Transactions of the Materials Research Society of Japan 29[4] 1147-1149 (2004)

Micro-Brillouin Scattering Study of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ Relaxor Ferroelctric Crystals

Do Han Kim[1], Jae-Hyeon Ko[2] and Seiji Kojima[1]
[1]Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan 305-8573
Fax: 81-29-853-5262, e-mail: dhkim@ims.tsukuba.ac.jp, kojima@bk.tsukuba.ac.jp
[2]Samsung Corning co. Ltd. 472 Sin-dong, Paldal-gu, Suwon-si, Gyeonggi-do, Korea 442-390
Fax: 82-31-219-7081, e-mail: jaehyeonko@hanmail.net

We have studied relaxor ferroelectric PZN-9%PT crystals. Dielectric measurements show that the from rhombohedral to tetragonal and from tetragonal to cubic phase transition temperatures were about 83 °C and 166 °C, respectively, in heating process. And a clear hysteresis was observed between cooling and heating cycles around the two transition temperatures. Acoustic anomalies were measured by Micro-Brillouin scattering technique in the backward scattering geometry. And the shape of Brillouin peaks show marked temperature variation in the conventional right angle scattering geometry. The Brillouin frequency shift and full width at half maximum (FWHM) showed marked changes on approaching rhombohedral-tetragonal and tetragonal-cubic phase transition temperatures.

Key words: ferroelectric, Brillouin, acoustic, phase transition, central peak, relaxor

1. INTRODUCTION

Recently, there are so much trial to clarify the origin of high piezoelectric properties of perovskite oxide materials such as Pb(Zr1-xTix)O (PZT), $Pb[(Zn_{1/3}Nb_{2/3})]_{1-x}Ti_x]O_3$ (PZN-xPT), $Pb[(Mg_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$ (PMN-xPT) etc. It has been reported that PZT has monoclinic phase near morphotropic boundary (MPB) between rhombohedral phase and tetragonal phase and theoretically, polarization of PZN-PT rotate with electric field. [1-3]

Relaxor based complex perovskite ferroelectric PZN-xPT and PMN-xPT single crystals are considered as good candidates for electromechanical application because of their huge piezoelectric effect. Ultrahigh piezoelectric coefficients (d_{33}) and ultrahigh strain levels with low hysteresis were observed in PZN-PT and PMN-PT.[4] PZN-xPT is solid solution of $Pb(Zn_{1/3}Nb_{2/3})O_3$ containing a few ratio of $PbTiO_3$. It has the piezoelectric response as an order of magnitude lager than PZT.[4] PZN-xPT has a cubic (C) perovskite structure in high temperatures range, and undergoes a ferroelectric phase transition from rhombohedral (R) into tetragonal (T) phases with increasing temperature. And it has high strain levels up to 1.7% and electromechanical coupling factors (k_{33}) more than 90% with the composition of MPB. [5] And PZN-xPT crystals experience morphotropic phase transition from R to T with increasing PT contents. The dielectric constants and dielectric loss changed like first order behavior as PT concentration was increased. [6] Noheda et al. investigated a monoclinic (M) phase between R and T in the ferroelectric PZN-PT at MPB by high-resolution synchrotron x-ray diffraction method.[1] They showed that M phase remains although electric field was removed. And Ohwada et al. studied phase transition from a R to M phases by neutron scattering and calculated lattice constants of PZN-xPT crystals.[7] Resently, they showed a successive (C)→(T)→(M_c) transition in the field cooling process.[8] The polarization reversals caused by electric field were investigated by Yin et al. and Ko et al. using ultrasonic and Brillouin scattering measurements, respectively.[9, 10] And Liu et al. investigated the behavior of rhombohedral PZN-xPT crystals as function of temperature and calculated electrostrictive coefficients of E-field induced tetragonal phase at high field.[11] PZN-PT crystals were investigated by Ozgul et al. as possibilities to apply Ferroelectric Random Access Momeries (FeRAMs). They tried to explain that the rhombohedral phase correlates the fatigue rates with respect to composition, orientation, temperature, and electric field strength.[12]

In this paper, we investigated the electric field effect of acoustic properties about PZN-9%PT crystals.

2. EXPERIMENTAL

Fig.1 is the 3+3 pass tandem Fabry-Perot interferometer (FPI) which has been used to measure the Brillouin spectra.[13] An Ar^+ ion laser was used to excite the sample with a wavelength 514.5nm and power of 100 mW. A conventional photon counting system and a multi-channel analyzer were used to detect and average the signals. Samples were put in a cryo-stat cell (THMS 600) with the temperature range −200~600 °C and the stability of ±0.1 °C.

An optical microscope (OLYMPUS BH-2) was combined with FPI to achieve a focal point of 1-2 μm for the backward scattering geometry. The sample cell with X-Y-Z adjustable stage was put on the stage of an optical microscope. And we used also a home made conventional furnace with temperature variation from room temperature to 800 °C for right angle scattering geometry. The propagation of phonon directions were [100] and [010] in the backward scattering geometry and the right angle scattering geometry, respectively. We applied 6kV/cm sufficiently to reverse polarization more than 2.5kV /cm which is well known by coercive field (E_c) to the applied field sample and started measuring after it kept as the state for 1 hour.[10]

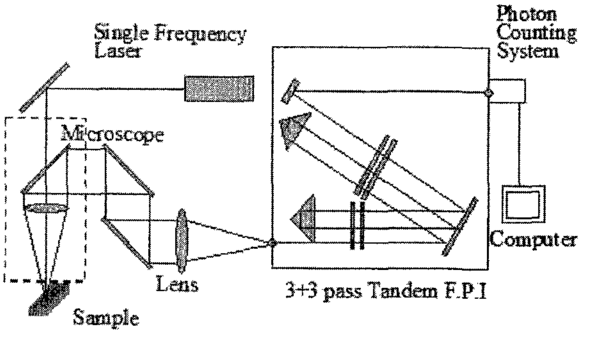

Fig. 1 The Brillouin scattering system with a tandem Fabry-Perot interferometer

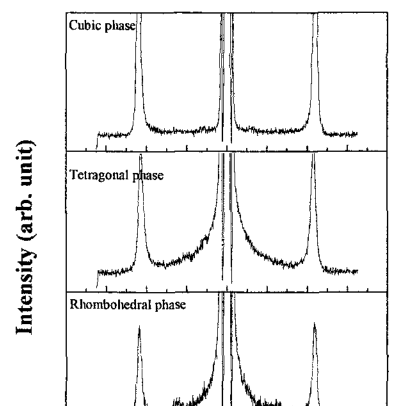

Fig. 2 Brillouin spectra obtained at the backward scattering geometry

3. RESULTS AND DISCUSSIONS

Fig. 2 shows Brillouin spectra of PZN-9%PT. There were a central peak and two peaks which were called transverse acoustic mode (TA-mode) and longitudinal acoustic mode (LA-mode) on the rhombohederal phase near the room temperature. Frequency shifts of LA-mode and TA-mode were about 42.2 GHz and 24.5 GHz, respectively. We measured temperature of Brillouin spectra. Intensity of LA-mode increases with respect to temperature, but that of TA-mode increases as shown in Fig 2. Jiang at al. explained that central peak is related to the fluctuation of polar microregions (PMRs) near the T_{T-C}.[14]

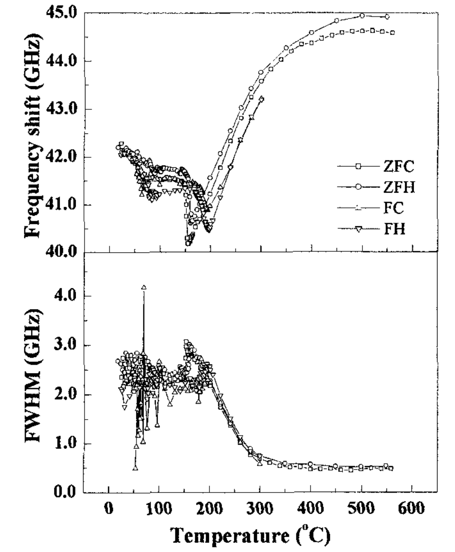

Fig.3 Temperature dependence of Brillouin shift and FWHM of PZN-9%PT

Fig. 3 shows the temperature dependences of LA-mode frequency and full with half maximum (FWHM). We studied zero field cooling (ZFC), zero field heating (ZFH), field cooling (FC) and field heating (FH). Generally the phase of PZN-xPT changes R-T(rhombohedral-tetragonal) and T-C(tetragonal-cubic) with respect to temperature. We also could find two phases anomalies as R-T and T-C. Intensity of LA-mode was increased on heating. That of TA-mode was decreased, then we could not find in the tetragonal phase and cubic phase as like Fig. 2. But central peak was remained at tetragonal phase, but disappeared at cubic phase.

T_{T-C} (transition temperature between tetragonal phase and cubic phase) on the FC process increased about 40 °C with comparing ZFC. T_{R-T} case was not clear because FC case could not measure clearly. T_{T-C} on FH process also increased about 35 °C. T_{R-T} case was decreased about 8 °C with comprаring ZFH. These results were in agreement with neutron diffraction study by Owada et al. FWHM increased near T_{R-T} and T_{T-C}.

Fig. 4 shows Brillouin spectra of right angle scattering geometry. We used polarizer to choose VV and VH geometries.

VV and VH spectra of R phase were similar at room temperature. There were LA-mode, TA-mode and central peak at room temperature. Frequency shifts of LA-mode and TA-mode were about 10.7 GHz and 6.9 GHz, respectively. LA-mode appeared as leakage in the VH geometry and TA-mode appeared as leakage in the VV geometry. So, LA-mode decreased with temperature but TA-mode didn't decrease in VH spectra. And TA-mode decreased with temperature but LA-mode didn't. These reasons were explained by Y.Gorouya et al. that there are the induced stresses in the sample near T_{R-T}. The crystal axes were not parallel to cubic axes near T_{R-T}, so VV and VH spectra didn't show any difference. [15]

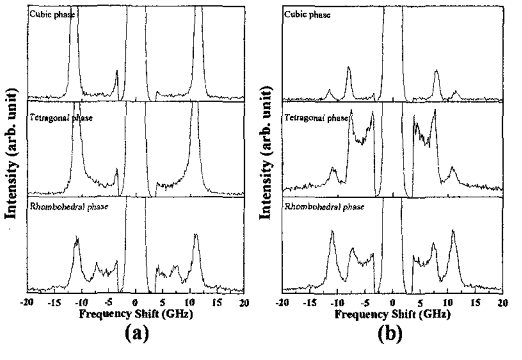

Fig 3. The Brillouin spectra at the right angle scattering geometry. (a) VV and (b) VH spectra

3. CONCLUSIONS

The successive phase transition of PZN-9%PT crystals has been investigated by Brillouin scattering. The thermal hysteresis was clearly observed for the two transitions. The electric filed effect on the two transition was also studied. It is found that the temperature range of the tetragonal phase increases under the electric field along [010] direction.

4. REFERENCES

[1] B. Noheda, J. A. Gonazalo, L. E. Cross, R. Guo, S.-E. Park, D. E. Cox and G. Shirane, Phys. Rev. B, 61, 8687-8695 (2000)
[2] B. Noheda, D. E. Cox, G. Shirane, S.-E. Park, L. E. Cross and Z. Zhong, Phys. Rev. Lett., 86, 3891-3894 (2001)
[3] H. Fu and R. E. Cohen, Nature, 403, 281-283 (2000)
[4] J. Kuwata, K. Uchino and Y. Yamashita, Jpn. J. Appl. Phys. 21, 1298 (1982)
[5] S. –E. Park and Thomas R. Shrout J. Appl. Phys. 82, 1804-1811 (1997)
[6] M. L. Mulvihill, S. E. Park, G. Risch, Z. Li, K. Uchino, Jpn. J. Appl. Phys.,35 3984-3990 (1996)
[7] K. Ohwada, K. Hirota, P. W. Rehrig, P. M. Gehring, B. Noheda, Y. Fujii, S. –E. Park and G. Shirane, J. Phys. Soc. Jpn., 70, No.9, 2778-2783 (2001)
[8] K. Ohwada, K. Hirota, P. W. Rehrig, Y. Fujii and G. Shirane, Phys. Rev. B, 109411-1-8 (2003)
[9] J. Yin and W. Cao, Appl. Phys. Lett. , 79, 4556-4558 (2001)
[10] J. –H. Ko and S. Kojima, Appl. Phys. Lett., 81, 1077-1079 (2002)
[11] M. Ozgul, K. Takemura, S. T-Mckinstry and C. A. Randall, J. Appl. Phys., 89, 5100-5106 (2001)
[12] M. Shen, J. Han and W. Cao, Appl. Phys. Lett. 83, 731-733 (2003)
[13] F. M. Jiang and S. Kojima, Appl. Phys. Lett., 77, 1271-1273 (2000)
[14] F. Jiang and S. Kojima, Ferroelectric, 266, 19-26 (2002)
[15] Y. Gorouya, Y. Tsujimi, Y. Yamashita, T. Ifukube and T. Yagi, Ferroelectics, 266, 165-169 (2002)

(Received October 11, 2003; Accepted March 10, 2004)