Evaluation of crystal structure in $TlInS_2$ by optical second-harmonic generation

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Abstract. Second-harmonic generation (SHG) in layered $TlInS_2$ crystals was studied over the temperature range of 77−300 K using a confocal laser microscope system. As expected, the SHG signal was observed in the low temperature ferroelectric phase of the layered compound. In addition, the polarization properties of the SHG signals of $TlInS_2$ were investigated in the 80−180 K range. The results are in good agreement with those of the symmetric space group C_2^3 in the ferroelectric phase.

1. Introduction
$TlMeX_2$ (Me = In, Ga; X = S, Se, Te) incommensurate materials with quasi-one- or two-dimensional lattice structures have attracted much attention because of their interesting electro-optic properties [1] and photo-induced memory effects [2]. Because the phase transition of such compound from the paraelectric to the ferroelectric state occurs via an intermediate incommensurate phase, composed supposedly of nanodomains polarized in opposite directions, the interaction of light waves with such materials is interesting from the viewpoint of basic science and practical applications. Layered $TlMeX_2$, such as $TlInS_2$, has a monoclinic crystal structure with a symmetric space group C_{2h}^6 at room temperature. However, the center of symmetry is lost when the temperature is decreased to that of the ferroelectric phase transition point, where the ferroelectric phase is asymmetric with the space group C_2^3. Second-harmonic generation (SHG) is possible only in materials with no center of symmetry; therefore, it is a very useful and sensitive method for the study of phase transition in $TlMeX_2$ compounds. However, there have been few studies on SHG in these materials [3, 4]. Recently, we reported on the temperature dependence of the SHG properties of $TlMeX_2$ [5]. In the present work, we report the polarization properties of the SHG signal in $TlInS_2$ below the ferroelectric phase transition temperature.

2. Experimental
The samples of $TlInS_2$ used for optical second-harmonic measurements were bulk single crystals grown using the Bridgman-Stockbarger method and then mechanically polished with alumina powder (particle size 0.1 μm). Each sample was mounted in a continuous-flow vibration-free cryostat (JANIS ST-500). Figure 1 is a schematic diagram of our SHG measurement system. A pulsed Ti:sapphire laser

(Spectra Physics Mai Tai VF-T1S), with a repetition rate of 80 MHz, wavelength of 845 nm, and pulse width of 100 fs, was used as the light source. The diameter of the laser beam at the focal point was estimated to be 20 μm. Reflection-type optical second-harmonic measurements were performed using a confocal microspectroscopy system (Tokyo Instruments extended Nanofinder 30) and a charge-coupled device detector (Tokyo Instruments DV420A-OE). The measurements were performed in the temperature range of 77−325 K.

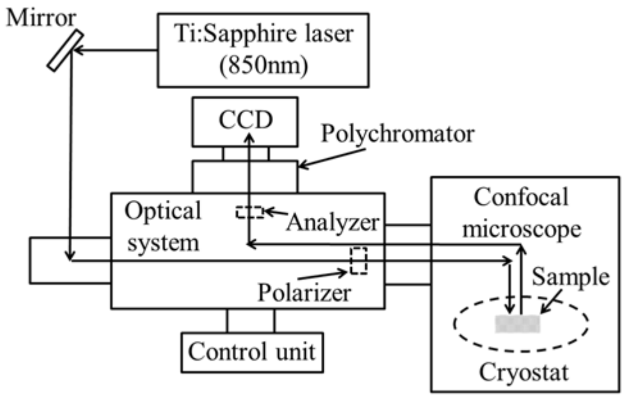

Figure 1. Schematic diagram of our SHG measurement system.

3. Results and Discussion

Figure 2 shows the temperature dependence of the intensity of SHG in the layered $TlInS_2$ crystal. The SHG signal is strong from 77 to 160 K, above which it rapidly decreases and then disappears at 192 K (Fig. 2, inset). The temperature at which $TlInS_2$ transitions from the low-temperature ferroelectric phase to the intermediate incommensurate phase was reported to be ~200 K [2]. Thus, SHG gives the more accurate value of 192 K for the phase-transition-point temperature and verifies that the average structure of the incommensurate phase has a center of symmetry. These results closely coincide with the data of Yamabi and Uchiki [4].

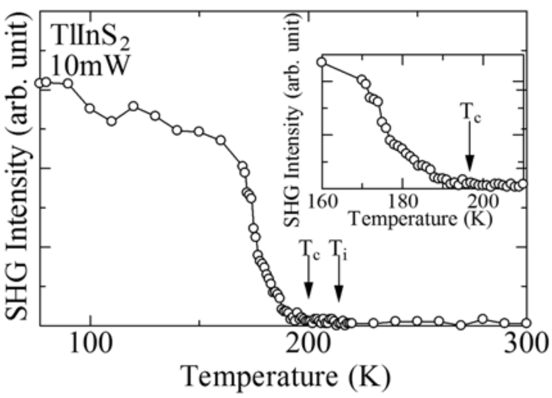

Figure 2. Temperature dependence of SHG intensity in $TlInS_2$.

In addition, we investigated the temperature dependence of the polarization of SHG in $TlInS_2$. Nonlinear polarization at 2ω in the symmetric space group C_2^3 is given by

$$\begin{pmatrix} P_x^{2\omega} \\ P_y^{2\omega} \\ P_z^{2\omega} \end{pmatrix} = \varepsilon_0 \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix} \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_yE_z \\ 2E_zE_x \\ 2E_xE_y \end{pmatrix} \quad (1)$$

The crystallographic a and b axes correspond to the x and y axes, respectively. Therefore, $P_x^{2\omega}$ and $P_y^{2\omega}$ are expressed as

$$P_x^{2\omega} = -\varepsilon_0 d_{16} \sin(2\phi) \quad (2)$$

and

$$P_y^{2\omega} = \varepsilon_0 \left(\frac{1}{2}d_{21} - \frac{1}{2}d_{21}\cos(2\phi) + \frac{1}{2}d_{22} + \frac{1}{2}d_{22}\cos(2\phi)\right) \quad (3)$$

Figures 3 and 4 show the dependence of the intensity of SHG on the fundamental light polarization detected along the a and b axes, respectively, in $TlInS_2$ in the temperature range of 80−180 K, together with results calculated using Eqs. (2) and (3). The observed results for $P_x^{2\omega}$ coincide with the calculated data, while those for $P_y^{2\omega}$ include the other peak. The results agree well with those of the symmetric space group C_2^3 in the ferroelectric phase, although there is the possibility that the samples are polycrystalline.

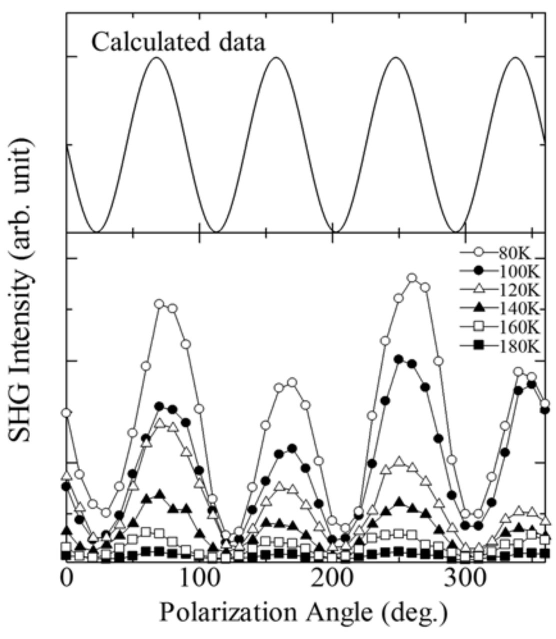

Figure 3. Fundamental light polarization dependence of the SHG intensity detected along a axis in the temperature range of 80 to 180 K in $TlInS_2$ in addition to the result calculated by eq. (2).

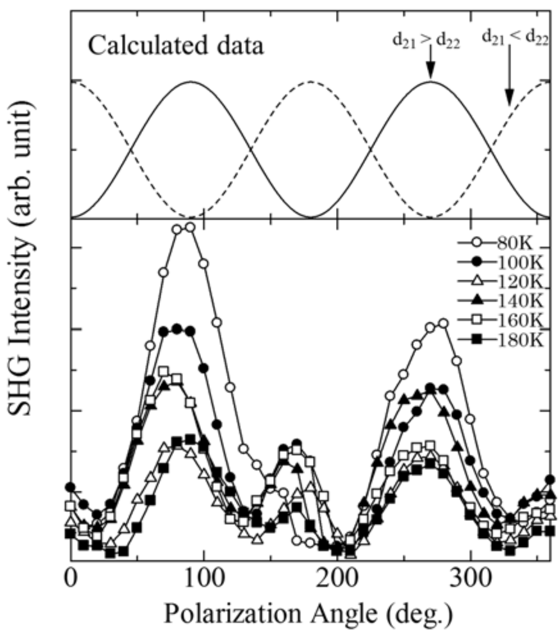

Figure 4. Fundamental light polarization dependence of the SHG intensity detected along b axis in the temperature range of 80 to 180 K in $TlInS_2$ in addition to the result calculated by eq. (3).

4. Conclusion

We performed an SHG experiment on layered $TlInS_2$ crystals in the temperature range of 77−300 K using a confocal laser microscope system. The SHG signal was observed in the low-temperature ferroelectric phase of the layered compounds, as expected. In addition, we investigated the polarization properties of SHG signals on $TlInS_2$ in the 80−180 K range. The results agree well with those of symmetric space group C_2^3 in the ferroelectric phase.

Acknowledgements

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