

## Low-frequency Raman scattering of ferroelectric $\text{LiH}_3(\text{SeO}_3)_2$ near the melting point

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### Abstract

The central peak of the Raman spectrum of  $\text{LiH}_3(\text{SeO}_3)_2$  was measured from 300 K to the melting point (383 K). With increasing temperature, the line width takes a minimum value around 360 K. As temperature was raised to the melting point, the anomalous increase in the line width was found. It is shown that the central peak around the room temperature is caused by the polarization fluctuation associated with the ferroelectric–paraelectric phase transition. The anomalous increase of the line width is discussed in relation to the melting of the crystal.

### 1. Introduction

Among the hydrogen-bonded ferroelectrics,  $\text{LiH}_3(\text{SeO}_3)_2$  (LTS) has somewhat unusual properties. The ferroelectric phase transition temperature  $T_c$  is higher than the melting point  $T_m$  (383 K), [1] i. e. the ferroelectric order remains up to the melting point in spite of the large thermal fluctuation associated with melting.

Low-frequency Raman scattering is a useful tool for the study of the thermal fluctuation because a so-called central peak reflects the dynamics of certain fluctuations. In this paper, we report the observation of the low-frequency Raman scattering from room temperature to  $T_m$ .

### 2. Experimental

Single crystals were grown by lowering the temperature of solutions of  $\text{SeO}_2$  and  $\text{Li}_2\text{CO}_3$ . Based on the

crystal habit and the cleavage plane, specimens were cut in shape of about 5 mm cubes the edges of which are parallel to the  $a$ ,  $b$  and  $c^*$  axes, where the  $c^*$  axis is perpendicular to the  $ab$  plane. In order to reduce the stray light due to the elastic scattering, silicon oil was used for refractive index matching and a pin-hole as a spacial filter. Temperature was maintained within  $\pm 0.5$  K.

Itoh et al. [2] showed that LTS is seriously damaged when its temperature is kept near the melting point for a long time. In fact, we observed that the crystal was colored brown when it was cooled down to room temperature after its temperature was raised above 360 K. Therefore, the scattering position was chosen with the spacial filter so that the scattered light from a crystal surface was masked.

### 3. Results and discussion

Fig. 1 shows the typical low-frequency spectra of LTS in the geometry  $a(c^*c^*)b$ . The intensity of a central peak depends on temperature and the direction of the

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scattering wave vector. Spectra in the  $a(c^*c^*)b$  show a rather intense central peak compared with those in the  $a(bb)c^*$  at 300 K. Spectra observed in the  $a(c^*c^*)b$  are analyzed with the Debye-type susceptibility,

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

where  $q$  is a scattering wave vector and a high-temperature approximation for the Bose factor is used. The temperature dependence of  $\Gamma$  is plotted in Fig. 2. It reaches a minimum value around 360 K and divergently increases with a further increase in temperature.

If we assume a temperature dependence of the Curie-Weiss type for  $\Gamma$  in the temperature range 300–360 K, it is expressed as

$$\begin{aligned} \Gamma_p(T)^{-1} &= \tau_p^{-1}(T) \\ &= 0.25 \times 10^{11}(T_c - T), \end{aligned} \quad (2)$$

with  $T_c = 417.6$  K, which is near the hypothetical ferroelectric–paraelectric phase transition point (420 K)

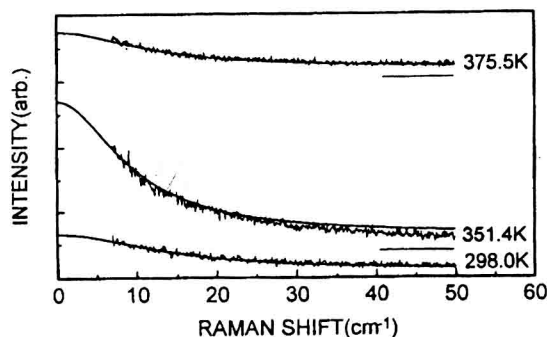


Fig. 1. Typical low-frequency spectra of  $\text{LiH}_3(\text{SeO}_3)_2$  observed in the geometries  $a(c^*c^*)b$ .

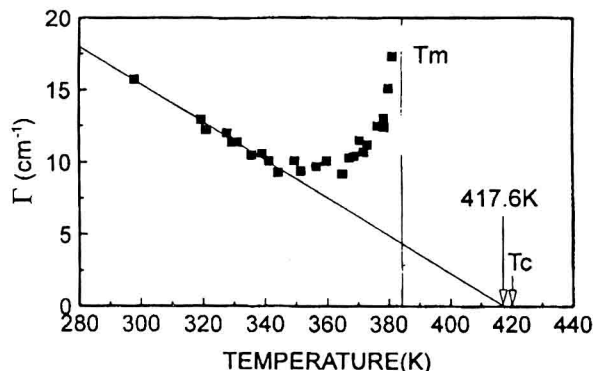


Fig. 2. Temperature dependence of  $\Gamma$  of the central peak in the geometry  $a(c^*c^*)b$ . Thin line expresses Eq. (2).

estimated from the dielectric measurements under hydrostatic pressure [3,4]. Therefore, the central peak in the lower-temperature region is inferred to be caused by the polarization fluctuation concerned with the ferroelectric–paraelectric phase transition.

The anomalous increase of  $\Gamma$  above 360 K is considered to be due to fluctuations other than the polarization fluctuations. The anomalous part,  $\Gamma_a(T)$ , is defined as the difference between the observed value and the extrapolated polarization part given by Eq. (2). The inverse of  $\Gamma_a(T)$  depends on temperature linearly as shown in Fig. 3 and is expressed by

$$\begin{aligned} \Gamma_a(T)^{-1} &= \tau_a(T) \\ &= 6.6 \times 10^{-14}(T_a - T), \end{aligned} \quad (3)$$

with  $T_a$  of 384.2 K which is slightly above the melting point (383 K) of LTS. In order to see if the analysis mentioned above is reasonable or not, the central peak was observed with  $q$  parallel to the  $c^*$  axis, because the polarization fluctuation is, in principle, not detected in this geometry. The result is shown in Fig. 4 and  $\Gamma_m(T)$  depends on temperature as

$$\begin{aligned} \Gamma_m(T)^{-1} &= \tau_m(T) \\ &= 5.2 \times 10^{-14}(T_m - T), \end{aligned} \quad (4)$$

where  $T_m = 388.1$  K and showing the good agreement with Eq. (3). Therefore, the fluctuation causing the broadening of  $\Gamma_a(T)$  is also attributable to that of  $\Gamma_m(T)$  and does not show the depolarization effect. We discuss some possible mechanisms of the fluctuation in the following.

At first, the ion hopping is supposed to be one of the candidates to give rise to the anomalous broadening, because the conductivity of LTS begins to increase above 360 K and  $\Gamma$  is proportional to the diffusion constant of ions in ionic conductor [5]. However, the independent hopping of ions leads to the temperature dependence of the diffusion constant of the Arrhenius type [5] which is quite different from Eq. (3).

Next we consider the fluctuation of the rotation of  $\text{SeO}_3^{2-}$  ions concerned with the melting. The correlation time of the hindered rotation of  $\text{SeO}_3^{2-}$  ions becomes short with increasing temperature and reaches the vanishing value of the free rotation at the melting point  $T_m$ . The hindered rotation about the threefold axis of the  $\text{SeO}_3^{2-}$  ion does not yield the polarization fluctuation. As a result, the intensity of the central peak shows no dependence on the direction of  $q$ . The temperature dependence of the correlation time given by Eqs. (3) and (4) implies presumably that there exists a collective rotation of  $\text{SeO}_3^{2-}$  ions.

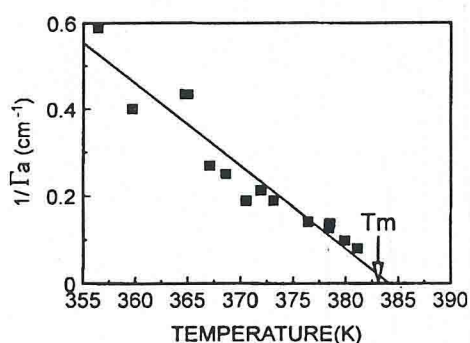


Fig. 3. Temperature dependence of the inverse of the anomalous part  $\Gamma_a$  near  $T_m$ .

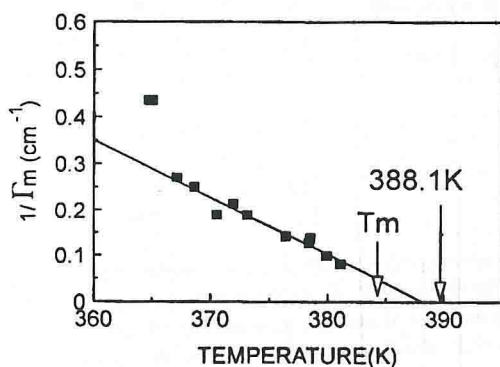


Fig. 4. Temperature dependence of the inverse of  $\Gamma_m$  observed with  $q$  parallel to the  $c^*$  axis.

Another possible mechanism is that  $\text{SeO}_3^{2-}$  connected through hydrogen bonds make a network like a cylinder along the  $c$  axis and no direct connection exists among cylinders [6]. If the thermal energy near  $T_m$  is sufficient to move the cylinder as a whole, this fluctuation does not cause a polarization fluctuation. It is revealed by the present study that the fluctuation near the melting has no (or weak) depolarization effect (Figs. 3 and 4) compared with the polarization fluctuation concerned with the ferroelectric-paraelectric phase transition. This means that the electric dipolar interaction in the ferroelectric phase is not disturbed by the fluctuation related with the melting and, as a result, the ferroelectric phase of LTS persists up to the melting temperature.

#### Acknowledgements

This work was partly supported by a Grant-in-Aid for scientific Research from the Ministry of Education, Science and Culture, No. 06402009.

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