Ferroelectric Properties of Ceramics in Lead Zirconate Titanate - Lead Magnesium Niobate System

Rattikorn Yimnirun[1*], Supon Ananta[1], and Pitak Laoratakul[2]

[1] *Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

[2] *National Metal and Materials Technology Center, Pathumtani 12010, Thailand*

Corresponding author. E-mail: rattikor@chiangmai.ac.th

ABSTRACT

The ferroelectric and piezoelectric properties of xPZT-(1-x)PMN were measured by means of a modified Sawyer-Tower circuit and LVDT strain gage, and d_{33}-meter, respectively. The P-E hysteresis loop measurements demonstrated that the ferroelectric properties of the ceramics in PZT-PMN system changed gradually from the normal ferroelectric behavior in PZT ceramic to the relaxor ferroelectric behavior in PMN ceramic. The s-E relations showed a so-called "butterfly" curve in some compositions, while the relation was of a quadratic electrostrictive nature in the PMN ceramic. Finally, the piezoelectric constant (d_{33}) decreased from, in the units of pm/V, 280 in piezoelectric PZT ceramic to less than 5 in electrostrictive PMN ceramic.

Key words: PZT-PMN, Ferroelectric properties, Hysteresis loops

INTRODUCTION

Lead–based perovskite-type solid solutions consisting of the ferroelectric and relaxor materials have attracted a growing fundamental and practical interest because of their excellent dielectric, piezoelectric and electrostrictive properties which are useful in actuating and sensing applications (Koval et al., 2003). Among the lead–based complex perovskites, lead zirconate titanate ($Pb(Zr_{1-x}Ti_x)O_3$ or PZT) and lead magnesium niobate ($Pb(Mg_{/3}Nb_{2/3})O_3$ or PMN) ceramics have been investigated extensively , both from academic and commercial viewpoints (Cross, 1996; Haertling, 1999). These two types of ceramics possess distinct characteristics that in turn makes each of them suitable for different applications. With the complementary features of PZT and PMN described in many publications (Wongsaenmai et al., 2003; Yimnirun et al., 2003), the solid solutions between PZT and PMN are expected to combine the properties of both normal ferroelectric PZT and relaxor ferroelectric PMN, which could exhibit better piezoelectric and dielectric properties than those of the single-phase PZT and PMN. Furthermore, the properties can also be tailored over a wider range by changing the compositions to meet the strict requirements for specific applications (Cross, 1987; He et al., 2001). In recent years, there have been several investigations on PZT-PMN system (Shilnikov et al., 1999; Burkhanov et al., 2000; Koval et al., 2003a). However, these previous works have focused only on a few compositions in the vicinity of the morphotropic phase boundary and of the end members. Therefore, the overall

purpose of this study was to determine the dielectric and ferroelectric properties of ceramics in the xPZT-(1-x)PMN (when x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1) binary system in the hope to gain some insights for possible applications. This article presents the ferroelectric properties of ceramics in this binary system.

MATERIALS AND METHODS

The $Pb(Zr_{0.52}Ti_{0.48})O_3$ - $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic composites were prepared from PZT and PMN powders by a mixed-oxide method. PZT powders were prepared by a more conventional mixed-oxide method, while perovskite-phase PMN powders were obtained via a well-known columbite method. The $(x)Pb(Zr_{0.52}Ti_{0.48})O_3 – (1-x) Pb(Mg_{1/3}Nb_{2/3})O_3$ (when x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0) ceramic composites were then prepared from the starting PZT and PMN powders by a mixed-oxide method at various processing conditions. The detailed descriptions of ceramics processing and characterizations were presented thoroughly in the earlier publications (Wongsaenmai et al., 2003; Yimnirun et al., 2003).

For ferroelectric properties characterizations, the sintered samples were lapped to obtain parallel faces, and the faces were then coated with silver paint as electrodes. The samples were heat-treated at 750°C for 12 min to ensure the contact between the electrodes and the ceramic surfaces. The samples were subsequently poled in a silicone oil bath at a temperature of 120°C by applying a dc field of 25 kV/cm for 30 min and field-cooled to room temperature.

The ferroelectric hysteresis (P-E) loops were characterized by using a computer controlled modified Sawyer-Tower circuit. The high voltage was applied to samples by a bipolar amplifier (Kepco BOP 1000M) and a high voltage AC amplifier (Trek 610C) with the input signals with a frequency of 0.1 Hz from a lock-in amplifier (Stanford Research System SRS 830). In addition, the strain-field (s-E) loops were also determined simultaneously by the same system, in which the strain was measured with a linear variation differential transformer (LVDT) strain gage (Radiant Technologies). The detailed description of this system has been described elsewhere (Jiang, 1992). Furthermore, the piezoelectric d_{33} constant of the poled ceramics (after 24 h aging at room temperature) was measured at 100 Hz by a piezoelectric d_{33}-meter (Channel Berlincourt d_{33}-meter).

RESULTS AND DISCUSSION

The experimental results on physical properties, the phase formation behavior and microstructure features of all the sintered ceramics have been discussed extensively in earlier publications (Wongsaenmai et al., 2003; Yimnirun et al., 2003). Hence, these results will not be shown here. However, it should be mentioned that the sintered ceramics were mainly in perovskite phase with tetragonal, cubic and pseudo-cubic crystal structure for PZT, PMN and all PZT-PMN ceramic composites, respectively. Table 1 summarizes the density, average grain-size and dielectric properties for all ceramic compositions.

Table 1. Characteristics of PZT-PMN ceramics with optimized processing conditions.

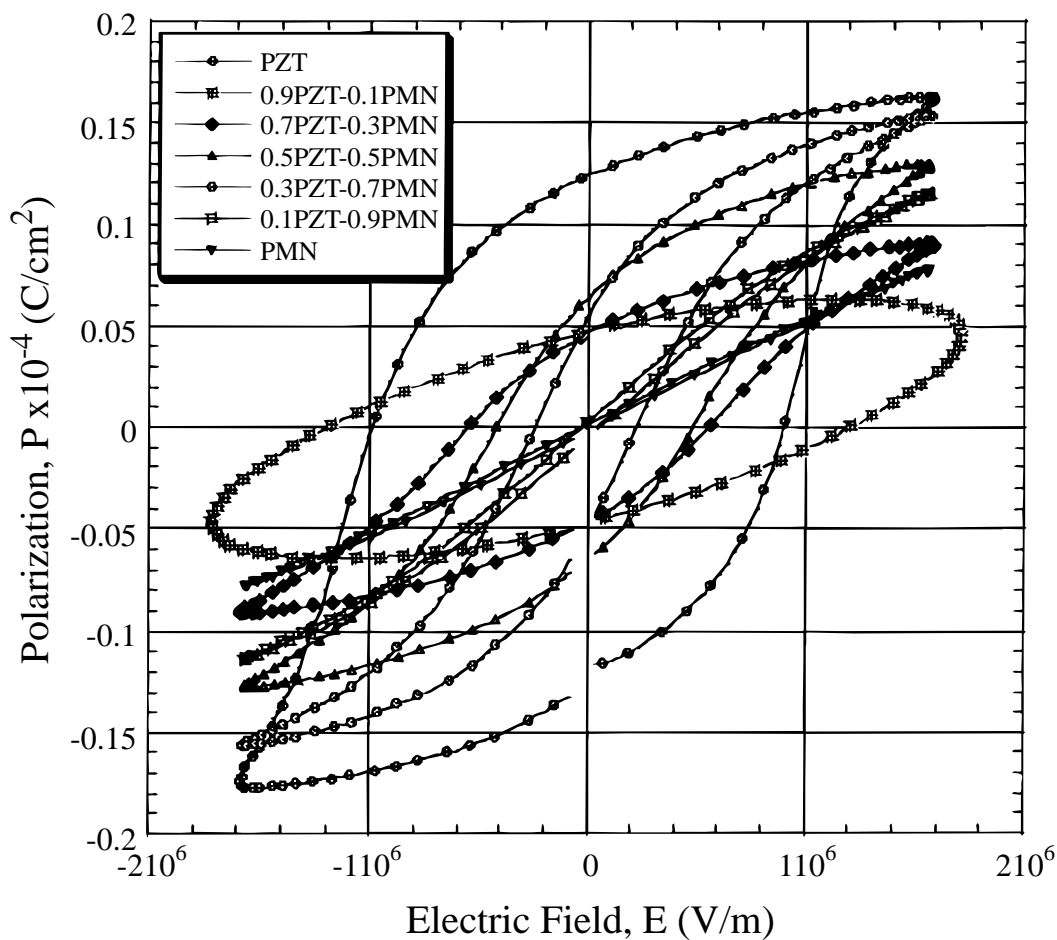| Ceramic	Density (g/cm³)	Grain Size Range (μm)	Average Grain Size (μm)	Maximum ε_r (1 kHz)	T_c (˚C)
PZT	7.59 ± 0.11	2-7	5.23	> 29,000	> 400
0.1PMN-0.9PZT	6.09 ± 0.11	0.5-2	0.80	3,700	~ 390
0.3PMN-0.7PZT	7.45 ± 0.10	0.5-3	1.65	3,800	160
0.5PMN-0.5PZT	7.86 ± 0.05	0.5-5	1.90	6,600	115
0.7PMN-0.3PZT	7.87 ± 0.07	1-4	1.40	11,000	71
0.9PMN-0.1PZT	7.90 ± 0.09	1-4	1.50	10,700	16
PMN	7.82 ± 0.06	2-4	3.25	7,600	-8

Figure 1. P-E hysteresis loops of xPZT-(1-x)PMN ceramics.

Figure 1 illustrates a series of polarization (P-E) hysteresis loops for the xPZT-(1-x)PMN ceramics. It is clearly evident that the shapes of P-E loops vary greatly with the ceramic compositions. The polarization loop of PZT is well-developed, showing large remnant polarization (P_r : remaining polarization when electric field is decreased to zero). The hysteresis loop is of a typical "square" form as a result of domain switching in an applied field. This is a typical characteristic of a phase that contains long-range interaction between dipoles in the ferroelectric micro-domain state (Koval et al., 2003a). This confirms that PZT is of a normal ferroelectric phase. From the loop, the remnant polarization Pr and the coercive field EC (indicating an electric field required to zero the polarization) are determined to be 12.5 $\mu C/cm^2$ and 10 kV/cm, respectively, as listed in Table 2. When more PMN content is added to the system, the hysteresis curves become more of "slim" hysteresis loops, a characteristic of the suppressed ferroelectric interaction (Koval et al., 2003a). This is typically found in the relaxor ferroelectrics with polar nano-regions. These results clearly indicate that an addition of PMN induces the relaxor behaviors of PMN into the PZT-PMN ceramic system. This also has resulted in the decrease in the values of both P_r and E_C, as seen in Table 2. Furthermore, the piezoelectric constant (d_{33}) also significantly decreases with increasing PMN content in the system. This is intuitively understandable from the decrease of the polarization in the ceramics and also from the fact that PMN is electrostrictive (the second harmonic property, in contrast to the first harmonic nature of piezoelectric ceramics, such as PZT). Therefore, it can be concluded that the ferroelectric properties of the ceramics in PZT-PMN system move gradually from the normal ferroelectric state in PZT to the relaxor ferroelectric state in PMN. It is also of interest to observe that the hysteresis loop of 0.9PZT-0.1PMN ceramic is not fully saturated. This is probably due to the limited capability of the measuring set-up used. However, it is expected that this composition should posses better ferroelectric properties, as reported in recent publication (Koval et al., 2003).

Table 2. Ferroelectric and piezoelectric properties of PZT-PMN ceramics.

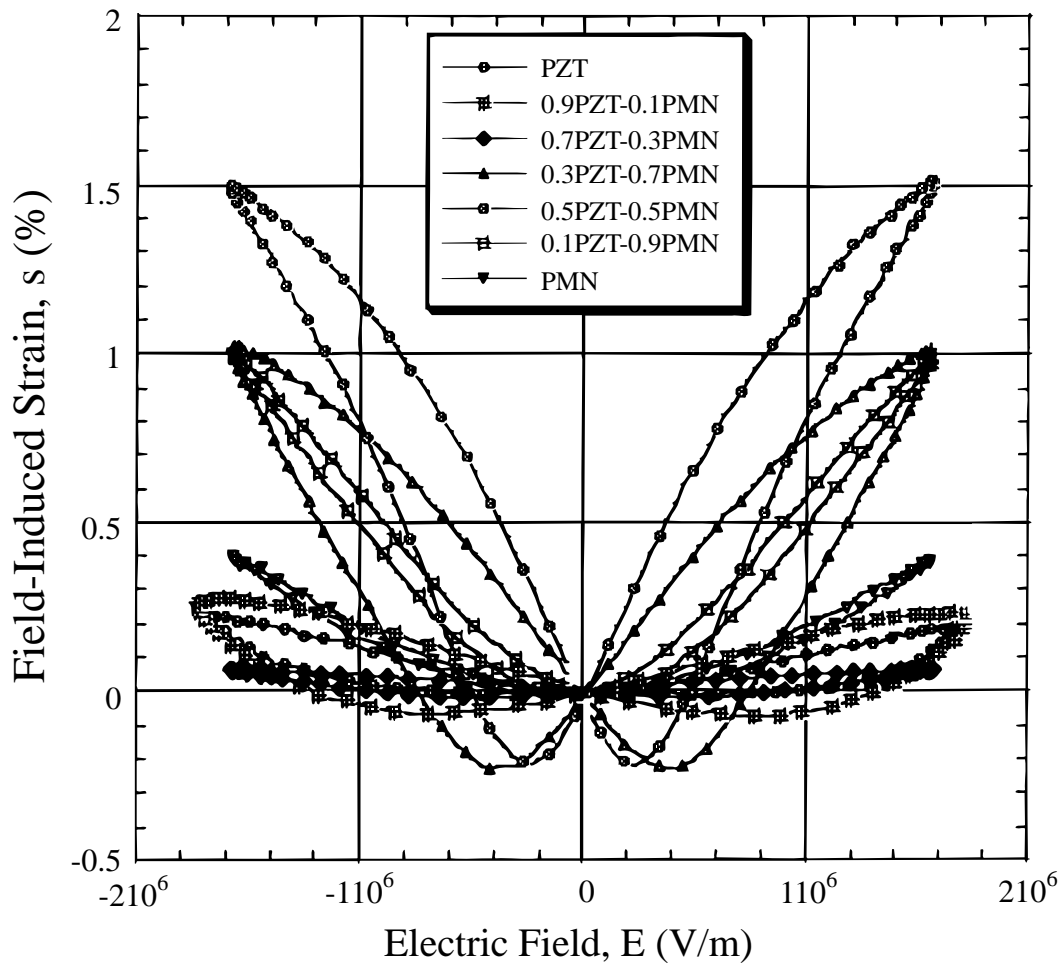| Ceramic	P_r ($\mu C/cm^2$)	E_C (kV/cm)	d_{33} (pm/V)
PZT	12.5	10	280
0.1PMN-0.9PZT	5	12	40
0.3PMN-0.7PZT	4.5	5.5	63
0.5PMN-0.5PZT	6.5	4.5	41
0.7PMN-0.3PZT	5.2	2.3	12
0.9PMN-0.1PZT	-	-	1
PMN	-	-	4

Figure 2. s-E relations of xPZT-(1-x)PMN ceramics.

The relationships between the field-induced strain (s) and the applied electric field (E) for the xPZT-(1-x)PMN ceramics are shown in Figure 2. The results show so-called "butterfly" curves, which are characteristics of ferroelectric materials in which an external field causes a domain switching mechanism that in turn creates strain in the material. In Figure 2, there are three distinct groups of s-E relationship. The first group is PMN and 0.1PZT-0.9PMN ceramics with slim loops, which follow quadratic relation at low field. This group signifies the electrostrictive relaxors. The second group consists of 0.3PZT-0.7PMN and 0.5PZT-0.5PMN ceramics with the large butterfly curves, a sign of more piezoelectric behavior. PZT-riched ceramics make up the last group, in which more open and larger butterfly curves are expected. However, the results obtained indicate that these ceramics are not fully poled due to limited capability of the set-up used.

CONCLUSIONS

The ferroelectric and piezoelectric properties of xPZT-(1-x)PMN (when x= 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0) ceramics prepared by a conventional mixed-oxide method were measured by means of a modified Sawyer-Tower circuit and LVDT strain gage, and d_{33}-meter, respectively. From the P-E hysteresis loop, it was shown that the ferroelectric properties of the ceramics in PZT-PMN system moved gradually from the normal ferroelectric state in PZT ceramic, with large P_r and E_C values, to the relaxor ferroelectric state in PMN ceramic. The s-E relations showed a so-called "butterfly" curve in some compositions, while the relation was of a quadratic electrostrictive nature in the PMN ceramic. Finally, the piezoelectric constant (d_{33}) decreased from, in the units of pm/V, 280 in piezoelectric PZT ceramic to less than 5 in electrostrictive PMN ceramic.

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