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Effect of preparation conditions on the low frequency Raman spectrum of glassy As_2S_3

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Low frequency Raman scattering was measured for glassy As_2S_3 samples, prepared by different quenched conditions. It was found that the boson peak position shifts to lower energy with increase of the initial temperature of the melt and with increase of quenching rate. The effect is interpreted in terms of the dissociation reaction of As_2S_3 at high temperature. This leads to softening of the elastic modules and a decrease in the sound velocity.

1. Introduction

It is well known that a prominent difference between the vibrational spectra of glassy and crystalline materials occurs in the low frequency region of their spectra [1, 2]. In this part of the spectrum the density of vibrational states of disordered materials can be seen in Raman scattering because of loss of momentum conservation [3]. The occurrence of a boson peak also in the neutron scattering spectra shows that coupling coefficient fluctuation cannot be main origin of the boson peak. This coupling coefficient $C(\omega)$ has a smooth dependence on ω [4], where $C(\omega)$ is proportional to omega.

In the present paper we will therefore proceed by assuming that the boson peak is a sign of elastic inhomogeneity. This parameter is describing an intermediate range of inhomogeneities and can be derived from the boson peak maximum [5]. This spectral feature gives information about the properties of the glass. It has been shown in [6–9] that the position of the boson peak of glasses is sensitive to the preparation conditions and the thermal treatment of the samples.

Glassy As_2S_3 is a convenient system for studying the influence of the preparation conditions on low frequency light scattering because this substance is known not to crystallize during slow cooling or long heat treatment.

2. Experimental procedure

Pure sulphur and arsenic (6 N) were weighed and mixed. The mixture was vacuum sealed in a quartz tube of 10 mm inner diameter. The tube was kept at 870 K for 8 h in a rocking furnace, and the tube was rotated. The samples were quenched from the melt with rate $0.01\ \mathrm{K\,s^{-1}}$. The obtained glass ingot was cut into cylindrical pieces, and each of them was again sealed in an evacuated quartz tube. The tubes were kept at a fixed temperature (without rotating) at 950 K or 1220 K or 1, 3 or 4.5 h, and then quenched with different cooling rates. The cooling rates are estimated to be about $10\ \mathrm{K\,s^{-1}}$ (ice-quenched), $1\ \mathrm{K\,s^{-1}}$ (in air) and $0.01\ \mathrm{K\,s^{-1}}$ (inside of the furnace). The specimens were cut to a rectangular shape and polished with diamond paste.

The Raman spectra from 5 to $500\ \mathrm{cm^{-1}}$ were measured in 90° scattering configuration (VO) using a Jobin Yvon U-1000 monochromator, at room temperature. As the light source, a Kr^+-ion laser (Spectra Physics, model 165, $\lambda = 676$ nm) of 100 mW was used. The spectral slit width gave a result of $1\ \mathrm{cm^{-1}}$. The Raman spectra had maximum signal intensities between 200 and 5000 counts $\mathrm{s^{-1}}$ depending on the particular sample. There was no sign of signal deterioration due to photodarkening effect.

3. Results

In Fig. 1, the low frequency (a) and vibration (b) parts of Raman spectra of As_2S_3 glasses, quenched with different cooling rate, are shown. Note that the peak position ω_p of spectra shifts to lower frequency and two new vibrational bands (at $189\ \mathrm{cm^{-1}}$ and $231\ \mathrm{cm^{-1}}$) appear as the cooling rate is increased. The boson peak position of the glass after synthesis is $26.5\ \mathrm{cm^{-1}}$.

In Figs 2 and 3 the dependence of the peak position on quenching rate is shown for various times of holding at $T = 950$ K and 1220 K, respectively. The peak position shifts to lower frequency upon increase of quenching rate as well as upon increase of time of holding the melt at a given temperature. For the same holding time (for example, 1 h, the peak position varies from $\omega_p = 25.4\ \mathrm{cm^{-1}}$ to $22.9\ \mathrm{cm^{-1}}$ at 950 K and from $23.3\ \mathrm{cm^{-1}}$ to $20.4\ \mathrm{cm^{-1}}$ at 1220 K.

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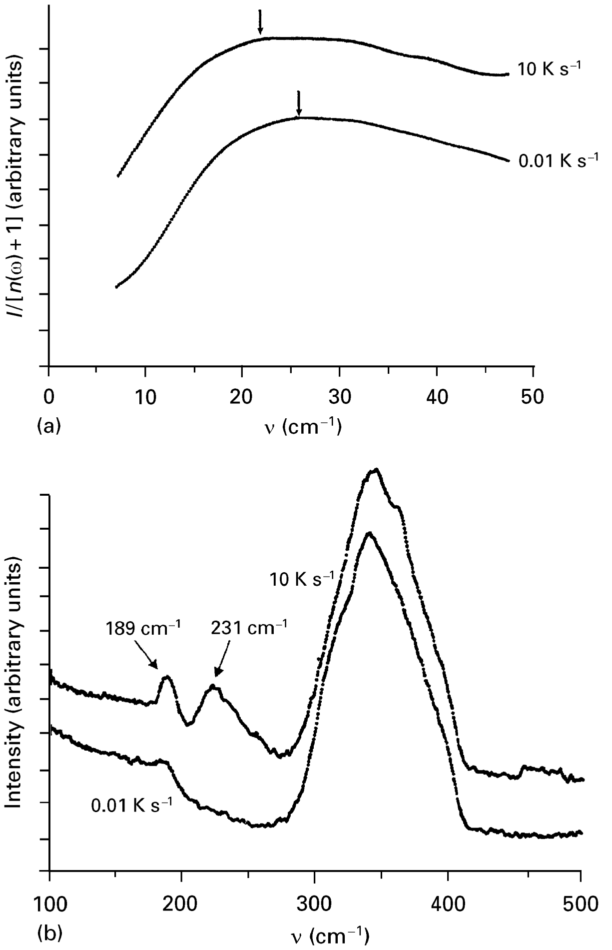

Figure 1 Raman spectra of As_2S_3 at different quenching conditions, after holding at 950 K for 1 h. Two curves on (a) and (b) are shifted upwards.

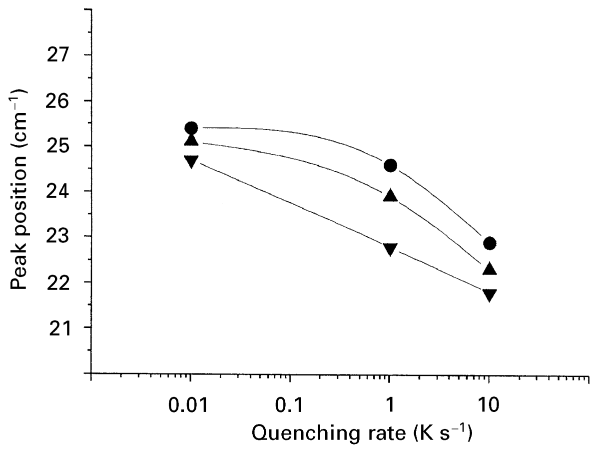

Figure 2 The position of the boson peak of As_2S_3 versus quenching rates from 950 K. (●) 1 h; (▲) 3 h; (▼) 4.5 h.

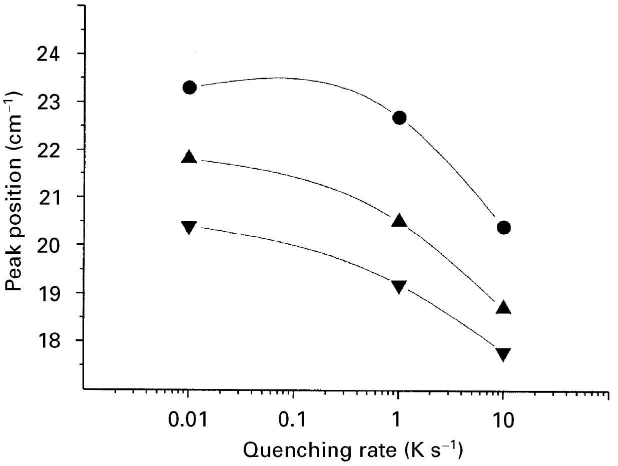

Figure 3 The position of the boson peak of As_2S_3 versus quenching rates from 1220 K. (●) 1 h; (▲) 3 h; (▼) 4.5 h.

4. Discussion

We mention here two models which have been proposed for the description of inelastic light scattering spectra of chalcogenide glasses in the low frequency region. One of them assumes that the low frequency peak is associated with the acoustic modes in an inhomogeneous medium with finite correlation length 2σ [10, 2]. The correlation length can be calculated from the peak frequency ω_p of spectrum by

$$2\sigma \cong \tilde{v}/\pi c\omega_p \qquad (1)$$

Here $\tilde{v}$ is the average of transverse and longitudinal velocity of acoustic waves, calculated by

$$\frac{1}{\tilde{v}^3} = \frac{1}{3}\left(\frac{1}{v_L^3} + \frac{1}{v_T^3}\right) \qquad (2)$$

where v_L and v_T are longitudinal and transverse velocity of acoustic waves, respectively.

Within the framework of the first model there are two possible reasons for the observed decrease of ω_p. First, a decrease of sound velocity and second, an increase of the correlation length. If we assume that the sound velocity is constant, i.e. does not depend on cooling rate, the correlation length may be calculated from the spectra using Equation 1 [1]. In such a case the correlation length will increase upon decreasing the quenching rate.

On the contrary, when thermodynamic arguments are used to estimate a correlation length from the shape of the excess specific heat around T_g [11], the conclusion is an increase of correlation length upon decreasing the quenching rate [12].

Let us therefore discuss the alternative that it is the (effective) sound velocity which changes by holding and quenching conditions [13]. In the first approximation we will assume the correlation length to be unchanged. Thus, the shift of the peak is due to the softening of the elastic constant of the glass. Above the melting point As_2S_3 may dissociate by endothermic reaction [14]

$$2As_2S_3 \rightleftharpoons As_4S_4 + S_2 \qquad (3)$$

At high temperatures the equilibrium shifts to the formation of As_4S_4 and S_2. The bands at 189 cm^{-1} and 231 cm^{-1} (Fig. 1b) are attributed to the bands to As_4S_4 [15]. The concentration of dissociation products depends on holding temperature and time [16, 17].

By fast cooling the melt it is possible to freeze the structural fragments produced by the dissociation because viscosity is high [18]. The sound velocity in As–S system is characterized by a strong and narrow maximum at the As_2S_3 composition which has been assigned to the formation of continuous network of trigonal structural units $AsS_{3/2}$ [14]. Replacement of a few of the strong covalent bonds in the $AsS_{3/2}$ network by weak van der Waals bonds between the chains and rings of the sulphur or molecular-like As_4S_4 fragments and network will decrease the sound velocity.

As follows from Figs 2 and 3, the position of the boson peak depends on the holding time at given temperature and cooling rate. Because of the high viscosity of this compound in the melt, the equilibrium in Equation 3 is not reached immediately and, therefore, concentration of the reaction products also depends on time. All those conditions which were shown here to decrease ω_p, namely high quenching rate, high holding temperature, and longer holding time, will lead to an increase of the reaction products of Equation 3 in the glass. Maximum peak position ω_p versus concentration of As_4S_4 in As_2S_3 is shown in Fig. 4. The concentration of As_4S_4 fragments have been determined by the X-ray emission spectroscopic method by Mamedov *et al.* [19], assuming Equation 3 occurs [20]. The peak position decreases upon increase of concentration of As_4S_4. As shown in Fig. 4, there are strong correlations between the boson peak position and the concentration of As_4S_4. Thus, the position of the peak at high temperature treatment is determined mainly by the concentration of reaction products.

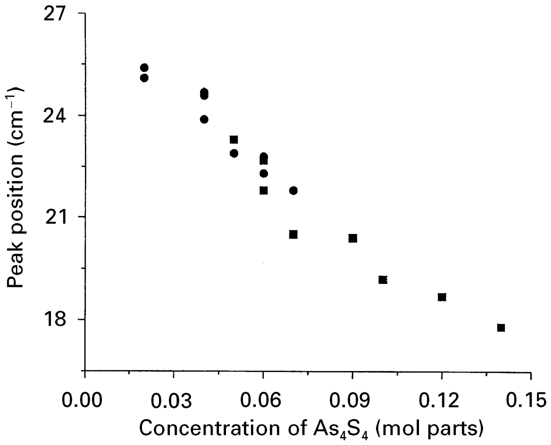

Figure 4 The position of the boson peak of As_2S_3 versus concentration of As_4S_4. (●) 950 K; (■) 1220 K.

Acknowledgements
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