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LOW-FREQUENCY INELASTIC LIGHT SCATTERING FROM As–S GLASSES

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Raman scattering from As–S glasses were observed in the low-frequency region, from 5 to 60 cm^{-1}. The spectral features depend on the quenching and annealing conditions as well as on the temperature and the composition. The spectrum was explained in terms of the vibration of the layer-like clusters coupled with each other through van der Waals forces.

THERE HAS BEEN much controversy on the origin of inelastic light scattering spectra of chalcogenides glasses in low-frequency region, from 5 to 60 cm^{-1}. Nemanich [1] has fitted his data to a model based on acoustic modes in a homogeneous amorphous medium. He has estimated "structural correlation length" $2R_0$ by fitting the data to the theoretical curve $I(\omega) = \omega^2 \exp{(\omega R_0/v)^2}$, where ω is the frequency, $I(\omega)$ the reduced Raman intensity and v the acoustic velocity. In contrast, Phillips [2] has suggested that the vibration of small layer-like cluster, which he called "outrigger raft" is responsible to the low-frequency spectrum. These rafts are stacked with van der Waals force operating between chalcogen atoms with lone pair electrons.

We measured the low-frequency spectra of As–S glasses for various quenching and annealing conditions. We also observed the change of the spectrum with the temperature and the composition. We found that the spectrum is sensitive to the medium range order and the model due to Nemanich is not preferable to explain our experimental results.

The Raman spectra were obtained with 90° scatter-configuration with the use of Jobin Yvon HRD-2 double monochromator furnished with 1800 grooves mm^{-1}, 0.5 μm blazed holographic gratings. As the light source, He–Ne laser (6328 A) of 50 mW was used. The polarization of the incident light was normal to the scattering plane and that of the scattered light was in the plane.

The 6*N* pure sulfur and arsenic were weighted and mixed in a mortar. The mixture was sealed in an evaucated quartz tube of inner diameter of 8 mm. The tube was kept at about 100°C above the melting temperature of the compound for ten hours. The specimens were quenched under various cooling rates.

In Fig. 1, the Raman spectra of vitreous As_2S_3 with different cooling conditions as well as of an annealed specimen were shown in the region from 5 to 60 cm^{-1}. Curve *a* is the spectrum for ice-quenched specimen. The cooling rate is about 10°C sec^{-1}. Curves *b* and *c* are those for cooled at the inside and outside of the furnace, respectively. The cooling rates are estimated to be about 100°C min^{-1} and 10°C min^{-1}, respectively. It is shown that the peak position moves to the higher frequency from 19.5 to 25.1 cm^{-1}, as the cooling rate is decreased. When the ice-quenched specimen is annealed at 170°C for one hour, peak position moves to 26.5 cm^{-1} as shown in curve *d*. The results are summarized in the following table. If the low-frequency spectrum is assumed to be associated with the acoustic modes in a homogeneous medium with the finite correlation length $2R_0$, according to Nemanich [1] and Martin *et al.* [3],

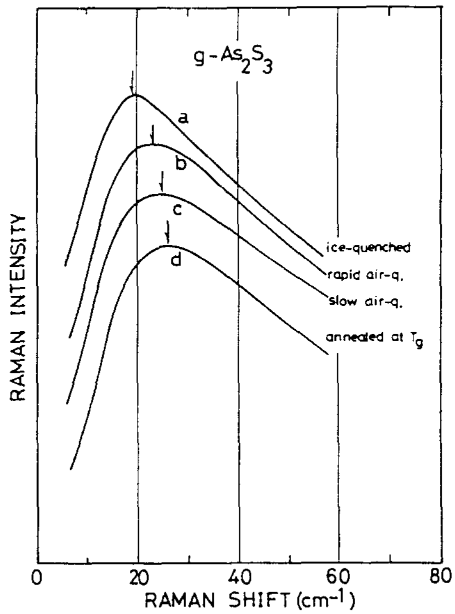

Fig. 1. Low-frequency Raman spectra of *g*-As_2S_3 of different quenching and annealing conditions, curve *a*: ice-quenched, curve *b*: rapidly air-quenched, curve *c*: slowly air-quenched and curve *d*: annealed at glass transition temperature.

Table 1

	Peak frequency ($1\ cm^{-1}$)	Correlation length $2R_0$ (A) in Nemanich model
Ice-quenched ($10°C\ sec^{-1}$)	19.5	7.61
Rapid air-quenched ($100°C\ min^{-1}$)	24.1	6.16
Slow air-quenched ($10°C\ min^{-1}$)	25.1	5.92
Annealed at 170°C for 1 hr	26.5	5.60

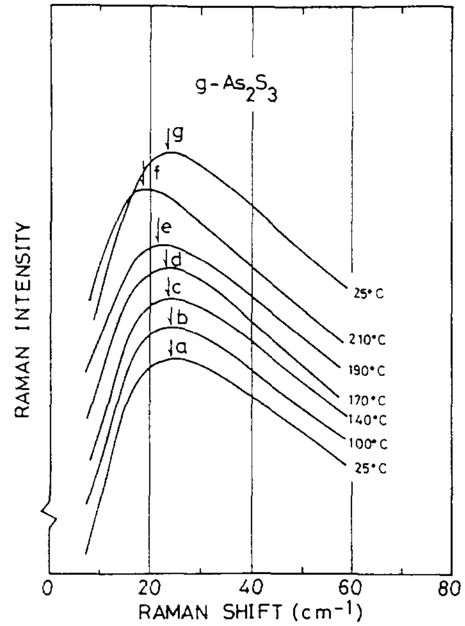

Fig. 2. Low-frequency Raman spectra of g-As_2S_3 at different temperatures. Curve a: 25°C, curve b: 100°C, curve c: 140°C, curve d: 170°C, curve e: 190°C, curve f: 210°C and curve g: 25°C.

the correlation length can be estimated from the peak frequency ω_{peak} of the spectrum with the use of the relation $\omega_{peak} = v/R_0$, where v is the acoustic wave velocity. On the last column of Table 1, the correlation length obtained in this way is listed. Though the order of magnitude is reasonable, it is quite irrational that the correlation length decreases as the quenching rate is slowed down and also with annealing. If this spectrum is ascribed to the vibration of the layer-like clusters of As_2S_3, the peak will move to the higher frequency as the result of the more ordered arrangement of the clusters. And the cluster may be "outrigger raft" in Phillips' model [2].

As shown in Fig. 2, Raman spectra of vitreous As_2S_3 were measured with raising the temperature from 25 to 210°C. The temperature was again lowered down to 25°C. In Fig. 3, the peak frequency is plotted vs temperature. The peak frequency is almost constant up to the glass transition temperature T_g (170°C), and then decreases rapidly above T_g. The spectrum is quite reproducible as shown in curve a and g in Fig. 2. The linear extrapolation of the curve in Fig. 3 meets the horizontal axis at about 315°C which is the melting temperature of As_2S_3. Above T_g, in the supercooled liquid, the separation between clusters may increase with the rise of temperature, resulting in the decrease of the frequency of vibration. At the melting temperature, these clusters may move freely, resulting in the vanishing of the stacking order of the clusters.

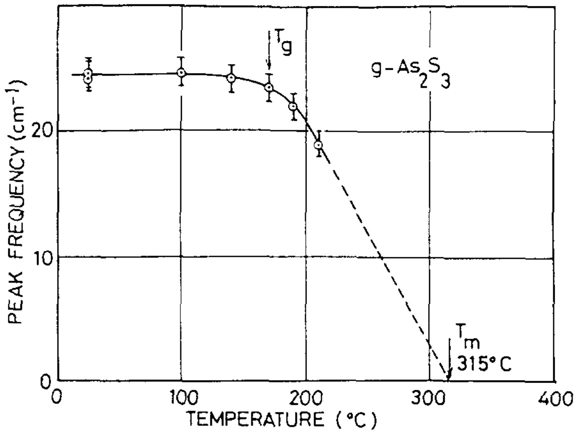

Fig. 3. Peak frequency of Raman spectrum of g-As_2S_3 vs temperature.

The Raman spectra of As_xS_{1-x} with various As composition x were measured. The specimens were all quenched in the air. Every spectrum has a broad band with a single peak, whose frequency is plotted as a function of x as shown in Fig. 4. The peak frequency is the highest for As_2S_3, decreasing with the deviation from the stoichiometry. It is reasonable that the coupling between the clusters decreases as the clusters themselves become more irregular owing to the deviation from the stoichiometry. Moreover, when the sulfur content is increased, eight-membered ring of the sulfur molecules are isolated in the inter-cluster space, blocking the van der Waals coupling of the clusters.

To summarize our conclusion, the low-frequency Raman scattering is associated with the vibration of clusters which are coupled with each other through van

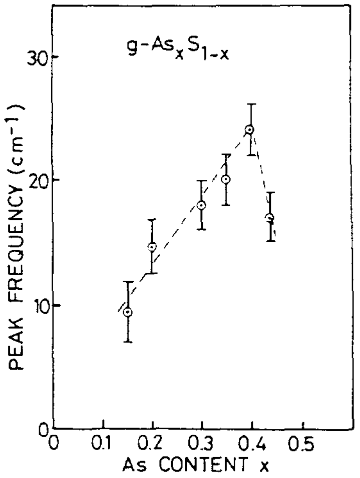

Fig. 4. Peak frequency of Raman spectrum of g-As$_x$S$_{1-x}$ vs As composition x.

der Waals force. The cluster may be the so called "outrigger raft", according to Phillips [2], stacked with lone-pair electrons of chalcogen atoms, vibrating with optic type shear mode. The frequency of the vibration increases with the increase of the order of the arrangement of the rafts. The order of the arrangement of the rafts may be large in the well annealed glass. It will decrease with the rise of temperature, especially above glass transition temperature, and will eventually disappear at the melting temperature, resulting in the vanishing of the resotring force for the vibration of the rafts. When the sulfur content is increased more than the stoichiometric composition of As_2S_3, the structure of the raft itself may become more irregular, resulting in the more random stacking of the rafts. With the further increase of the sulfur content, eight-membered rings of the sulfur may be isolated into the interlayer space between rafts, resulting in the increased separation of the rafts. From these arguments it can be concluded that the low-frequency Raman spectrum is quite sensitive to the medium range order of the glassy state.

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