described above.

The phases present in the sintered pellets were analysed by X-ray diffraction pattern and the lattice constants were determined from (220), (321), (303) and (330) reflections. The relative amounts of the pyrochlore phase and the perovskite phase were determined by measuring the major X-ray peak intensities for the perovskite and pyrochlore phases, (110) and (222), respectively. The percentage of perovskite phase was calculated using the following equation.

$$\%\,\text{perov.} = \frac{100 \times I_{\text{perov.}}}{(I_{\text{perov.}} + I_{\text{pyro.}})}$$

Theoretical densities were calculated from lattice parameter measurements and densities were determined geometrically. Microstructures of the fracture surfaces were examined by scanning electron microscopy. For dielectric measurements, the flat surfaces of the pellets were ground parallel and silver electrodes fired on at 600 °C and then the measurement was carried out using a LCR meter (ANDO, AG4303, Japan) and a temperature controller.

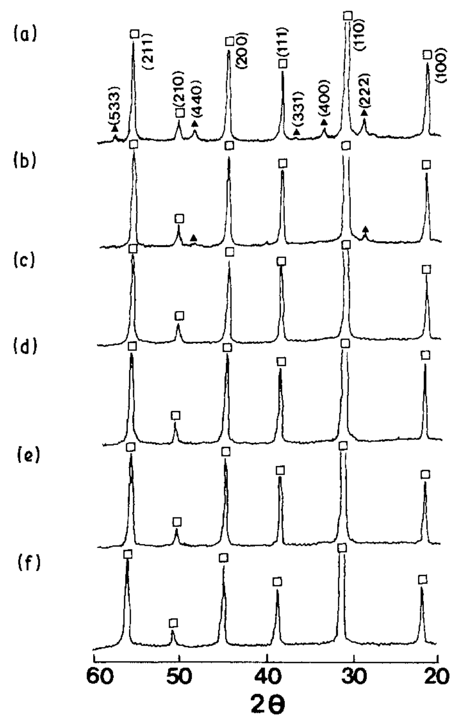

Figure 1 XRD patterns of (a) PB-0, (b) PB-1, (c) PB-2, (d) PB-3, (e) PB-5, and (f) PB-6 compositions. (□ PMN, ▲ P_3N_2)

3. Results and discussion

3.1. Sintering and XRD analysis

The sintering conditions, percentage perovskite phase, fired densities and lattice constants for all the compositions are given in Table I.

Higher sintering temperatures were necessary to obtain sufficient densities for compositions containing larger fractions of $BaTiO_3$. The higher content of excess PbO (5 w/o) than that of Guha's result (2 w/o) was used as a sintering aid because of the $BaTiO_3$ character [7]. The sintering temperature was, however, lowered by the addition of the 5 w/o excess PbO as compared to $Pb(Zn_{1/3}Nb_{2/3})O_3$–$BaTiO_3$ (PZN–BT), PZN–$PbTiO_3$ (PZN–PT), PZN–$SrTiO_3$ (PZN–ST) ceramics with no sintering flux [5, 6]. The percentage of perovskite phase increased with the addition of $BaTiO_3$ as shown in Table I. Compositions containing $\geqslant$ 5 m/o $BaTiO_3$ did not have any pyrochlore phase. According to Shrout *et al.*, the increase in the tolerance factor and electronegativity difference of lead-based compounds due to the addition of $BaTiO_3$ or $SrTiO_3$ served highly successfully to stabilize the perovskite structure [1]. The pyrochlore phase in PZN also was completely eliminated by the addition of 6 to 7 m/o $BaTiO_3$ or 10 m/o $SrTiO_3$, respectively [5, 6].

In the case of PMN, a number of methods have been tried to reduce the pyrochlore phase, resulting in the conclusion that excess MgO in the range of 5 to 12 m/o should be added to obtain 100% pure perovskite PMN ceramics [1]. In this experiment, however, it is clear that the formation of the pyrochlore phase in PMN can be completely avoided by adding 4 to 5 m/o $BaTiO_3$ without addition of excess MgO. This can similarly be explained as the result of the larger electronegativity difference and tolerance factor of the $BaTiO_3$ compared with those of PMN.

Fig. 1 shows the XRD patterns of the sintered specimens as a function of $BaTiO_3$ content. The pyrochlore phase peak ($Pb_3Nb_4O_{13}$, (222)) present initially was eliminated completely in PMN compositions with $BaTiO_3$ content of 4 to 5 m/o or more and the PMN peaks shifted slightly to higher angle with added $BaTiO_3$. No peak for residual PbO showed up in the XRD patterns.

SEM photographs of selected specimens are shown in Fig. 2. The grain size was in the range of 3 to 3.5 μm for compositions up to 0.7PMN–0.3BT and decreased for the 0.5PMN–0.5BT specimen (Fig. 2). The microstructural changes observed between the excess-PbO-added 0.95PMN–0.05BT and no-excess-PbO-added 0.95PMN–0.05BT specimens clearly demonstrate that the liquid phase formed by the addition of excess PbO significantly enhanced grain growth (Fig. 2a and b). The microstructure differences were also very similar to the Guha microstructure, which exhibits the effect of excess PbO on PMN–PT ceramics [7]. The specimen of Fig. 2b has been sintered at 1200 °C for 2 h to achieve a comparable density value to that of Fig. 2a.

3.2. Dielectric properties

The temperature dependence of the dielectric constant (at 1 kHz) as a function of composition is shown in Fig. 3. All compositions show a broad maximum for the dielectric constant. The maximum value for the dielectric constant increases slightly with addition of $BaTiO_3$ up to 5 m/o and then decreases with further addition of $BaTiO_3$. The initial increase in the maximum value for the dielectric constant with the addition of $BaTiO_3$ resulted from the elimination of the pyrochlore phase in the ceramic. In the compositions with higher than 10 m/o $BaTiO_3$, the drastic decrease in the maximum value of the dielectric constant even

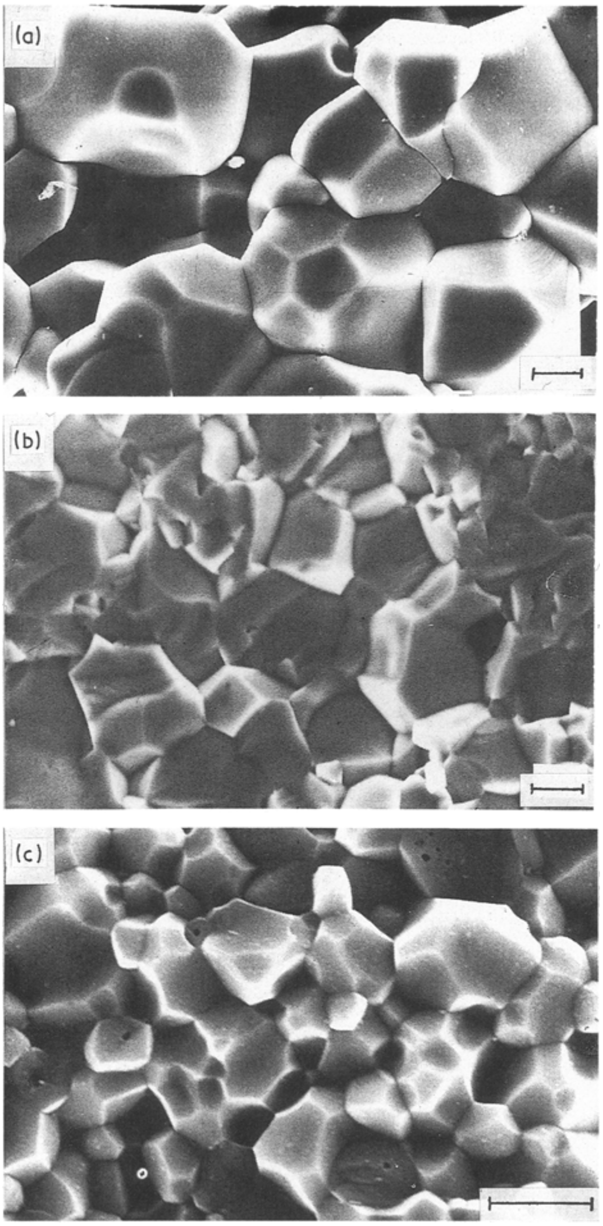

Figure 2 SEM photographs of (a) PB-2, (b) no excess PbO added PB-2, and (c) PB-6 compositions. (bar = 2 μm)

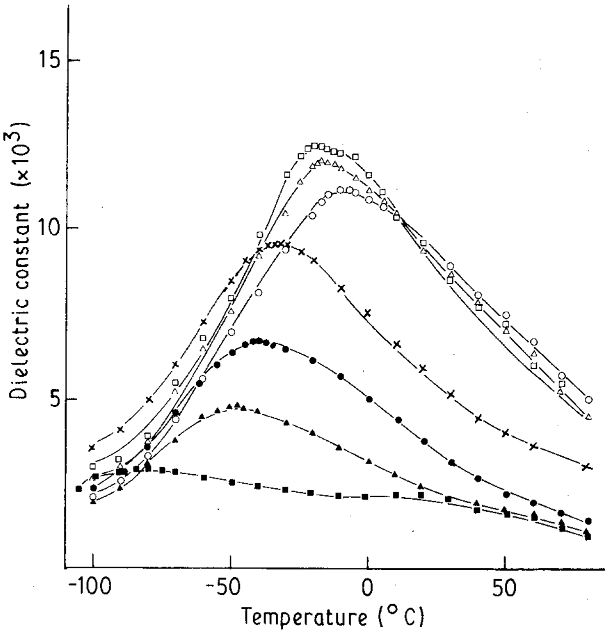

Figure 3 Dielectric constant plotted against temperature for various PMN–$BaTiO_3$ compositions at 1 kHz (○ PB-0, △ PB-1, □ PB-2, × PB-3, ● PB-4, ▲ PB-5, ■ PB-6).

when no pyrochlore phase was found to be present occurred mainly due to the detrimental effect of the low permittivity of $BaTiO_3$. Halliyal *et al.* and Belsick *et al.* observed that up to the composition at which the pyrochlore phase was eliminated the dielectric constant increased but decreased for higher addition of $BaTiO_3$ or $SrTiO_3$ in PZN, respectively [5, 6].

The transition temperature (T_c) is shifted to lower temperatures by the addition of $BaTiO_3$, with results similar to that of PZN–BT ceramics [5]. This is probably related to the decrease in lattice constant with $BaTiO_3$ addition as shown in Table I. The relation between the dissipation factor and the temperature for various compositions is represented in Fig. 4. The dissipation factors for all compositions had values lower than 0.01 near room temperature.

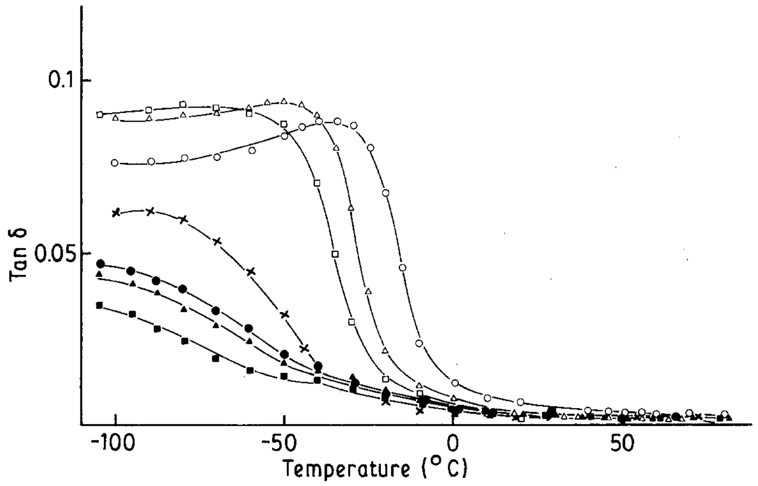

Figure 4 Dissipation factor plotted against temperature for various PMN–$BaTiO_3$ compositions at 1 kHz. (symbols as Fig. 3)

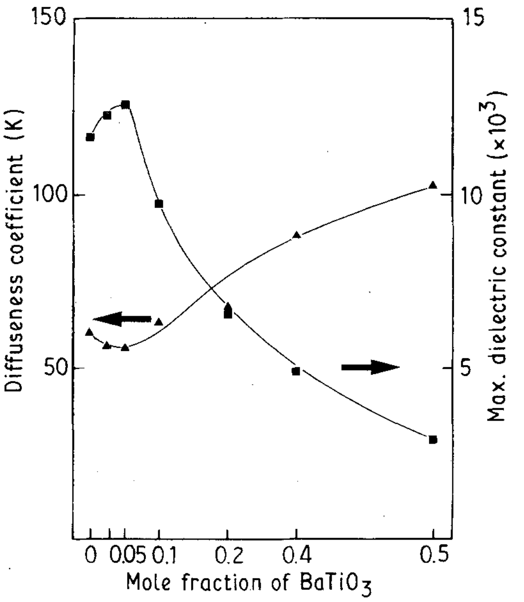

Figure 5 Diffuseness coefficient, δ, and maximum dielectric constant, K_{max}, plotted against mole fraction of $BaTiO_3$ for PMN–$BaTiO_3$ compositions.

From the results of hysteresis analysis, the remanent polarization near $-80\,^{\circ}C$ decreased with $BaTiO_3$ addition, from 5.4 $\mu C\,cm^{-2}$ for PB-0 to 2.7 $\mu C\,cm^{-2}$ for the PB-6 composition. This may be due to the addition of $BaTiO_3$ which has a lower value of remanent polarization ($\sim 2.0\,\mu C\,cm^{-2}$) [8].

3.3. Diffuse phase transition

As is apparent from Fig. 3, these specimens showed a diffused phase transition. The law $1/K \sim (T - T_0)^2$ has thus been shown to hold over a wide temperature range instead of the normal Curie–Weiss law [10]. The values of the diffuseness coefficient, δ, which indicate the intensity of the diffused phase transition were calculated from the slopes of the plots of $1/K$ against $(T - T_0)^2$ and are shown as a function of composition in Fig. 5. The increase in diffuseness coefficient with the amount of $BaTiO_3$ corresponds to the decrease in dielectric constant (K_{max}). Similar results have been reported for PZN–BT, PZN–ST and PZN–PT–BT ceramics [5, 6, 9].

3.4. Compositions for capacitors

In order to confirm the effect of $BaTiO_3$ addition in 10 m/o $PbTiO_3$ added PMN, whose composition has been studied as capacitor material by Swartz *et al.* [11], the phases present in the 0.9PMN–0.1PT and 0.87PMN–0.1PT–0.03BT specimens were analysed by XRD and the temperature dependence of the dielectric constants are shown in Fig. 6. The corresponding temperature dependence of the dissipation factor was observed simultaneously. For the 0.87PMN–0.1PT–0.03BT specimen, the pyrochlore phase, which was detected at 2 to 3% for 0.9PMN–0.1PT, was eliminated completely by the addition of $BaTiO_3$ and the dielectric constant increased slightly. The transition temperature was also lowered to near room temperature and the values of δ were 43 and 39 for 0.9PMN–0.1PT and 0.87PMN–0.1PT–0.03BT, respectively, which are lower than those for the compositions containing no $PbTiO_3$, indicating a narrower phase transition.

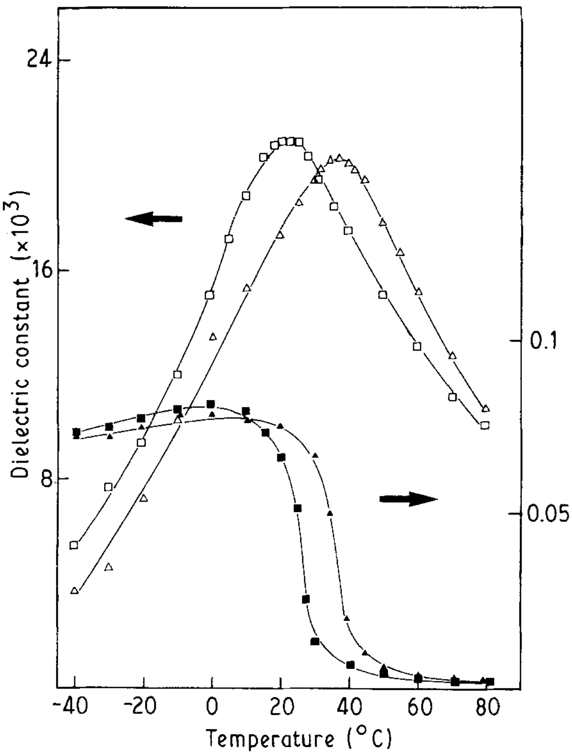

Figure 6 Dielectric constant and dissipation factor plotted against temperature for 0.9PMN–0.1$PbTiO_3$ (△ ▲) and 0.87PMN–0.1PT–0.03$BaTiO_3$ (□ ■) compositions.

Plots of the temperature coefficient of capacitance (TCC) for the 0.9PMN–0.1PT and 0.87PMN–0.1PT–0.03BT compositions are shown in Fig. 7. These compositions satisfy the Z5U and Y5U TCC specifications for capacitors.

4. Conclusions

This study confirmed that $BaTiO_3$ is also very effective in suppressing the formation of the pyrochlore phase in PMN ceramics. With the addition of 4 to 5 m/o $BaTiO_3$, the pyrochlore phase was completely

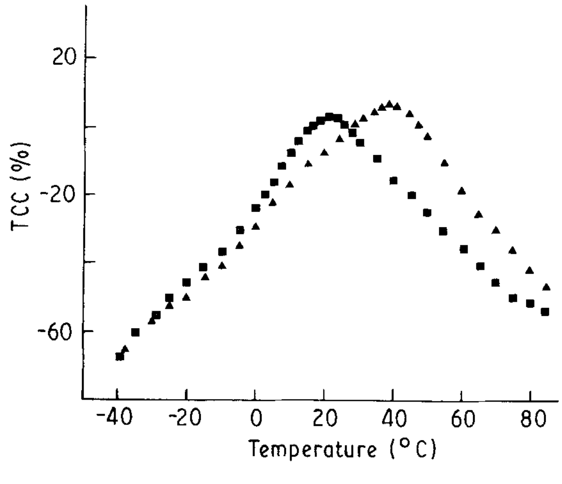

Figure 7 TCC plotted against temperature for 0.9PMN–0.1$PbTiO_3$ and 0.87PMN–0.1PT–0.03$BaTiO_3$ compositions.

eliminated and the dielectric constant was increased slightly. Further addition of $BaTiO_3$, however, caused a degraded dielectric constant even though no pyrochlore phase was found to be present. Compositions near 0.87PMN–0.1PT–0.03BT have been identified to have high dielectric constants (~ 21 000) near room temperature and low temperature coefficient of capacitance (TCC) values.

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