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AMORPHOUS, VITREOUS, AND POROUS SEMICONDUCTORS

The Boson Peak in Raman Spectra of As_xS_{1-x} Glasses

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Abstract—The Raman spectra of As_xS_{1-x} glasses with $x < 40$ at % ($Z < 2.4$) have been studied in a wide temperature range (20–300 K). A well resolved boson peak is observed in the low-frequency portion of the spectrum, not withstanding the appearance of floppy modes in the glasses under study. It is shown that the boson peak is characterized by two parameters: intensity and the peak position. A comparison of the intensity variation for the boson peaks indicates that the degree of disorder increases as x decreases. This effect is caused by floppy modes in the glass network and by sulfur phase separation. Studies of reduced boson peaks in the Raman spectra of As_xS_{1-x} glasses confirms the theoretical assumption that the shape of the peaks is independent of composition and temperature. *© 2005 Pleiades Publishing, Inc.*

The low-frequency portion of the first-order Raman spectrum in glasses has been studied intensively using experimental and theoretical methods for more than 25 years. In this spectral region ($\omega < 100$ cm^{-1}), a well pronounced broad peak, referred to as the boson peak, is observed. As is well known, the boson peak is a universal special feature of the Raman spectra of unordered materials and is not observed in the Raman spectra of corresponding crystalline materials. The intensity of the measured boson peak $I_m(\omega, T)$ depends heavily on the temperature factor $n(\omega, T) = 1/[\exp(h\omega/kT) - 1]$, where $n(\omega, T)$ is the Bose–Einstein distribution at a temperature T for the vibrational energy $h\omega$ [1, 2]. Therefore, in order to determine the characteristic parameters of the boson peak, the reduced intensity $I_R(\omega, T)$ is often used and can be written as

$$I_R(\omega, T) = I_m(\omega, T)/\{\omega[n(\omega, T) + 1]\},$$

where $I_m(\omega, T)$ is the measured intensity of the boson peak. Shuker and Gammon [1] showed that the spectral dependence $I_R(\omega, T)$ should be identical to the shape of the curve for the density of vibrational states in unordered solids. The scattering mechanism responsible for boson-peak manifestation in the Raman spectra of glasses has not yet been completely clarified and is still debatable.

In this paper, we report the results of studying the Raman spectra of As_xS_{1-x} glasses with $x < 40$ at %. The average coordination number Z characterizing the degree of connectedness present in the glass network is smaller than 2.4 for the glasses under consideration. The critical value $Z = 2.4$ corresponds to the stoichiometric composition, As_2S_3 ($As_{0.4}S_{0.6}$). An excess of sulfur in the chosen compositions is conducive to the appearance of additional degrees of freedom (floppy modes) and brings about an increase in the degree of disorder in the glasses' structure. The network of such glasses becomes more flexible and the corresponding glasses are referred to as low-coordinated (low-constrained). The Raman spectra were measured in a wide temperature range in order to determine the effect of temperature on the boson-peak parameters. The objective of this study was to gain insight into the local structure and determine the degree of disorder of As–S glasses with $Z < 2.4$ using Raman spectroscopy. When analyzing the Raman spectra, we paid most attention to the low-frequency region with the aim of obtaining information about the manifestation and nature of the boson peak in these glasses.

Glasses belonging to the As_xS_{1-x} series were obtained by quenching the melt. The mixture of As and S elements (with a 99.999% purity) was put in a quartz cell; the cell was then evacuated, sealed, and heated for 24 h at 950°C in a swinging furnace. The melt was quenched by cooling the cells in air. The samples to be used in the Raman studies were fabricated in the form of thoroughly polished platelets. The Raman spectra were recorded in the wave number range 5–600 cm^{-1}. The pump radiation was emitted from a Kr$^+$ laser (the 647.1-nm line) with a power density of 40 W/cm^2. We used backscattering geometry. The signal was analyzed using a SPEX 1403 double monochromator and was detected by an RCA cooled photomultiplier. The spectral resolution was 1.5 cm^{-1}. *HH*- and *VH*-polarized components were measured independently. The boson-peak parameters were determined with higher confidence when the *VH* component was measured, since the level of quasi-elastic scattering is lower in the *VH* component than in the polarized *HH* component. The samples were mounted in a helium-filled cryostat during the measurements, which were performed in a wide temperature range (20–300 K).

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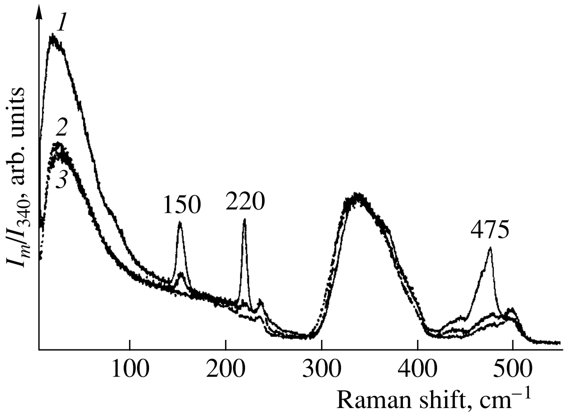

Fig. 1. Raman spectra of As_xS_{1-x} glasses with x = (*1*) 0.2, (*2*) 0.29, and (*3*) 0.31. The temperature of the measurements was 23 K.

The *VH* Raman spectra of three As_xS_{1-x} glasses with $x = 0.2$ ($Z = 2.2$), 0.29 ($Z = 2.285$), and 0.31 ($Z = 2.309$) were measured at a temperature of 23 K and are shown in Fig. 1. The spectra are normalized to the intensity of the band at 340 cm^{-1} in order to make it possible to compare the boson peaks for the three glasses. As is well known, the band at ~340 cm^{-1} is caused by As–S vibrations in $AsS_{3/2}$ pyramids. It is clearly seen from Fig. 1 that the boson-peak intensity increases as the sulfur content increases. The boson-peak intensity is at its highest for the $As_{0.2}S_{0.8}$ glass with $Z = 2.2$. For this composition, the degree of disorder is high due to the increased degree of freedom in the glass matrix. This inference is confirmed by the appearance of intense bands at 150, 220, and 475 cm^{-1}, which are typically attributed to phase-stratified S_8 rings, in the Raman spectrum of the $As_{0.2}S_{0.8}$ glass. The position of the boson peak ω_B shifts to higher frequencies as x (or Z) increases. These results are in good agreement with previously obtained composition dependences for the boson-peak parameters of As_xS_{1-x} glasses [3]. It is worth noting that, both in the reduced spectra and in the original Raman spectra, the composition dependences of the boson-peak parameters are similar. Since the intensity and the position of the boson peak vary as the glass composition is varied, we analyzed the reduced spectra.

The reduced Raman spectra are normalized in the low-frequency region by ω_B, (ω/ω_B), on the horizontal axis and by $I_{R\max}$, ($I_R/I_{R\max}$), on the vertical axis. The curves obtained in this way are often referred to as master curves and make it possible to compare the shape of the curves. After this procedure, we found that the boson-peak curves for the three glasses under study coincided completely; i.e., the shape of the curve $I_R(\omega, T = \text{const})$ is independent of the glass composition. The universality of the boson-peak spectral shape suggests that the nature of the low-energy vibrational states in As_xS_{1-x} glasses with $Z < 2.4$ should be identical. In contrast, we obtained a very complex composition dependence of the boson-peak spectral shape for Ge–As–S glasses [4]. This dependence is related to variation in the connectedness of the network in ternary glasses as the composition varies (the value of Z varied from 2.4 to 2.8 for the Ge–As–S glasses studied).

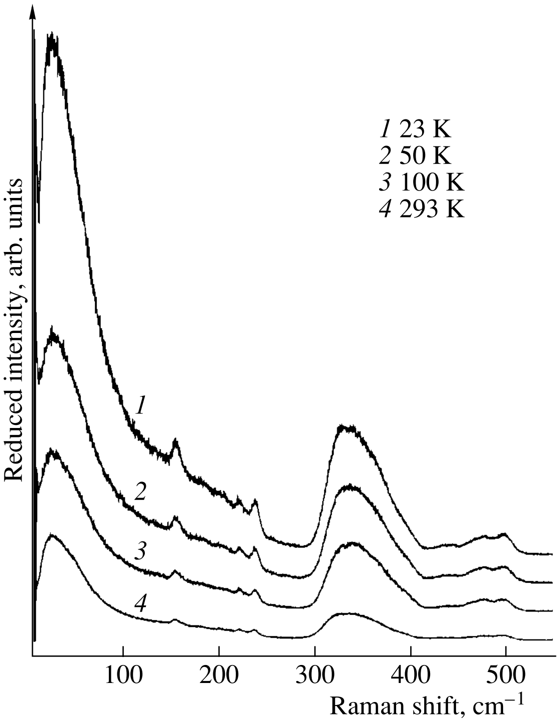

Fig. 2. Reduced Raman spectra of $As_{0.29}S_{0.71}$ glass ($Z = 2.285$) at four chosen temperatures. The scale on the intensity axis is the same for all temperatures.

Studies of the effect of temperature on the boson-peak parameters are hampered by the fact that the thermal factor $n(\omega, T)$ profoundly affects the low-frequency region of the spectrum as the temperature is lowered. Typically, the measured boson-peak intensity decreases drastically as the temperature decreases, and the Raman signal is also reduced if measured in the full-range spectrum. In Fig. 2, we show the reduced Raman spectra for the $As_{0.29}S_{0.71}$ glass ($Z = 2.285$) at four chosen sample temperatures. It can clearly be seen from Fig. 2 that the boson-peak intensity $I_{R\max}$ increases as the temperature decreases (in contrast to the above statement). However, the intensity of the band at about 340 cm^{-1} decreases; therefore, we do not suggest any quantitative correlations. It can be seen from Fig. 2 that ω_B is independent of temperature. We compared the shape of the reduced boson peak (using the method of master curves) for the three glasses under study at different temperatures. The comparison shows that the curves $I_R(\omega, T)$ coincide completely at temperatures ranging from 23 to 293 K. The universality (in particular, the temperature independence) of the boson-peak shape manifests itself to a greater extent in the binary As–S glasses under study than in the ternary Ge–As–S glasses. An additional broad temperature-independent peak at ~140 cm^{-1} is found to be superimposed on the boson peak for ternary glasses [5].

As a result of our studies of the Raman scattering, we established that a well-resolved boson peak is observed in the As_xS_{1-x} glasses with $Z < 2.4$ in spite of the appearance of floppy modes. The boson peak is characterized by two parameters: intensity and position of the maximum. A comparison of the boson-peak intensities shows that the degree of disorder increases as the average coordination number Z decreases. This circumstance is due to flexibility of the glass network (the so-called low-constrained glasses) and the existence of phase separation of sulfur. Studies of the shape of the reduced boson-peak Raman spectra for the As_xS_{1-x} glasses confirmed theoretical predictions concerning the independence of the boson peak from the composition and temperature.

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