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Central Peak of Ferroelectric $LiH_3(SeO_3)_2$ near the Melting Point Studied by Raman Scattering

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The central peak of the Raman spectrum of ferroelectric $LiH_3(SeO_3)_2$ was observed as a function of temperature from 300 K to the melting point (383 K). With increasing temperature, the linewidth takes a minimum around 360 K and then shows anomalous broadening near the melting point. The temperature dependence of the linewidth is decomposed into two components; one component decreases linearly with temperature and the other one shows an anomalous increase toward the melting point. The analysis shows that the former is caused by the critical slowing down of the fluctuating electric polarizations in the ferroelectric phase and the latter by the activation of the ionic motion due to the premelting phenomena.

KEYWORDS: $LiH_3(SeO_3)_2$, Raman scattering, central peak, polarization fluctuation, melting

§1. Introduction

The crystal $LiH_3(SeO_3)_2$ (LTS) is one of the well studied ferroelectrics.[1] The ferroelectric axis was reported to be approximately parallel to the c^* axis in the ac^* plane,[2] where the c^* axis is perpendicular to the a and b axes. Among the hydrogen-bonded ferroelectrics, this crystal has distinct properties. First, the ferroelectric phase transition temperature T_c is higher than the melting point T_m of 383 K,[1] that is, the ferroelectric order remains up to T_m in spite of the large thermal activation of ionic motion near T_m. Second, in spite of the strong anisotropy of the depolarization field effect which is expected in the uniaxial ferroelectrics, the dielectric constants along the a and b axes show the behaviors similar to that along the c^* axis. This effect has been considered to be caused by the increase in the ionic mobility near T_m.[1] Since the two kinds of dynamical process mentioned above coexist near T_m, the spectroscopic study is helpful for understanding dynamically of distinct properties of LTS.

Low-frequency Raman scattering is a useful tool for the study of dynamical phenomena, because a so-called central peak reflects directly the slow dynamics and fluctuations. For example, the relaxation time of the polarization fluctuations in the ferroelectric phase transition have been obtained from the linewidth of the central peak.[3] The central peak also gives useful information to study ionic conduction,[4] because the linewidth depends on the hopping rate of ions. The ionic mobility is estimated if one knows a step distance of the hopping. In addition to these results, the anisotropy of the fluctuations can be obtained easily from the angular dependence of the spectral width with respect to the crystal axis.

In this paper, we report the observation of the central peak in the Raman scattering spectra from room temperature to T_m. Section 2 is devoted to the experimental method and §3 to results and discussion for the two dynamical aspects in LTS.

§2. Experimental

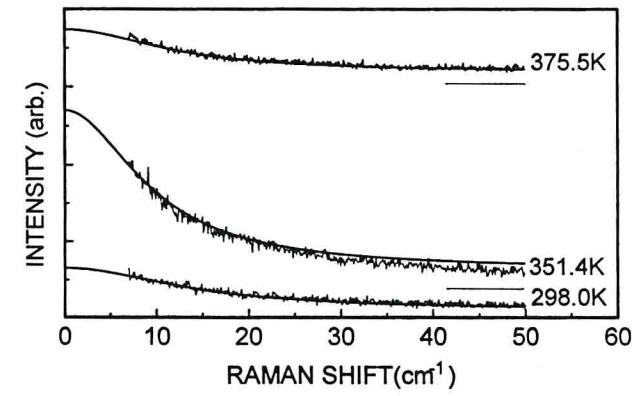
Single crystals were grown by lowering the temperature of stoichiometric solutions of SeO_2 and Li_2CO_3. Based on the crystal habit and the cleavage plane,[5] specimens were cut in shape of about 5 mm cubes of which edges are parallel to the a, b and c^* axes. Surfaces of specimens were polished with wet filter papers. Cylindrical specimens with the axis parallel to the crystal b axis were provided for the measurements of the angular dependence of the central peak.

Instrument for Raman scattering is described previously.[6] In order to reduce the stray light due to the elastic scattering from surfaces of a specimen, silicon oil (Toshiba Silicone TSF433) was used for refractive index matching and a pin-hole as a spatial filter. The stability of temperature was controlled within ± 0.5 K.

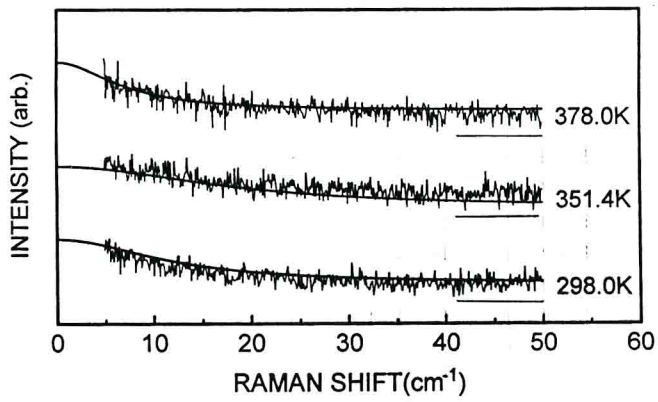
Itoh *et al.*[7,8] reported that LTS is seriously damaged when it is kept at temperature near T_m for a long period. In fact, we observed that the crystal was colored brown when it was cooled down to room temperature after its temperature was kept above 360 K for several hours. Neverthless, we were successful to reduce the parasitic scattering light and the stray light from crystal surfaces to a descent level by carefully choosing the scattering position with a spatial filter. After that, the excellent reproducibility in the temperature dependence of the Raman spectrum was obtained in the temperature region above 360 K. Below 360 K, there was no such problem in the observation of spectra.

§3. Results and Discussion

Figures 1(a) and 1(b) show several examples of the central peaks of LTS in the geometries $a(c^*c^*)b$ and $a(bb)c^*$. As shown in the figures, its intensity depends on both of temperature and the direction of the scattering wave vector q. So we denote the central peak intensity as $I(\omega, q)$. The spectra $I(\omega, q)$ in $a(c^*c^*)b$ are rather intense than those in $a(bb)c^*$ at 300 K. As a trial, the



(a)



(b)

Fig. 1. Typical low frequency spectra of $LiH_3(SeO_3)_2$ observed in the geometries (a) $a(c^*c^*)b$ and (b) $a(bb)c^*$.

spectra observed in $a(c^*c^*)b$ is analyzed with the Debye type susceptibility with a relaxation time $\tau(q) = \Gamma(q)^{-1}$ and a static susceptibility $\chi(0, q)$,

$$I(\omega, q) = \frac{\chi(0, q)\Gamma(q)}{\omega^2 + \Gamma^2(q)}, \tag{1}$$

where a high temperature approximation for the Bose factor is used. It was found that all spectra are well represented by this equation. The temperature dependence of $\Gamma(q)$ obtained by the numerical fit with eq. (1) is plotted in Fig. 2. It reaches the minimum value around 360 K and increases divergently near T_m. Hence, we assume that the central peak consists of two components, one with a decreasing linewidth with increasing temperature and the other with a linewidth divergent near T_m.

Since the ferroelectric order of LTS decreases with increasing temperature, we infer that the decrease of $\Gamma(q)$ with increasing temperature is due to the slowing down of the fluctuations of electric polarization. Hereafter we denote this component as $\Gamma_p(T)$. The temperature dependence of the relaxation time $\tau_p(T)$ or $\Gamma_p(T)^{-1}$ of the polarization is given as follows,

$$\tau_p(T) = \Gamma_p(T)^{-1} = \frac{4.05 \times 10^{-11}}{T_c - T}, \tag{2}$$

where the temperature dependence of the Curie-Weiss type is assumed with $T_c = 417.6$ K. The value of T_c is nearly equal to the hypothetical ferroelectric-paraelectric

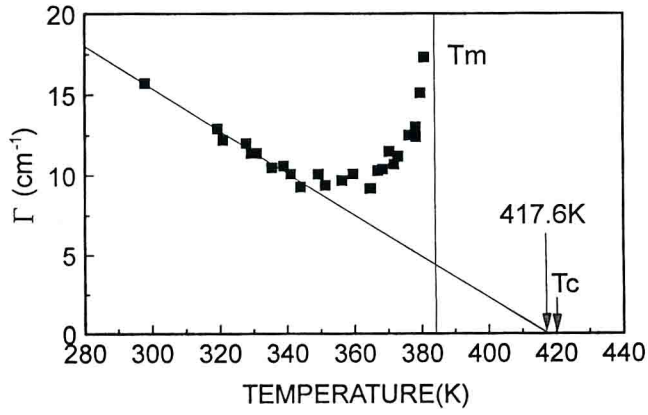


Fig. 2. Temperature dependence of $\Gamma(q)$ of the central peak in the geometry $a(c^*c^*)b$. Thin line expresses eq. (2). The thin vertical line indicates the melting temperature T_m. The arrows show the hypothetical ferroelectric phase transition temperature estimated from the dielectric measurements under high pressure.

phase transition point (420 K) estimated from the dielectric measurements under hydrostatic pressure.[9-11] Thus, $\Gamma_p(T)$, the decreasing part of $\Gamma(q)$ given by eq. (2) is well expressed by the straight line in the lower temperature region as shown in Fig. 2. Therefore, the central peak in the lower temperature region is concluded to be caused by the polarization fluctuations concerned with the ferroelectric-paraelectric phase transition. The Curie constant of τ_p given by eq. (2) is almost the same as that of KH_2PO_4. The τ_p of KH_2PO_4 was given by $1.8 \times 10^{-11}/(T - T_c)$ from the Brillouin scattering spectra.[12]

In the case where the central peak is caused by the polarization fluctuations, the peak height $\chi(0, q)$ depend on the direction of q due to the depolarization effect.[13] Its angular dependence is given as $[q + a_1 \cos^2\theta + a_2(T_c - T)]^{-2}$, where θ is the angle between the scattering vector and the polar c^* axis. Figure 3 shows the angular dependence of the peak height of the central peak observed in the cylindrical sample at several temperatures. One can see the slight disagreement between the experimental results and theoretical calculation; there is an asymmetry in the pattern with respect to the a axis. However, this disagreement seems to be due to the experimental factors such as the misalignment of the specimen and the change of the leakage of the stray light as a specimen was rotated. Thus, we can conclude that Fig. 3 shows the anisotropy of the depolarization effect of the fluctuations. Furthermore, a small peak appears in the rotation pattern around q nearly parallel to the c^* axis and its intensity does not seem to depend on temperature. At present, we do not know the origin of this small peak. The weak angular dependence in Fig. 3(c) is due to small contribution of the polarization fluctuations to the anomalous broadening which is discussed below.

The anomalous increase of $\Gamma(q)$ above 360 K is considered to be due to fluctuations other than the polarization fluctuations. The anomalous component $\Gamma_a(T)$ is defined as the difference between the observed value and the extrapolated $\Gamma_p(T)$ which is shown with a thin

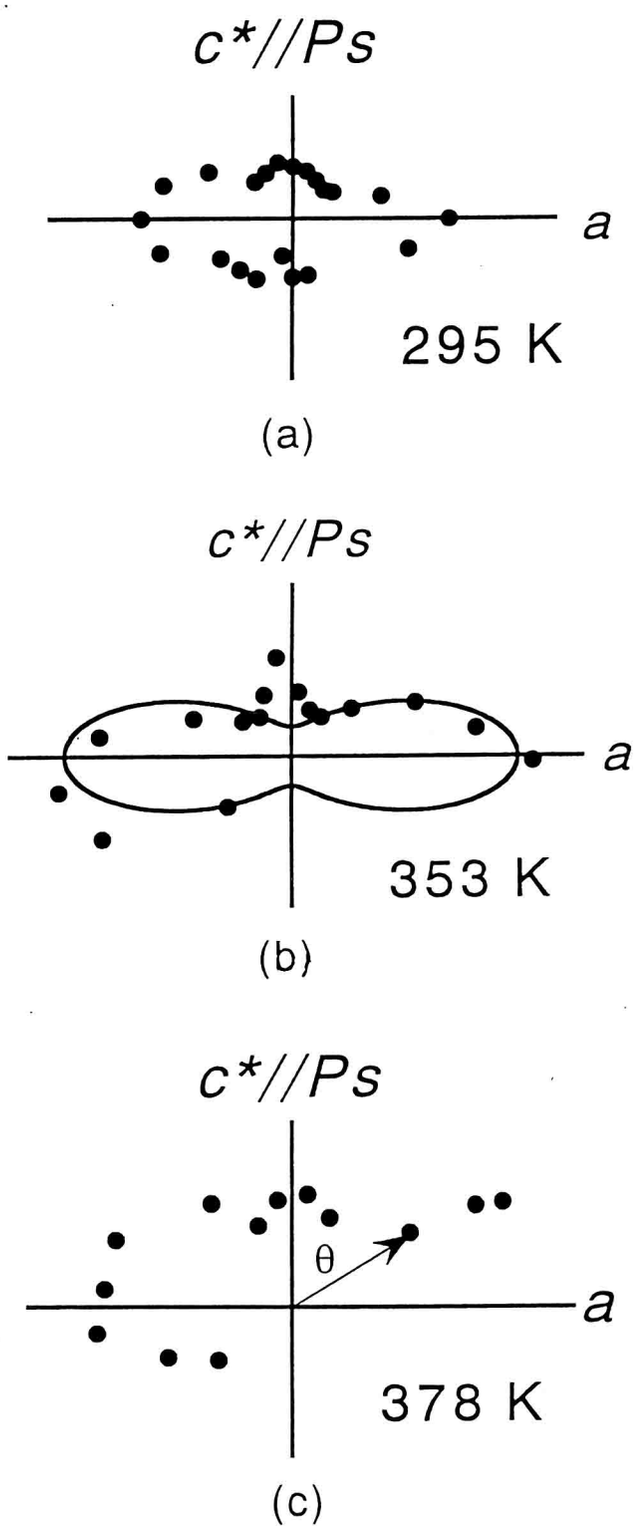


Fig. 3. Angular dependence of the peak height of the central peak observed in the ac^* plane at (a) 295, (b) 353 and (c) 378 K. The direction of radius vector from the origin to each point is the direction of the scattering wave vector and its length indicates the peak height as shown in (c). In (b), the solid line shows the depolarization effect.

line in Fig. 2. The inverse of the anomalous part $\Gamma_a(T)$ depends on temperature linearly as shown in Fig. 4 and is expressed by

$$\tau_a(T) = \Gamma_a(T)^{-1} = 6.6 \times 10^{-14}(T_a - T), \qquad (3)$$

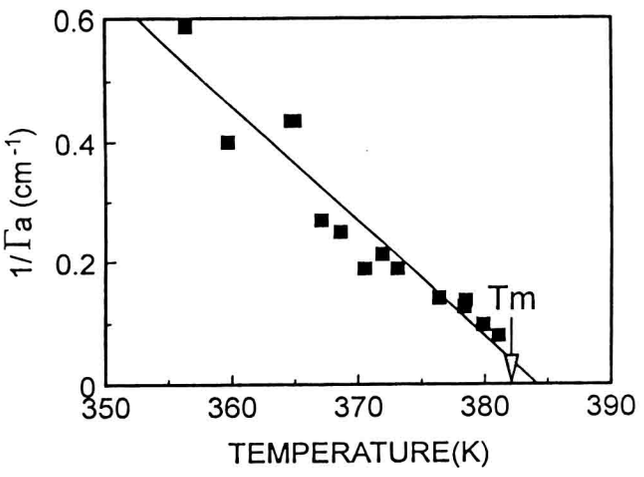


Fig. 4. Temperature dependence of the inverse of the anomalous part Γ_a near T_m.

with T_a of 384.2 K which is nearly equal to T_m (383 K) of LTS. In order to confirm if the analysis mentioned above is reasonable or not, the central peak was observed with q parallel to the c^* axis, because the polarization fluctuations are, in principle, suppressed in this geometry. Then the anomalous component in this direction is considered to be caused by the fluctuations related to the melting process. We denote the linewidth in this case by $\Gamma_M(T)$. The temperature dependence of Γ_M is shown in Fig. 5 and is well represented by

$$\tau_M(T) = \Gamma_M(T)^{-1} = 5.2 \times 10^{-14}(T - T_M), \qquad (4)$$

with $T_M = 388.1$ K which is also nearly equal to T_m. Thus, we can conclude that Γ_M and Γ_a are caused by the same origin which does not show anisotropy. It is most probable to assume that there exist two types of fluctuations, one is associated with the paraelectric-ferroelectric phase transition which contributes to $\Gamma_p(T)$ and the other one with the melting of the crystal which contribute to $\Gamma_a(T)$.

As shown in Fig. 3(c), the central peak at 378 K shows weaker angular dependence than that in the lower temperature case shown in Fig. 3(b). This implies that the pattern in Fig. 3(c) contains two components, $\Gamma_p(T)$ and $\Gamma_a(T)$ almost in equal magnitude. In the following, let's discuss about the possible mechanisms of the origin of Γ_a.

First, the ion hopping is supposed to be the one of possible candidates for the mechanism, because the conductivity of LTS begins to increase drastically above 360 K and $\Gamma(q)$ is proportional to the diffusion constant of ions in ionic conductor.[4] In this case, however, eq. (3) leads to the unrealistic result in which the diffusion constant is infinite at T_m, whereas it actually is finite even just above T_m. In addition, the independent ionic hopping leads the temperature dependence of the diffusion constant to that of the Arrhenius type,[4] which has quite different temperature dependence from eq. (3).

Another possible origin is the fluctuation of the rotation of SeO_3^{2-} ions concerned with the melting. According to the computer simulation for $NaNO_2$ performed by Lu *et al.*,[14] the librational motion of NO_2^- ions increases

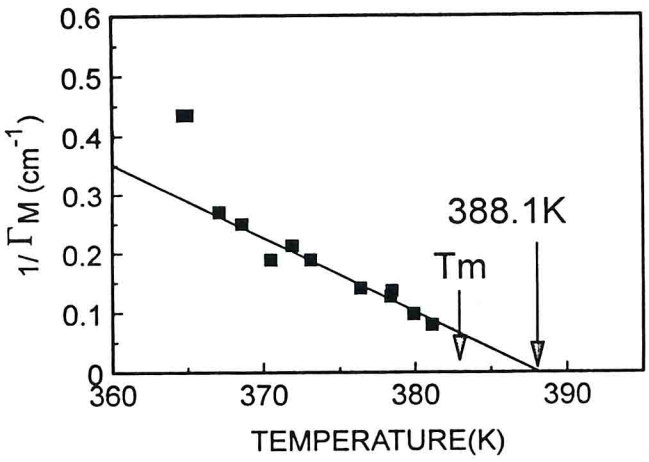


Fig. 5. Temperature dependence of the inverse of Γ_M observed with q parallel to the c^* axis.

in amplitude with increasing temperature and further increase of temperature causes the decrease of the hindered rotation. The collective free rotation commences above the phase transition temperature. The rotation of NO_2^- ions increases suddenly above 510 K and they concluded that this temperature corresponds to the melting point 554 K of $NaNO_2$.

In the case of SeO_3^{2-} ions in LTS, the correlation time of the hindered rotation of SeO_3^{2-} ions becomes short with increasing temperature and reaches to the vanishing value of the free rotation at T_m. The hindered rotation about the three fold axis of a SeO_3^{2-} ion does not yield the polarization fluctuations. This is consistent with the present result, that is, the intensity of the central peak near T_m shows a weak dependence on the direction of q. The temperature dependence of the correlation time given by eq. (3) implies presumably that there exits the collective rotation of SeO_3^{2-} ions.

Selenite ions SeO_3^{2-} connected with hydrogen bonds make a network like a cylinder along the c axis and no direct hydrogen bonded connection exists among cylinders.[15] It is highly probable that thermal energy near T_m is sufficient to move the cylinder as a whole. Even so, this fluctuation has little effect on the polarization fluctuations. Thus, this is another possible mechanism to produce the fluctuations without the depolarization effect.

We found the fluctuations related to the melting of LTS. Presumably, this fluctuations is not caused by the diffusion of ions as discussed above and its correlation time becomes short with the increase of temperature. Thus, it is not the origin of the increase of the susceptibility along the direction perpendicular to the polar axis near T_m. It is revealed that the fluctuations related to the melting has a weak angular dependence (Fig. 3(c)) compared with the polarization fluctuations concerned with the ferroelectric-paraelectric phase transition. This means that the electric dipolar interaction in the ferroelectric phase is not disturbed by the fluctuations related with the melting and, as a result, the ferroelectric phase of LTS persists up to the melting temperature.

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