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Composites of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ prepared by a sol-gel method: effect of atmosphere powders

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Dielectric and electrical properties of relaxor ferroelectric 0.9PMN-0.1PT ceramics prepared by a sol-gel method were investigated as a function of $PbZrO_3$ atmosphere powders. The proper amount of atmosphere powders led to better properties of dielectric constant, polarization, and strain by preventing PbO volatilization from ceramics. Excessive amount of atmosphere powder, however, resulted in aging characteristics such as decreases in dielectric constant and loss exhibiting saddle-shaped dielectric constant and loss vs. temperature curves. A propeller-shaped P-E hysteresis curve indicating aging characteristics was also observed when an excessive amount of atmosphere powder was used during sintering. The aging of ceramics caused by absorption of PbO into the ceramics resulted in decreased polarization and strain. These aging characteristics associated with defects by excessive PbO absorption could not be reversed even though the aged ceramics underwent a heat-treatment above the dielectric maximum temperature.

1. Introduction

Relaxor ferroelectric ceramics such as lead magnesium niobate (PMN)-based materials have been widely studied for electrostrictive applications including ultra-precise position actuators and non-linear optical devices because the assets of PMN are a high dielectric constant and a relatively large strain [1–4]. Especially, Relaxors based on the PMN-$PbTiO_3$ (PT) ceramics exhibit excellent dielectric and piezoelectric/electrostrictive properties along with various compositional modifications [5].

The properties of Pb-based materials mainly depend on the method of preparation and processing conditions. The main problem in making pure PMN ceramics having only a perovskite structure is the formation of pyrochlore phases such as $Pb_3Nb_4O_{13}$, $Pb_2Nb_2O_7$ and $Pb_5Nb_4O_{15}$ because of the volatilization of PbO and the differences of the reactive temperature between Pb-Nb and Pb-Mg [6, 7]. In order to overcome these problems, new preparation and process methods such as columbite method [8] and molten salt synthesis [9] have been developed. An alternative method is a sol-gel processing technique [10] which leads to almost pure perovskite phase at low temperature with an improvement in the properties of PMN ceramics. An additional advantage of this processing is that it leads to fine particles which in turn lead to relatively high density of ceramics. We have already shown the superiority of the sol-gel processing which used a PMN core enclosed by a PZT shell (solution + powder processing) [11]. This method provided fine particles and a higher dielectric constant compared to those of conventional powder processing.

A limitation to the utilization of PMN in device application has been the lack of a simple, reproducible fabrication technique for ceramic PMN. Previous studies have been primarily concerned with processing characteristics and dielectric properties of the solid solution in which it has been demonstrated that both the starting materials and sintering conditions greatly influenced the densification process and dielectric properties of the resulting ceramics. Guha *et al.* [12] reported that the optimum conditions for obtaining PMN-PT ceramics with high densities and improved dielectric properties were a nominal addition of 1 wt % excess PbO which contributed to a homogenous distribution of PbO, and saturation with PbO throughout the grains. In contrast, the decrease of the dielectric constant by excess PbO is attributed to an increase of the PbO layer in the grain boundaries [13]. Moreover, the control of PbO stoichiometry during sintering is also important because the high volatility of PbO degrades the densification and dielectric properties of ceramics. To prevent PbO volatilization, Pb-based ceramics are usually fired with atmosphere powders of same composition or $PbZrO_3$ (PZ) in a closed alumina crucible. The effect of excess PbO on the structural and dielectric properties of PMN-based materials has been widely explored [13, 14]. However, effect of atmosphere powders have been rarely reported but Katayama *et al.* [9] investigated the variation of the phases and densities according to PZ + PbO atmosphere powders.

The objective of this paper was to explore the effect of PZ atmosphere powders on the 0.9PMN-0.1PT ceramics prepared by a composite sol-gel processing route. Dielectric and electrical properties have been measured and discussed with respect to the amount of atmosphere powders.

2. Experimental

The fabrication procedures of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ composite ceramics prepared by a sol-gel processing were reported elsewhere [11]. PMN and PT solutions were first prepared using a sol-gel processing and then PT powders were prepared by hydrolyzing, drying, and calcining from the solutions. In order to make PMN-PT composites PT powders were added to PMN solution, which consisted of a PT core enclosed by a PMN shell. The solution and powder mixture was dried at 150 °C for 48 h and then calcined at 850 °C for 2 h. The calcined powders were uniaxially pressed to form pellets of 6.35 mm diameter and 1 mm thickness in a steel die at 10 MPa and then cold isostatically pressed at 280 MPa. PMN-PT ceramics were fabricated at 1200 °C for 4 h in a closed alumina crucible whose volume was $\sim$102 cm^3. Various amounts of $PbZrO_3$ powders in the range of 0 to 5 g were added to help control Pb stoichiometry in the sample.

Phase identification of powders was performed by a Scintag X-ray diffractometer with CuK_α radiation (Model DMC 105, USA) to check for phase purity. No second phase pyrochlore, within the detection limits of the X-ray diffractometer, was observed. Morphological investigation of the particles and the fractured surface was performed with a scanning electron microscope (Model ISI-DS 130, Akashi Beam Technology Corporation, Japan). Dielectric properties of the specimens were measured semi-continuously at various frequencies in the temperature range of 150 to −50 °C at cooling or heating rates of 2 °C/min during a temperature programmed sequence using an LCR meter (HP 4274A, USA) controlled by a computerized automatic measuring system.

For electrical characterization, samples were prepared by polishing with silicon carbide and alumina polishing powders to achieve flat and parallel surfaces onto which gold electrodes were sputtered. High-field measurements included polarization and strain hysteresis using a modified Sawyer-Tower circuit and a linear variable displacement transducer (LVDT) driven by a lock-in amplifier (Stanford Research Systems, Model SR830). During testing, the samples were submerged in Fluorinert (FC-40, 3M, St. Paul, MN), an insulating liquid, to prevent arcing.

3. Results and discussion

3.1. Dielectric properties

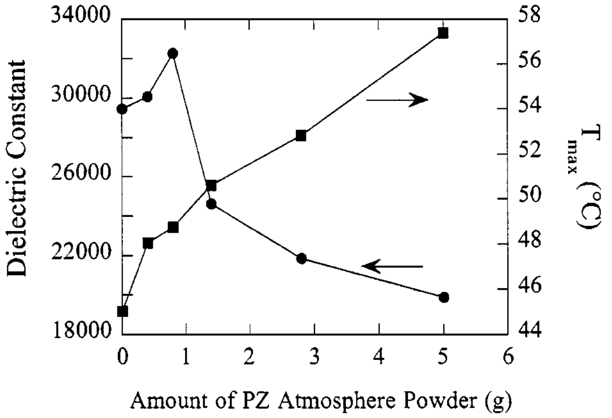

Figure 1 Dielectric constant and dielectric maximum temperature (T_{max}) at 1 kHz for 0.9PMN-0.1PT ceramics as a function of $PbZrO_3$ atmosphere powder.

Fig. 1 presents dielectric constant at dielectric maximum temperature (T_{max}) and variation of T_{max} as a function of PZ atmosphere powder. A maximum dielectric constant of 32,200, not achievable with a conventional powder processing, was observed for the sample with 0.8 g PZ powder and then the dielectric constant abruptly decreased with further increase in PZ amount. The higher dielectric constants are due to the composite sol-gel processing which leads to fine particle size and subsequently higher densification as previously reported [11]. The values of the dielectric constant for the samples containing PZ $\geq$ 2.8 g decreased as much as 10,000 compared to those for the samples with PZ $\leq$ 0.8 g. An excessive amount of PbO from atmosphere powder might penetrate into samples during sintering. The T_{max} continuously increased with increasing PZ powder. The excessive atmosphere powders led to excessive absorption of PbO evidently into the samples as revealed from weight gain after sintering as shown in Fig. 2. The fact that the dielectric constant decreased for the samples containing excessive PbO is in good agreement with Wang's result [13], even though addition methods of PbO are different. The excess PbO addition resulted in the decrease of the dielectric constants due to an increase of PbO layer apparently in the grain boundaries [13]. Since both sides of the measured samples were gound using silicon carbide powders, the absorbed PbO did not exist only near the surface. Observation of the surface and fracture surface, however, revealed no significant second phases.

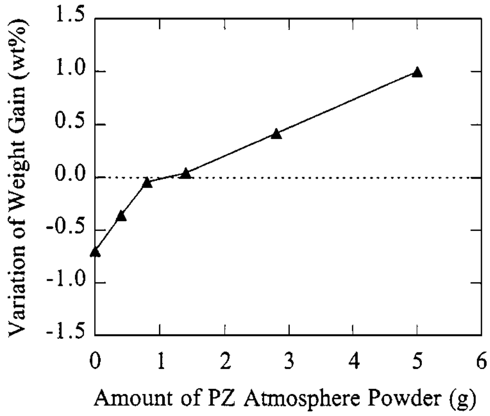

Figure 2 Variation of weight gain for 0.9PMN-0.1PT ceramics as a function of $PbZrO_3$ atmosphere powder.

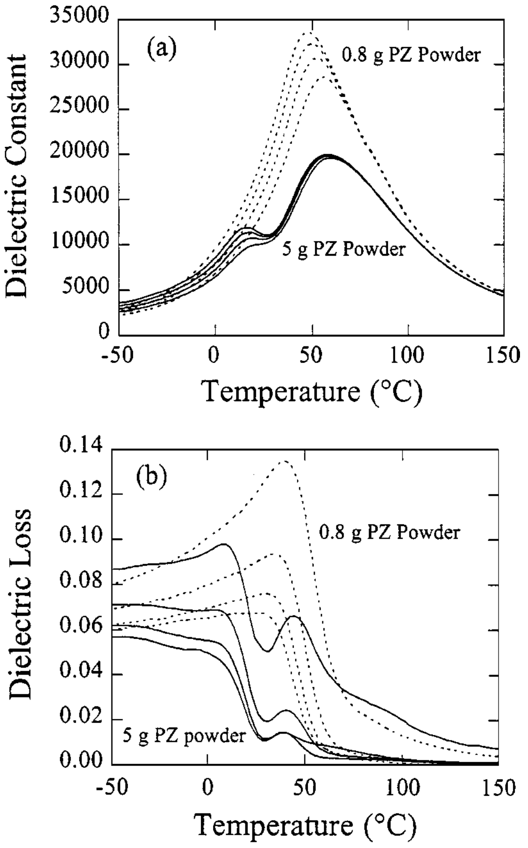

Figure 3 Temperature dependence of (a) dielectric constant and (b) loss at various frequencies for 0.9PMN-0.1PT ceramics sintered with 0.8 and 5 g $PbZrO_3$ atmosphere powders. The measurement frequencies from the top to the bottom curves for (a) are 0.1, 1, 10, and 100 kHz and for (b) 100, 10, 1, and 0.1 kHz.

Dielectric constant and loss vs. temperature curves at various frequencies for the samples with 0.8 and 5 g of PZ powder are shown in Fig. 3. Saddle-shaped depressions in the dielectric constant (Fig. 3a) were observed for the samples with 5 g PZ powder. The characteristics saddle in dielectric constant reflects the reduction of the dielectric constant as a result of aging [15, 16] caused by the excessive PbO absorption. The aging rate of dielectric constant is strongly frequency dependent, especially at lower frequencies. The aging of the dielectric loss (Fig. 3b) is further distorted than of dielectric constant with similar frequency dependence. The aging rates of dielectric properties caused by the excessive PbO absorption are much greater than that by isothermal aging associated with time [16]. The aging associated with time and temperature can be partially reversed by external stimulus of electric, mechanical or thermal energy and completely by heating above the dielectric maximum temperature in paraelectric phase. However, the aging effects in samples of this study can not be reversed because defects occurred by excessive PbO absorption which resulted in the aging characteristics. The effects of PZ atmosphere powder on the dielectric properties are illustrated in Fig. 4 by comparing the dielectric constants at a frequency of 1 kHz. The dielectric constant and loss of the samples with PZ $\geq$ 1.4 g dramatically decreased due to an increase in PbO layer, being a much lower dielectric layer. Dielectric loss maxima could not be determined for the aged samples.

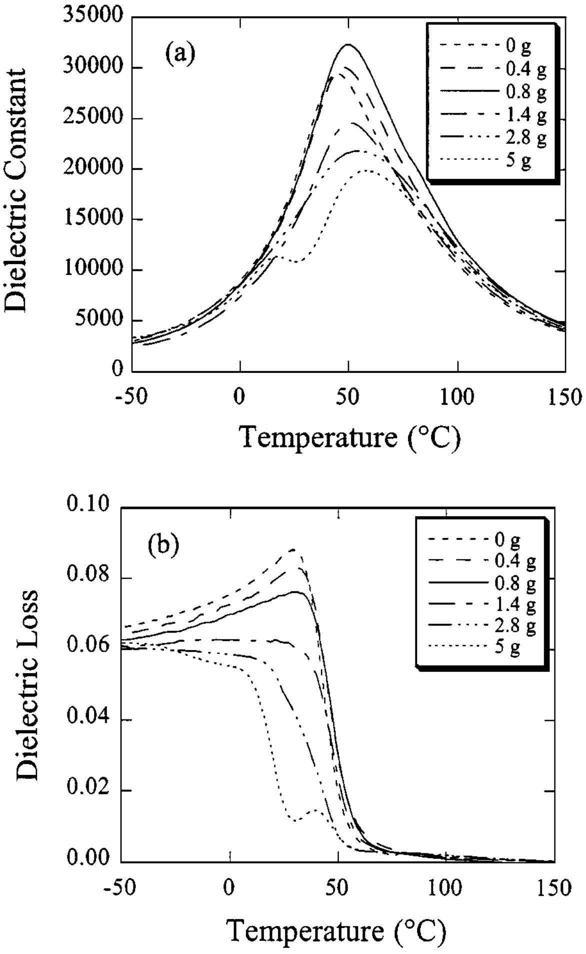

Figure 4 Temperature dependence of (a) dielectric constant and (b) loss at 1 kHz for 0.9PMN-0.1PT ceramics as a function of $PbZrO_3$ atmosphere powder.

From the above results, it is obvious that a proper amount of atmosphere powder improves the dielectric properties by controlling the volatilization of PbO. However, as the excessive PbO absorption prevents the condensation of long range order characteristic of the ferroelectric phase [17], it is natural that the dielectric properties decrease also. The distorted state may contribute more strongly to the low frequency dielectric constant. These aging characteristics were mainly observed in generating cation vacancies as higher valence cations substituted for lower valence cations, i.e., La^{3+} substituted for Pb^{2+} in PLZT system [18]. In the case of this study, even though same valence substituent was added, the aging behavior was observed. The use of excessive amount of atmosphere powder also results in defects by the absorbed PbO into the samples analogous to the doping effect.

3.2. Hysteresis and strain behavior

Electrical properties of 0.9PMN-0.1PT ceramics including polarization and strain behaviors under high fields were investigated as a function of PZ atmosphere powder. P-E hysteresis behaviors for the samples with various amounts of PZ powders are shown in Fig. 5. The hysteresis curves for the samples with PZ $\geq$ 2.8 g were distorted into propeller shapes and the remanent

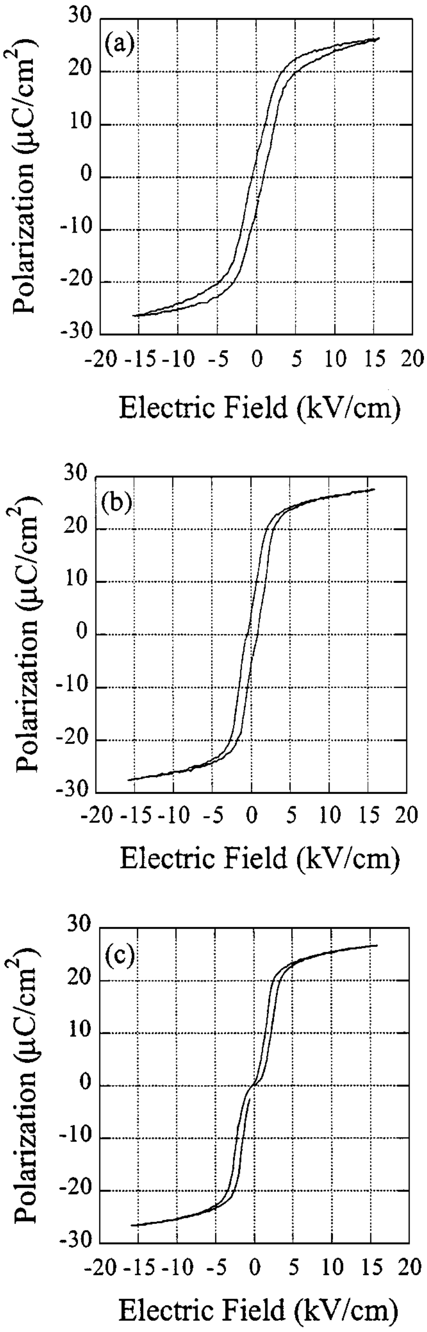

Figure 5 Polarization vs. Electric field curves at room temperature for 0.9PMN-0.1PT ceramics sintered with (a) 0 g, (b) 0.8 g and (c) 5 g of $PbZrO_3$ atmosphere powders.

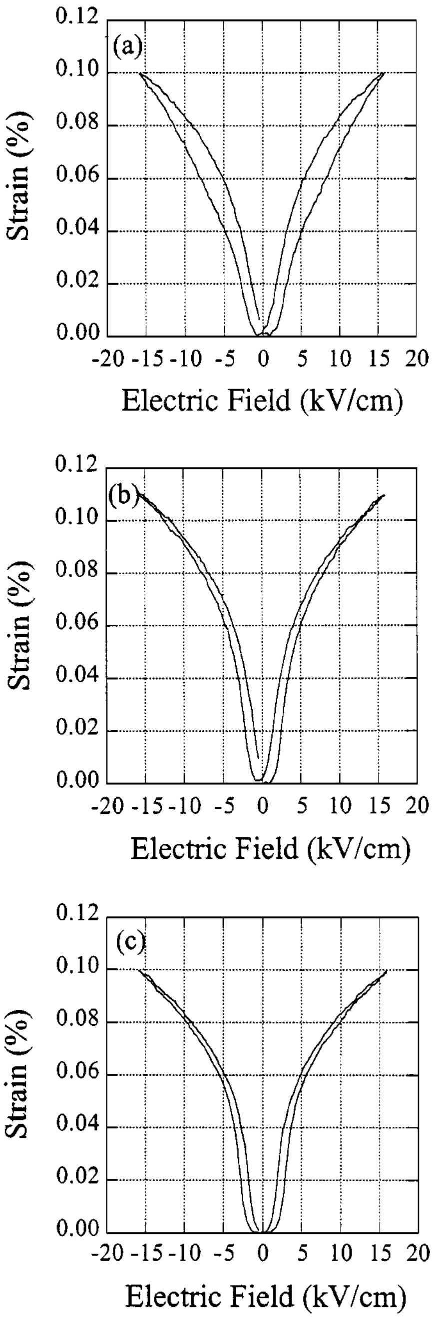

Figure 6 Strain vs. Electric field curves at room temperature for 0.9PMN-0.1PT ceramics sintered with (a) 0 g, (b) 0.8 g and (c) 5 g of $PbZrO_3$ atmosphere powders.

polarization appeared to drop to approximately zero at room temperature. The saturated polarization of the aged sample by 5 g PZ powder decreased as much as 5% compared to that of the unaged sample sintered with 0.8 g PZ powder. Although the values of the saturated polarization were not severely changed when compared to the results of the dielectric constants, the propeller shaped hysteresis curve leads to reduction of polarization while a maximum polarization is achieved for the sample with 0.8 g PZ powder.

Strain vs. electric field behavior corresponds to the hysteresis behavior as shown in Fig. 6. However, the shapes of the strain vs. electric field curves did not change as shown in hysteresis curves while the strain levels decreased with increasing amounts of PZ powders. The strain level decreased as much as 12%, at a greater rate than that of polarization. The hysteresis as shown in Figs 5 and 6 decreased with increasing amounts of PZ powders due to restraint of nucleation of space charge layer by preventing PbO volatilization [19].

Fig. 7 summarizes polarization and strain relations as a function of the amounts of PZ powder used for atmosphere control. The excessive PbO highly affects strain level compared to polarization because strain is proportional to the square of the polarization in electrostrictive materials. The distorted and decreased polarization and the decreased strain behavior are attributed to the aging, generated by defects due to the excessive PbO absorption as previously described. The aging of electrical properties at high fields can be assumed by stability of the domain structure as previously reported by Schulze

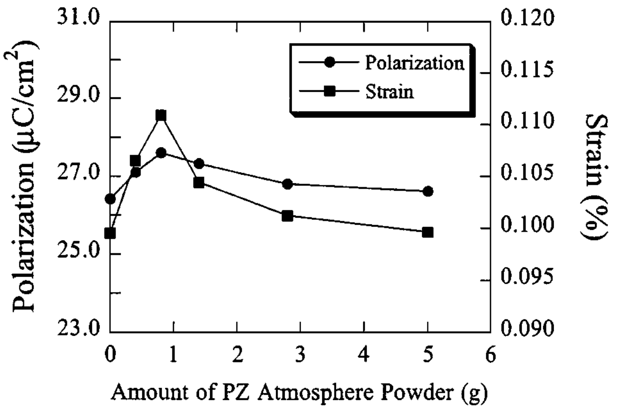

Figure 7 Polarization and strain at 15 kV/cm and room temperature for 0.9PMN-0.1PT ceramic as a function of $PbZrO_3$ atmosphere powder.

[15]. The stabilization of domain configurations (micro polar region) is considered to be due to defects. The aging behavior resulted from defects, readjusting their orientation so as to lower the energy and stabilizing the domain state [20]. Among the several mechanisms of the domain stability, the possible explanation for the results of this study may be that the accumulated charge and ordering of defects caused by the excessive PbO absorption exist to compensate flux discontinuities at grain boundaries. The difficulty of this study was that the exact amount of the absorbed PbO could not be determined quantitatively because atmosphere powders penetrated into both the samples and alumina crucible. Further detailed analysis including FESEM or TEM will be required in order to directly observe existence and behavior of the excessive PbO in the ceramics.

4. Conclusion

An optimum amount of atmosphere controlling powder led to increased dielectric properties and polarization and strain behaviors by preventing PbO volatilization. However, the peak dielectric constant of 0.9PMN-0.1PT ceramics sintered with excessive amounts of atmosphere powder dramatically decreased by as much as ~60% of the maximum dielectric constant obtained for the sample exposed to optimum atmosphere powder. This result may be due to defects associated with the excessive PbO absorption. The excessive PbO gain resulted in property degradation indicating aging behavior, i.e., a lower and saddle-shaped dielectric constant and a propeller-shaped hysteresis curve. The polarization and strain level also decreased by as much as 5% and 12%, respectively, with increasing amounts of atmosphere powder. Therefore, the control of atmosphere powder is also another important parameter to achieve reproducible ceramics.

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