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Piezoelectric properties in PMN–PT relaxor ferroelectrics with MnO_2 addition

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Abstract

The temperature dependence of piezoelectric properties in the PMN–PT relaxor ferroelectric system with MnO_2 addition was studied in the temperature range from −40 to 30°C. Samples were poled at −40°C and the piezoelectric properties were measured by resonance–antiresonance method. Q_m increased by increasing the doping contents of Mn. When 0.5 wt.% MnO_2 was doped, Q_m increased from 95 to 480. From the experimental results, it is predicted that Mn behaves as an acceptor and a domain pinning element. The effects of MnO_2 observed in PZT-based normal ferroelectrics were also confirmed in PMN-based relaxor ferroelectrics.

Keywords: Functional applications; Impurities; Perovskite; Piezoelectric properties; Sintering

1. Introduction

Relaxor ferroelectric materials, which may be distinguished from normal ferroelectrics by diffuse phase transition and strong frequency dependence of the dielectric properties, have been extensively studied.[1–6] The ferroelectric–paraelectric transition and all the related properties in these systems are characterized not by abrupt changes, but rather by gradual diffuse changes which occur over a temperature range which is often referred to as permittivity maximum temperature. Among many electrostrictive materials, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN)-based materials have received special attention because of their better dielectric and electrostrictive properties.[7–10]

In the temperature range below the T_m, relaxors exhibit ferroelectric and piezoelectric properties. There are many reports devoted to the dielectric, pyroelectric, electrostrictive properties in PMN.[11–13] However, there is few report on the piezoelectric properties of PMN in the temperature range below the T_m. Although, the PMN -based relaxor materials are generally used for high permittivity dielectric materials and electrostrictive materials, it is necessary to study the piezoelectric properties in the phase transition temperature range to comprehend the ferroelectric–paraelectric transition and all the related properties in these systems.

In this study, the effect of Mn addition on the piezoelectric properties of PMN relaxors will be studied. Mn was selected as a dopant because the studies of Mn addition on PZT-based normal ferroelectric materials are most frequently found in the literature. In PZT systems, both the planar coupling coefficient (K_p) and Q_m increased with Mn addition. In PZT-based normal ferroelectrics, Mn was reported to behave as an acceptor and domain pinning element.[14,15]

Among the many compositions of PMN-based relaxor ferroelectrics, $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ (0.9 PMN–0.1 PT) was the most studied system because of its large dielectric constant and electrostriction. This composition is used for the present study.

2. Experimental

Powders were prepared from the oxide forms of Pb, Mg, Nb, and Ti via a columbite precursor method. The details of sample preparation are described elsewhere.[4,11] Dielectric constants were measured at 100 Hz, 1 kHz, 10 kHz, and 100 kHz with an LF impedance analyzer

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(4192A, Yokogawa-Hewlett-Packard, Tokyo, Japan). The oscillating level was 1.1 volt.

To measure the piezoelectric properties, samples were poled at −40°C under the electric field of 1.5 kV/mm. Piezoelectric properties were determined from the impedance spectrum with LF impedance analyzer via resonance-antiresonance method.[16] The temperature of measurement was controlled in the range of −40–120°C using test chamber.

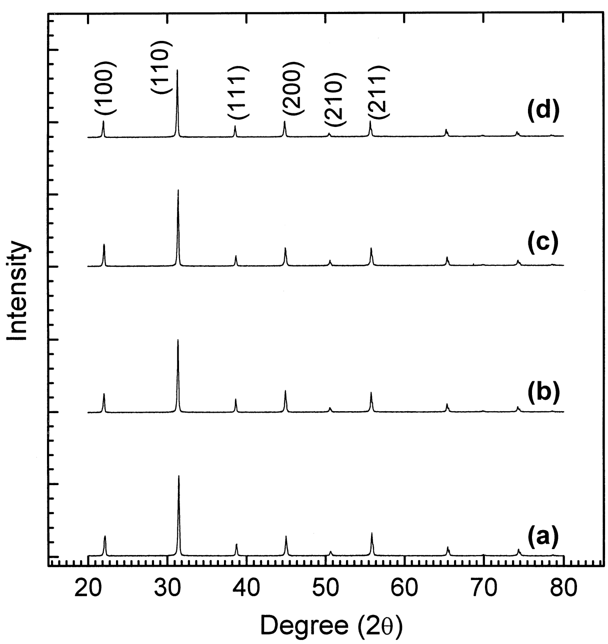

Fig. 1. XRD patterns for 0.9 PMN–0.1 PT with MnO_2 addition.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the sintered specimen. In all the specimen, pyrochlore phases and second phases due to the addition of MnO_2 are not found. Fig. 2 shows the scanning electron micrographs of the samples. The grain size increased with 0.1 wt.% MnO_2 addition. However, the grain size decreased little with the MnO_2 addition above 0.5 wt.%. From the above results, it seems that there were no significant modifications in microstructure and crystallographic phase with the MnO_2 addition in 0.9PMN–0.1PT.

Fig. 3 shows the temperature dependence of the low-field dielectric properties measured at 1 kHz in 0.9 PMN–0.1 PT. The maximum dielectric constant of 0.9 PMN–0.1 PT reaches up to 20,000, which was also reported elsewhere. The temperatures of maximum dielectric constants (T_m) vary with MnO_2 addition: they are ca. 38, 42, 60, and 65°C when the added amount of MnO_2 is 0, 0.1, 0.5, 1.0 wt.%. As the amount of MnO_2 increases, T_m increases and the maximum dielectric constant decreases.

Fig. 4 shows the temperature dependence of the impedance spectrum of the poled samples. At temperatures far below T_m, the spectrum exhibits a typical resonant spectrum. However, as the temperature increases up to the phase transition temperature, the span of resonant-antiresonant frequency becomes narrower and the magnitude of the resonance becomes smaller. This schematically shows that the magnitude of piezoelectricity becomes smaller as the temperature increases up to the phase transition range.

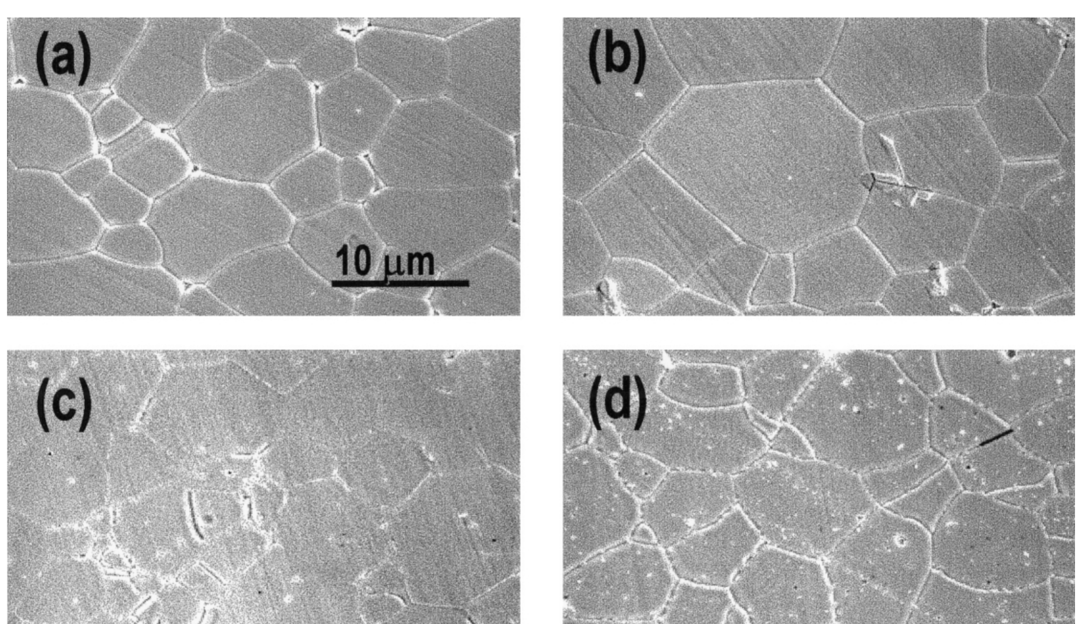

Fig. 2. SEM photographs of polished surface for 0.9 PMN–0.1 PT + x wt.% MnO_2, where (a) $x=0$, (b) $x=0.1$, (c) $x=0.5$, (d) $x=1$.

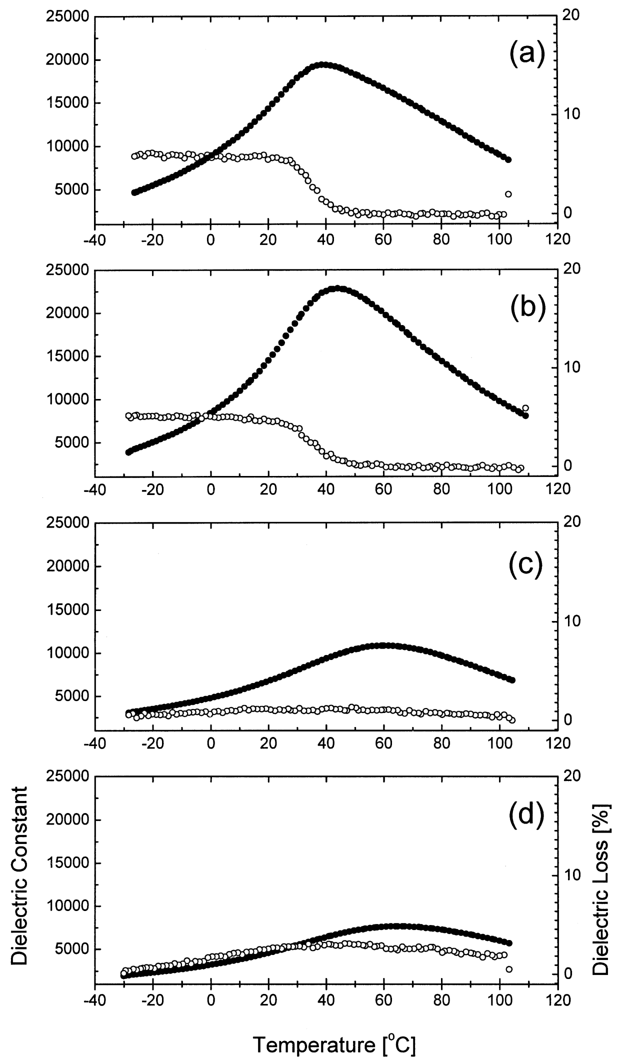

Fig. 3. Temperature dependence of dielectric properties for 0.9 PMN–0.1 PT + x wt.% MnO_2, where (a) $x=0$, (b) $x=0.1$, (c) $x=0.5$, (d) $x=1$.

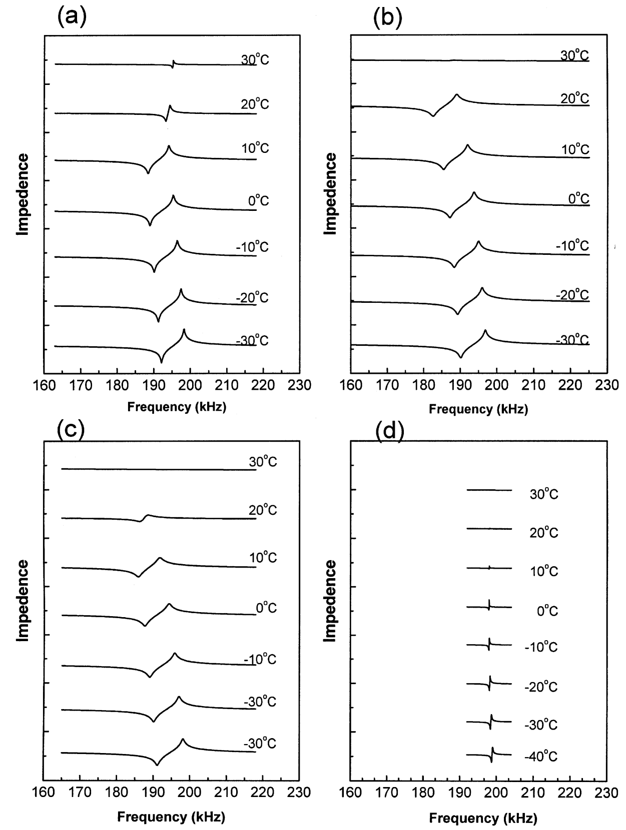

Fig. 4. Frequency dependence of impedance in the temperature range from −40 to 30°C.

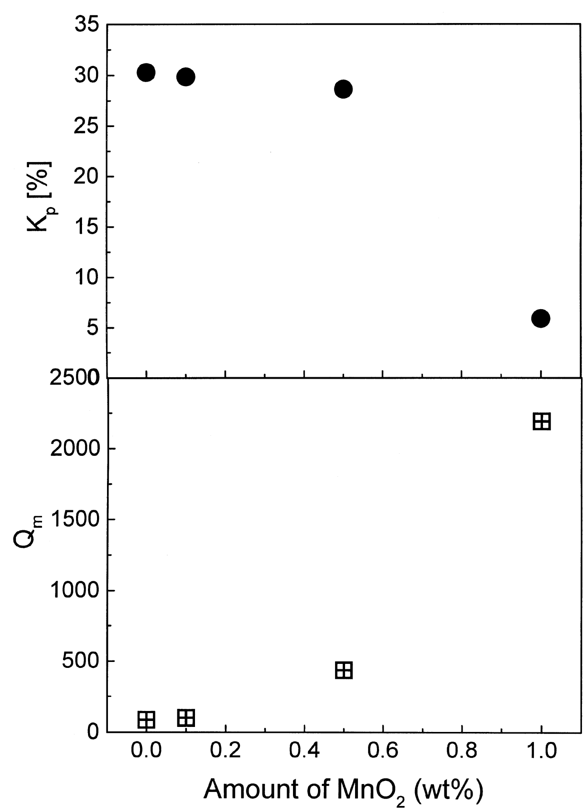

Fig. 5. Variation of K_p and Q_m of 0.9 PMN–0.1 PT ceramics as a function of MnO_2 concentration at −30°C.

As the added amount of MnO_2 increases, the electromechanical coupling factor of the samples decrease when compared at the same temperature. It is very notable that, even though T_m increases with amount of MnO_2 in Fig. 3, the electromechanical coupling factor in the temperature range between 10 and 30°C decrease as shown in Fig. 4. Considering the experimental results from Figs. 4 and 5, it is predicted that Mn behaves as an acceptor and a domain pinning element. In the previous reports in PZT-based normal ferroelectrics, Mn was also judged to behave as an acceptor and domain pinning element.[14,15] Fig. 5 summarizes the temperature dependence of the electromechanical coupling factor (K_p) and mechanical quality factor (Q_m) calculated from the impedance spectrum. K_p decreases significantly at temperatures far below T_m. Q_m increases significantly with MnO_2 addition.

4. Summary and conclusion

The temperature dependence of piezoelectric properties in PMN–PT relaxor ferroelectric system with MnO_2 addition was studied in the temperature range from −40 to 30°C. Q_m increased by increasing the doping contents of Mn. When 0.5 wt.% MnO_2 was doped, Q_m increased from 95 to 480. Considering the experimental results, it is predicted that Mn behaves as an acceptor and a domain pinning element. The effects of MnO_2 observed in PZT-based normal ferroelectrics were also confirmed in PMN-based relaxor ferroelectrics.

References

1. Smolenskii, G. A. and Agranoviskaya, A. I., Dielectric polarization of a number of complex compounds. *Soviet Physics Solid State*, 1959, **1**, 1429–1437.
2. Uchino, K., Electrostrictive actuators: materials and applications. *Am. Ceram. Soc. Bull.*, 1986, **65**, 647–652.
3. Uchino, K., *Piezoelectric/Electrostrictive Actuators*. Morikita Press, Tokyo, 1986 pp. 1-40..
4. Park, J. H., Kim, B. K. and Park, S. J., Electrostrictive coefficients of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ relaxor ferroelectric ceramics in the ferroelectricity-dominated temperature range. *J. Am. Ceram. Soc.*, 1996, **79**, 430–434.
5. Cross, L. E., Relaxor ferroelectrics. *Ferroelectrics*, 1987, **76**, 241–267.
6. Nomura, S. and Uchino, V., Electrostrictive effect in $Pb(Mg_{1/3}Nb_{2/3})O_3$ type materials. *Ferroelectrics*, 1982, **41**, 117–132.
7. Bouquin, O., Formation of the perovskite phase in the $Pb[Mg_{1/3}Nb_{2/3}]O_3$–$PbTiO_3$ system. *J. Am. Ceram. Soc.*, 1991, **74**, 1152–1156.
8. Ho, J. C., Liu, K. S. and Lin, I. N., Study of ferroelectricity in the PMN-PT system near the morphotrophic phase boundary. *J. Mater. Sci.*, 1993, **28**, 4497–4502.
9. Zhang, Q., Pan, W., Bhalla, A. and Cross, L. E., Electrostrictive and dielectric response in lead magnesium niobate lead titanate [0.9PMN–0.1PT] and lead lanthanum zirconate titanate [PLZT 9.5/65/35] under variation of temperature and electric-field. *J. Am. Ceram. Soc.*, 1989, **72**, 599–604.
10. Choi, S. W., Shrout, T. R., Jang, S. J. and Bhalla, A. S., Morphotrophic phase boundary in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ system. *Mater. Lett.*, 1989, **8**, 253–255.
11. Park, J. H., Kim, B. K., Song, K. H. and Park, S. J., Temperature dependence of the electric field induced strains in $Pb(Mg_{1/3}Nb_{2/3})O_3$-based relaxor ferroelectrics. *J. Ceram. Soc. Jpn.*, 1995, **103**, 16–19.
12. Park, J. H., Hong, K. S. and Park, S. J., Frequency dependence of the phase transition in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ relaxor ferroelectrics. *J. Appl. Phys.*, 1997, **81**, 2039–2041.
13. Swartz, S. L., Shrout, T. R., Shulze, W. A. and Cross, L. E., Dielectric properties of lead-mganesium niobate ceramics. *J. Am. Ceram. Soc.*, 1984, **67**, 311–314.
14. Kamiya, T., Susuki, T. and Tsurumi, T., Effects of manganese addition on piezoelectric properties of $Pb(Zr_{0.5}Ti_{0.5})O_3$. *Jpn. J. Appl. Phys.*, 1992, **31**, 3058–3060.
15. Park, J. H., Kim, B. K., Song, K. H. and Park, S. J., Piezoelectric properties of Nb_2O_5 doped and MnO_2–Nb_2O_5 co-doped $Pb(Zr_{0.53}Ti_{0.47})O_3$ ceramics. *J. Mater. Sci.: Materials in Electronics*, 1995, **6**, 97–101.
16. IRE standards on piezoelectric crystals: measurements of piezoelectric ceramics. *Proc. IRE*, 1962, 49, 1161–1170.