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Study of Acoustic Anomalies in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Relaxor Single Crystal by Brillouin Scattering

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Acoustic anomalies of [001] lead magnesium niobate-lead titanate (PMN-PT) single crystals of new morphotropic phase boundary (MPB) composition have been investigated by 90A Brillouin scattering technique. The Brillouin spectra consisted of one longitudinal acoustic (LA) and one transverse acoustic (TA) phonon modes. Brillouin frequency shift and damping of the LA mode clearly showed two anomalies at cubic-tetragonal T_{C-T}, and tetragonal-rhombohedral T_{T-R} phase transition temperatures. The respective anomalies in TA mode were similar to those of LA mode. A strong quasielastic central peak (CP) was also observed showing maximum intensity close to ~85±5 °C.

Key words: Ferroelectrics, relaxor, PMN-PT, morphotropic phase boundary, Brillouin scattering

1. INTRODUCTION

The complex perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) belongs to the class of ferroelectrics known as relaxor. Relaxors are characterized by a number of unusual properties, such as frequency dependent temperature of dielectric maximum (T_m~−8 °C at 1 kHz for PMN), very broad permittivity versus temperature response, lack of macrosymmetry changes near and below the dielectric anomaly, and by slim-loop hysteresis character near T_m. Relaxors have glasslike features, resembling to spin and dipolar glasses [1,2]. A Vogel-Fulcher-type freezing of polarization fluctuations was observed by the analysis of dielectric and acoustic relaxation [3]. Relaxor properties can be attributed to the self-assembled ordered/ disordered nanostructures and the formation of local polar micro-regions (PMRs). The development of the long-range order (LRO) is prevented by the frustration of the local polarizations. Micro- to macrodomain ferroelectric phase transition can only be established by the application of an electric field along [111] pseudocubic direction. On the other hand, lead titanate $PbTiO_3$ (PT) shows a typical ferro-paraelectric phase transition at T_c~490 °C with LRO occurring below T_c.

The solid solutions of PMN and PT, i.e., the $(1-x)$(PMN)$-x$(PT) with a morphotropic phase boundary (MPB) located at x~0.33-0.35, are expected to combine the properties of both relaxor ferroelectric PMN and ferroelectric PT. MPB separates the rhombohedral (relaxor side) and tetragonal (ferroelectric side) phases. High-resolution synchrotron x-ray studies [4] on an unpoled ceramics have revealed the presence of an intermediate monoclinic phase between the rhombohedral and tetragonal phases. However, piezoelectric response in the monoclinic phase was not so strong as that observed in the crystals containing the rhombohedral phase with a composition near the MPB [5]. Rather 90° domain rotation [6] has been considered to be at the origin of the anomalous enhancement of piezoelectric constants near MPB. Single crystals of PMN-PT with a composition near the MPB are technologically important materials due to their excellent electromechanical properties, with a very high piezoelectric constant (d_{33} >2500 pC/N), very large electromechanical coupling factor (k_{33}>94%), and high strain levels up to 1.7% [7,8] along crystal directions which are inclined by certain angles with respect to the polar axis [9]. Therefore, compositions near MPB are very attractive for broadband ultrasonic transducers and other devices like ferroelectric nonvolatile random access memories (NVRAMs) and in high bit density metal-oxide-semiconductor (MOS) dynamic random access memories (DRAMs).

The origins of their outstanding performance have been attributed to the polarization rotation under external electric field [10]. However, quenched random fields have been suggested [11,12] as facilitators for the formation of metastable ferroelectric monoclinic and orthorhombic phases. Inspite of extensive investigations on MPB compositions, acoustic properties have hardly been reported. In the study reported here, we show our recent results of the Brillouin scattering investigation of structural phase transitions in a PMN-PT MPB [001] single crystal.

2. EXPERIMENT

PMN-PT MPB [001] crystals were grown by Bridgman method. Sample of the approximate size of 10x10x2 mm^3 was polished to optical quality and used for present measurements. A 3+3 pass tandem Fabry-Perot interferometer was used to measure the Brillouin spectra by employing 90A scattering geometry. Since the acoustic wave vector is independent of the refractive index of the sample, 90A geometry is more appropriate to study the acoustic properties. The sample was excited with a single mode Ar^+-ion laser with a wavelength of 514.5 nm at a power of ~100 mW. A conventional photon-counting system was used to detect and average the signals. The Brillouin spectra were recorded from room temperature to 200 °C by using a home-made high-temperature furnace specially designed

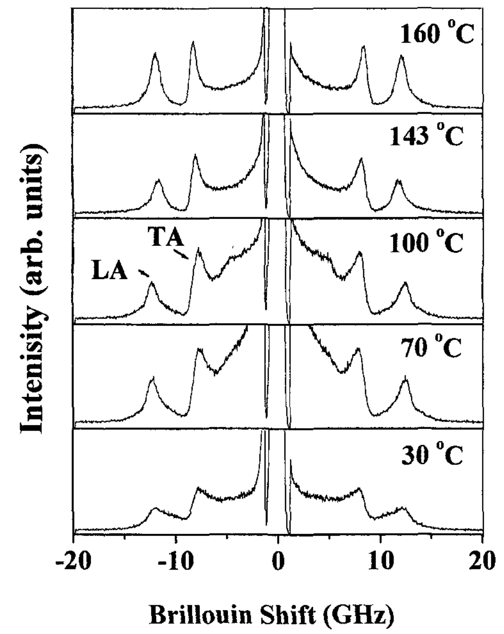

Fig. 1 Typical Brillouin spectra of a PMN-PT [001] MPB single crystal measured at some selected temperatures.

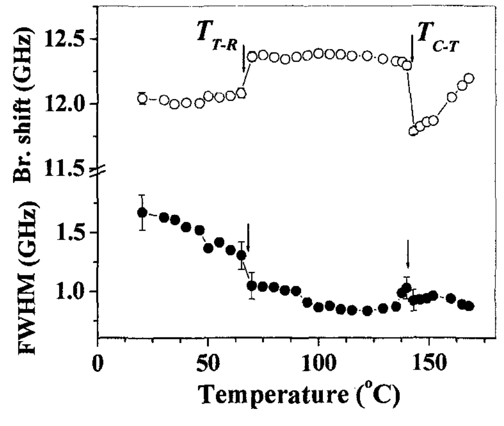

Fig. 2 Temperature dependences of the Brillouin frequency shift (open circles) and FWHM (filled circles) of the LA mode of a PMN-PT [001] oriented MPB single crystal.

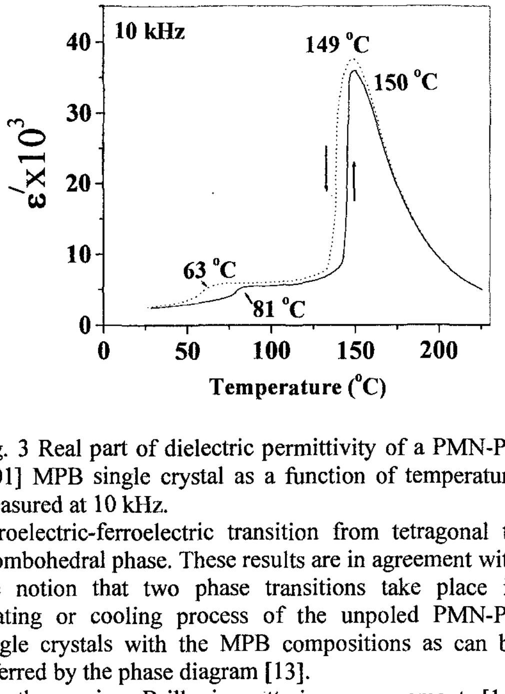

Fig. 3 Real part of dielectric permittivity of a PMN-PT [001] MPB single crystal as a function of temperature measured at 10 kHz.

for optical experiments. Temperature was monitored with a CHINO KP-1000 digital temperature controller and the measurements were accurate within ±5 °C.

3. RESULTS AND DISCUSSION

Figure 1 shows the Brillouin spectra of PMN-PT at some selected temperatures, which are composed of one LA mode and one TA mode. In addition, a quasielastic central peak (CP) can be seen clearly in the spectra shown. These spectra were taken in heating the crystal from room temperature to ~200 °C. In order to obtain the frequency shift and full width at half maximum (FWHM, more accurately known as damping) of the phonon modes, data were analyzed using peak fitting module (PFM) for Origin version 6.0 (Microcal™ Software, Inc.). By assuming the instrumental function as Gaussian, LA and TA phonon peaks were fitted with the Lorentzian function to obtain frequency shift and FWHM. Their resulting temperature dependences for the LA phonon mode are shown in Fig. 2. Dielectric permittivity of the crystal was also measured by using a Solartron Impedance analyzer (SI1260). Measurements were done at a heating/cooling rate of 1 °C/min and 1 volt probing ac-signal. The temperature dependent real part of the permittivity exhibits a typical ferroelectric behaviour as is evident from Fig. 3.

The frequency shift and FWHM showed two clear anomalies at ~63 °C and ~142 °C corresponding to T_{C-T} and T_{T-R} phase transitions; respectively. TA phonon mode showed similar changes in the frequency shift, whereas the two anomalies in FWHM were not observable clearly in this case. The sharp change at ~142 °C corresponds to a first order paraelectric-ferroelectric phase transition from cubic to tetragonal, and the low temperature anomaly at ~63 °C corresponds to the ferroelectric-ferroelectric transition from tetragonal to rhombohedral phase. These results are in agreement with the notion that two phase transitions take place in heating or cooling process of the unpoled PMN-PT single crystals with the MPB compositions as can be inferred by the phase diagram [13].

In the previous Brillouin scattering measurements [14] of PMN-PT with x=0.35, the low temperature anomaly could not be observed clearly. One possibility may be that those experiments were done with very large free spectral range (FSR=100 GHz) in the backscattering geometry so the relatively smaller change was masked out. It is advantage of the 90A scattering geometry that because the scattering wave vector is small, therefore by employing a smaller FSR very small change in stoke and anti-stoke Brillouin components can be observed more precisely. Moreover; in this kind of geometry bulk phonon modes are probed rather than any kind of surface states. In principle, when a laser of incident frequency ω_i and wave vector $\boldsymbol{k}_i$ is scattered from the sample through an angle θ, then, the scattered frequency ω_s and wave vector $\boldsymbol{k}_s$ are defined by the energy and momentum conservation laws: $\omega_s = \omega_i \pm \Delta\omega$ and $\boldsymbol{k}_s = \boldsymbol{k}_i \pm \boldsymbol{k}$. Here, $\Delta\omega$ and $\boldsymbol{k}$ are the frequency and wave vector $[(4\pi/\lambda_i)\sin(\theta/2)$, where $\theta \approx 90°$ in present case] of the scattered phonon, respectively. Here λ_i is the wavelength of the incident light in vacuum.

The differences in two transition temperatures can be justified by the smaller PT concentration (x~0.33) in present crystal. Due to smaller PT contents $T_{C\text{-}T}$ transition point shifts to lower values while $T_{T\text{-}R}$ becomes bit higher. Although the low temperature phase could not be observed in the dielectric and pyroelectric experiments [15] on unpoled PMN-PT ceramics near MPB, it is apparent in single crystals.

The dielectric permittivity curve (Fig. 3) clearly indicates that MPB crystal studied here shows normal ferroelectric behaviour, so the phase transitions can be explained according to the simple ABO_3 perovskite structural model. The paraelectric cubic to ferroelectric tetragonal transition can be associated with either the distortion of the BO_6 octahedra from the ideal cubic structure or B-site atomic displacement along $[001]_{cub}$. It has also been reported that atomic displacement results from A- and B-site atomic shifts along $[111]_{cub}$ directions in the PMN relaxor, and tilting/rotation of $(Mg/Nb/Ti)O_6$ octahedra [16].

From Fig. 1 it can be seen that a quasielastic central peak is present in almost the whole investigated temperature range. Its intensity increases with heating the crystal from room temperature up to ~85±5 °C and then it decreases with further rise in temperature. In the Raman spectra of disordered crystals the appearance of CP near the second-order structural phase transitions has been considered to be a precursor effect which indicates a crossover from displacive to an order-disorder type of transition behaviour. The origin of CPs has been associated with the interaction of the soft mode with some relaxational degrees of freedom such as symmetry breaking defects. In PMN, CP has been investigated by Raman scattering [17] caused apparently by the displacement of off-centre ions. In case of PMN-PT MPB the coexistence of tetragonal and rhombohedral symmetries complicates to explain such phenomena quantitatively. Most probably the atomic disorder created by the A- and B-site atomic shifts, displacement of Pb ions, and presence of stoichiometric nonuniformities and defects may be responsible for the CP.

Recent studies [18] on PZN single crystals show that the system does not have rhombohedral symmetry at room temperature. The rhombohedral phase is rather a surface state whereas; the bulk of the crystal is of nearly cubic symmetry. While; PMN-PT has rhombohedral symmetry down to low temperatures.

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