

Dynamical Properties of Relaxor Ferroelectric Lead Scandium Tantalate Probed by Micro-Brillouin Scattering

Fuming JIANG, Jae-Hyeon KO, Sergey LUSHNIKOV¹ and Seiji KOJIMA*

Institute of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
¹*A Foffe Physical Technical Institute, Russian Academy of Sciences, St Petersburg, 194021, Russia*

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We report the Brillouin scattering of a disordered $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ crystal with degree of order $S = 0.29$. In $z(x, x + y) = \bar{Z}$ scattering geometry, the broad minimum of longitudinal acoustic mode (LA) shifts and the broad maximum of LA width were observed around 245 K corresponding to the maximum temperature T_m of low frequency dielectric constant. Relaxation times were determined by assuming a complex elastic constant from LA modes, and they were attributed for the first time to the fluctuations of polar microregions. In addition, central peaks with marked temperature dependences were observed below 400 K showing a sharp anomaly at 293 K. Concerning specific heat, no anomaly was found for the as-grown crystal, while two broad anomalies around 293 and 270 K for PST ($S = 0.31$), and only one marked anomaly at 293 K for PST ($S = 0.85$) were observed in the cooling process, respectively. A two-phase transition model (Fm $\bar{3}$ m-R3m, $Z = 2$; Pm3m-R3m, $Z = 1$) was proposed to explain the experimental results.

KEYWORDS: relaxor, micro-Brillouin scattering, elastic constant, hypersonic damping, phase transition, PST, specific heat

1. Introduction

Lead scandium tantalate $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST) is a well-known relaxor ferroelectric material with complex perovskite structure $\text{A}(\text{B}'\text{B}'')\text{O}_3$.¹ It has attracted much attention due to its high permittivity, high electrostriction and high pyroelectricity. From a structural point of view, PST is also a very important model object to understand the relationship of relaxor behaviors to the related sublattice structural disorders since the degree of chemical order at the B-site can be controlled by thermal treatment.^{2–4} PST can be ordered or disordered showing normal or typical relaxor ferroelectric behaviors depending on the degree of chemical order S at the B-site.^{2,5–7} The degree of chemical order at the B-site has been revealed by superlattice reflection in patterns of X-ray diffraction and F-spots in selected area electron diffraction (SAED) studies.^{2,8–10}

Dielectric responses of PST with different degrees of chemical order at the B-site change from a broad dispersive anomaly in disordered samples to a “classical” normal ferroelectric anomaly in ordered samples.^{5–7} A spontaneous relaxor to ferroelectric transition was observed in partially ordered PST samples^{5,6} below the maximum temperature T_m of broad dielectric anomaly indicating the development of long-range ferroelectric order. Corresponding anomalies were also observed in specific heat measurement.^{2,6} Raman and IR spectroscopy studies in the high-temperature paraphase show that there are strong lattice modes inconsistent with the average disordered space group Pm $\bar{3}$ m ($Z = 1$). These strong modes are due to the B-site 1:1 ordered nanoregions with space group Fm $\bar{3}$ m ($Z = 2$), and they increase in intensity and become narrower in width with the increase of B-site chemical order.^{10–14} No evidence of soft optical modes has ever been observed, however Raman and IR studies both show that there exists low-frequency inelastic scattering indicating relaxation contributions.^{12,14} Petzelt *et al.*¹⁵ reported microwave dielectric properties at 33 GHz of B-site ordered and disordered PST ceramics, and their results show that for

high-frequency relaxation, not much difference is observed between ordered and disordered PST.¹⁵

Interestingly, this 33 GHz frequency falls within the window of Brillouin scattering. Brillouin scattering is a very useful tool to study the relaxation properties in the 1 GHz to 100 GHz region. The purpose of the present research is to clarify the GHz dynamics of the disordered PST crystals using high contrast Brillouin scattering. Temperature dependences of elastic constants c_{33} , which are very important for application purposes, are determined from the frequency shifts of the longitudinal acoustic modes. Relaxation times are determined using a Debye model. To illustrate the results obtained by Brillouin scattering, specific heat of the as-grown crystal and two other ceramic powder samples with degree of order $S = 0.31$ and 0.85 were measured using modulated differential scanning calorimetry (MDSC).

2. Experimental

A thin plate PST sample of size $3 \times 5 \times 1 \text{ mm}^3$ with (001) orientation was prepared from disordered crystals grown by spontaneous crystallization. The degree of order S was determined to be 0.29 by X-ray structural analysis according to the procedure suggested by Setter and Cross.² Based on our dielectric measurement, this sample is abbreviated as PST-DV (disordered with lead vacancy).¹⁶ Two ceramic powder samples PST-D ($S = 0.31$) and PST-O ($S = 0.85$) were prepared using appropriate thermal treatment similar to that described by Setter and Cross.²

A 3 + 3 pass tandem Fabry-Perot interferometer combined with an optical microscope was used.^{17–19} The sample was excited by a single mode Ar^+ ion laser with a wavelength of 514.5 nm and power of 50 mW and backward scattering geometries were used. The sample was put in a cryostat cell (THMS 600) situated on the stage of an optical microscope (Olympus BH-2) with X–Y–Z adjustments. The temperature could be varied from 600 to -190°C with a stability of $\pm 0.1^\circ\text{C}$.

Specific heat was measured on powder samples using MDSC (TA Instruments 2920) during both cooling and heat-

*E-mail address: kojima@bk.tsukuba.ac.jp

ing processes. The dielectric constant was measured using the impedance gain/phase analyzer (Solartron SI 1260).

3. Brillouin Scattering Results

Typical Brillouin spectra at various temperatures are shown in Fig. 1, these spectra were measured on a (001)-plate PST-DV with a free spectral range (FSR) of 200 GHz and a scan range of ± 1.5 FSR. Except the Rayleigh line, a Brillouin doublet which arises from the longitudinal acoustic mode was clearly seen. No transverse acoustic mode was observed in our experiment down to liquid nitrogen temperature. Based on our dielectric measurement of PST-DV and those reported by Chu *et al.* and Ko *et al.*,^{5,16} the as-grown crystal is a typical relaxor with lead vacancies. According to the random field theory,^{20,21} introducing lead vacancies will prevent the development of long-range ferroelectric order.⁵ It will be seen later that no specific heat anomaly was observed in PST-DV. Therefore it is inferred that the crystal remains averagely cubic or pseudocubic. In addition, broad central peaks (CPs) with marked temperature dependence appear below 400 K. CPs with marked temperature dependence are likely common features for relaxor ferroelectrics since they have also been observed in PMN, PMN-PT, PZN-PT, PLZT and SBN relaxors.^{17–19,22,23} CPs can have different microscopic origins in relaxor ferroelectrics due to the related nature of relaxation process. Discussion of the CPs in PST-DV will be presented

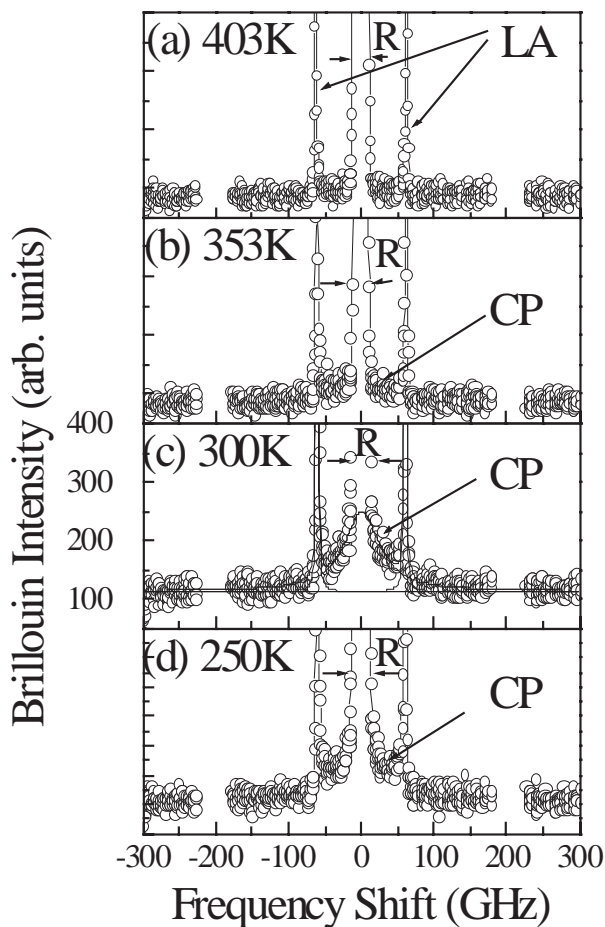


Fig. 1. Typical Brillouin spectra at various temperatures using a FSR of 200 GHz and scanning range of ± 300 GHz, a fitting example is shown in (c).

elsewhere.²⁴

3.1 Elastic constant and hypersonic damping

Elastic constants can be determined according to the Brillouin frequency shift if density and refractive index of the sample under investigation are known. To determine the Brillouin frequency shifts accurately, a FSR of 75 GHz and a scan range of 60 GHz were used. A convolution process was employed to subtract the instrumental broadening,²⁵ the LA modes were described by damped harmonic oscillator models, and the CPs were fitted with a Lorentzian centered at zero frequency assuming a single relaxation process. The obtained LA mode frequency shift and full-width at half maximum (FWHM) are shown in Fig. 2. For comparison, the dielectric constant measured at 26.8 Hz for the same sample was plotted in the same figure. There is no sharp anomaly in temperature dependences of LA frequency shift and FWHM, only a very broad dip and hump are observed for LA shifts and FWHM around 245 K, consistent with the broad peak of the dielectric constant within the acceptable range of experimental accuracy.

For the LA mode with a wavevector $q \parallel (001)$, the corresponding elastic stiffness constant is $c_{33} = \rho V_{LA}^2(001) = \rho [f_{LA}(q \parallel 001) \lambda_0 / 2n]^2$, where, ρ , λ_0 , and n are density, wavelength of incident light in vacuum, and refractive index of PST, respectively. A theoretical value of 9.22 g/cm^3 for ρ is estimated from the lattice parameter at room temperature ($a = 4.072 \text{ \AA}$), n is taken to be 2.7. Temperature dependences of elastic constant c_{33} are shown in Fig. 3. The room temperature value of c_{33} is $17.3 \times 10^{10} \text{ N/m}^2 \sim 17 \times 10^{11} \text{ dyn/cm}^2$, and this value is typical for perovskite ferroelectric materials, for example, c_{33} is $16.2 \times 10^{10} \text{ N/m}^2$ at room temperature for

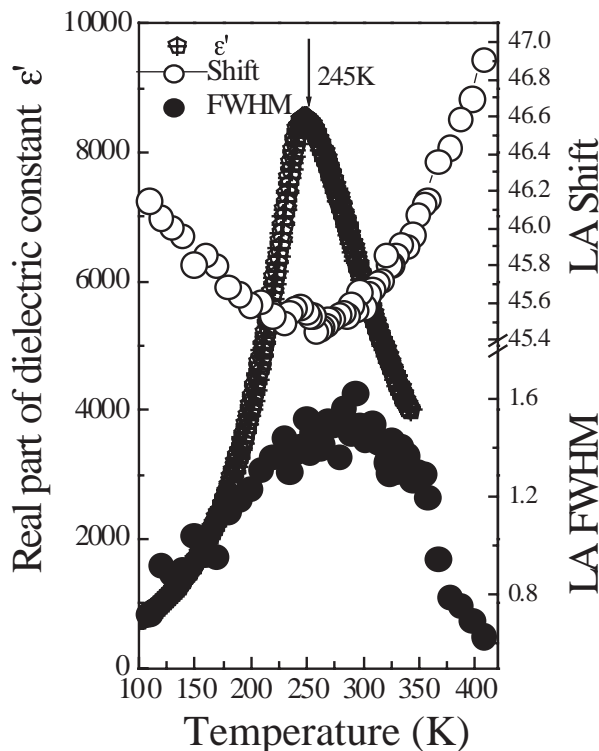


Fig. 2. Temperature dependences of LA mode frequency shift and FWHM, real part of the dielectric constants measured at 26.8 Hz were plotted in the same figure for comparison.

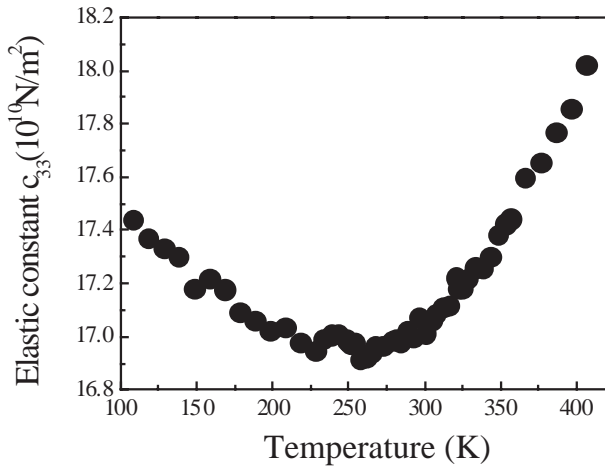


Fig. 3. Temperature dependences of the elastic stiffness constant c_{33} .

PMN.²⁷⁾ Sound velocity of PST-DV at room temperature is $V_{LA} \sim 4.33 \times 10^3$ m/s.

3.2 Relaxation time determined from Brillouin components

The theory employed is that of a complex elasticity with a single relaxation time. The expression for the complex elastic stiffness constant $c(\omega)$ is as

$$c(\omega) = c(\infty) - \frac{\Delta c}{1 - i\omega\tau(T)}, \quad (1)$$

where a real part is proportional to the longitudinal sound velocity

$$\rho V_{LA}^2 = \Re\{c\} = c(\infty) - \frac{\Delta c}{1 + \omega^2\tau^2(T)}, \quad (2)$$

and an imaginary part is proportional to the attenuation

$$\Gamma(T) = \Im\{c\} \frac{q}{2\pi\rho V_{LA}} + \Gamma_\infty = \Gamma_\infty + \frac{\Delta c\tau(T)}{1 + \omega^2\tau^2(T)} \frac{q^2}{2\pi\rho}. \quad (3)$$

Combining eqs. (2) and (3), a simple expression for the relaxation time can be obtained.^{28,29)}

$$\tau(T) = \frac{\Gamma(T) - \Gamma_\infty}{c(\infty) - c(T)} \frac{2\pi\rho}{q^2}. \quad (4)$$

Note that Γ_∞ is due to additional decay or attenuation mechanisms not included in eq. (3). In the present case, we use the high-temperature value Γ of LA mode to represent Γ_∞ since it is quite common for relaxor ferroelectrics that FWHMs are nearly temperature independent above a Burns temperature T_D .^{17,18,30)} Below T_D , it is well known that typical relaxor properties are observed due to the formation of polar microregions (PMRs).^{1,30)} Consequently, we propose that the broad hump in the temperature dependence of FWHM of the LA mode has at least some contributions due to the fluctuations of PMRs. This is most likely the reason that FWHMs of the acoustic modes in relaxor ferroelectrics are much larger and exist over a much wider temperature range than those for normal ferroelectrics.

Since the value of c_∞ is not available, an approach frequently used in the liquid-glass transition is employed here to obtain the relaxation time from the LA mode. PST-DV is a

typical relaxor,¹⁶⁾ therefore we assume:³¹⁾

$$\omega\tau = 1 \text{ at } T_m \text{ where } \Gamma(T) \text{ is maximum } \Gamma_m. \quad (5)$$

In this way, Δc can be determined at T_m , and it is assumed here to be nearly temperature independent. In this way, a physically reasonable relaxation time can be obtained:

$$\tau = \frac{\frac{\Delta\Gamma_m}{\Delta\Gamma}\omega_m - \sqrt{\left(\frac{\Delta\Gamma_m}{\Delta\Gamma}\omega_m\right)^2 - \omega^2}}{\omega^2}, \quad (6)$$

where $\Delta\Gamma = \Gamma(T) - \Gamma(\infty)$ and ω_m is Brillouin frequency shift at T_m . Relaxation frequency and relaxation time thus obtained are shown in Fig. 4. The lattice relaxation slows down markedly to T_m upon cooling. The temperature behaviors in Fig. 4 are similar to those reported by Setter *et al.*, but here the relaxation frequency f_r is nearly two orders of magnitude larger than that by dielectric measurement. Such a difference in relaxation frequency has been reported in clustered glass-forming materials.^{32,33)} Similarly, dielectric relaxation in relaxors reflects the behavior of polar microclusters which dominate the dielectric strength, whereas the mechanical relaxation occurs through those on the outside of the clusters which respond much more rapidly to the applied stress.^{32,33)}

It is interesting to discuss the origins of the relaxation behaviors. Since the PMR in PST is of 3 nm order in size D , its elastic resonance vibrational frequency can be estimated as:

$$f_r^{-1} \sim D/V_{LA} \sim$$

$$3 \times 10^{-9} \text{ m} / (4.33 \times 10^3 \text{ m/s}) \sim 0.69 \times 10^{-12} \text{ s},$$

and this value is clearly in agreement with our results shown in Fig. 4. Therefore the relaxation time determined from the LA mode is most likely attributed to the elastic fluctuations

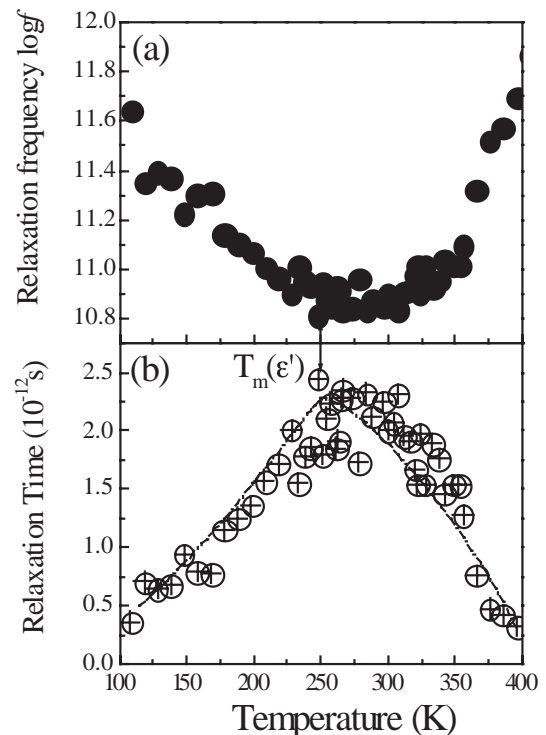


Fig. 4. Relaxation time τ and relaxation frequency $\log f$ obtained from the LA mode by assuming the Debye model.

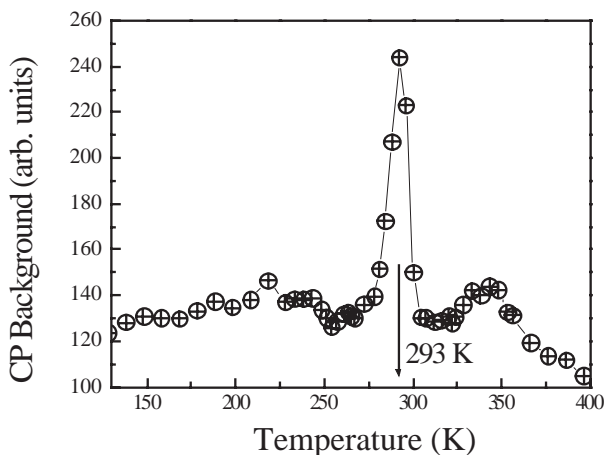


Fig. 5. Temperature dependences of the CP background.

of PMRs, since the PMRs can couple to the strain through $\Delta x_{jj} = (Q_{11} + 2Q_{12})P_s^2$,¹⁾ where Q_{11} and Q_{12} are electrostrictive coupling coefficients, and P_s is the local polarization ($\langle P_s \rangle = 0$, while $\langle P_s^2 \rangle \neq 0$).

3.3 Sharp anomaly in the temperature dependence of CPs

Temperature dependences of integrated intensity, and the FWHM of the CPs of the PST-DV crystal were reported.²⁴⁾ Interestingly, a sharp anomaly was observed near 293 K in the cooling process. This is also seen in the background of CPs as shown in Fig. 5. This sharp anomaly has no correspondence in the temperature dependence of LA mode. No sharp anomaly was observed in our dielectric measurement.¹⁶⁾ The result is reproducible. Therefore, the question arises as to what the origin might be for this sharp anomaly. To answer this question, the specific heats of the crystal PST-DV, and of two other ceramic powder samples PST-D ($S = 0.31$) and PST-O ($S = 0.85$) were measured by MDSC.

4. Specific Heat Results

Specific heat was measured during both cooling and heating processes for all three PST samples in the temperature range of -100 to 300°C with a temperature variation rate of $\pm 5^\circ\text{C}/\text{min}$, and the results are reproducible. They are shown in Fig. 6. The as-grown crystal does not show any anomaly during either heating or cooling processes. Two weak broad anomalies with thermal hysteresis are observed in the specific heat for PST-D ($S = 0.31$), while only one sharp anomaly with thermal hysteresis appears in the specific heat of PST-O ($S = 0.85$). It is to be noted that the high-temperature anomaly for PST-D appears at the same temperature as that of the PST-O during both heating and cooling processes. The

temperatures at 293 K for PST-O and at 270 K for PST-D are similar to those reported by other experimental methods.⁵⁾ Interestingly, the sharp anomaly for PST-DV in CP behavior occurs also near 293 K. Consequently, it is expected that three PST samples with different degrees of chemical order have some common microscopic origins.

5. Discussion

Structures of PST have been studied by various experimental methods.^{1,2,8,9)} It is now clear that Sc and Ta are distributed randomly at B-sites with a short range order of 3 nm. The short range order at B-sites has been confirmed by F-spots in SAED and superlattice reflection peaks in X-ray diffraction. Vibrational spectroscopic studies revealed a space group of $Fm\bar{3}m$ associated with the ordered nanoregions.¹²⁻¹⁴⁾ A group theoretical analysis suggests two phase transition sequences for disordered and ordered PST:^{13,14)}

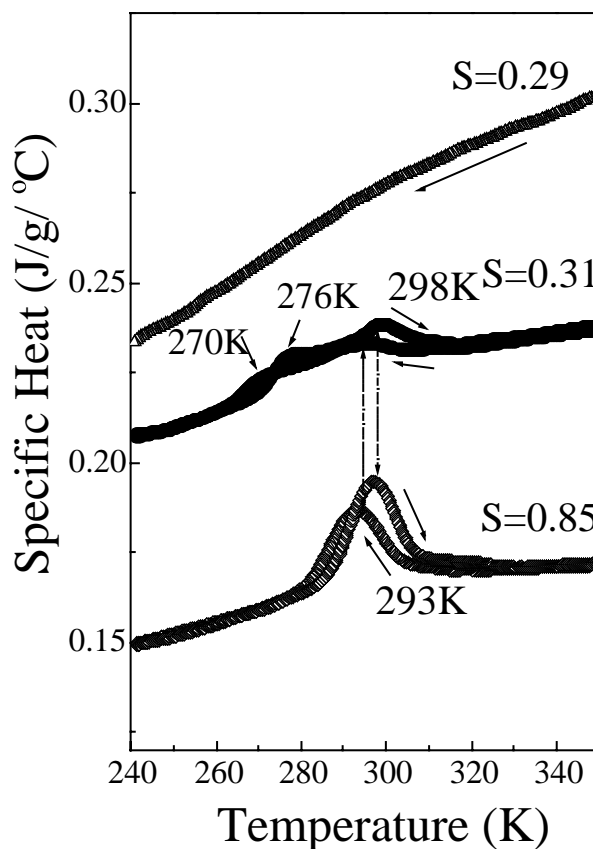
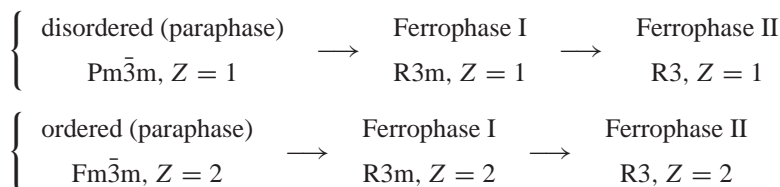


Fig. 6. Specific heat of PST-DV ($S = 0.29$), PST-D ($S = 0.31$) and PST-O ($S = 0.85$). No anomaly was found for PST-DV, two for PST-D, and one for PST-O; Thermal hysteresis was observed for PST-D and PST-O.



From IR studies, the R3 ferrophases are improbable.¹⁴⁾ Therefore two probable transitions can be expected depend-

ing on the degree of order. Returning to our experimental results of PST, we can ex-

pect only one phase transition ($Fm\bar{3}m \rightarrow R3m$, $Z = 2$) for the PST-O, since for ordered PST-O with nearly pure $Fm\bar{3}m$ phase, it behaves like a normal ferroelectric, as evidenced by dielectric and thermal heat flow measurement. Consequently a sharp first order transition was observed by our specific heat measurement. As for the PST-D sample, short-range ordered nanoregions with space group $Fm\bar{3}m$ are dispersed in the disordered matrix with an averaged space group $Pm\bar{3}m$. Therefore, two phase transitions are possible from $Fm\bar{3}m \rightarrow R3m$ ($Z = 2$) and $Pm\bar{3}m \rightarrow R3m$ ($Z = 1$). These two transitions are observed by our specific heat measurement for PST-D, since the high-temperature anomaly corresponds to $Fm\bar{3}m \rightarrow R3m$ ($Z = 2$), it is reasonable that it occurs at nearly the same temperature as that for PST-O. Two anomalies in specific heat measurement for disordered PST were observed for the first time. Thermal flow and specific heat measurement by Setter *et al.* using differential scanning calorimetry with a heating or cooling rate of $10^\circ\text{C}/\text{min}$ revealed only one anomaly for disordered PST.^{2,5)} The reason might be the high sensitivity of MDSC used in our measurement. The result for our PST-D is reasonable, since spontaneous transitions ($Pm\bar{3}m \rightarrow R3m$) have been observed at a temperature below a broad dielectric maximum T_m by dielectric measurement for both disordered PST and PSN.⁵⁻⁷⁾ In comparison with the anomaly in specific heat for PST-D, two anomalies for PST-D are weak and broad due to the low degree of order.

It was suggested that introducing the lead vacancy would prevent the development of long-range order in PST-D due to the random field effect. PST-D behaves like a typical relaxor ferroelectric, and therefore no anomaly was observed in our specific heat measurement. However, a sharp anomaly was revealed by Brillouin scattering in the temperature dependence of CPs for PST-DV, and it appeared near the temperature of $Fm\bar{3}m \rightarrow R3m$ ($Z = 2$) for ordered PST. We think that it is likely related to the dynamics of ordered nanoregions with space group $Fm\bar{3}m$. Recently, Petzelt *et al.*¹⁵⁾ reported microwave measurement at 33 GHz of PST-O, PST-D, and PST-DV samples, and they observed sharp anomalies for all PST samples at nearly the same temperature, 300 K. There are controversies regarding the high-frequency relaxation as to whether Pb hopping or B-site disorder plays the main role, but it seems that they are related to the ordered nanoregions.^{14,34)} It is to be noted that the microwave frequency at 33 GHz falls in the frequency window of Brillouin scattering, and our Brillouin scattering of CPs reveals a sharp anomaly at nearly the same temperature of the dielectric anomaly by microwave measurement. Therefore, it is proposed that they are related to the ordered nanoregions.

6. Conclusions

We have reported a Brillouin scattering study of an as-grown single crystal PST-DV. Elastic constant c_{33} and hyper-sonic damping were determined, and relaxation times were calculated from the LA mode assuming a complex elastic constant. They are attributed to the fluctuations of PMRs. CPs with marked temperature dependence revealed a sharp

anomaly at 293 K in the cooling process. To illustrate the sharp anomaly of CPs in PST-DV, specific heats of PST-DV, PST-D ($S = 0.31$) and PST-O ($S = 0.85$) were measured. The results can be explained by a two phase transition model: $Fm\bar{3}m \rightarrow R3m$ ($Z = 2$) for ordered PST, and $Pm\bar{3}m \rightarrow R3m$ ($Z = 1$) spontaneous transition for disordered PST.

Acknowledgements

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