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Invited lecture

STRUCTURE AND DYNAMICS OF Ge-As-S CHALCOGENIDE GLASSES MONITORED BY LOW-FREQUENCY RAMAN SCATTERING

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The Raman scattering spectra of several "stoichiometric" $(GeS_2)_x(As_2S_3)_{1-x}$ glasses have been measured over temperatures ranging from 20 K, through the respective glass transition temperature T_g and up to a temperature close to melting point. For comparisons, similar temperature-dependent Raman spectra have been obtained for the "non-stoichiometric" $Ge_{0.30}As_{0.10}S_{0.60}$ glass which is rich in Ge in relation to the above stoichiometry. All glasses studied belong to the stress-rigid network regime (mean coordination number $\boldsymbol{r} \geq 2.475$). Emphasis is given on the study of the low-frequency Boson peak (BP) and, in particular, its variation with composition and temperature which is related to the dynamics of the glassy network. The relative intensity of the BP to the high-frequency main molecular band is practically composition-independent in the stoichiometric glasses, but in the non-stoichiometric one is much larger, thus reflecting the higher degree of disorder in the latter. The Boson peak frequency decreases with increasing Ge-content in the $(GeS_2)_x(As_2S_3)_{1-x}$ glasses, while that of the $Ge_{0.30}As_{0.10}S_{0.60}$ glass is the lowest than any stoichiometric composition, implying a higher correlation length of the medium-range order for the latter glass. The temperature dependence of the BP up to the respective T_g is manifested by either a slight smooth softening with increasing temperature, or by an almost temperature-independent frequency over this range of temperatures (20 K – T_g). As T_g is approached, all glasses show discontinuous (abrupt) changes in their BP characteristics (intensity and frequency), signifying the transition to a less rigid network regime. Further increase of temperature results in a sharp drop of the BP intensity for most glasses, which implies a transition to a more ordered network. The results confirm the close correlation between the BP and the medium-range order in network glasses. Also, it has been shown that monitoring the spectral characteristics of the BP constitutes a reliable technique for detecting critical phenomena in rigid glassy networks around T_g.

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Keywords: Chalcogenide glasses, Boson peak, Glassy network dynamics,
Raman spectroscopy, Temperature dependence, Phase transitions

1. Introduction

Ternary $Ge_xAs_yS_{1-x-y}$ chalcogenide glasses display remarkable properties, such as structural (bond) flexibility and consequently extended compositional ranges [1-5], long term stability as well as good transmission in the visible and near-infrared parts of the spectrum [2,6]. These properties make them useful candidate materials for nonlinear optical [7,8] and photonic applications [6,9,10].

In general, amorphous chalcogenides are *network glasses*, with their structure being described fairly well by the continuous random network (CRN) model [1], and are classified, on the whole, as *strong glass formers*. The constraint theory [11,12] developed for network glasses suggests that the structure and physical properties of such glasses are critically dependent on the mean coordination number $\boldsymbol{r}$. Bearing in mind the coordination numbers for Ge (4), As (3) and S (2), for the $Ge_xAs_yS_{1-x-y}$ glasses of this work, the mean coordination number is: $\boldsymbol{r} = 4x + 3y + 2(1 - x - y)$. For $\boldsymbol{r} < 2.4$, the glassy network is characterized as floppy (soft) in which atoms display high degrees

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of freedom, while for $\boldsymbol{r} > 2.4$ a rigid network is obtained. Thus, according to this model [11,12], a rigidity percolation transition occurs at $\boldsymbol{r} = 2.4$.

The dynamics of network glasses can be described by either relaxational [13-17] or vibrational [14,15,18-25] processes which give overlapping low-frequency spectral components in light scattering experiments. Specifically, relaxational processes are responsible for the central component known as quasi-elastic (or excess) light scattering [13] which decays with frequency and is highly-dependent on temperature. On the other hand, the low-frequency vibrational spectrum has been related with the non-central, asymmetric scattering component which is commonly known as the *Boson peak* (BP) and is a characteristic feature in the Raman spectra of the glassy state [18-25]. The two scattering components often overlap at an extent depending on the type of glass. It has been reported [26,27] that in strong glass formers the contribution of the relaxational component to the overall low-frequency scattering is significantly reduced compared to that of the vibrational one, at least for frequencies $\boldsymbol{\omega} \geq 10$ cm^{-1}, i.e. over the spectral region where the BP is observed. Therefore, in strong glass formers like the chalcogenides, the observed BP band practically coincides with the low-frequency vibrational spectrum; however, at elevated temperatures, and particularly around T_g, the contribution of the quasi-elastic scattering may be not be negligible in the overall intensity of the BP, first because the quasi-elastic component is strongly dependent on temperature and as a result of the network softening at T_g.

A number of theories have been developed for the origin of the vibrational spectrum of the BP, with the most prominent being those of the acoustic phonon model [18,19,22] and the soft potential model [25]. Furthermore, the BP has been associated [20,22] with the intermediate structure (or medium range order, MRO, as is often referred to) of glasses and the characteristic correlation length *R* of the MRO. This aspect has been supported by a recent composition- and temperature-dependent Raman study (20 – 300 K) in Ge-As-S glasses [28]. Elsewhere, the BP has been attributed to vibrations between small clusters [29] or localized vibrations within the clusters [30].

In this work we report Raman scattering from $(GeS_2)_x(As_2S_3)_{1-x}$ glasses for various compositions (x = 0.40, 0.60, 0.80, 0.83, 0.90) in which the Ge:S and As:S ratios are equal to the stoichiometric ones, i.e, along the lines of the GeS_2 and As_2S_3 binary compounds, as well as from the “non-stoichiometric” $Ge_{0.30}As_{0.10}S_{0.60}$ glass (with some Ge-excess relatively to “stoichiometry”). All these glasses belong to the rigid network regime, ranging from $\boldsymbol{r} = 2.475$ ($x = 0.40$) to $\boldsymbol{r} = 2.625$ ($x = 0.90$) for the “stoichiometric”, and up to $\boldsymbol{r} = 2.7$ for the $Ge_{0.30}As_{0.10}S_{0.60}$ glass. For three of the “stoichiometric” glasses, namely those corresponding to x = 0.40, 0.83 and 0.90, Raman spectra under variable temperature are also reported from 20 K up to a temperature well above T_g. The aim of these experiments is to investigate the temperature dependence of both the high-frequency (molecular) Raman scattering and the low-frequency Boson peak and to obtain evidence about possible structural variations or dynamical effects in the glassy network. Furthermore, the evolution of the BP is studied to test the feasibility of using this peak for monitoring critical phenomena in rigid glasses around T_g.

2. Experimental details and data analysis

Samples of Ge-As-S glasses were prepared by quenching in air melts of the desired atomic contents. The melts were sealed in silica cells under vacuum and kept at 950 ^{0}C for 20 hours inside a tilting furnace with continuous rocking. After preparation, all glasses were annealed for ~ 1 hour at a temperature just below the respective T_g in order to reduce the residual mechanical stress. Samples aimed for Raman measurements were cut and polished in the shape of platelets.

Excitation of the Raman spectra was realized by the 647.1 nm line of a Kr^+ laser at a power density of ~ 40 W/cm^2 using a pseudo-backscattering geometry and line focusing (cylindrical lens) of the incident beam. Scattered light was analyzed and detected by a SPEX 1403 double spectrometer in combination with a cooled photomultiplier. Both HH and VH Raman spectra were recorded separately corresponding to parallel (HH) and crossed (VH) polarizations between the incident and scattered light. The VH polarization component was preferred at temperatures around T_g as it provided a better resolution of the BP due to the much lower level of the elastic and quasi-elastic scattering associated with this component. At room temperature, mixed polarization HH + VH spectra were obtained in order to study, in a more reliable way, the composition dependence of spectral intensities.

A closed cycle He optical cryostat (20 – 300 K) was used for the low-temperature Raman measurements. For the high-temperature experiments, a vacuum operated optical furnace (300 – 1200 K) of very small temperature gradients [31] was employed; at high-temperatures, the glass sample was held inside an appropriately positioned silica cell under inert gas atmosphere in order to avoid oxidation.

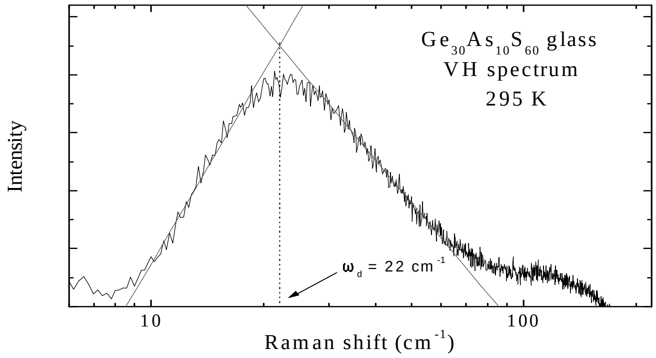

Fig. 1. Linear-log, $I(\omega)$-$\log_{10}\omega$ plot of the Boson peak spectrum of $Ge_{0.30}As_{0.10}S_{0.60}$ glass and linear fittings on both the low- and high-frequency sides of it, giving the crossover frequency $\omega_d \equiv \omega_{bos}$.

Due to the broad and asymmetric spectral profile of the BP, evaluation of its peak frequency ω_{bos} is not straightforward using normal fitting procedures. We have overcome this difficulty by considering $I(\omega)$ – $\log_{10}\omega$ plots of the recorded spectra, a procedure which makes the BP narrower and almost symmetric as is illustrated in Figure 1 for the room temperature spectrum of the $Ge_{0.30}As_{0.10}S_{0.60}$ glass. This procedure has allowed us to perform linear fittings on both low- and high-frequency sides of the modified BP and from the interception of the two fittings a reliable value for $\omega_{bos} \equiv \omega_d$ has been obtained.

3. Results and discussion

3.1. Composition dependence of Raman spectra of Ge-As-S glasses

The unpolarized (HH + HV) room-temperature Raman spectra of four “stoichiometric” $(GeS_2)_x(As_2S_3)_{1-x}$ glasses are given in Figure 2 for x = 0.40, 0.60, 0.80 and 0.90, corresponding to the atomic-content formulas: $Ge_{0.095}As_{0.286}S_{0.619}$, $Ge_{0.158}As_{0.210}S_{0.632}$, $Ge_{0.235}As_{0.118}S_{0.647}$ and $Ge_{0.281}As_{0.063}S_{0.656}$. In the inset of Fig. 1, the BP frequency ω_{bos} of the as-recorded spectra is plotted against composition for all stoichiometric glasses studied in this work, plus the two binary (edge) components of the series: As_2S_3 (x = 0) and GeS_2 (x = 1.0); the BP frequencies of the binary glasses have been taken from previous Raman studies on As_2S_3 [3] and GeS_2 [32]. The ω_{bos} frequencies have been evaluated from the fitting procedures described in the previous section and illustrated in Fig. 1.

Prior to the discussion on the composition variation of the BP characteristics (intensity, frequency), we comment briefly on the high-frequency molecular spectrum which is related to the local (chemical) structure of glasses. Specifically, a series of unresolved bands is observed in all spectra of Fig. 2 between 300 and 450 cm^{-1}. Both the intensity and lineshape of these bands depend strongly on composition, and are attributed mainly to heteropolar Ge-S and/or As-S bond vibrations in $Ge(S_{1/2})_4$ tetrahedra and $As(S_{1/2})_3$, respectively, which are the structural units in the two (binary) compound GeS_2 [33] and As_2S_3 [5] glasses. It is interesting that the overall intensity of the spectra of Fig. 2 increases with increasing As-content and this result most likely reflects partly the higher polarizability of As (relative to Ge) and partly to resonance effects as the optical band-gap of the glassy Ge-As-S system becomes narrower with increasing As-content [34].

It has been argued [19,22] that the intensity of the BP is a measure of the disorder of the glassy network. However, it is risky to compare absolute intensities of different spectra and, particularly, when glasses of variable composition are involved. In a previous publication, we have suggested [28] that a more objective parameter giving the degree of disorder is the *ratio of* *intensities between the BP and the high-frequency molecular band*. This ratio is ~ 1.1 and, more or less, composition-independent for the stoichiometric $(GeS_2)_x(As_2S_3)_{1-x}$ glasses (Fig. 2), indicating that there is negligible proportion of defective (homopolar) bonds in the network and that disorder in these stoichiometric glasses is purely *topological*. In contrast, this ratio is ~ 2.5 for the non-stoichiometric $Ge_{0.30}As_{0.10}S_{0.60}$ glass (see Fig. 3 of Ref. 28), thus confirming its higher degree of disorder; it is reminded that this glass has an excess in Ge compared to the stoichiometric $Ge_{0.25}As_{0.10}S_{0.65}$ one which results in the appearance of homopolar Ge-Ge bonds. Therefore, apart from the topological, there is also a contribution of *defective* disorder in non-stoichiometric Ge-As-S glasses. The suggestion that the relative intensity (ratio) of the BP to the high-frequency molecular band is the key parameter for determining the degree of disorder is further justified by the temperature-dependent Raman data from these glasses in the following section.

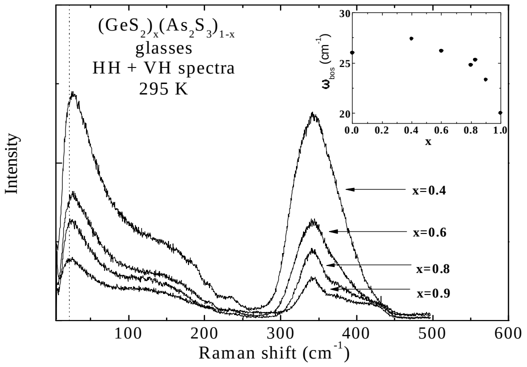

Fig. 2. As-recorded, room temperature unpolarized (HH + VH) Raman spectra of $(GeS_2)_x(As_2S_3)_{1-x}$ glasses at four compositions; all spectra correspond to the same intensity scale. In the inset, the Boson peak frequency ω_{bos} is plotted against x (Ge-content).

It is evident from Fig. 2 (and its inset) that the BP of the $(GeS_2)_x(As_2S_3)_{1-x}$ glasses shifts, on the whole, towards the lower frequencies with increasing Ge-content. In a simple harmonic oscillator approximation for the BP and bearing in mind the nearly equal atomic masses of Ge and As, this shift can be interpreted in terms of a lower 'mean' force constant of oscillators containing higher Ge-contents. This implies that the vibrating units responsible for the BP (and the glassy network as a whole) should be less compact in the case of Ge-rich glasses than the As-rich ones. The compactness can be related to the free volume and the correlation length R of the MRO [22], i.e. the more compact the network, the smaller the free volume and the lower the R. In this situation, an increase of the MRO size is concluded with increasing Ge-content in $(GeS_2)_x(As_2S_3)_{1-x}$ glasses. The observed shift of the BP frequency with x (Fig. 2) can be explained in terms of the higher free volume (lower compactness) displayed by glasses of high Ge-content [35,36]. As the Ge-content increases, the structure of these ternary glasses gradually changes from a predominantly two-dimensional pyramidal to a three-dimensional tetrahedral one, with the latter possessing a higher free volume than the former. The compositional dependence of the free volume is the same with that of the mean atomic volume [37] which shows a marked increase for compositions close to $x = 1$, i.e. for compositions where ω_{bos} is low (see inset of Fig. 2). Therefore, we propose that the downward shift of the BP with increasing Ge-content in $(GeS_2)_x(As_2S_3)_{1-x}$ glasses is related with an increase of the free volume and this concept is compatible with the increase of the correlation length of the MRO with increasing Ge-content.

The non-stoichiometric $Ge_{0.30}As_{0.10}S_{0.60}$ glass displays a BP frequency $\omega_{bos} = 22$ cm^{-1} (Fig. 1) which is the lowest than any stoichiometric $(GeS_2)_x(As_2S_3)_{1-x}$ glass (Fig. 2). This implies that the MRO of this glass is larger in comparison to that of the stoichiometric ones. Again, we interpret this result in terms of the higher free volume displayed by the $Ge_{0.30}As_{0.10}S_{0.60}$ glass. Bearing in mind that this glass is enriched in Ge, some of the Ge atoms take the positions of S atoms in $Ge(S_{1/2})_4$ tetrahedra, resulting in the formation of $S_3Ge\text{-}GeS_3$ structural units which are larger in size than the former and the $As(S_{1/2})_3$ pyramidal units. In this way, the presence of $S_3Ge\text{-}GeS_3$ units in the network causes an enlargement of the average size of the MRO and an increase of the free volume of the glass.

3.2. Temperature dependence of Raman spectra of Ge-As-S glasses

The Raman spectra of all ternary Ge-As-S glasses have been recorded for a large number of temperatures up to and well above the respective T_g. Typical results showing the evolution with temperature of the polarized HH spectrum of the stoichiometric $Ge_{0.25}As_{0.10}S_{0.65}$ glass ($x = 0.83$) are given in Figure 3. The glass transition temperature T_g of this glass is known [37] to be ~ 600 K. Therefore, the spectra of Fig. 3 cover a temperature range of 100 K above T_g. At a first view, both the Boson peak and the high-frequency molecular bands appear to soften with increasing temperature. However, for an accurate temperature dependence of either the low- or high-frequency scattering, it has been necessary to perform the appropriate for each occasion fitting: the two sides of the $I(\omega) - \log_{10}\omega$ spectrum of the BP have been linearly fitted according to the procedures described in section 2, while the high-frequency molecular spectrum has been fitted to 4 mixed character functions (33% Lorentzian, 67% Gaussian) because of the variable width of the individual bands involved. Plots of the BP frequency ω_{bos} (main frame) and the frequency of the strongest molecular band at ~ 340 cm^{-1} (inset) are given in Figure 4 for the stoichiometric $Ge_{0.281}As_{0.063}S_{0.656}$ glass as they have obtained from the fittings.

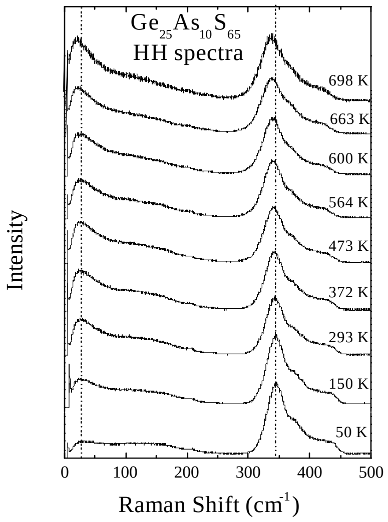

Fig. 3. Evolution with temperature of the as-recorded polarized (HH) Raman spectrum of the "stoichiometric" $Ge_{0.25}As_{0.10}S_{0.65}$ ($x = 0.83$) glass in the range 50 – 698 K.

As seen from Fig. 4, the BP frequency, having an initial value of 25.5 cm^{-1} (at 20 K), decreases slightly up to 200 K, it remains temperature-independent up to about $T_1 = 620$ K and then drops sharply to a value of ~ 19 cm^{-1}. The temperature at which the BP frequency decreases sharply is very close (in fact, slightly below) to the nominal T_g value [37] for the $Ge_{0.281}As_{0.063}S_{0.656}$. On the other hand, the high-frequency molecular band of this glass at ~ 340 cm^{-1} softens continuously and smoothly over the entire temperature range (inset of Fig. 4), thus showing normal mode (quasi-harmonic) behaviour and without sensing the incipient reverse glass transition. These contrasting results provide unambiguous evidence and conclusions about the structure (local and intermediate) and dynamics of these rigid, strong glass formers. First, the strong, covalent binding which dominates all the atomic (chemical) bonding at local level does not "feel" the changes taking place over longer ranges in the glassy network near and above T_g; the smooth softening of the molecular bands is simply explained in terms of the thermal expansion and anharmonic effects in the network. Therefore, the basic structural units from which the network is built *remain intact well above the glass transition temperature* T_g. The temperature dependence of the BP frequency (almost temperature-independent in the region 200 – 620 K and abruptly decreasing near T_g) confirms the close connection of the BP with the intermediate structure and generally the glassy network. It is then concluded that the ω_{bos} variation with temperature (Fig. 4) can be used as a measure of the rigidity of the glassy network and to monitor the structural and dynamical changes occurring around T_g. Similar temperature dependence of the BP frequency has been observed in the other glasses of this study, with the abrupt drop occurring in each occasion at a temperature T_1 just below the nominal T_g. As another example, in Figure 5 the plot of the BP frequency against temperature is shown for the stoichiometric $Ge_{0.095}As_{0.286}S_{0.619}$ glass in which the sharp softening takes place at a T_1 ~ 460 K.

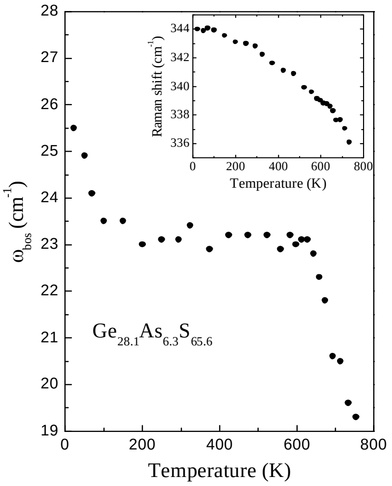

Fig. 4. Boson peak frequency ω_{bos} of the $Ge_{0.281}As_{0.063}S_{0.656}$ glass plotted against temperature. The inset shows a similar frequency plot of the molecular band at 340 cm^{-1}.

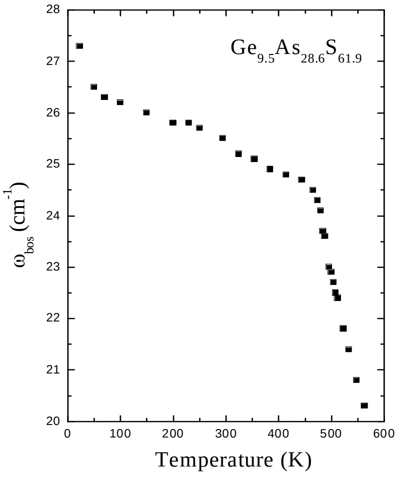

Fig. 5. BP frequency ω_{bos} plotted against temperature for the $Ge_{0.095}As_{0.286}S_{0.619}$ glass.

Apart from the frequency, the BP intensity can also be used to monitor critical structural and dynamical effects in these glasses. Specifically, the normalized BP intensity to the high-frequency molecular band at 340 cm^{-1} is a reliable parameter for this purpose as it represents a measure of disorder of the glass [28]. A plot of the relative intensity I_{bos}/I_{mol} against temperature is given in Figure 6 for the stoichiometric $Ge_{0.281}As_{0.063}S_{0.656}$ glass. This parameter increases in a continuous way with increasing temperature up to about T_2 = 530 K, reflecting the anticipated increasing degree of disorder as the temperature is raised. Above 530 K, I_{bos}/I_{mol} increases discontinuously and rather sharply, indicating that the glass has sustained a transition to a more disordered phase. Note that the temperature T_2 = 530 K is well below the critical temperature T_1 = 620 K which corresponds to the sharp drop of the BP frequency for this glass. Therefore, the relative intensity I_{bos}/I_{mol} serves as a precursor for the incipient rigidity percolation transition. Further, this parameter sustains another sharp change at a temperature T_3 = 700 K for the $Ge_{0.281}As_{0.063}S_{0.656}$ glass (Fig. 6), that is well above T_g. This change is manifested by a very abrupt drop of I_{bos}/I_{mol} which, in fact, corresponds to a likewise drop of the absolute intensity of the BP. This is an ordering effect in the network and signifies the onset of a transition to a more ordered structure which eventually will lead to crystallization. The critical temperature T_3 can be connected with the crossover temperature T_c which is a key parameter in relaxational dynamics studies [14-17] of glasses. Similar BP intensity dependence has been observed in the other glasses of this study.

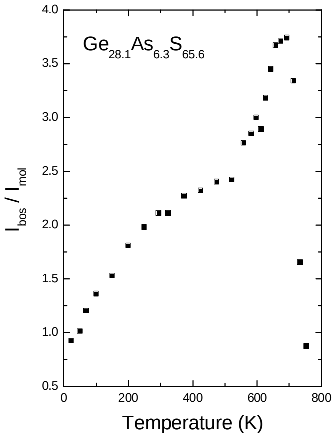

Fig. 6. The Boson peak intensity of the $Ge_{0.281}As_{0.063}S_{0.656}$ glass normalized to the molecular band at 340 cm^{-1} and plotted against temperature.

4. Conclusions

The compositional dependence of Raman scattering from "stoichiometric" $(GeS_2)_x(As_2S_3)_{1-x}$ glasses has revealed a shift of the Boson peak frequency towards the lower frequencies with increasing Ge-content which implies an increase of the intermediate structure and is interpreted in terms of the higher free volume (lower compactness) displayed by high Ge-content members of this glassy system. The "non-stoichiometric" $Ge_{0.30}As_{0.10}S_{0.60}$ glass displays the lowest Boson peak frequency than any "stoichiometric" one which is explained by the presence of a large number of homopolar (defective) bonds and the formation of larger, modified structural units in the network, leading to an enlarged intermediate structure.

It has been shown that the Boson peak can be used as a probe for the study of temperature-induced critical phenomena in rigid, strong glass formers. Thus, the variation of the Boson peak frequency with temperature provides a fairly accurate method for determining the glass transition temperature T_g of rigid glasses. Further, the relative intensity of the Boson peak to the high-frequency main molecular band I_{bos}/I_{mol}, which is a measure of disorder in the glass, varies discontinuously around T_g manifested first by a sharp increase (well below T_g) and then by an more abrupt decrease; in its first discontinuity it serves as a precursor for the incipient glass transition and in the second as a probe parameter for the commence of ordering of the glassy network. These results confirm the close relation between the Boson peak and the intermediate structure of glasses, and prove that the low-frequency Raman scattering is a useful technique for studying the dynamics of strong glass formers.

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