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Processing and properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$-based ceramics

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Abstract

Ceramic compositions of a combination between lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$, and lead titanate, $PbTiO_3$, were fabricated using the $Mg_4Nb_2O_9$ precursor technique. Their electrical properties with respect to temperature and frequency were examined and the effect of sintering conditions on phase formation, densification, microstructure and electrical properties of the ceramics were examined. It has been found that optimisation of sintering conditions can lead to a highly dense and pyrochlore-free PMN–PT ceramics. The gradual decrease of the physical properties of the sintered ceramics was related to the gradual decrease of density and inhomogeneous microstructure. The results also revealed that for the lower concentration of lead titanate, a relaxor behaviour is noticed with a high electrostrictive effect, which was almost hysteretic free. However, higher amount of lead titanate led to a normal ferroelectric behaviour.

Keywords: C. Dielectric properties; C. Ferroelectric properties; Lead magnesium niobate titanate

1. Introduction

The complex perovskite lead magnesium niobate–lead titanate, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT), are extensively used as multilayer capacitors, electrostrictive actuators, sensors and many other electronic and microelectromechanical devices [1,2]. This is due to their excellent electrical and electromechanical properties including high relative permittivity, a broad maximum in the dielectric constant, large electrostrictivity, associated with a low thermal expansion and excellent voltage stability [1–3]. The Columbite method [4], in which prefabricated $MgNb_2O_6$ is reacted with an appropriate proportion of PbO, has been widely used in the synthesized of phase-pure perovskite PMN-based ceramics. To our knowledge, there are no reports so far on the preparation of PMN–PT ceramics using a corundum $Mg_4Nb_2O_9$ precursor. From our previous works, pure perovskite PMN could be obtained using $Mg_4Nb_2O_9$ precursor. In the present study, ceramics in the $(1-x)$PMN–xPT system were fabricated by the solid-state reaction technique with $Mg_4Nb_2O_9$ as a key B-site precursor. Their electrical properties with respect to temperature and frequency were examined, compared and explained on the basis of their final composition, densification, and structural development.

2. Experimental procedure

The system under investigation is $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ or $(1-x)$PMN–xPT, where x changed from 0.1 to 0.5. The starting materials were commercially available oxide powders of PbO, MgO, Nb_2O_5 and TiO_2 (Aldrich, 99.9% purity) with an average particle size of 3–5 μm. PMN powders were first synthesized from these oxides using a modified mixed oxide synthetic route [5]. In this method, MgO and Nb_2O_5 are reacted at 950 °C for 2 h to form the corundum precursor $Mg_4Nb_2O_9$ [6], prior to reaction with PbO and TiO_2 at 800 °C for 2 h with heating/cooling rates of 30 °C/min [5]. The mixing process was carried out by vibro-milling the mixture of raw materials for 2 h with corundum media. After wet-milling, the slurry was dried, sieved and calcined in closed alumina crucibles. Green pellets were pressed into disks and sintered at various temperatures between 900 and 1250 °C. Densities of the sintered pellets were determined by the Archimedes principles. Room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) was used to identify the phases formed and optimum sintering condition, with the microstructural development examined by scanning electron

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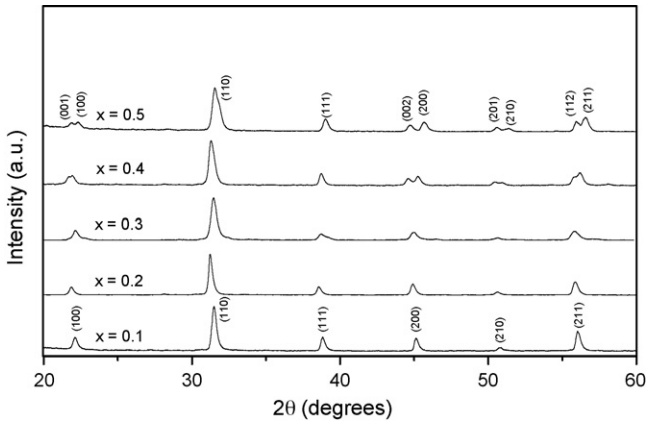

Fig. 1. XRD patterns of the $(1-x)$PMN–xPT ceramics sintered at their optimum conditions.

microscopy (SEM; JEOL JSM-840A). For the electrical measurements, the ceramics were sputtered with gold. The dielectric measurements were made using an automated measurement system, i.e. an LCR meter (HP-4174A) and furnace (9023 Delta design). Hysteresis measurements were made using a modified Sawyer-Tower circuit, with simultaneous measurement of strain using an LVDT and lock-in amplifier (SR830 DSP, Stanford Research).

3. Results and discussion

The X-ray diffraction patterns from sintered PMN–PT ceramics with maximum perovskite and bulk density are given in Fig. 1, where complete crystalline solutions of perovskite structure were formed throughout the whole composition ranges. In general, only a pseudo-cubic symmetry was observed at low values of PT concentration, in good agreement with other researchers [7–9]. With a further increase in PT concentration, however, several peaks were split at $x \geq 0.4$, indicating the development of tetragonal symmetry. For example, (0 0 2)/(2 0 0) peaks were split at 2θ of 44–46° confirming their tetragonal symmetry and being consistent with literature [7,10].

The densification data of all compositions is given in Table 1. In general, the bulk density was found to slightly decrease with x, which could be due to the low melting point of PT. It can be seen that the ceramic sintered at 1220–1240 °C exhibited the highest relative density with grain size range of about 0.4–3.7 μm. This sintered ceramic was of the best interest for further investigation. SEM micrographs of both

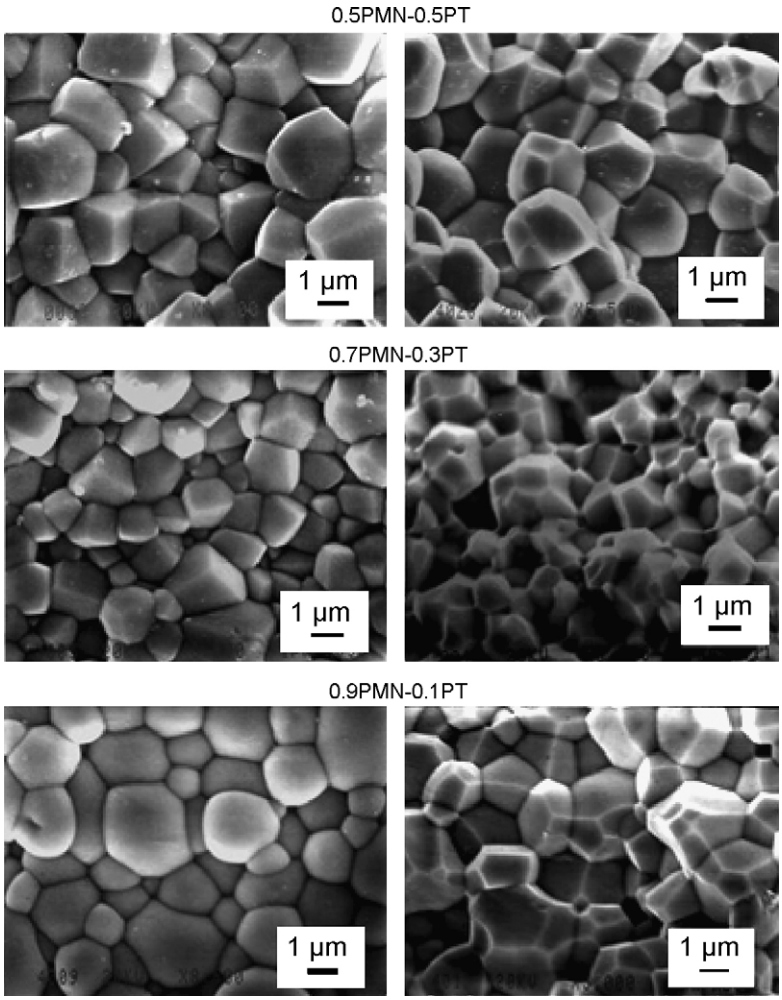

Fig. 2. SEM micrographs of the $(1-x)$PMN–xPT ceramics sintered at their optimum conditions.

Table 1
Phase and densification characteristics of $(1-x)$PMN–xPT ceramics from various sintering conditions

x	Optimum sintering condition (°C for 2 h)	Concentration of perovskite phase (%)	Density[a] (g/cm^3)	Grain size[b] (μm)
0.1	1240	100	7.98	0.42–3.66
0.2	1240	100	7.94	0.44–3.02
0.3	1240	100	7.86	0.41–2.80
0.4	1220	100	7.83	0.41–3.45
0.5	1220	100	7.78	0.48–3.72

[a] The estimated precision of the density is ±0.05 g/cm^3.
[b] The estimated precision of the grain size is ±0.05 μm.

as-fired and fracture surfaces of all compositions are shown in Fig. 2. In general, similar microstructural characteristics were observed in these samples, i.e. uniformly sized grains with a high degree of grain close-packing. By applying the linear intercept method to these micrographs, mean grain sizes of about 0.3–3.35 μm were estimated as given in Table 1.

The dielectric properties, e.g. dielectric constant (ε_r) and loss tangent (tan δ), are measured as functions of both temperature and frequency, as shown in Fig. 3a and b. As listed in Table 2, the Curie temperature (T_C) (determined at measuring frequency of 1 kHz) increases from 38 °C for 0.9PMN–0.1PT to 250 °C for 0.5PMN–0.5PT. This is a direct result of PT addition to PMN ($T_C \sim -8$ °C) since PT itself has a Curie temperature of 490 °C [11]. As shown in Fig. 3a, for 0.9PMN–0.1PT ceramic, both ε_r and tan δ exhibit strong temperature–frequency dependence below the transition temperature. The dielectric properties then become frequency independence above the transition temperature [12]. This is a typical behaviour of relaxor ferroelectrics [13]. Small addition of PT to PMN causes an increase in T_C, but the strong relaxor behaviour still exists. In addition, since 0.9PMN–0.1PT ceramic has a pseudo-cubic symmetry, it is therefore intrinsically electrostrictive (i.e. its electrically induced strain is quadratically proportional to the applied electric field and is non-hysteretic, as shown later in Fig. 4b) [14].

Further increase in PT contents leads to more observable normal ferroelectric behaviour because PT is intrinsically a normal ferroelectric [14]. For instance, the dielectric properties of 0.7PMN–0.3PT ceramic, as plotted in Fig. 3b, exhibit a mixture of both normal and relaxor characteristics, in which the transition temperature is not shifted as much as for relaxor 0.9PMN–0.1PT ceramic. Similar tendency has also been observed in several prior investigations [12,15,16]. The 0.5PMN–0.5PT ceramic, on the other hand, exhibits a normal ferroelectric behaviour (not shown). It should also be noted here that the dielectric properties in all ceramics increase significantly at high temperature as a result of thermally activated space charge conduction [15]. It can be concluded that when PT is added to form the binary system with PMN, the T_C increases monotonically, as shown in Table 2 and Fig. 3, and the dielectric behaviour is shifted from relaxor ferroelectric towards normal ferroelectric.

Fig. 4a illustrates a series of polarization–field (P–E) hysteresis loops for the PMN–PT ceramics. With large amount of normal ferroelectric PT contents, the polarization loops of 0.5PMN–0.5PT and 0.6PMN–0.4PT are well developed showing large remnant polarization (P_r: remaining polarization when electric field is decreased to zero). The hysteresis loops are of a typical ''square'' form as a result of domain switching in an applied field. This confirms that these compositions are of a normal ferroelectric phase with tetragonal symmetry, as indicated by the dielectric measurements and XRD analysis. The 0.7PMN–0.3PT ceramic shows largest polarization values with small coercive field (E_C), confirming that the composition

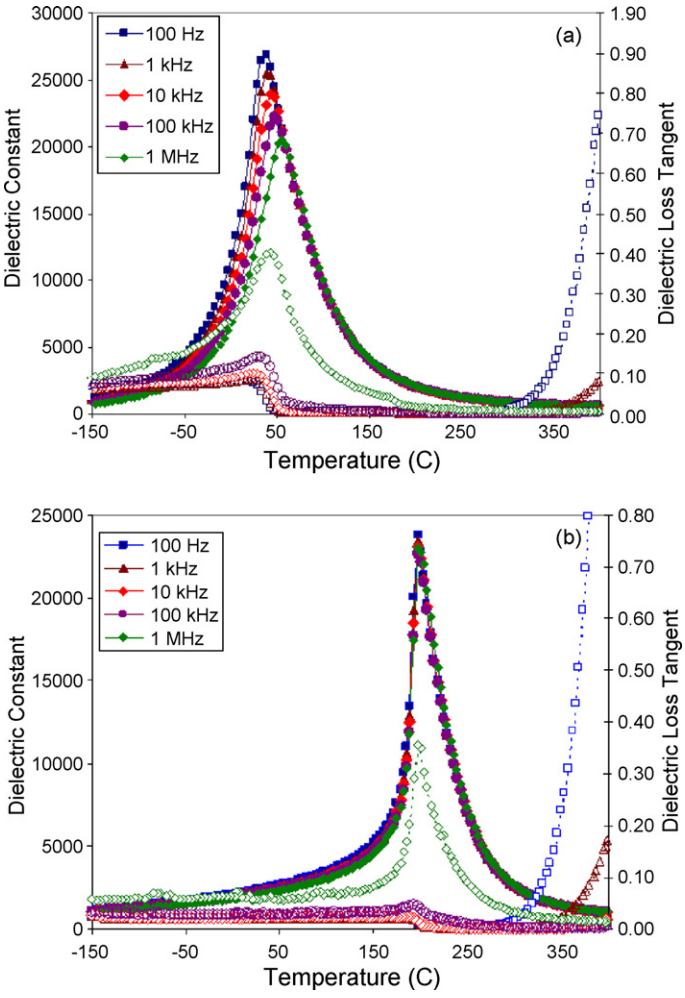

Fig. 3. Temperature and frequency dependences of dielectric properties of (a) 0.9PMN–0.1PT and (b) 0.7PMN–0.3PT ceramics (open markers with dotted lines indicate data for the dielectric loss tangent (tan δ) at the same frequency).

Table 2
Dielectric and ferroelectric properties of $(1-x)$PMN–xPT ceramics

Composition, x	T_C (°C)	Dielectric properties[a]		Ferroelectric properties[b]		
		ε_r	tan δ	P_{sat} (mC/m^2)	P_r (mC/m^2)	E_C (MV/m)
0.1	38	19,400 (16,500)[c]	0.087 (0.13)[c]	100	13	0.196
0.2	140	3,520	0.043	160	55	0.236
0.3	197	2,320 (3,782)[c]	0.022 (0.034)[c]	179 (460)[c]	100	0.391
0.4	220	2,134 (2,097)[c]	0.021 (0.016)[c]	127.5 (270)[c]	84	0.891
0.5	250	1,010	0.025	75	53	1.279

[a] Measured at 25 °C and 1 kHz.
[b] Measured at 25 °C and 0.1 Hz.
[c] Available properties for ceramics prepared by Columbite method.

is near the MPB of PMN–PT system. The other compositions with more PMN content show more of "slim" hysteresis loops, a characteristic of the suppressed ferroelectric interaction [13]. This also has resulted in decreasing of the values of both P_r and E_C, as seen in Table 2, due to an increased pseudo-cubic non-ferroelectric phase content [15,16]. A similar behaviour is also observed from the strain–electric field (s–E) relation, as plotted in Fig. 4b. As can be seen, the near hysteresis-free electrostrictive behaviour normally observed in relaxor ferroelectric is obtained in 0.9PMN–0.1PT ceramic. With increasing amount of PT, the s–E loops become more of "butterfly" type

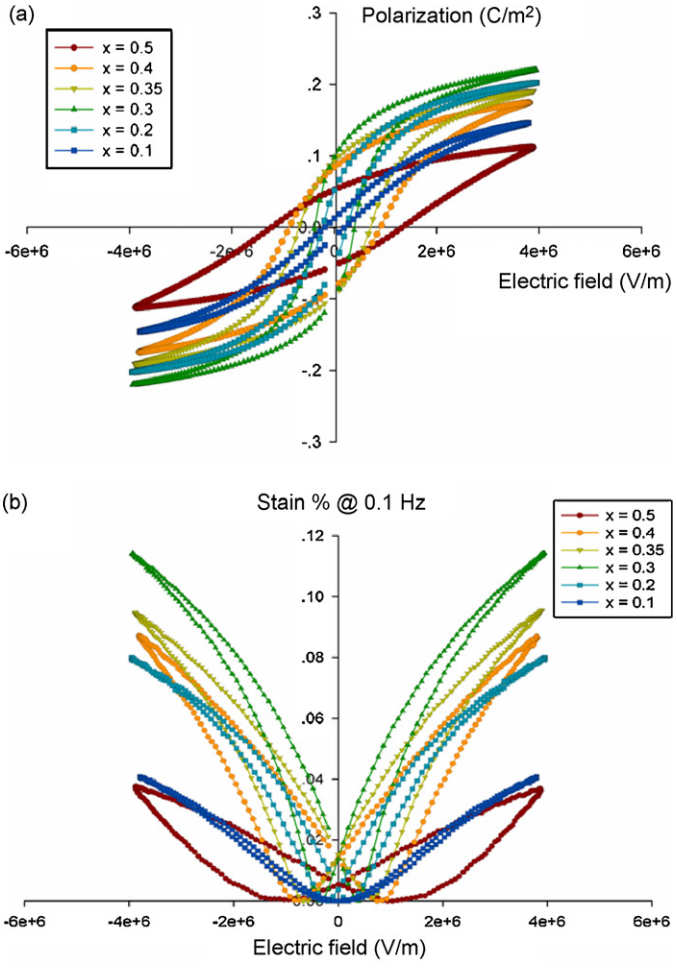

Fig. 4. (a) P–E and (b) s–E hysteresis loops of $(1-x)$PMN–xPT ceramics.

typically obtained in normal ferroelectric state. The field-induced strain increases with increasing amount of PT to 30 mol.% (near MPB composition), reaching the maximum value of ~0.12%. Further increase in the PT content results in the decrease of the induced strain. Therefore, it can be concluded that the ferroelectric properties of the ceramics in PMN–PT system move gradually from the relaxor ferroelectric state in PMN to the normal ferroelectric state in 0.5PMN–0.5PT, crossing the MPB near 0.7PMN–0.3PT [13]. In addition, it is worth noting that the measured values of the electrical properties in the present work are in good agreement with the previous works on PMN–PT ceramics prepared by the conventional Columbite method [17,18], as listed in Table 2.

4. Conclusions

Dense and pure perovskite PMN–PT relaxor ceramics could be produced using corundum $Mg_4Nb_2O_9$ as a B-site precursor. They possess very high dielectric constants and fundamental dielectric and electromechanical properties, similar to those found for the Columbite method, which can be greatly varied by composition and sintering condition. Dielectric relaxor behaviour for the rhombohedral sample was found to lower concentration of PT, where high electrostrictive effect was observed. A higher amount of lead titanate induced a normal ferroelectric behaviour with high polarization value and high electric field-induced strain.

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