High-temperature Raman and DSC studies of ternary floppy chalcogenide glasses

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The Raman scattering spectra of two ternary floppy ($Z < 2.4$) Ge-As-S chalcogenide 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. Additional Differential Scanning Calorimetry (DSC) measurements have been carried out in these glasses at high temperatures from which values of T_g have been determined. The purpose of this work is twofold: (i) to study, through the Raman spectra and in particular the Boson peak (BP), critical phenomena around the T_g and make comparisons with the results obtained by DSC, and (ii) to make overall comparisons of the present Raman results and conclusions with those reported in a previous Raman study [Boulmetis *et al*, J. Opt. Adv. Materials **7**, 1209 (2005)] on rigid ($Z > 2.4$) Ge-As-S glasses. It has been found that the study of the Boson peak is a reliable technique for predicting and determining the onset of the transition to the supercooled liquid phase in floppy chalcogenide glasses.

1. Introduction

The Raman spectra of ternary Ge-As-S chalcogenide glasses were measured systematically under variable temperature in recent works [1-3] from which valuable evidence was obtained regarding the structural changes and dynamics of these glasses over extended temperature regions. It should be pointed out that all glasses studied in those works [1-3] were on the rigid side of compositions, that is, with mean coordination number $Z > 2.4$. Briefly, the results of the particular studies [1-3] have confirmed the correlation between the Boson peak (BP) and the medium range order of glasses, and demonstrated the usefulness of this characteristic Raman band of glasses for the study of critical effects near the glass transition temperature, T_g. Besides, detailed quantitative analysis of the BP has suggested [3,4] that rigid chalcogenide glasses are strong glass formers and this is concluded [3,4] from the low values of the fragility ratio

$$r\ (T_g) = \frac{I_{R\min}}{I_{R\max}} \qquad (1)$$

at T_g for such glasses, where I_{Rmin} and I_{Rmax} are reduced intensities related with the BP, i.e., the reduced intensities at the low-frequency minimum (valley) and at the peak position, respectively. As an empirical criterion characterizing a strong glass former, it has been proposed [4,5] that $r(T_g) < 0.85$ while for $r(T_g) > 0.85$, the glass is characterized as fragile. It has been found [3] that rigid Ge-As-S chalcogenide glasses follow this criterion and therefore, they can be classified as strong glass formers.

Furthermore, it has been established [2,3] that in rigid glasses the normalized temperature slopes

$$k = (\frac{1}{\omega_0})(\frac{\partial \omega}{\partial T}) \qquad (2)$$

are much higher (around T_g) for the Boson peak in comparison to the high-frequency molecular bands, indicating that the changes induced by varying the temperature affect mainly the medium range order rather than the local structure in this temperature region. In particular abrupt changes have been observed in the spectral characteristics (frequency and intensity) of the BP at temperatures close and above T_g and attributed to critical effects related with the glass transition.

In the present work, we extend the temperature dependence studies to floppy-type Ge-As-S glasses ($Z < 2.4$) with motivation to find out whether the evolution of the BP with temperature can provide similar evidence on the structural changes and dynamics of such glasses, and to make overall comparisons with the previously studied rigid Ge-As-S glasses [2,3]. In particular, in this article we present the Raman spectra of the floppy glasses $Ge_{0.04}As_{0.225}S_{0.735}$ ($Z = 2.31$) and $Ge_{0.08}As_{0.20}S_{0.72}$ ($Z = 2.36$). In order to cross-check critical point values obtained from the Raman experiments, we have performed additional Diferential Scaning Calorimetry (DSC) experiments which are known to give fairly accurate values of T_g.

2. Experimental details and data analysis

The Raman spectra were excited by the 647.1 nm line of a Kr[+] laser at a power density of about 50 W/cm^{2} before the cryostat or the optical furnace. A nearly backscattering geometry along with a cylindrical focusing lens for the incident beam were used. Scattered light was analyzed and detected by a SPEX 1403 double spectrometer in

combination with a cooled photomultiplier. Both (HH) and (VH) spectral components were recorded separately, corresponding to parallel and cross polarizations between the incident and scattered light, respectively. A closed cycle He optical cryostat (20-300 K) and a vacuum operated optical furnace (300-1200 K) were used for the low- and high- temperature Raman measurements. At high-temperatures, the glass sample was held inside a silica cell under argon atmosphere in order to avoid oxidation.

The BP frequency ω_{bos} was determined by the interception of the two linear fittings on both low- and high-frequency sides of the BP after converting the Raman spectra in $I(\omega)$-$\log_{10}\omega$ plots [1-3]. Analysis of molecular bands (see section 3) was done by means of a least-squares numerical fitting of the spectra using Lorenzian, Gaussian or mixed-type profiles. The VH polarization component was preferred for the study of the BP because the level of elastically scattered (stray) light was lower than that of the HH component, thus enabling to obtain better resolution of the BP profile. In contrast, since the intensity of the high-frequency molecular bands was higher in the HH component, the latter was used for the study of these bands.

Finally, for the DSC measurements a heat flux Differential Scanning Calorimeter was used with a heating rate of 10 K/min in nitrogen atmosphere. The T_g value was determined as the temperature corresponding to $\Delta C_p/2$, where ΔC_p is the total C_p variation over the entire endothermic process, which is associated with the glass transition (see section 3 for details).

3. Results and discussion

Raman spectra of the two glasses have been obtained at several temperatures from 20 K up to and well above the respective T_g s and in small intervals in the vicinity of T_g. The T_g values had been predetermined accurately through DSC measurements. Representative spectra (covering the respective temperature regions) of the $Ge_{0.04}As_{22.5}S_{0.735}$ (HH component) and $Ge_{0.08}As_{0.20}S_{0.72}$ (VH component) glasses are given in Figs. 1 and 2. All spectra display two very broad spectral features: the low-frequency Boson peak ranging from about 10 to 200 cm^{-1}, and a high-frequency envelope of strongly overlapping molecular bands between 300 and 450 cm^{-1}. The lineshapes of the two spectral features are almost the same in the two glasses. The high-frequency bands (300-450 cm^{-1}) should be attributed primarily to heteropolar As-S bond vibration in $As(S_{1/2})_3$ pyramidal units [1,6] and less so to Ge-S bond ones in $Ge(S_{1/2})_4$ tetrahedra [1,7] since the ratio of Ge to S favours the former bonds for the two glasses of the present study.
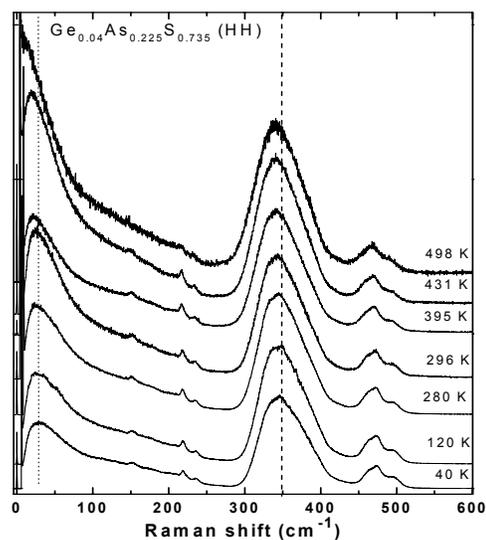

Fig. 1. Evolution with temperature of polarized (HH) Raman spectrum of the $Ge_{0.04}As_{0.225}S_{0.735}$ glass in the range 40-498 K.
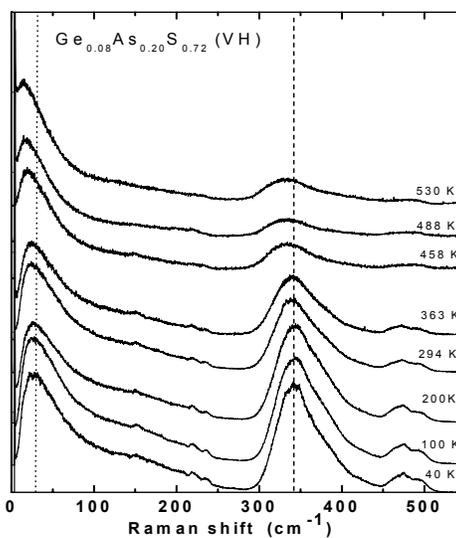

Fig. 2. Evolution with temperature of depolarized (VH) Raman spectrum of the $Ge_{0.08}As_{0.20}S_{0.72}$ glass in the range 40-530 K.

Given that the two glasses in hand are rich in sulphur, that is, their composition is off the "stoichiometric" system $(GeS_2)_x(As_2S_3)_{1-x}$, a proportion of the sulphur content cannot be bonded to Ge or/and As to form tetrahedral and pyramidal units. In this situation, the excess sulphur forms cluster-like S_8 rings or S_N chains which are embedded in the glassy network of tetrahedra and pyramids [3,7-9]. The bands at about 470 and 495 cm^{-1} have been attributed [3,7,8] to symmetric vibrations of homopolar S-S bonds in S_8 rings and S_N chains, respectively. Similarly, two weak, but relatively, narrow bands at about 150 and 218 cm^{-1} have been attributed [3,8] to bending vibrations of S atoms in S_8 rings. Finally, another weak band at about 230 cm^{-1} may be due to internal vibrations in isolated As_4S_4

molecules which form in glasses containing As and S as a result of local atomic concentration fluctuations [10].

The determination of the BP frequency is rather awkward by conventional means as it is difficult to fit accurately the asymmetric BP profile to a particular function. In order to minimize the asymmetry, we have transformed each BP spectrum by taking the logarithm of the frequency axis. Then, the peak frequency has been determined by the interception of the linear fittings performed on either side of the BP [1-3]. The BP frequencies ω_{bos} obtained from this procedure for the two glasses of study as well as for two Ge-rich "stoichimetric" ternary glasses [2] (for comparisons) are given in Table 1.

Table 1. Various physical quantities for the floppy and rigid Ge-As-S glasses. Z: mean coordination number, ω_{bos}: Boson peak frequency (at 20K), T_1 and T_2: temperatures of onset and completion of the endothermic process, respectively, corresponding to the transition to the supercooled phase, T_g: glass transition temperature determined from the DSC experiments, T_d: temperature at which the BP frequency drops abruptly, $k=(\partial\omega/\partial T)/\omega_0$: normalized temperature slope (Eq. 2), $r(T_g)$: fragility ratio I_{Rmin}/I_{Rmax} of intensities at the minimum and maximum of the BP.

Glass	Z	T_1 (K)	T_2 (K)	ω_{bos} (cm^{-1})	T_g (K) (DSC)	T_d (K) (Raman)	k (10^{-3}K^{-1})	$r(T_g)$
Ge$_{0.04}$As$_{0.225}$S$_{0.735}$	2.31	398	468	27	433	414	3.52	0.76
Ge$_{0.08}$As$_{0.20}$S$_{0.72}$	2.36	424	504	25	458	433	2.66	0.71
Ge$_{0.281}$As$_{0.063}$S$_{0.656}$	2.63	-	-	25[a]	620[b]	617[a]	1.00[a]	0.355
Ge$_{0.095}$As$_{0.286}$S$_{0.619}$	2.48	-	-	27[a]	510[b]	461[a]	1.60[a]	0.428

[a] Values from Ref. [2]
[b] Values from Ref. [11]

Before discussing the evolution of the Raman spectra with temperature, we present the thermogram of the Ge$_{0.04}$As$_{0.225}$S$_{0.735}$ glass in the region 370-540 K (Fig. 3). A similar thermogram has been obtained for the second glass of the study. If the specific heat increase over the entire endothermic effect associated with the glass transition is ΔCp, the T_g is estimated as the temperature corresponding to an increase of $\Delta Cp/2$. In the DSC curve of Fig. 3, the temperatures T_1 and T_2 (indicated by arrows) correspond to the commencement and completion of the endothermic effect, respectively. The values of T_g obtained in this way are 432 and 458K for the Ge$_{0.04}$As$_{0.225}$S$_{0.735}$ and Ge$_{0.08}$As$_{0.20}$S$_{0.72}$ glasses, respectively (see also Table 1, where the T_1 and T_2 values are also shown).

the lower frequencies with increasing temperature. Similar temperature dependence is also observed for the bands at 470 and 495 cm^{-1} due to S-S bonds. This overall band softening is illustrated better in the frequency-temperature plots of Figs. 4 and 5 for the BP and peak (~ 340 cm^{-1}) of the convoluted bands between 300 and 450 cm^{-1} (insets). The molecular peak has a rather continuous decrease of frequency with temperature for either glass. In contrast, the BP is practically temperature-independent in the region 20 K -T_g, but as T_g is approached, its frequency drops abruptly (discontinuously) for both glasses at a temperature T_d. Compared to the DSC measured values (Fig. 3 and Table 1), T_d is lower than T_g, but quite close to the commencement temperature T_1. Therefore, we suggest that T_d corresponds to the onset of the transition to the supercooled state.
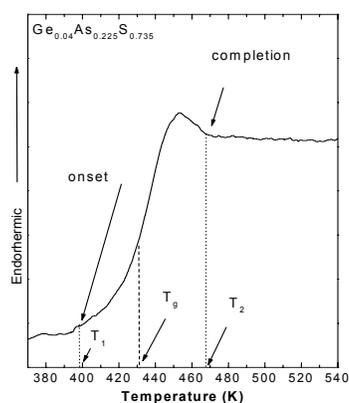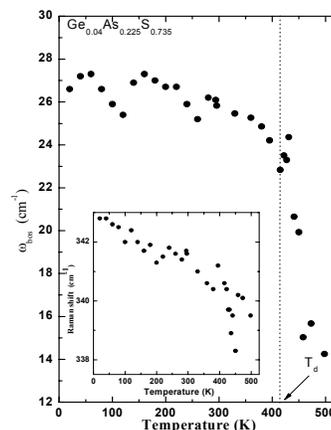

Fig. 3. DSC curves for Ge$_{0.04}$As$_{0.225}$S$_{0.735}$ glass. The arrow indicates the glass transition temperature Tg.

It is evident from the Raman spectra of Figs 1 and 2 that both the BP and high-frequency molecular bands are temperature dependent and specifically they shift towards

Fig. 4. Boson peak frequency ω_{bos} of the Ge$_{0.04}$As$_{0.225}$S$_{0.735}$ glass plotted against temperature. The inset shows a similar frequency plot of the molecular band at 340 cm^{-1}.
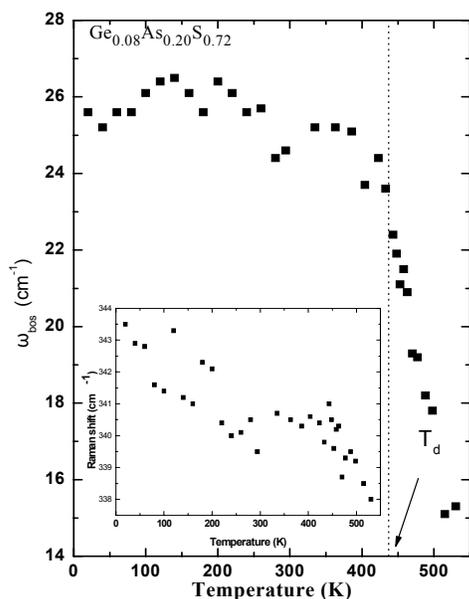
Fig. 5. Boson peak frequency ω_{bos} of the $Ge_{0.08}As_{0.20}S_{0.72}$ glass plotted against temperature. The inset shows a similar frequency plot of the molecular band at $340\ cm^{-1}$.

Fig. 6. The Boson peak intensity of the $Ge_{0.04}As_{0.225}S_{0.735}$ glass normalized to the molecular band at $340\ cm^{-1}$ and plotted against temperature.

The above results are similar to those obtained in rigid Ge-As-S glasses where, again, the drop temperature T_d is lower than the DSC estimated T_g value (see Ref. 2 and Table 1). It must be pointed out that in the previous work [2] there were no DSC measurements, so the comparisons relied on different DSC data [11] for the T_g values, thus there were no values for T_1 and T_2. However, in comparison to the previous report [2] on rigid chalcogenide glasses, the BP frequency drop is more abrupt, a result which is also reflected by the higher normalized slopes (Eq. 2) for the floppy glasses (Table 1).

Further, as T_g is approached, apart from the abrupt frequency drop, a noticeable increase of the BP intensity is observed. This effect is illustrated in Figs. 6 and 7 which give the relative peak intensity I_{bos}/I_{mol} between BP and high-frequency molecular ($340\ cm^{-1}$) bands for the glasses $Ge_{0.04}As_{0.225}S_{0.735}$ and $Ge_{0.08}As_{0.20}S_{0.72}$, respectively. In order to reduce the error level, the VH spectra were preferred for I_{bos} and the HH ones for the I_{mol}. It is obvious from Fig. 6 that a sharp increase of the relative intensity occurs for the $Ge_{0.04}As_{0.225}S_{0.735}$ at a temperature $T_i \approx 380$ K which is below both T_1 and T_d. Therefore, the sharp increase of this intensity ratio acts as a warning for the incipient transition to the supercooled liquid phase.
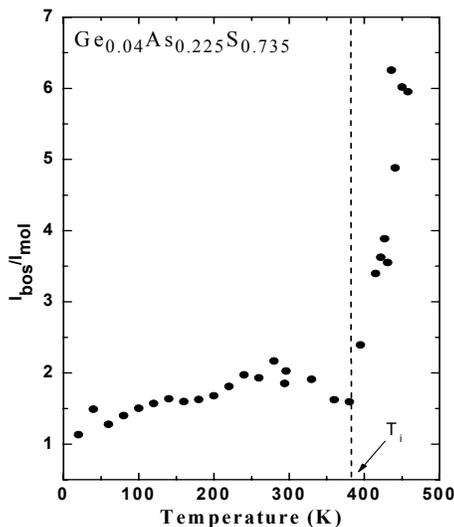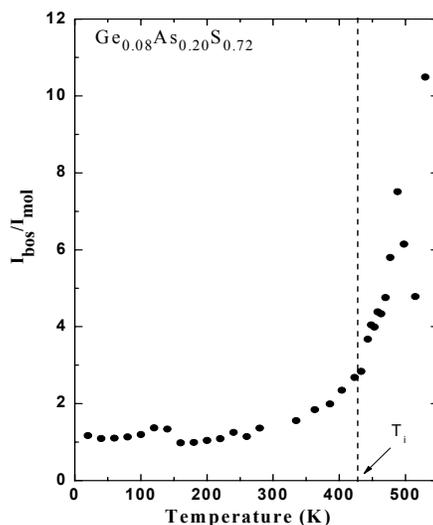

Fig. 7. The Boson peak intensity of the $Ge_{0.08}As_{0.20}S_{0.72}$ glass normalized to the molecular band at $340\ cm^{-1}$ and plotted against temperature.

Finally the values of fragility ratio $r(T_g)$ are < 0.85 for both glasses (Table 1), so we can conclude that these floppy glasses are strong glass formers [4], but relatively more fragile than the rigid ones of the series.

4. Conclusions

The comparative Raman and DSC studies have shown that the spectral characteristics of the Boson peak can be used for the study of critical phenomena around the glass

transition temperature T_g in the case of floppy Ge-As-S chalcogenide glasses. Indeed, the temperature of the abrupt frequency drop of the BP almost coincides with the onset of transition to the supercooled liquid phase. In comparison to the rigid Ge-As-S glasses, the frequency drop is steeper in the floppy ones, a result which is compatible with the (generally accepted) lower bulk modulus [12] and higher fragility of the latter. On the other hand, the sharp increase of the BP intensity, prior to the onset of the transition to the supercooled liquid, can be considered as a precursor of the incipient transition.

Acknowledgments

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