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Far-infrared study of low-frequency vibrational states in As_2S_3 glass

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Far-infrared absorption and reflection spectra of As_2S_3 glass have been measured in the frequency range 10–60 cm^{-1} at room temperature. The absorption coefficient $\alpha(\nu)$ has been determined as a function of frequency ν and found to deviate from the quadratic frequency dependence. A broad absorption peak corresponding to a boson peak is clearly found at about 27 cm^{-1}. Infrared coupling coefficient $C_{ir}(\nu)$ is determined experimentally from $\alpha(\nu)$ and the density of vibrational states previously reported. It is found that $C_{ir}(\nu)$ shows the frequency dependence similar to that of the Raman coupling coefficient $C_r(\nu)$ obtained in the same manner for As_2S_3 glass and is not described by the Martin-Brenig model. Both $C_{ir}(\nu)$ and $C_r(\nu)$ show no peak and the frequency dependence close to that predicted by a fractal model. The far-infrared absorption peak may be interpreted as a result of the phonon-fracton crossover.

Amorphous materials or glasses exhibit physical properties different from crystalline solids. The most important differences occur in low-frequency vibrational states (≤ 100 cm^{-1}). The nature of low-frequency vibrational states in glasses has been extensively investigated by a variety of experimental techniques and theoretical models, but it is still unclear. These vibrational states are mainly investigated by means of heat capacity, inelastic neutron scattering, Raman scattering, and infrared absorption. In particular, Raman-scattering studies in glasses are extensively made. In contrast to this, little study is made by far-infrared spectroscopy.

As_2S_3 glass is one of the most-studied glasses. The density of low-frequency vibrational states $g(\nu)$ in As_2S_3 glass has been determined from both inelastic-neutron-scattering[1] and heat capacity[2] measurements, and found to be non-Debye form. Ahmad *et al.*[2] obtained the dependence of the absorption coefficient $a(\nu)$ of As_2S_3 glass on frequency ν, from absorption measurements using far-infrared laser lines in the range 22–50 cm^{-1}, although their data points were separate and did not lie on a smooth curve. Matsuishi *et al.*[3] also measured absorption spectra of As_2S_3 glass in the range 8–22 cm^{-1} with a Lamellar-grating Fourier transform spectrometer and reported the ν^2 frequency dependence of $a(\nu)$. This result is different from the frequency dependence of $a(\nu)$ by Ahmad *et al.*[2] The aim of this study is to determine $a(\nu)$ of As_2S_3 glass in the wider frequency range and the frequency dependence of the infrared coupling coefficient $C_{ir}(\nu)$, which is a measure of interactions between the infrared light and vibrational modes, and to interpret low-frequency vibrational dynamics in As_2S_3 glass.

In the present paper the frequency dependence of $a(\nu)$ in As_2S_3 glass has been obtained from far-infrared absorption and reflection measurements in the range 10–60 cm^{-1} and shown not to be interpreted by empirical[4] and Schlömann[4,5] models which have been applied to the analysis of far-infrared absorption in glasses. The frequency dependence of $C_{ir}(\nu)$ obtained from $a(\nu)$ and $g(\nu)$ mentioned above is compared with that of the Raman coupling coefficient $C_r(\nu)$ obtained in the same manner and is discussed by a model proposed by Martin and Brenig[6,7] (MB) and a fractal model.[8–10]

Samples of As_2S_3 glass were prepared by melting the mixture of high-purity (6*N*) elements As and S in evacuated fused silica ampoules of 10 mm inner diameter with rocking for 10 h at 700 °C and then air quenching. After that the glass samples were annealed for 20 h at 192 °C. Disk-shaped samples were cut from the ingots obtained above with a wire saw and both surfaces were optically polished with diamond paste. For absorption measurements four plane parallel slabs of different thicknesses 0.51, 1.0, 2.0, and 3.37 mm depending on frequency range, and for reflection measurements a wedged-shaped sample about 10 mm thick were used. Far-infrared absorption and reflection measurements were made with a Martin-Puplett Fourier transform spectrometer[11,12] in the range 10–60 cm^{-1} at room temperature. A liquid-He-cooled Si bolometer was used as a detector. The far-infrared absorption coefficient was determined from absorption and reflection measurements by using the usual expression for the transmission *T* through a plane parallel slab. For normal incidence the expression for the transmission *T* through a plane parallel slab of thickness *d* in the high-absorption region is

$$T=\frac{(1-R)^2e^{-\alpha d}}{1-R^2e^{-2\alpha d}}, \tag{1}$$

where $R=(n-1)^2/(n+1)^2$ is the single surface reflectivity at normal incidence and n is the index of refraction.

The obtained $a(\nu)$ for As_2S_3 glass is shown in open circles as a function of frequency on a log-log plot in Fig. 1. According to Strom and Taylor[4] the far-infrared absorption in chalcogenide glasses above 10 cm^{-1} is expressed in the following empirical form:

$$\alpha(\nu)\propto\nu^{\beta}, \tag{2}$$

where $\beta\leq 2.0$. They report $\beta=2$ over the frequency range 10–100 cm^{-1} for chalcogenide glasses like As_2S_3 and As_2Se_3. Matsuishi *et al.*[3] also reported $\beta=2$ for As_2S_3 glass in the range 8–22 cm^{-1}. But, a nonquadratic frequency dependence of the far-infrared absorption was also reported for As_2S_3 (Ref. 2) and As_2Se_3 (Ref. 13)

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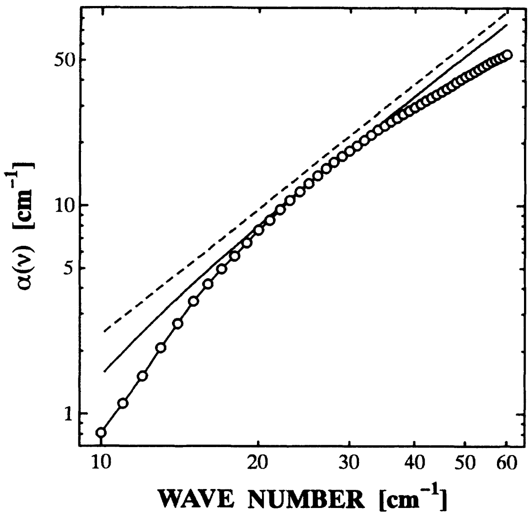

FIG. 1. Far-infrared absorption coefficient $a(\nu)$ as a function of frequency ν at room temperature for As_2S_3 glass in a log-log scale (open circle, ○); a dashed line, $a(\nu)\sim\nu^2$ curve; a solid line, frequency dependence of $a(\nu)$ calculated by the Schlömann model, Eq. (3).

glasses. The dashed line in Fig. 1 shows the line of $\beta=2$. It is evidently found from this figure that $a(\nu)$ obtained here for As_2S_3 glass deviates from the ν^2 frequency dependence even in the narrow range 10–60 cm^{-1}, is more complicated and cannot be described in terms of a single value of β.

No microscopic theory for infrared absorption in amorphous materials presently exists. Far-infrared absorption in amorphous materials has been often explained on the basis of ideas developed for crystals with imperfections. The disorder-induced far-infrared absorption can be expressed by a charge-fluctuation model[4,5] as follows:

$$\alpha(\nu)\propto\nu^2\left[1-\frac{1}{\{1+(\nu/\nu_0)^2\}^2}\right], \tag{3}$$

where $\nu_0=\kappa/l$, κ is the velocity of sound and l is a correlation length. Matsuishi *et al.*[3] reported that the frequency dependence of $a(\nu)$ in the range 8–22 cm^{-1} for As_2S_3 glass was well represented by Eq. (3). The solid line in Fig. 1 is the curve calculated on the basis of Eq. (3) using the same values of κ (1.426×10^5 cm/sec) and l (7.2 A) as used in Ref. 3. As seen in this figure, the curve calculated above does not fit the absorption data in the low-frequency range 10–20 cm^{-1} observed here. We could not find out physically significant values of the correlation length l to fit our data.

The far-infrared absorption for amorphous materials can be written as follows:[14]

$$a(\nu)=C_{\rm ir}(\nu)g(\nu), \tag{4}$$

where $C_{\rm ir}(\nu)$ is the infrared coupling coefficient and $g(\nu)$ is the density of vibrational states. The intensity of reduced Raman scattering, $I_r(\nu)$ in amorphous materials is usually expressed in the form[7,15]

$$I_r(\nu)=\frac{I(\nu)\nu}{\{n(\nu)+1\}}=C_r(\nu)g(\nu), \tag{5}$$

where $I(\nu)$ is the intensity of Raman scattering, $n(\nu)$ is the Bose population factor, and $C_r(\nu)$ is the Raman coupling coefficient.

A log-log plot of $a(\nu)/\nu^2$ versus ν (solid line) is shown in Fig. 2 together with $I_r(\nu)/\nu^2$ versus ν (solid squares) obtained at 8 K by Nemanich[7] for As_2S_3 glass. In this figure, open circles represent absorption coefficients of As_2S_3 glass obtained by Ahmad *et al.*[2] It is seen from this figure that $a(\nu)$ obtained here is in good agreement with that reported by Ahmad *et al.*[2] and shows the frequency dependence similar with $I_r(\nu)$ by Nemanich.[7] This result indicates that the frequency dependence of both $C_{\rm ir}(\nu)$ and $C_r(\nu)$ are nearly identical in As_2S_3 glass in the observed frequency range. For As_2S_3 glass $g(\nu)$ has been determined in the frequency range 1.25–15 meV (10–120 cm^{-1}) from inelastic neutron scattering[1] and in the range 0–50 cm^{-1} from heat capacity.[2] Consequently, we can obtain $C_{\rm ir}(\nu)$ or $C_r(\nu)$ by dividing $a(\nu)$ or $I_r(\nu)$ by $g(\nu)$. The frequency dependence of $C_{\rm ir}(\nu)$ and $C_r(\nu)$ obtained in this manner is shown in Fig. 3. The Raman data at 8 K were taken from Nemanich[7] and $g(\nu)$ from Malinovsky *et al.*[1] $C_{\rm ir}(\nu)$ and $C_r(\nu)$ show the similar frequency dependence in the observed frequency region, although small deviation is observed below 17 cm^{-1}. Ahmad *et al.* indicated that $C_{\rm ir}(\nu)$ and $C_r(\nu)$ can be described in terms of a single coupling coefficient for As_2S_3 glass[2] in the region 22–50 cm^{-1} and for SiO_2 glass[16] in the region 22–82 cm^{-1}.

According to the MB model[6,7] which has been extensively used for the interpretation of Raman scattering

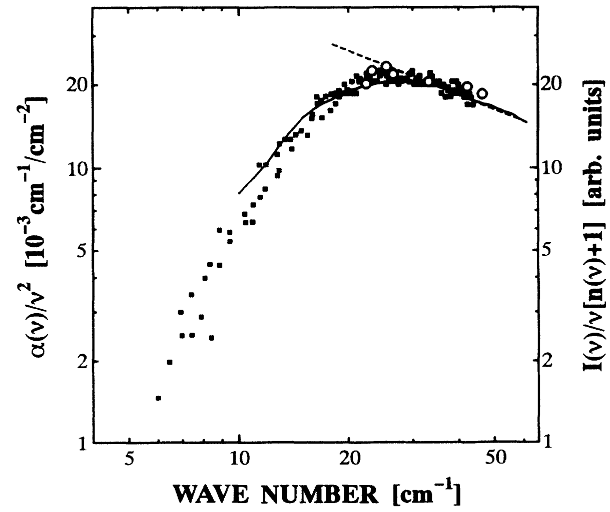

FIG. 2. Comparison of absorption coefficients $a(\nu)$ with reduced Raman scattering $I_r(\nu)$ for As_2S_3 glass in a log-log scale. A solid line, absorption coefficient $a(\nu)/\nu^2$ vs ν at room temperature, solid squares (■), reduced Raman scattering $I_r(\nu)/\nu^2$ vs ν (Raman data at 8 K from Ref. 7); open circles (○), absorption coefficient $a(\nu)/\nu^2$ vs ν (infrared data at room temperature from Ref. 2); a dashed line, $a(\nu)/\nu^2\sim\nu^{-0.54}$.

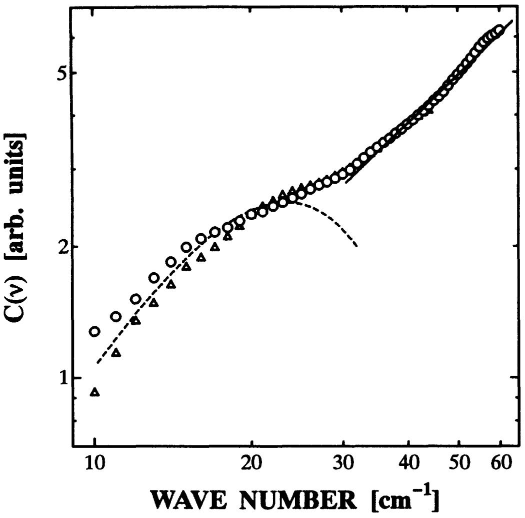

FIG. 3. Comparison of experimentally determined and calculated coupling coefficients $C(\nu)$ for As_2S_3 glass. Open circles (○), infrared coupling coefficient $C_{ir}(\nu)$; open triangles (△), Raman coupling coefficient $C_r(\nu)$ (Raman data at 8 K taken from Ref. 7); a dashed line, calculated coupling coefficient $C(\nu)$ by the Martin-Brenig model, Eq. (6); a solid line, calculated coupling coefficient $C_f(\nu)$ by the fractal model, Eq. (9).

from glasses, $C_r(\nu)$ is expressed in the form

$$C_r(\nu)\propto \nu^2 \exp[-(2\pi\nu\sigma/\kappa)^2] \ , \tag{6}$$

where κ is the velocity of sound and 2σ is the structural correlation range. Nemanich[7] found a good agreement between the Raman data and the MB model for As_2S_3 glass, assuming the Debye form $g(\nu)\sim\nu^2$. $C_r(\nu)$ was calculated on the basis of Eq. (6) using the same values of κ and σ used by Nemanich.[7] The result is shown in a dashed line in Fig. 3. It is seen from this figure that the MB model cannot explain the frequency dependence of $C_r(\nu)$ and $C_{ir}(\nu)$ determined experimentally for As_2S_3 glass in the range 10–60 cm^{-1} in disagreement with Nemanich's result. This is due to the difference in $g(\nu)$ used. Ahmad *et al.*[2] and Ahmad[16] indicated that the MB model is not valid for the interpretation of the Raman coupling coefficients in As_2S_3 glass[2] and SiO_2 glass[16] if $g(\nu)$ determined from heat capacity is used.

Now let us consider the infrared absorption of As_2S_3 glass by the fractal model. According to the fractal model[8–10] the density of states $g_f(\nu)$ and the Raman-scattering intensity $I_f(\nu)$ for fractons can be written as

$$g_f(\nu)\propto \nu^{\tilde{d}-1} \ , \tag{7}$$

$$I_f(\nu)\propto \nu^{(2\tilde{d}/d_f)+\tilde{d}-2}\{n(\nu)+1\} \ , \tag{8}$$

where $\tilde{d}$ is the fracton (spectral) dimension and d_f is the fractal dimension. We obtain the Raman coupling coefficient $C_r^f(\nu)$ for fractons from Eqs. (7) and (8) as follows:

$$C_r^f(\nu)\propto \nu^{2\tilde{d}/d_f} \ . \tag{9}$$

If we describe the infrared absorption coefficient as $\alpha_f(\nu)=C_{ir}^f(\nu)g_f(\nu)$ for fractons as in Eq. (4), we may write $\alpha_f(\nu)$ in the form of Eq. (10) as evidenced from the experimental result that the frequency dependence of $C_{ir}(\nu)$ is nearly identical with that of $C_r(\nu)$. Here $C_{ir}^f(\nu)$ is the infrared coupling coefficient for fractons.

$$\alpha_f(\nu)=C_{ir}^f(\nu)g_f(\nu)\propto \nu^{(2\tilde{d}/d_f)+\tilde{d}-1} \ . \tag{10}$$

We obtain $\tilde{d}-1=0.35$ and then $\tilde{d}=1.35$ from Eq. (7) and the value 0.35 of the slope of $g(\nu)$ in the frequency range 30–50 cm^{-1} in Fig. 1 of Ref. 1. Similarly, we obtain $d_f=2.43$ from Eq. (10) and the value -0.54 of the slope of $a(\nu)/\nu^2$ in the same range 30–50 cm^{-1} in Fig. 2 (dashed line). Theoretical values[8] of the fracton and fractal dimensions predicted for a three-dimensional percolating network are $\tilde{d}=1.42$ and $d_f=2.5$. These values are close to the above values determined experimentally. The theoretical value 1.1 of the exponent $(2\tilde{d}/d_f)$ in Eq. (9) is identical to the experimentally obtained value 1.1. The theoretical frequency dependence of $C_r^f(\nu)$ calculated for fractons are shown in a solid line in Fig. 3. It is found that $C_r^f(\nu)$ calculated on the basis of the fractal model is nearly in agreement with $C_{ir}(\nu)$ and $C_r(\nu)$ determined experimentally, at least above 30 cm^{-1}. Therefore, it seems plausible to think that the broad far-infrared absorption peak at about 27 cm^{-1} corresponding to the boson peak is interpreted as a result of the phonon-fracton crossover. The above agreement seems not to be fortuitous, but presumably to indicate the fractality of the distribution of elastic constants or the size distribution of clusters making up glasses, which are considered to determine frequencies of the low-frequency vibrational modes in glasses. However, it is certainly not obvious why the structure in As_2S_3 glass should exhibit dynamical properties analogous to the percolating network.

In summary, the nonquadratic frequency dependence of the absorption coefficient in As_2S_3 glass has been clearly observed in the far-infrared region 10–60 cm^{-1}. It is found that the infrared coupling coefficient exhibits the frequency dependence similar with that of the Raman coupling coefficient and the frequency dependence close to that predicted by the fractal model, and is not described by the Martin-Brenig model. The far-infrared absorption peak in As_2S_3 glass may be interpreted as a result of the phonon-fracton crossover.

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