Growth and Optical Properties of TlGaSe$_2$ and β-TlInS$_2$

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TlGaSe$_2$ and β-TlInS$_2$ were studied for crystal growth and optical properties. Both materials have wide transparency regions, from 0.61 to 20 μm for the former and 0.5 to 12.5 μm for the latter. X-ray studies of single crystals show that these compounds are monoclinic, space group $P2_1/m$. Raman spectra are presented.

1. Introduction

Compounds of the General Formula ABX$_2$, where A is a univalent cation, B is a trivalent cation, and X may be S, Se or Te have been of interest for use as nonlinear optical, acousto-optical and infrared window materials.

In the work reported here, we studied two compounds, TlGaSe$_2$ and β-TlInS$_2$, to obtain information on crystal growth and optical properties. These compounds were first described as semiconductors which were photoconducting (*1*). Later studies showed that there were two forms of TlInS$_2$ (*2*, *3*), the high-temperature polymorph being labeled β and the low-temperature α (*3*). The space group for both forms was given as I4/mcm (*3*). TlGaSe$_2$ was also thought to be tetragonal with the same space group (*2*). More recent work (*4*, *5*) has shown that none of these compounds was tetragonal, and that there was fairly extensive polymorphism in TlInS$_2$.

2. Experimental Details

The compounds were made by heating high-purity elements (99.999 + wt% from ASARCO) together in evacuated silica-glass ampoules. When the material was completely melted, the tubes were shaken a number of times over a period of a few hours to ensure homogeneity. They were then allowed to cool slowly to room temperature by shutting off the power to the furnace. The resulting reactants were seen to be composed of small platy crystals, some of which measured as much as 5 mm across the face.

Large single crystals were grown of TlGaSe$_2$ and β-TlInS$_2$ using a modified Stockbarger technique (*6*). The polycrystalline reactants were sealed in silica-glass crystal-growing tubes under a pressure of 0.8 atm of pure dry argon gas. These tubes had a necked-in section of approximately 1 mm to initiate the growth of single crystals. We used a steep temperature gradient of 15°C/mm for each run, and slow growth rates of from 11 to 17.5 mm/day. The melting point of TlGaSe$_2$ is approximately 780°C, while that of β-TlInS$_2$ is approximately 760°C.

TlGaSe$_2$ has a deep red color, β-TlInS$_2$ a yellow-orange color, and α-TlInS$_2$ a blackish color.

Small crystals of TlGaSe$_2$ and β-TlInS$_2$ were examined under the polarizing microscope, and by single crystal X-ray diffraction using the Buerger precession technique.

Larger crystals of these compounds were examined for optical transmission. We did not study the β form of TlInS$_2$ as it is highly conducting and opaque.

3. Results

Our X-ray studies on the symmetries of TlGaSe$_2$ and β-TlInS$_2$ show that these compounds are pseudo-tetragonal, but actually

monoclinic, space group P2$_1$/m (4, 5). The lattice parameters are $a \cong b = 7.60 \pm 0.08$ Å, $c = 31.36 \times 2 \pm 0.08$ Å, $\beta = 90°20' \pm 5'$ for TlGaSe$_2$ and $a \cong b = 7.76 \pm 0.01$ Å, $c = 30.01 \pm 0.02$ Å, $\beta = 90°10' \pm 5'$ for β-TlInS$_2$.

Substantial polymorphism was found within the so-called β-TlInS$_2$, and we have labeled only the highest temperature member β (5). It is this polymorphism that prevents us from growing large single crystals of good optical quality.

Optical Transmission and Raman Data

A. β-TlInS$_2$. The optical transmission of β-TlInS$_2$ in the 0.5 μm–25 μm region is shown in Fig. 1a. The band edge is at 0.526 μm, in agreement with the results of Guseinov and his co-workers (3, 7). An optical loss region extends from this edge, well into the infrared. In the 0.8 μm to 10 μm region, the optical transmission, T, of this sample can be reasonably well approximated by an empirical expression of the form

$$T = 0.225 + 0.085 \ln \lambda,$$

with λ in micrometers. We believe that it is likely that the optical loss mechanism responsible for this behavior in β-TlInS$_2$ is scattering from long, needle-like refractive index discontinuities associated with cleavage plane boundaries in the crystal. In the microscope, these discontinuities appear to be about 1 μm in diameter, and spaced of the order of 25 μm

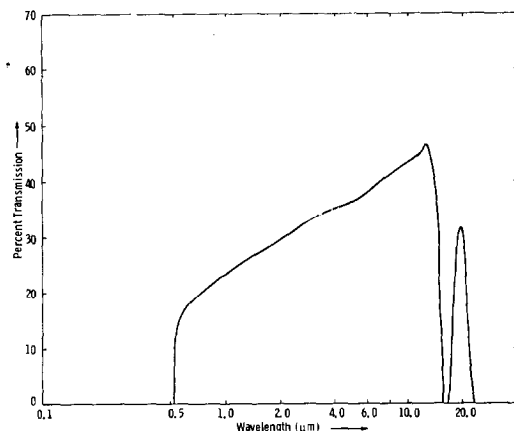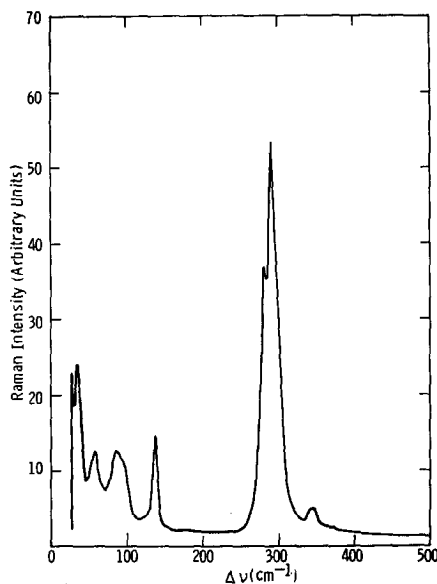FIG. 1b. Raman spectrum of TlInS$_2$. Resolution 6.7 cm^{-1}.

apart in a given plane of observation; they intersect at approximately 90° when viewed along the pseudo four-fold axis. Extinction curves for scattering by similar refractive index discontinuities have been calculated by H. C. Van de Hulst (8). The optical transmission of β-TlInS$_2$ extends beyond 800 cm^{-1} (12.5 μm), with strong lattice absorptions at 610 cm^{-1}, and below 400 cm^{-1}.

The Raman spectrum of β-TlInS$_2$, obtained with a Spex Ramalog system using a 50 mW He–Ne laser as the source, is shown in Fig. 1b. The exciting light was incident normal to the prominant cleavage faces in the crystal. The observed frequencies are shown in Table I.

TABLE I

$\Delta\nu$ (cm^{-1})	Relative intensity	Relative linewidth
35	Moderate	Medium
57	Moderate	Broad
85	Moderate	Broad
137	Moderate	Narrow
279[a]	Strong	Narrow[a]
289[a]	Strong	Narrow[a]
343	Weak	Medium

[a] Overlapped lines.

FIG. 1a. Percent transmission vs wavelength for a 1 mm thick plate of β — TlInS$_2$.

No further Raman activity was observed out to $\Delta v = 1000$ cm^{-1}. Without specific Raman orientational intensity data and detailed infrared absorption spectra below 500 cm^{-1}, it is difficult to make any conclusions other than that the above frequencies most likely correspond to external modes of vibration of the molecules in the crystal lattice, the strongest being the doublet at 279–289 cm^{-1}. It is possible that the infrared absorption peak at 610 cm^{-1} is the result of a 2-phonon absorption process associated with these prominent lattice modes.

B. *TlGaSe$_2$*. The optical transmission of TlGaSe$_2$ is shown in Fig. 2a. The band edge in this material is at 0.61 μm. The wavelength dependence of transmission is considerably different from that of β-TlInS$_2$; the band tail is absent, and the transmission curve is closer to the "square-window" appearance of most optical materials. Inspection by microscope also shows that the prominent cleavage plane discontinuities observed in β-TlInS$_2$ are absent in TlGaSe$_2$. The long wavelength transmission of TlGaSe$_2$ extends well beyond 800 cm^{-1}, and the lattice absorption frequencies appear to be lower than those of β-TlInS$_2$, as might be expected on the basis of the higher mass of TlGaSe$_2$ molecules compared to β-TlInS$_2$ molecules. Lattice absorption peaks appear in TlGaSe$_2$ at about 490 cm^{-1}, 435 cm^{-1}, and below 400 cm^{-1}.

Fig. 2b – Raman spectrum of TlGaSe$_2$. Resolution 2 cm^{-1}

FIG. 2b. Raman spectrum of TlGaSe$_2$. Resolution 2 cm^{-1}.

The Raman spectrum of TlGaSe$_2$ is shown in Fig. 2a. The observed frequencies are found in Table II.

The absolute Raman intensities observed at 0.6328 μm in TlGaSe$_2$ are at least ten times higher than those from β-TlInS$_2$; this is in part a result of the better optical quality of the TlGaSe$_2$ crystals, but it is also a result of the closeness of the wavelength of the exciting line, 0.6328 μm, to the absorption edge, 0.61 μm, in
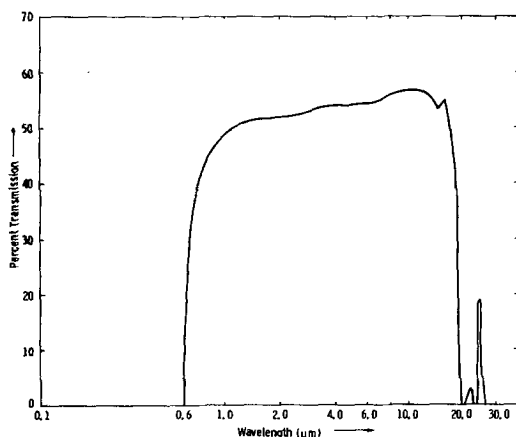

Fig. 2a – Percent transmission vs wavelength for a 1.8 mm thick plate of TlGaSe$_2$

FIG. 2a. Percent transmission vs wavelength for a 1.8 mm thick plate of TlGaSe$_2$.
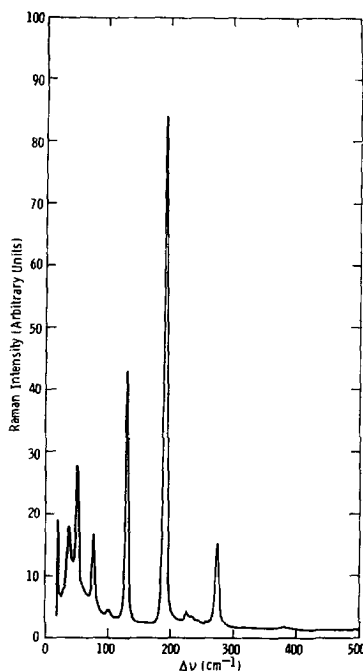
TABLE II

Δv (cm^{-1})	Relative intensity	Relative linewidth
42	Moderate	Narrow
56	Moderate	Narrow
82	Moderate	Narrow
105	Weak	Narrow
135	Strong	Narrow
196	Very strong	Narrow
230	Very weak	Narrow
240	Very weak	Narrow
279	Moderate	Narrow

TlGaSe$_2$. It should be noted that in this case, we are approaching the interesting situation of resonance Raman scattering in TlGaSe$_2$, with the photon energy near that of an exciton transition.

As in β-TlInS$_2$, no Raman active modes were found from 400 cm^{-1} to 1000 cm^{-1}. Although the low-frequency infrared absorption data is still incomplete, subject to further work we can conclude that this is evidence that both crystal structures are centrosymmetric, since in such systems no vibrational modes are simultaneously Raman and infrared active. This conclusion is consistent with the fact that neither crystal exhibited piezoelectric behavior.

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