Dielectric and relaxation behaviors of (PbMg1/3Nb2/3O3)0.67(PbTiO3)0.33 single crystal

Authors: C.-S. Tu, V.H. Schmidt, H. Luo, and F.-C. Chao

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Dielectric and Relaxation Behaviors of $(PbMg_{1/3}Nb_{2/3}O_3)_{0.67}(PbTiO_3)_{0.33}$ Single Crystal

CHI-SHUN TU[a]*, V. H. SCHMIDT[b], H. LUO[c] and F.-C. CHAO[a]

[a]*Department of Physics, Fu-Jen University, Taipei, Taiwan 242, R.O.C.,* [b]*Department of Physics, Montana State University, Bozeman, MT 59717 and* [c]*Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, P.R. China*

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Dielectric permittivity along the [111] direction has been measured as a function of temperature for a relaxor ferroelectric single crystal $(PbMg_{1/3}Nb_{2/3}O_3)_{0.67}(PbTiO_3)_{0.33}$ (PMN-33%PT). A sharp ferroelectric phase transition was observed near 425 K and 429 K for cooling and heating processes, respectively. As temperature decreases, a diffuse phase transition (which begins near 330 K upon cooling) was detected. In addition, the nature of the thermal hysteresis for the dielectric permittivity confirms that these transitions (near 330 and 425 K upon cooling) are diffuse first-order and first-order, respectively. The frequency-dependent dielectric data $\varepsilon''_{111}(f,T)$ prove the existence of an electric dipolar relaxation process between 350 and 400 K. The activation energy, the Vogel-Fulcher temperature and attempt frequency corresponding to this relaxation process are also calculated.

Keywords: Dielectric permittivity; frequency dispersion; phase transition

INTRODUCTION

Relaxor ferroelectrics generally mean the complex ABO_3-type unit cell and are crystals in which unlike-valence cations belonging to a given site (A or B) are presented in the correct ratio for charge balance, but are situated randomly on these cation sites. These randomly different cation charges give rise to random fields. These random fields tend to make the phase transitions "diffuse" instead of sharp as in normal ferroelectrics.[1-12] The physical properties of relaxor ferroelectrics near transitions depend on the cation ordering degree. The ordering tendency depends on several things such as method of crystal growth, cation valence, thermal treatment, and aging effects.

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), is one of the most interesting relaxor ferroelectric (FE) materials. PMN has a disordered complex structure in which the Mg^{2+} and Nb^{5+} cations exhibit only short range order on the B-site. PMN undergoes a diffuse phase transition near 280 K and has cubic symmetry at room temperature with space group *Pm3m*, whereas below 200 K a small rhombohedral distortion (pseudo-cubic) was observed.[1-2] The $PbTiO_3$ has tetragonal symmetry with space group *P4mm* at room temperature and has a sharp FE phase transition taking place at T_c=760 K.[3]

The mixed system $(PbMg_{1/3}Nb_{2/3}O_3)_{1-x}(PbTiO_3)_x$ (PMN-*x*PT) naturally has a morphotropic phase boundary (MPB) [tetragonal$\leftrightarrow$rhombohedral], where huge dielectric and piezoelectric constants appear, as is similar to the case in the $PbZrO_3$-$PbTiO_3$ (PZT) system.[4-5] The piezoelectric constants and the electromechanical coupling factors so far reported for the PMN-*x*PT crystals are larger than those in the PZT family of ceramics.[4-6] Several papers have reported the large piezoelectric constants ($d_{33}>1500 \times 10^{-12}$ C/N) and electromechanical coupling parameters ($k_{33}>70$ %) of PMN-PT based crystals.[4-6] Single crystal growth of PMN-PT by the flux technique is also easier than for PZT which makes PMN-PT a promising material for high performance transducers. However, the understanding of dielectric anomalies near the MPB is still lacking. This motivated us to carry out dielectric measurements on PMN-33%PT.

EXPERIMENTAL PROCEDURE

The lead magnesium niobate-lead titanate single crystal PMN-~33%PT was grown by the high temperature flux solution method. The sample was cut perpendicular to the [111] direction and were coated with silver paste electrodes. The sample dimensions are $5 \times 5 \times 2$ mm^3. A *Wayne-Kerr Precision Analyzer Model PMA3260A* with four-lead connections was used for the frequency range 500 Hz-2.5 MHz. A *Janis Model CCS-450* closed cycle refrigerator was used with a *Lakeshore Model 340* temperature controller for temperature-dependent measurements. The heating rate was 1.5 K/min.

RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependences of both the real and imaginary parts (ε'_{111} and ε''_{111}) of the dielectric permittivity for the frequency range 10 kHz-1 MHz. The insets of Fig. 1 are enlargements of both ε'_{111} and ε''_{111} for temperatures below 410 K to clarify the dispersion behaviors. Compared with the relaxor ferroelectric crystal $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) which has a diffuse phase transition near 280 K, PMN-33%PT exhibits a narrower frequency dispersion and stronger dielectric maximum near 425 K (upon cooling) due to the PT content. For temperature below 400 K, a broad weaker dispersion anomaly appears in both ε'_{111} and ε''_{111}. Fig. 2 shows the temperature-dependent data of ε'_{111} from both cooling and heating runs at measuring frequency f=50 kHz. Two thermal hystereses were observed in the regions of ~300-350 K and ~380-430 K, respectively. The inset of Fig. 2 shows the reciprocal of ε'_{111} in which a typical first-order FE phase transition appears near 425 K and 429 K for cooling and heating processes, respectively.[13]

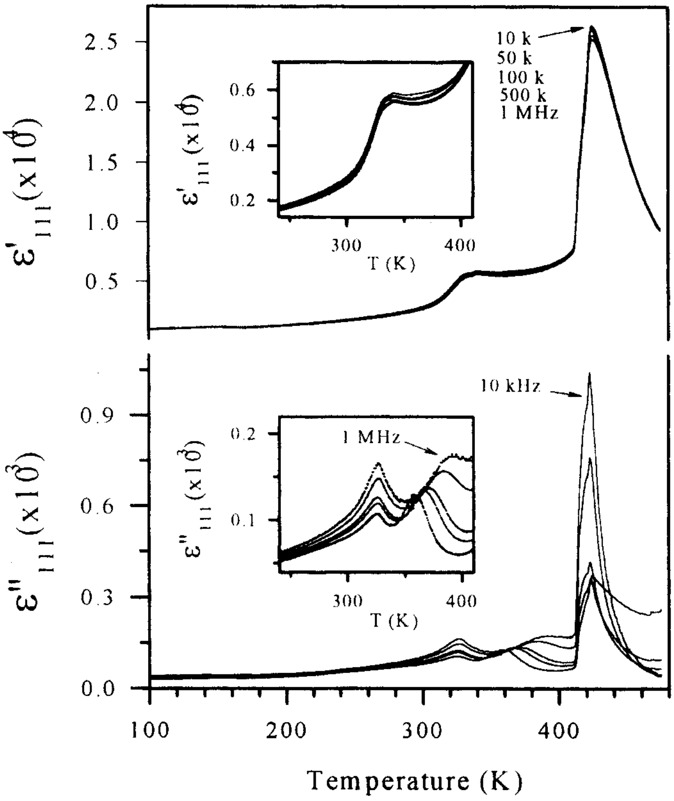

FIGURE 1 Temperature dependences of ε'_{111} and ε''_{111} for PMN-33%PT upon cooling. The insets are enlargements below 410 K.

What are the origins of the dielectric phenomena shown in Figs. 1-2 near 425 K? For a typical FE phase transition, the transition temperature occurs where the dielectric permittivity has an abrupt change.[13] In PMN-33%PT, the real part ε'_{111} (Fig. 1) exhibits a steep change and an obvious thermal hysteresis near 425 K (Fig. 2). Such an anomaly is usually attributed to a rapid growth of long-range electric ordering. Thus, the PMN-33%PT crystal possesses a sharp first-order FE phase transition near 425 K (upon cooling). This value is consistent with the temperature 430±5 K (cubic paraelectric ↔tetragonal FE) predicated from the MPB in Ref. 14.

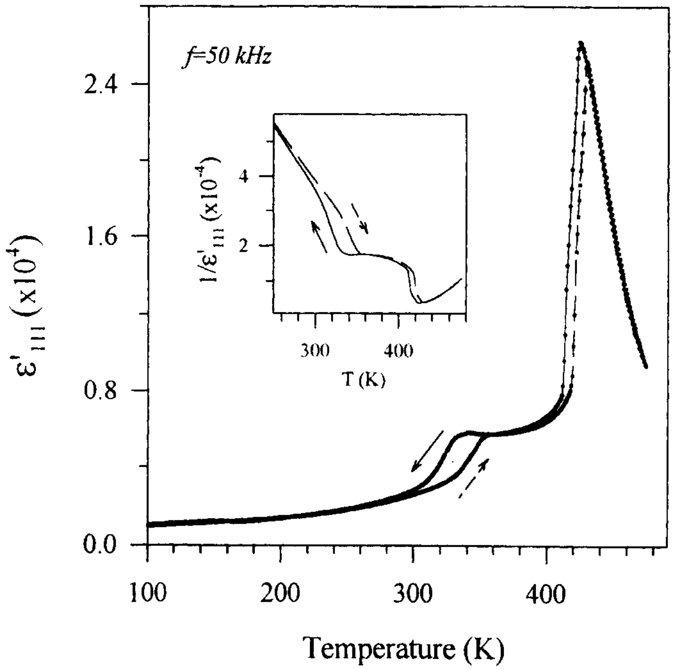

FIGURE 2 Thermal hysteresis of the dielectric permittivity $\varepsilon'_{111}(f,T)$. The inset is the reciprocal of ε'_{111}.

In the lower temperature region (below 350 K), the real part ε'_{111} of dielectric permittivity (Figs. 1 and 2) exhibits a gradual change with a extensive frequency dispersion (or diffuse phase transition) and an clear thermal hysteresis. Accordingly, the imaginary part ε''_{111} shows a obvious frequency dispersion in the same temperature region. A similar dielectric anomaly was

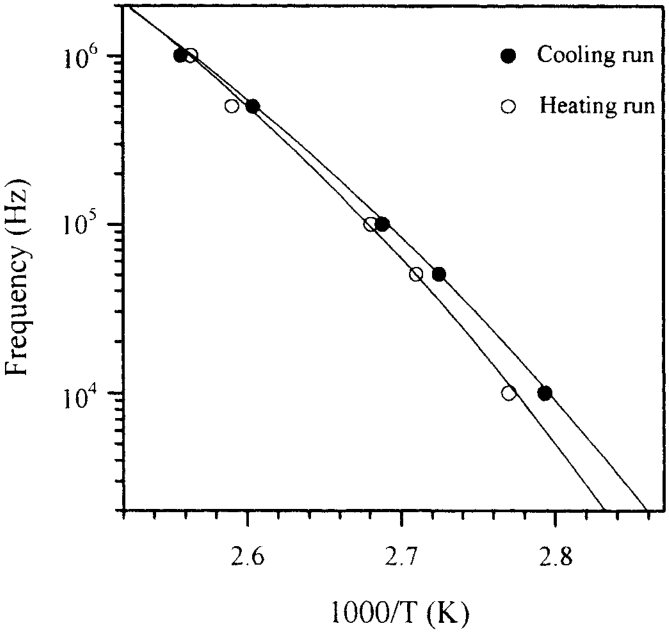

FIGURE 3 Measuring frequency vs. 1000/T. "*T*" is the temperature corresponding to the maximum value of ε''_{111} between 350 and 400 K. The solid lines are fits of Eq. (1) with parameters listed in the text.

seen in PMN.[15] In the supposedly disordered PMN crystal, a nanometric microstructure with 1:1 (B' : B") cation ordering was reported.[16,17] Such 1:1 ordering, when charge naturally requires 1:2 stoichiometry, implies locally charged regions causing fields which can induce order parameter fluctuations. Thus, the diffuse phase transition near 330 K could be triggered by the local structural fluctuations, perhaps between rhombohedral and tetragonal symmetries. We call this a first-order transition for two reasons. First, the thermal hysteresis in the permittivity shows that the system is metastable in this temperature region. Metastability can occur for first- but not second - order transitions. Second, the point groups of the tetragonal and rhombohedral phases do not have a group-subgroup relation, so a transition between these phases must be of first order. The distinctions between first- and second-order transitions, such as discontinuity in dP/dT, do not apply for diffuse transitions.

In addition to the dielectric anomalies seen near 330 and 425 K in the cooling run, the imaginary part ε_{111}'' of dielectric permittivity also shows an obvious frequency dispersion in the region 360-400 K. This anomaly has almost the same magnitude as the one that appears near 330 K (inset of Fig. 1). This origin of this anomaly is not known. One possibility is the response of the domain walls between the domains polarized along, and opposite to, the [001] direction. To check this possibility, the experiment should be repeated with a crystal completely poled along [001].

Precise measurements at temperatures between 350 and 400 K proved the existence of an electric dipolar relaxation process that is evidenced in the imaginary part $\varepsilon_{111}''(f,T)$ of the dielectric permittivity, which is illustrated in the insets of Fig. 1. It was found that the relaxation occurring in this temperature region obeys the exponential Vogel-Fulcher equation that has been used to describe other relaxation processes, especially for mixed systems:

$$f = f_o e^{\frac{-E_a}{k_B(T_g - T_o)}}, \tag{1}$$

where f is the measured frequency, f_o is the attempt frequency, and E_a is the activation energy for orientation of electric dipoles. T_o is the Vogel-Fulcher temperature and T_g is the temperature where the imaginary part ε_{111}'' of the dielectric permittivity reaches its maximum value. Fig. 3 shows the reciprocal temperature dependences of measuring frequency for both heating and cooling processes. The solid lines are fits of Eq. (1) with parameters listed below: E_a=159 meV (1850 K), f_o=2.6 × 10^{12} Hz, T_o=265 K (heating run) and E_a=171 meV (1980 K), f_o=2.4 × 10^{12} Hz, T_o=255 K (cooling run). What is the significance of these parameters? First, the attempt frequency is in the usual range for vibration frequency. Second, E_a is an average activation energy for various clusters in this partly disordered system to reorient, perhaps between rhombohedral and tetragonal local symmetries. Third, T_o is the temperature at which, based on an unjustified extrapolation of the Vogel-Fulcher formula beyond the range of the data, all reorientation would cease. The fact that the Vogel-Fulcher formula fits better than the Arrhenius formula for many disordered systems reflects the fact that, as temperature decreases, a greater number of cooperative steps must occur in the course of a reorientation event.

CONCLUSIONS

From the temperature-dependent dielectric permittivities (ε'_{111} and ε''_{111}) of PMN-33%PT with decreasing temperature, two successive phase transitions are evidenced near 425 K (cubic paraelectric phase ↔ tetragonal FE phase) and 330 K (a diffuse phase transition), respectively. In addition, an intermediate anomaly which may be associated with the response of the domain walls between the domains polarized along, and opposite to, the [001] direction, was also observed in the region 360-400 K. The thermal hysteresis behaviors of dielectric permittivity confirm that both phase transitions (near 425 K and 330 K upon cooling) are first-order. The frequency-dependent dielectric data proved the existence of an electric dipolar relaxation process between 350 and 400 K. The activation energies, the Vogel-Fulcher temperatures and attempt frequencies corresponding to this relaxation process are also calculated for both heating and cooling processes.

Acknowledgments

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References

[1] L.E. Cross, Ferroelectrics **76,** 241 (1987).
[2] L.A. Shebanov. P. Kaspostins, and J. Zvirgzds, Ferroelectrics **56,** 1057 (1984).
[3] M.L. Mulvihill. S.E. Park, G. Risch, Z. Li, and K. Uchino, Jpn. J. Applied Phys. **35** (part 1), 3984 (1996).
[4] S.-E. Paek and T.R. Shrout, J. Appl. Phys. **82,** 1804 (1997).
[5] Y. Yamashita, Jpn J. Appl. Phys. **33** (part 1), 5328 (1994).
[6] S.W. Choi, T.R. Shrout, S.J. Jang and A.S. Bhalla, Ferroelectrics **100,** 29 (1989).
[7] J. Kuwata, K. Uchino and S. Nomura, Ferroelectrics **37,** 579 (1981).
[8] J. Kuwata, K. Uchino and S. Nomura, Jpn. J. Appl. Phys. **21,** 1298 (1982).
[9] S. Nomura, H. Arima and F. Kojima, Jpn. J. Appl. Phys. **12,** 531 (1973).
[10] S.E. Park, M.L. Mulvihill, G. Risch, and T.R. Shrout, Jpn. J. Appl. Phys. **36** (part 1), 1154 (1996).
[11] S. Nomura, T. Takahashi, and Y. Yokomizo, J. Phys. Soc. Jpn. **27,** 262 (1969).
[12] J. Kuwata, K. Uchino, and S. Nomura, Ferroelectrics **37,** 579 (1981).
[13] M.E Lines and A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials,* (Oxford, London, 1977).
[14] T.R. Shrout, Z.P. Chang, N. Kim. and S. Markgraf, Ferroelectrics Letters **12,** 63 (1990).
[15] C.-S. Tu, V. H. Schmidt, and I.G. Siny, J. Appl. Phys. **78,** 5665 (1995).
[16] A.D. Hilton, D.J. Barber, C.A Randall, and T.R. Shrout, J. Mater. Sci. **25,** 3461 (1990).
[17] S.B. Vakhrushev, A.A. Nabereznov, Y.P. Feng, S.K. Sinha, S.M. Shapiro, T. Egami, H.D. Rosenfeld, and D.E Moncton, Bull. Am. Phys. Soc. **39,** 680 (1994).