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Improvement in shape memory in magnesium niobate modified PZST

Abhishek Pathak [a], Ratnamala Chatterjee [a], Chandra Prakash [b,*]

[a] Advanced Ceramic Laboratory, Department of Physics, Indian Institute of Technology, New Delhi 110016, India
[b] Directorate of ER & IPR, DRDO, DRDO Bhawan, New Delhi 110105, India

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Abstract

A modified lead zirconate stannate titanate system (PZST) has been studied for shape memory effect. Addition of magnesium niobate (MN) slows down the dipole relaxation process, leading to increased (~3-fold improvement) remnant strain in the PZST system (0.99PZST–0.01PMN). Room temperature X-ray diffraction patterns before poling (antiferroelectric (AFE) tetragonal) and after poling (ferroelectric (FE) rhombohedral), clearly demonstrate that the transition to the ferroelectric phase is stable even in the absence of any electric field. A small applied electric field (~1.7 kV/cm) in the opposite direction was required to bring the sample back to its original shape. Field-induced strain butterfly loops taken at 50 Hz show that the material response time is quite small.
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Keywords: Shape memory materials; Ferroelectrics; PZST

1. Introduction

Piezoelectric materials show induced strain of the order of ~0.1–1% on application of electric field, which normally disappears after the removal of electric field. However, if in a sample this field-induced strain remains even after the removal of the electric field and a small electric field in opposite direction is required to bring the sample back to its original shape, the material is called a shape memory ceramics [1]. In these ceramic materials, stress, temperature or electric field-induced antiferroelectric (AFE) to ferroelectric (FE) phase transition is responsible for the shape memory effect [2–7]. In recent years the shape memory effect has received increasing attention among researchers and large recoverable strains have been reported in metallic alloys like Nitinol (an alloy of nickel and titanium, ~8%) [8], Heusler alloy Ni–Mn–Ga (~5–10%) [9]. An important difference between the ceramic piezoelectric actuators and these metallic shape memory alloys lies in their comparative band-widths. The band-widths of ceramic materials are ~100 kHz, leading to quick response time; in comparison, the metallic shape memory alloys show comparatively much smaller band-width ~100 Hz [1]. Thus, although remnant strain is quite small in shape memory ceramics, their small response time, high durability and less power consumption are expected to be the positive features making them more attractive for industrial use. The electric field driven shape memory in niobium modified (at *A*-site) lead zirconate stannate titanate (PNZST) ceramic was first reported by Uchino and Nomura [10]. Till date, researchers have shown field-induced strain properties in various doped PZST systems *viz*., PYZST [11], PNbZST [10,12], PLaZST [13] and PNdZST [14].

We present here the results of our studies on dielectric, ferroelectric and strain behavior of PZST–PMN (lead zirconate stannate titanate–lead magnesium niobate), where magnesium niobate is doped at *B*-site. Initially, a series of PZST ceramic samples with chemical formula Pb $[(Zr_{0.7}Sn_{0.3})_xTi_{(1-x)}]O_3$, where x was varied as $x = 0.93$, 0.94, were prepared. Composition $x = 0.93$ was found to be FE (rhombohedral) at room temperature whereas the composition with $x = 0.94$ was observed to be AFE (tetragonal). Value of x was then varied up to the third decimal point between $0.93 < x < 0.94$ to approach the exact MPB. The pinched polarization hysteresis loop of composition $x = 0.938$ indicates the coexistence of AFE and FE phases [3]. Remnant strain (0.06%) in this undoped composition is found to be comparable [6,11,15,17] or smaller [12,16] than the values reported for doped PZST systems.

In order to increase the remnant strain by slowing down the phase change mechanism, we introduce PMN, a well known

* Corresponding author. Tel.: +91 11 2300 7350.
E-mail address: cprakash@hqr.drdo.in (C. Prakash).

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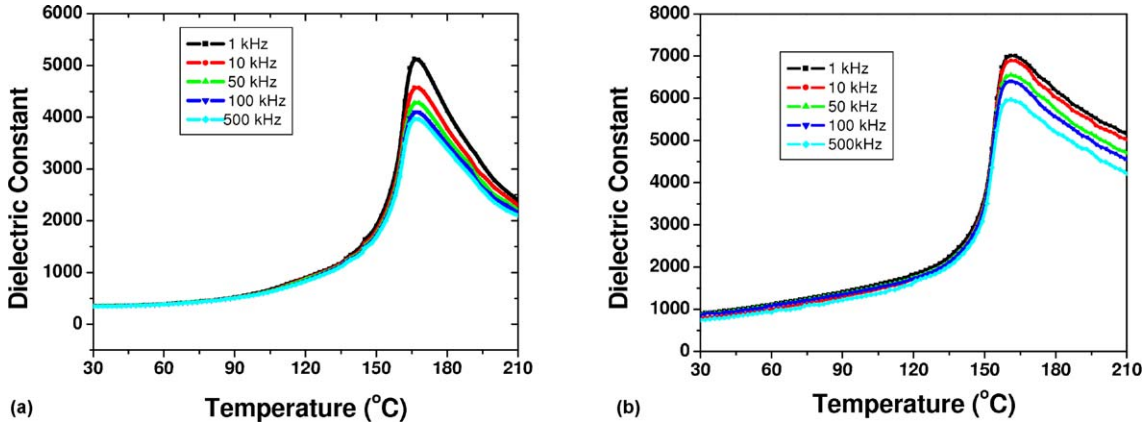

Fig. 1. Variation of dielectric constant (ε') of unmodified and modified PZST composition with temperature (30 °C ≤ T ≤ 210 °C), at different frequencies (1 kHz ≤ f ≤ 500 kHz).

relaxor ferroelectric in this unmodified composition ($x = 0.938$). Magnesium niobate modification is expected to slow down the dipole reorientation; the induced FE phase that remains even on decreasing the electric field down to zero is expected to produce larger remnant strain.

In this paper the composition at exact MPB, $Pb[(Zr_{0.7}Sn_{0.3})_{0.938}Ti_{0.062}]O_3$ is modified at *B*-site by magnesium niobate (0.99PZST–0.01PMN) and is studied for the shape memory effect. The AFE–FE MPB of this new composition 0.99PZST–0.01PMN is observed at 45 °C. Increasing the content of magnesium niobate is observed to shift the MPB to higher temperatures.

2. Experimental procedure

The samples were prepared by the solid-state route using raw materials of 99.9% (Aldrich Chem. Ltd.) purity. Mixed powders were calcined at 950 °C for 1 h and pellets were sintered at 1250 °C for 2 h with heating and cooling rate of 5 °C/min in air atmosphere. The density was found to be better than 95% of theoretical density. The coulombite method was used to prepare magnesium niobate modified compositions. For electrical characterizations, the sintered samples were polished to obtain parallel and smooth faces and gold electrodes were made by thermal evaporation on the faces of the pellets. After electroding, the samples were heat-treated at 450 °C for 30 min to ensure better contact between the electrodes and the ceramic surfaces. The dielectric properties of the sintered samples were studied as functions of both temperature and frequency using an HP 9142A impedance analyzer. The capacitance and the dielectric loss tangent were determined in the temperature range 30 °C ≤ T ≤ 220 °C with the frequency ranging from 1 kHz ≤ f ≤ 500 kHz. Measurements were carried out at heating rate of 0.5 °C/min. The ferroelectric hysteresis (*P–E*) loops were measured using Radiant Technology's work station at 0.1 Hz frequency. Field-induced strain measurements were carried out on a LVDT based strain meter (SS 50 strain measurement system, Sensor Tech. Ltd., Canada).

3. Results and discussion

Fig. 1(a) and (b) shows the representative plots for the variation of the dielectric constant vs temperature at different frequencies, for unmodified and magnesium niobate modified samples, respectively. Although the ordering temperatures for both compositions are found to be independent of frequencies (non-relaxor behavior), MN modified PZST shows a broader transition with decrease in transition temperature and increase in dielectric constant (∼1.5 times).

Fig. 2 shows *P–E* hysteresis loops of 0.99PZST–0.01PMN at different temperatures (30 °C ≤ T ≤ 70 °C). At room temperature the sample goes through an induced FE phase transition and shows a clear ferroelectric loop. MN modification in the sample introduces a slower relaxation process leading to larger (in comparison to the unmodified PZST) remnant polarization (P_R), although the spontaneous polarization (P_S) in both unmodified and modified compositions are comparable (see inset for *P–E* loop of unmodified PZST). On increasing the temperature, at 45 °C, a pinched shape loop in the MN modified composition is observed; indicating coexisting AFE and FE phases. With further increase of temperatures ≥60 °C the sample finally becomes pure AFE.

Fig. 3 shows electric field-induced strain butterfly loops for MN modified composition at different temperatures (30 °C ≤ T ≤ 70 °C). The measurements are made at 50 Hz frequency (unlike *P–E* measurements that are made at 0.1 Hz). Value of *remnant strain* at 45 °C is found to increase more than three times (∼0.19%) as compared to the largest value (0.06%) for the parent composition. A small reverse electric field (∼1.78 kV/cm), which is quite smaller than previously reported values [6,12,11,15,17] is required to bring the sample back to zero strain. This is an important feature for device applications. Further increase in temperature decreases the *remnant strain* due to the dominance of AFE phase at these temperatures. It was noted that after 70 °C *remnant strain* completely disappears. An important point to note is that the values of strains shown in this report are all measured at 50 Hz frequency (due to experimental

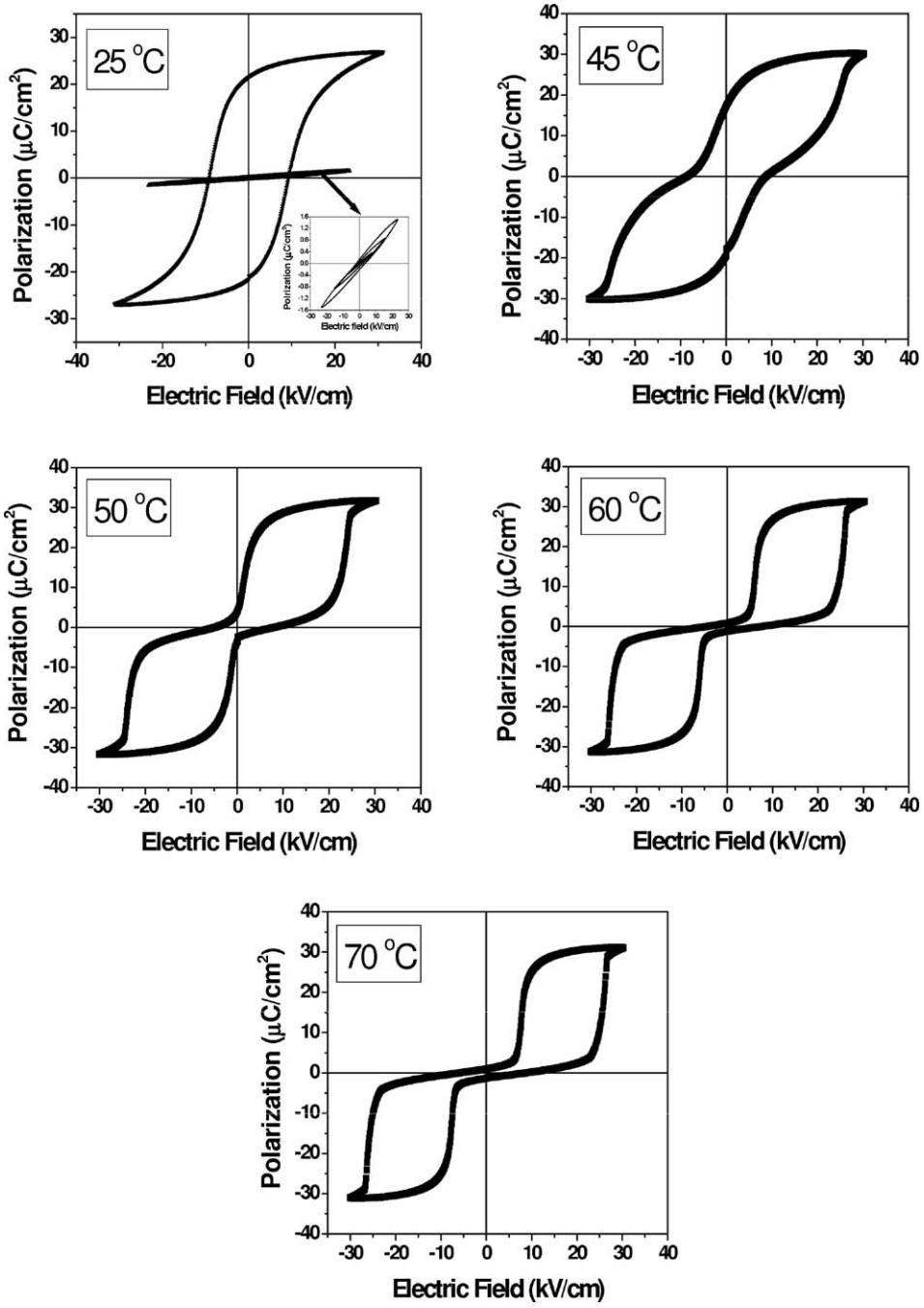

Fig. 2. *P–E* hysteresis loops of 0.99PZST–0.01PMN composition at different temperatures.

limitations); corresponding values at lower frequencies are expected to be comparatively larger.

In order to prove that addition of magnesium niobate slows down the dipole reorientation and the induced FE phase to remain even after removal of electric field, electric field was applied to unmodified composition and after its removal no change in structure was observed. On the other hand the modified composition shows change in structure on application of the electric field. Fig. 4(a) shows the XRD pattern of the modified composition before applying the electric field. Doublet of (2 0 0) peak and singlet of (1 1 1) peak confirm the tetragonal structure. After applying and removing the electric field (≥25 kV/cm) doublet of (1 1 1) peak and singlet of (2 0 0) peak reveal rhombohedral structure (Fig. 4(b)). These results confirm that in modified composition, field-induced FE phase remains after the removal of the electric field.

A comparison of relevant properties of Pb-based systems with those obtained for the PZST–PMN (present work) is shown in Table 1.

4. Conclusions

Magnesium niobate modified PZST system (0.99PZST–0.01PMN) shows remarkable changes in dielectric, ferroelectric and piezoelectric properties. After modification, the value of dielectric constant increases 1.5 times, *remnant strain*

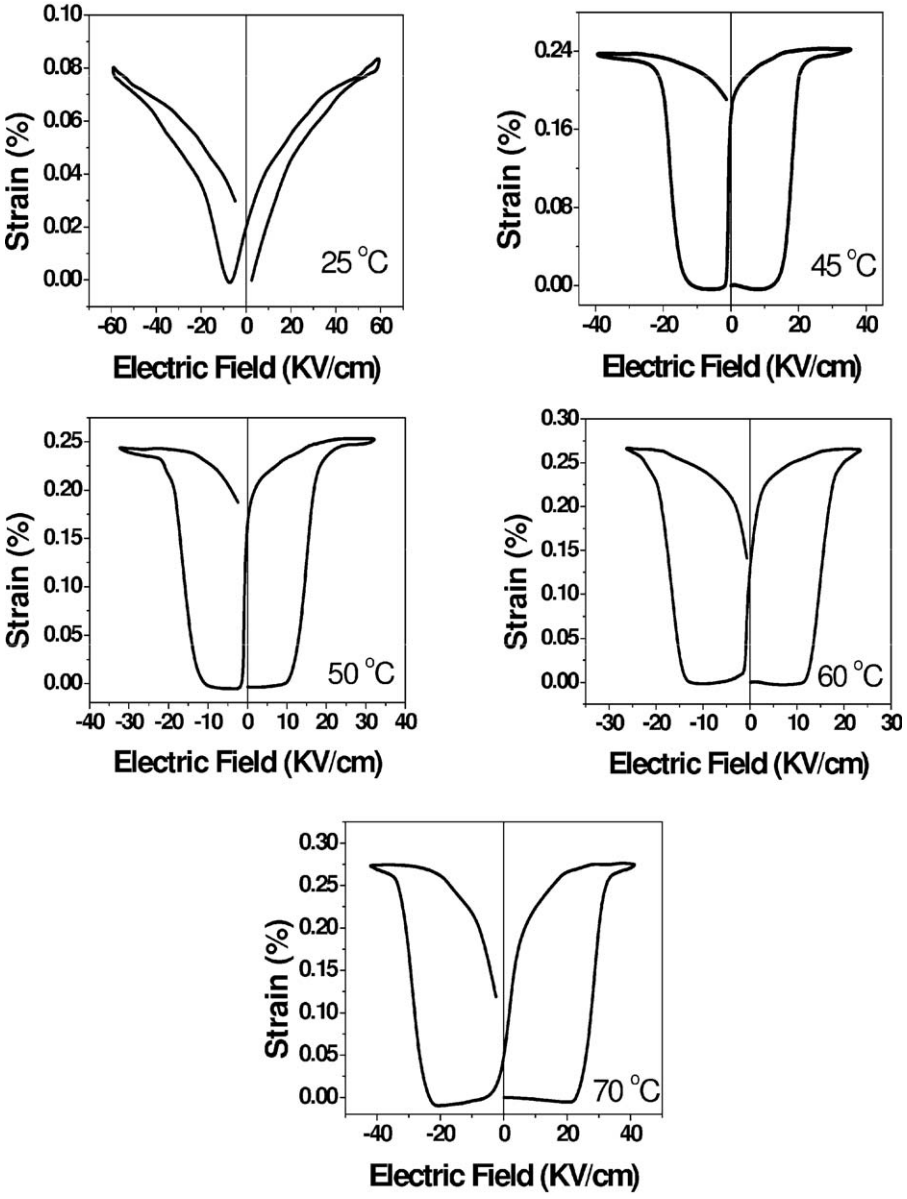

Fig. 3. Field-induced strain loops of 0.99PZST–0.01PMN composition at different temperatures.

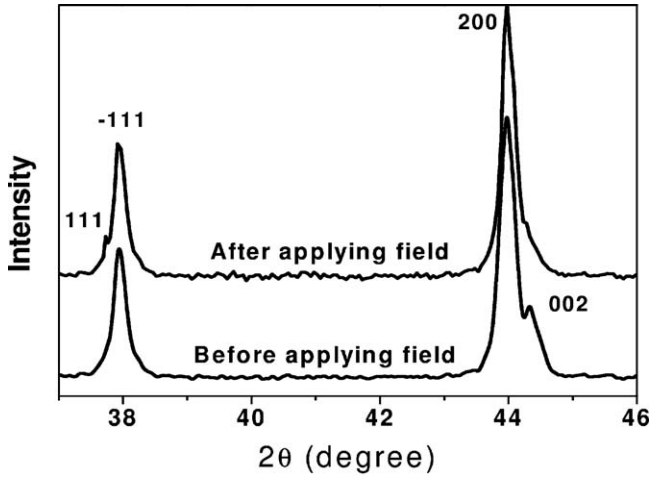

Fig. 4. X-ray diffraction of modified composition before and after application of electric field.

Table 1
A comparison of relevant properties of Pb-based systems with those obtained from present work.

Materials	Dielectric constant	References	Remnant strain (%)	Reverse field for 0% strain (kV/cm)
0.99PZST–0.01PMN	7500	Present work	0.19[a]	1.7
PNbZST	–	12	0.22[b]	10
PLaZST	–	6	0.05	10
PYZST	3500	11	0.06	15
0.8PZST–0.2PMN	14,000	15	0.04	07
PZSrT	–	17	0.06	20
PZN–PT	32,000	16	0.1	–

[a] The reported value of *remnant strain* is for 50 Hz.
[b] The reported value of *remnant strain* is for 0.05 Hz.

increases ∼3 times and the reverse electric field for strain butterfly loop decreases ∼10 times, compared to those of unmodified composition. These properties make this system a good candidate for shape memory applications.

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