Optical absorption spectra of liquid As_2S_3 and As_2Se_3 over a wide temperature range

LETTER TO THE EDITOR

Optical absorption spectra of liquid As$_2$S$_3$ and As$_2$Se$_3$ over a wide temperature range

Shinya Hosokawa, Yoshifumi Sakaguchi, Hiroko Hiasa and Kozaburo Tamura

Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima 730, Japan

Abstract. We have measured the optical absorption coefficient of liquid As$_2$S$_3$ and As$_2$Se$_3$ up to 900 °C in a wide absorption range up to about 3×10^5 cm^{-1}. We have developed an optical cell of our own design with a sample thickness of about 2000 Å. The optical gap obtained from the spectra decreases rapidly with increasing temperature, eventually becoming zero at about 950 °C for liquid As$_2$Se$_3$, where the semiconductor-to-metal transition starts to occur.

Arsenic chalcogenides such as As$_2$S$_3$ and As$_2$Se$_3$ are well known as prototype materials having a strong glass-forming tendency. The glassy states are easily obtained by cooling down their melts. Physical properties of glassy As$_2$S$_3$ and As$_2$Se$_3$ have been intensively investigated from both an experimental and theoretical point of view [1]. However, investigations for the liquid states have so far been less common and have been limited to a relatively small temperature range near the melting points.

The results of the neutron diffraction [2] and the infrared absorption measurements [3] for liquid As$_2$Se$_3$ revealed that the short-range atomic arrangements in the crystal [4], in which three-fold coordinated As and two-fold coordinated chalcogen atoms are covalently bonded with each other, are largely preserved on melting. Due to the preservation of covalent bonding the main features of the electronic structures of these liquids are semiconducting near the melting points, which is consistent with the results of the measurements of electrical conductivity and thermopower [5]. By raising temperature the scission of covalent bonds occurs as confirmed by the results of viscosity measurements for As$_2$S$_3$ [6, 7] and As$_2$Se$_3$ [6, 8]. This gives rise to the change of the electronic structure including the generation of the defect states at high temperatures. It is obvious that useful information about the behaviour of the electronic structure of these liquids can be obtained from studies of the optical properties, particularly if measurements of optical absorption coefficients, α, are performed in the wide absorption range; absorption spectra in the relatively low absorption range will give information about defects produced by the bond scission and in the high absorption range, about the interband transition. In this paper we report for the first time the results of the measurements of α for liquid As$_2$S$_3$ and As$_2$Se$_3$ over the wide temperature region exceeding the boiling temperature at normal pressure.

In order to measure α beyond 10^5 cm^{-1} of liquid As$_2$S$_3$ and As$_2$Se$_3$, we developed the optical cell of our own design with a sample thickness of about 2000 Å, which is
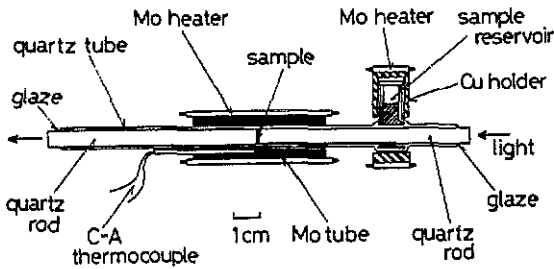
Figure 1. The construction of quartz cell used for the optical absorption measurements.

illustrated in figure 1. It should be noted that it is extremely difficult to construct an optical cell keeping such a liquid thin film, especially with high vapour pressure, stable. As seen in figure 1 two quartz rods with diameter 6.5 mm and length 80 mm, the ends of which were polished to have optically flat surfaces, were put in a quartz tube with inner diameter 6.5 mm, outer diameter 8 mm and length 150 mm. The cell had a uniform gap between the rods as a sample space, in which the liquid sample was introduced from the sample reservoir. The quartz rods and tube were cemented by a high temperature glaze [Vitta: type P-1015]. We had measured α of liquid Se using a cell of the same type [9]. We will give a detailed description of how to construct a cell with such a thin sample thickness elsewhere.

We used commercial samples with a purity of 99.999%. The sample was heated by a heating element made of Mo wire. In order to reduce the temperature gradient around the sample, a Mo tube was put between the cell and the heater. The temperature was measured by two chromel–alumel thermocouples attached on the outside wall of the cell through the holes drilled in the Mo tube. The sample reservoir was covered by a Cu holder in order that the As chalcogenide vapour could not escape. Another heating element made of Mo wire was put around the Cu holder to keep the temperature of the reservoir about 50 °C higher than the melting point of the sample. We performed the measurements of α at a high pressure of 20 bar, which enabled us to measure α at high temperatures exceeding the boiling point at normal pressure. For this we used a high-pressure vessel with two optical windows made of sapphire [10]. We measured α in the wide photon wavelength range from 330 to 2500 nm, which corresponds to the energy range from about 0.50 to 3.75 eV. In order to obtain α from the measured optical transmittance, we took account of various effects in correction, of which the following four were very important: optical reflectance, interference fringes, temperature variations of the sample thickness and those of the optical absorption of the quartz cell.

Figure 2 shows the logarithmic plots of α of liquid As_2S_3 as a function of photon energy at various temperatures up to 900 °C at a pressure of 20 bar. The spectra for glassy and supercooled liquids are also presented. The optical path lengths were about 0.5 mm, 40, 4, 1 μm, 4000 and 2000 Å, which enabled us to measure α in the wide absorption range from 5 to 3×10^5 cm^{-1}. Our results for the glassy As_2S_3 are in good agreement with the previous data of Kosek and Tauc [11]. The absorption curves shown in the figure can be split into three parts as usually seen in amorphous semiconductors: a weak shoulder in the low absorption region, the intermediate part with an exponential variation, and the high absorption part with a power dependence on photon energy. As clearly seen in the figure the curve of α shifts to the low energy side with increasing temperature. Note that all the curves in the high absorption region seem to be focused on a fixed point (about 4 eV, 4×10^5 cm^{-1}). The slope of the exponential tail becomes

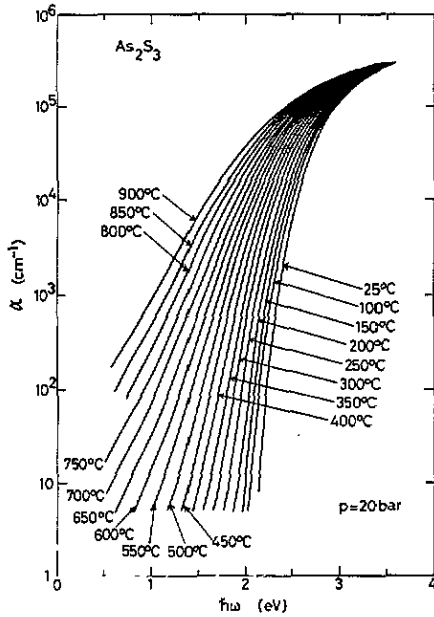**Figure 2.** Logarithmic plots of α of liquid As_2S_3 as a function of photon energy at various temperatures up to 900 °C at pressure of 20 bar.

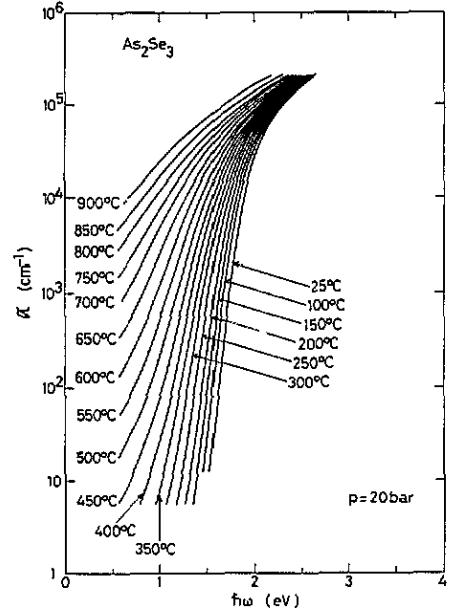**Figure 3.** Logarithmic plots of α of liquid As_2Se_3 as a function of photon energy at various temperatures up to 900 °C at pressure of 20 bar.

smaller with increasing temperature. The shoulder clearly seen at low temperatures grows with temperature eventually merging into the exponential tail. The shoulder may be attributed to the defects produced by the thermal breaks of the As–S covalent bonds.

Figure 3 shows the logarithmic plots of α for liquid As_2Se_3 as a function of photon energy. The results for glassy and supercooled liquids are also presented. The optical path lengths were about 0.5 mm, 40, 4, 1 μm and 3000 Å which enabled us to measure α in the range from 5 to 2×10^5 cm^{-1}. Our result for glassy As_2Se_3 is in good agreement with the previous data of Edmond [5], who also measured α of liquid As_2Se_3 in the limited and low absorption range from 5 to 2×10^2 cm^{-1}. Our results are in good agreement with the data in the absorption range around 10^2 cm^{-1}, but less consistent in the lower absorption region. The gross feature of the absorption curves is quite similar to that for liquid As_2S_3. The curves at low temperatures may be also focused on a fixed point in the high absorption region (about 3.2 eV, 4×10^5 cm^{-1}). Note that the curves in the high absorption region at temperatures higher than 850 °C seem to shift almost in parallel.

From a detailed analysis of these spectra of liquid As_2S_3 and As_2Se_3 in the high absorption region, we obtained the optical gap E_g defined by the conventional relation $(\alpha\hbar\omega)^n \propto \hbar\omega - E_g$, where $\hbar\omega$ is the photon energy and n is a constant [12]. It is well known that n is $\frac{1}{2}$ in the glassy As chalcogenide [12]. The temperature variations of E_g for As_2S_3 and As_2Se_3 are shown in figure 4 and the values of E_g and n are summarized in table 1. As seen in figure 4, E_g of As_2S_3, indicated by empty circles (O), decreases with increasing temperature and the decrease becomes substantial at higher temperatures. In the figure, E_g of As_2Se_3, indicated by full circles (●), decreases rapidly with increasing temperature, eventually becoming zero at about 950 °C, where the semiconductor-to-

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Table 1. The values of E_g and n obtained using the conventional relation $(\alpha\hbar\omega)^n \propto \hbar\omega - E_g$ for As_2S_3 and As_2Se_3 at various temperatures.

T (°C)	As_2S_3		As_2Se_3	
	E_g	n	E_g	n
25	2.40	0.50	1.68	0.50
100	2.34	0.50	1.63	0.50
200	2.24	0.50	1.56	0.50
300	2.15	0.50	1.49	0.50
400	2.06	0.50	1.41	0.50
500	1.96	0.50	1.24	0.45
600	1.87	0.50	1.04	0.40
700	1.76	0.50	0.88	0.40
800	1.64	0.50	0.56	0.33
900	1.50	0.50	0.26	0.30
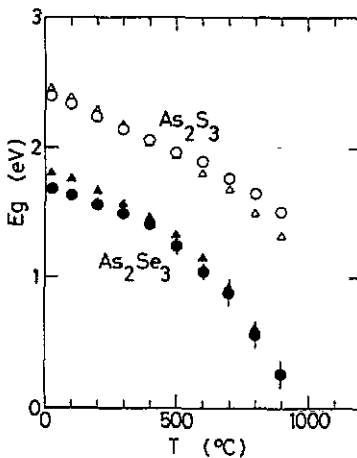
Figure 4. Empty (○) and full (●) circles indicate the optical gap E_g of As_2S_3 and As_2Se_3 as a function of temperature, respectively. Empty (△) and full (▲) triangles show the value of energy at which α becomes 3×10^3 cm^{-1} for As_2S_3 and As_2Se_3, respectively.

metal (SC-M) transition starts to occur. This is consistent with the recent results of electrical conductivity up to 1400 °C at 600 bar [13]. The value of conductivity increases substantially with increasing temperature and becomes about 300 Ω^{-1} cm^{-1} at 1150 °C. Empty (△) and full (▲) triangles show the value of energy at which α becomes 3×10^3 cm^{-1} for As_2S_3 and As_2Se_3, respectively. It is interesting that both values show a similar temperature-dependence to that of E_g. As seen in table 1, the obtained value of n for As_2S_3 is $\frac{1}{2}$ in the present temperature range. Note that n for As_2Se_3 at temperatures lower than 400 °C is also $\frac{1}{2}$, but becomes smaller when the SC-M transition temperature is approached.

Recently, we measured x-ray diffraction [14], EXAFS [15] and mass density [14] for liquid As_2Se_3 up to about 1500 °C under high pressure to obtain information on the mechanism of the SC-M transition. We have found that remarkable structural changes accompanied by the volume contraction occur around the SC-M transition region.

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