ORIGINAL ARTICLE

Dielectric properties of ceramics in lead zirconate titanate - lead magnesium niobate system

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Abstract

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Dielectric properties of ceramics in lead zirconate titanate - lead magnesium niobate system

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In this study, the $xPb(Zr_{0.52}Ti_{0.48})O_3$ - $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$ (when x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0) ceramic composites are prepared from PZT and PMN powders by a conventional mixed-oxide method. The dielectric properties of the ceramics are measured as functions of both temperature (-150 - 400ºC) and frequency (100 Hz - 1 MHz). The results indicate that the dielectric properties of the pure phase PZT and PMN are of normal and relaxor ferroelectric behaviors, respectively. The dielectric behaviors of the 0.9PZT - 0.1PMN and 0.7PZT - 0.3PMN ceramics are more of normal ferroelectrics, while the other compositions are obviously of relaxor ferroelectrics. In addition, the transition temperature decreases and the maximum dielectric constant increases with increasing PMN content in the system. These results clearly show the significance of PMN in controlling the dielectric behavior of the PZT-PMN system.

Key words : PZT, PMN, PZT-PMN, dielectric properties

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สมบัติไดอิเล็กตริกของสารเซรามิกในระบบเลดเซอร์โคเนตไทเทเนต-เลดแมกนีเซียมไนโอเบต

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ในการวิจัยนี้ได้ทำการเตรียมสารผสมเซรามิกในระบบ $(x)Pb(Zr_{0.52}Ti_{0.48})O_3$-$(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$ เมื่อ x = 0.0 0.1 0.3 0.5 0.7 0.9 และ 1.0 ด้วยวิธีการผสมออกไซด์แบบดั้งเดิม และได้ทำการวัดสมบัติไดอิเล็กตริกของสารเซรามิกที่เปลี่ยนแปลงตามอุณหภูมิ (ในช่วง -150 ถึง 400°C) และความถี่ (ในช่วง 100 เฮิรท์ซ ถึง 1 เมกะเฮิรท์ซ) ผลการทดลองชี้ให้เห็นว่าสมบัติไดอิเล็กตริกของสารเซรามิก PZT และ PMN บริสุทธิ์ จะมีพฤติกรรมแบบสารเฟร์โรอิเล็กตริกแบบปกติและแบบรีแลกเซอร์ ตามลำดับ พฤติกรรมไดอิเล็กตริกของสารเซรามิก 0.9PZT - 0.1PMN และ 0.7PZT-0.3PMN จะเป็นแบบสารเฟร์โรอิเล็กตริกแบบปกติมากกว่า ในขณะที่สารเซรามิกที่มีส่วนผสมอื่น ๆ จะมีพฤติกรรมไดอิเล็กตริกที่เป็นแบบสารเฟร์โรอิเล็กตริกแบบรีแลกเซอร์ที่ชัดเจน นอกจากนี้ ยังพบว่าเมื่อมีปริมาณสาร PMN เพิ่มมากขึ้นในระบบ จะทำให้อุณหภูมิการเปลี่ยนเฟสลดลง ในขณะที่ค่าคงที่ไดอิเล็กตริกสูงสุดจะมีค่าเพิ่มขึ้น ซึ่งผลการทดลองนี้แสดงให้เห็นถึงความสำคัญของสาร PMN ในการควบคุมสมบัติไดอิเล็กตริกของสารเซรามิกในระบบ PZT-PMN

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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 ($Pb(Mg_{1/3}Nb_{2/3})O_3$ or PMN) ceramics have been investigated extensively, from both academic and commercial viewpoints (Haertling, 1999). These two types of ceramics possess distinct characteristics that in turn make each ceramic suitable for different applications. Piezoelectric transducers with compositions near the tetragonal-rhombohedral morphotropic phase boundary (MPB) have been among the primary applications of PZT ceramics. The closer the composition is to the MPB, the better the piezoelectric properties (Shaw *et al.*, 1993). The component closest to the MPB then becomes the main research focus for PZT ceramics. However, PZT ceramics are fairly lossy as a result of their highly hysteretic behavior. This makes them unsuited for applications that require high delicacy and reliability. Furthermore, PZT ceramics normally have very high Curie temperature (T_C) in the vicinity of 400ºC (Las *et al.*, 2001). Usually many applications require that T_C is close to ambient temperature. Therefore, there is a general interest to reduce the T_C of PZT ceramics to optimize their uses. Alternative materials that also offer some the same desirable features as in PZT ceramics are electrostrictive materials that possess a very interesting combination of large electrostrictive strains and a minimal or negligible hysteresis in the strain-field dependence (Koval *et al.*, 2003). PMN is nowadays acknowledged as the representative of relaxor electrostrictive materials. PMN exhibits high dielectric constant (~18000 for ceramics and ~ 20000 for single crystals) and a broad range transition of dielectric constant, with temperature as a function of frequency (Park and Shrout, 1997). This makes PMN a good candidate for a large number of applications in electronics and microelectronics, such as multilayer capacitors, sensors and actuators. However, PMN ceramics have relatively low electromechanical coupling coefficients, as compared to PZT. With the complementary features of PZT and PMN, 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. In addition, the properties can also be changed over a wider range by changing the compositions to meet the stringent requirements for specific applications (He *et al*., 2001). Therefore, the overall purpose of this study is to investigate the PZT-PMN binary system in hope of gaining some insights for possible applications of the ceramics in this system. This article is particularly aimed to present the dielectric properties of ceramics in PZT-PMN system as functions of both temperature and frequency.

Materials and Methods

The $Pb(Zr_{0.52}Ti_{0.48})O_3$ - $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic composites are prepared from PZT and PMN powders by a mixed-oxide method. PZT powders are prepared by a more conventional mixed-oxide method, while perovskite-phase PMN powders are obtained via a well-known columbite method (Swartz and Shrout, 1982). PZT powders are prepared from reagent-grade PbO (99%), ZrO_2 (99%), and TiO_2 (98.5%) starting powders (Fluka, Switzerland). These powders are ball-milled for 24 hours and later calcined at 850ºC for 2 hours. For PMN powders, the magnesium niobate powders are first prepared by mixing starting MgO (>98%) (Fluka, Switzerland) and Nb_2O_5 (99.9%) (Aldrich, Germany) powders and then calcining the mixed powders at 1050ºC for 2.5 hours. This yields a so-called columbite powder ($MgNb_2O_6$). The columbite powders are subsequently ball-milled with PbO (99%) for 24 hours. The mixed powders are calcined at 800ºC for 2.5 hours. The analysis of the X-ray diffraction pattern confirms the perovskite phase of PMN.

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 are prepared from the starting PZT and PMN powders by a mixed-oxide method at various processing conditions. Initially, the PZT and PMN powders for a given composition are weighed and then ball-milled in ethanol for 24 hours. After drying process, the mixed powders are pressed hydraulically to form disc-shaped pellets 15 mm in diameter and 2 mm thick, with 5 wt.% polyvinyl alcohol (PVA) as a binder. The pellets are stacked in a covered alumina crucible filled with PZ powders to prevent lead loss. Finally, the sintering is carried out at a sintering temperature for 2 hours with 5 min/ºC heating and cooling rates. The firing profile includes a 1-hour dwell time at 500ºC for binder burn-out process to complete. For optimization purpose, the sintering temperature is varied between 1000ºC and 1300ºC depending upon the compositions. The ceramics are characterized thoroughly with the same techniques described in an earlier publication (Yimnirun *et al*., 2003).

The dielectric properties of the sintered ceramics are studied as functions of both temperature and frequency with an automated dielectric measurement system. The computer-controlled dielectric measurement system consists of an LCR-meter (Hewlett-Packard Precision LCR-Meter HP 4284A), a temperature chamber (Delta Design 9023), and a computer system. The detailed description of this system is explained elsewhere (Jiang, 1992). For dielectric property characterizations, the sintered samples are lapped to obtain parallel faces, and the faces are then coated with silver paint as electrodes. The samples are heat-treated at 750ºC for 12 min to ensure the contact between the electrodes and the ceramic surfaces. The capacitance and the dielectric loss tangent are determined over the temperature of -150 and 400ºC with the frequency ranging from 100 Hz to 1 MHz. The measurements are carried out on cooling continuously. Before each cooling run, the samples are first heated up to 400ºC and then cooling run is performed at the rate of 3ºC/min.

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

Ceramic	Density (g/cm^3)	Grain Size Range (μm)	Average Grain Size (μm)
PZT	7.59±0.11	2-7	5.23
0.1PMN - 0.9PZT	6.09±0.11	0.5-2	0.80
0.3PMN - 0.7PZT	7.45±0.10	0.5-3	1.65
0.5PMN - 0.5PZT	7.86±0.05	0.5-5	1.90
0.7PMN - 0.3PZT	7.87±0.07	1-4	1.40
0.9PMN - 0.1PZT	7.90±0.09	1-4	1.50
PMN	7.82±0.06	2-4	3.25

The dielectric constant is then calculated from $\varepsilon_r = Cd / \varepsilon_0 A$, where C is the capacitance of the sample, d and A are the thickness and the area of the electrode, respectively, and ε_0 is the dielectric permittivity of vacuum (8.854×10^{-12} F/m).

Results and Discussion

The experimental results on physical properties, the phase formation behavior, and microstructure features of all the sintered ceramics are presented and discussed thoroughly elsewhere (Yimnirun *et al.*, 2003). Hence, these results will not be shown here. However, it should be stated here that the sintered ceramics are 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 and averaged grain-size for all ceramic compositions.

The dielectric properties, e.g. dielectric constant (ε_r) and tan δ, are measured as functions of both temperature and frequency, as shown in Figure 1 (a-d). The dielectric properties of PZT ceramic, as plotted in Figure 1 (a), change significantly with temperature, but are nearly independent of frequency, except in the vicinity of the phase transformation temperature. This is a typical characteristic of ferroelectric ceramics with a long-range ordered structure (Koval *et al.*, 2003). The Curie temperature (T_C) for PZT ceramic is not determinable in this study as a result of limited range of the measuring set-up, though is widely known to be close to 400ºC (Las *et al.*, 2001). While PZT exhibits a normal ferroelectric behavior, PMN is a well-known relaxor ferroelectric material as a result of a short-range ordered structure with a nanometer scale heterogeneity in composition (Koval *et al.*, 2003). In typical relaxor ferroelectrics, both dielectric constant (ε_r) and dielectric loss tangent (tan δ) exhibit strong temperature-frequency dependence below the transition temperature, as shown in Figure 1 (d) for PMN ceramic. In this case, the temperatures of maximum dielectric constant and dielectric loss tangent are shifted to higher temperature with increasing frequency. The maximum value of the dielectric constant decreases with increasing frequency, while that of the dielectric loss tangent increases. The dielectric properties become independent of frequency above the transition temperature (Koval *et al.*, 2003). When PMN is added to form the binary system with PZT, the dielectric behavior is shifted towards the relaxor behavior, in which the dielectric properties vary significantly with frequency below the phase transition temperature. The results shown in Figure 1 (a-d) clearly indicate such a trend. However, with smaller amount of PMN added, such as in 0.9PZT-0.1PMN and 0.7PZT-0.3PMN ceramics, the dielectric properties exhibit a mixture of both normal and relaxor characteristics, for instance as shown in Figure 1 (b) in which the transition temperature is not shifted as much as for other

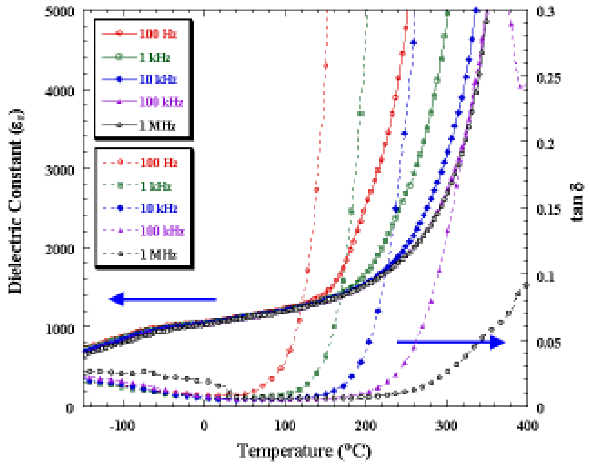

Figure 1. **(a) Temperature and frequency dependences of dielectric properties of PZT ceramic. (dotted lines indicate data for the dielectric loss tangent (tan δ) at the same frequency)**

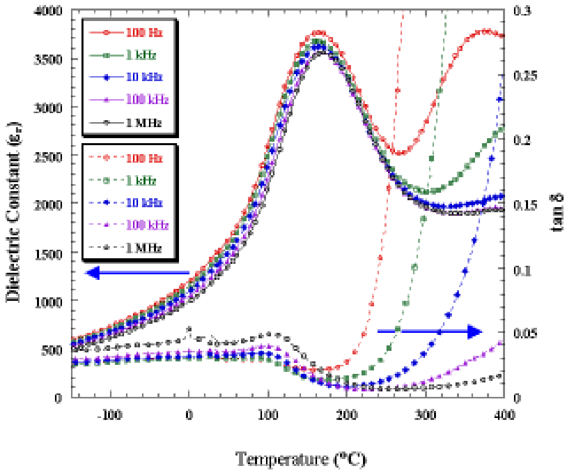

Figure 1. **(b) Temperature and frequency dependences of dielectric properties of 0.7PZT - 0.3PMN ceramic. (dotted lines indicate data for the dielectric loss tangent (tan δ) at the same frequency)**

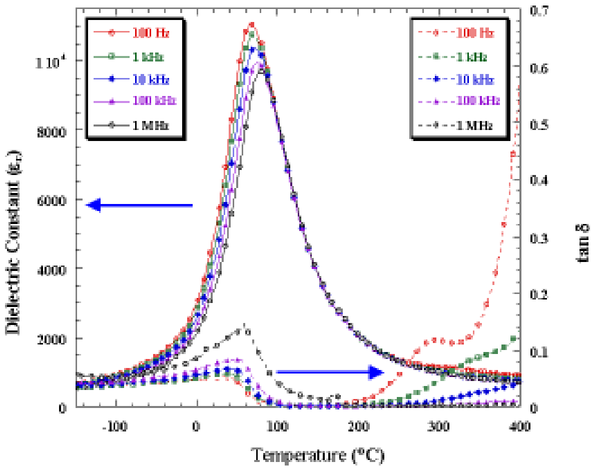

Figure 1. **(c) Temperature and frequency dependences of dielectric properties of 0.3PZT - 0.7PMN ceramic. (dotted lines indicate data for the dielectric loss tangent (tan δ) at the same frequency)**

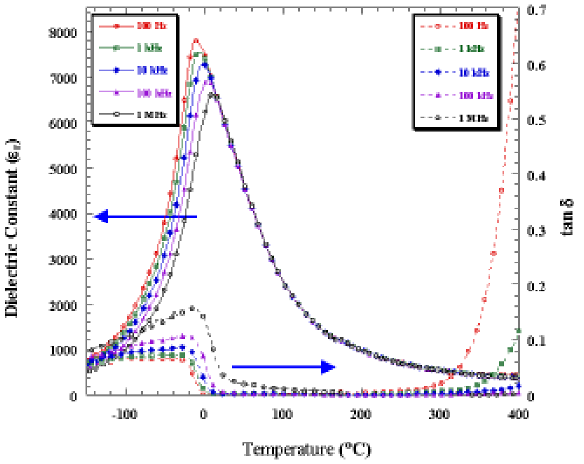

Figure 1. **(d) Temperature and frequency dependences of dielectric properties of PMN ceramic. (dotted lines indicate data for the dielectric loss tangent (tan δ) at the same frequency)**

predominantly relaxor-like ceramics. 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.

More importantly, as shown in Table 2 since the transition temperature of PMN is very low (-8ºC at 1 kHz) and its maximum dielectric constant is very high (~7600 at 1 kHz), it is also expected to observe that the transition temperature

Table 2. Curie temperature and dielectric properties of PZT-PMN ceramics (1 kHz).

Ceramic	T_C (ºC)	Maximum Properties		Room Temp. Properties	
		ε_r	tan δ	ε_r	tan δ
PZT	*	> 29000	0.010	1100	0.006
0.1PMN - 0.9PZT	*	~ 3700	0.020	700	0.020
0.3PMN - 0.7PZT	160	3800	0.030	1400	0.030
0.5PMN - 0.5PZT	115	6600	0.045	2200	0.040
0.7PMN - 0.3PZT	71	11000	0.057	5600	0.057
0.9PMN - 0.1PZT	16	10700	0.077	10300	0.001
PMN	-8	7600	0.073	6000	0.001

*** Not determinable as a result of measuring set-up.**

decreases and the maximum dielectric constant increases with increasing amount of PMN in the system. This is clearly evident in Figure 2. Figure 3 shows that the transition temperature (at 1 kHz for this case) moves towards lower temperature almost linearly with the average rate of ~ -2.4ºC/mol% as the molar fraction of PMN in the composition increases. However, it is noted that this relationship does not cover the compositions 0.9 PZT - 0.1PMN and pure-phase PZT, which are expected to have the transition temperature near 400ºC, shown in Figure 3 as open circles. The reason is not clearly known, but could be attributed to the pseudo-binary nature of this system, as described in the earlier publication (Yimnirun *et al.*, 2003), in which PZT and PMN do not form a solid solution, but rather a composite. Figure 4 shows an example of SEM micrographs demonstrating separated PZT (large) and PMN (small) grains. In this case, depending upon the composition, the properties of PZT or those of PMN strongly control the properties of the system.

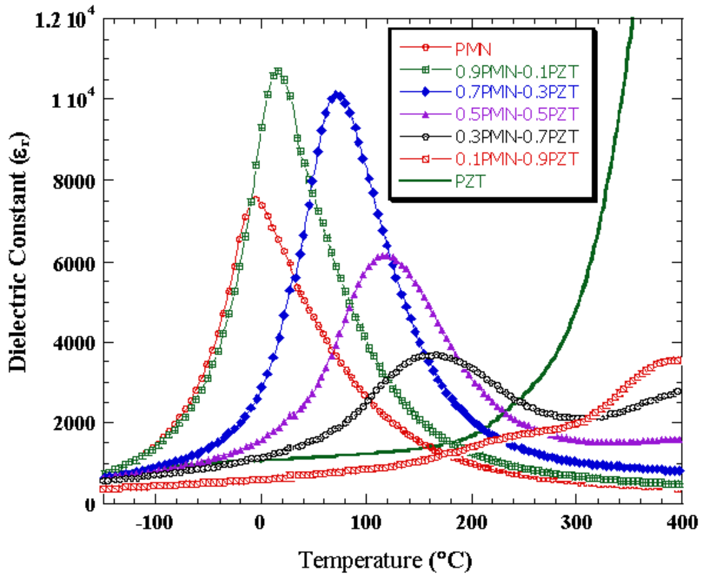

Figure 2. Temperature dependence of dielectric constant of xPZT-(1-x)PMN ceramics. (measured at 1 kHz)

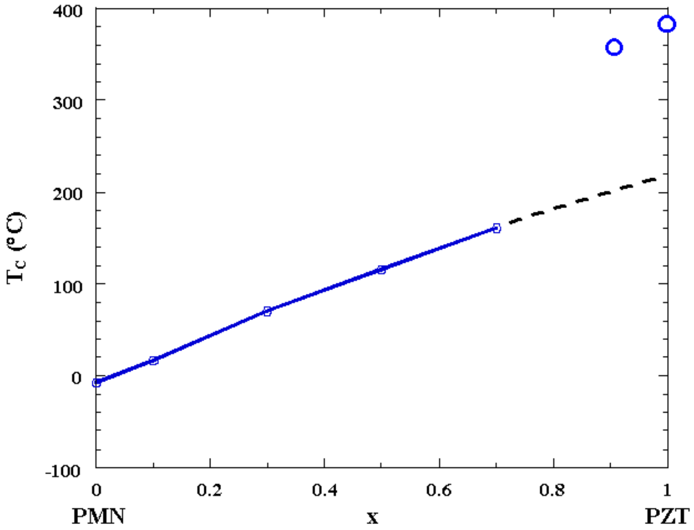

Figure 3. Curie temperature of xPZT - (1-x)PMN ceramics (measured at 1 kHz) (Data for PZT and 0.1PMN - 0.9PZT (open circles) are estimated from references by Las *et al.* (2001) and Koval *et al.* (2003), respectively)

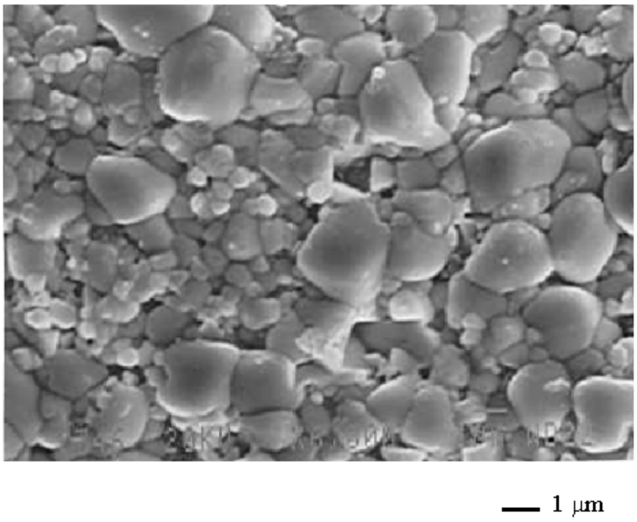

Figure 4. SEM micrograph of 0.5PZT - 0.5PMN ceramic.

However, it should still be noted that the reasons for such behavior require further investigation.

Conclusion

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 are prepared from PZT and PMN powders by a mixed-oxide method. The dielectric properties of the ceramics are determined as functions of both temperature and frequency with an automated dielectric measurement system. The measurement takes place over the temperature range of -150ºC and 400ºC with measuring frequency between 100 Hz and 1 MHz. The results indicate that the dielectric properties of the pure phase PZT and PMN follow that of normal and relaxor ferroelectric behaviors, respectively. The dielectric behaviors of the 0.9PZT - 0.1PMN and 0.7PZT - 0.3PMN ceramics are more those of normal ferroelectrics, while the other compositions are obviously those of relaxor ferroelectrics. It is also observed that the transition temperature decreases and the maximum dielectric constant increases with increasing amount of PMN in the system. Most importantly, this study shows that the dielectric properties of the PZT-PMN ceramics are not linearly dependent of the amount of the end members over the whole compositional range of PZT-PMN as a result of the composite nature of the materials.

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