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Structural study of Ge–Bi–S glasses by Raman spectroscopy

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The glass-forming ability in the Ge–Bi–S system and some basic physical properties of Ge–Bi–S glasses were reported in 1976 by Frumar *et al.* [1]. After the discovery of anomalous n-type conductivity in these glasses [2], their electrical properties were studied more thoroughly and reviewed later in papers by Elliott and Steel [3] and Frumar and Tichy [4].

Recent studies of glass formation in the Ge–Bi–S system [5] corrected the extension of the glass-forming region towards the glasses with a higher Bi_2S_3 content in accordance with the formation of a eutecticum in the pseudo-binary GeS_2–Bi_2S_3 system (Fig. 1).

The structure of Ge–Bi–S glasses, especially the bonding of Bi in them, is still a matter of discussion. Generally it is assumed that in the glasses lying on the tie-line GeS_2–Bi_2S_3 (Fig. 1) the structural network consists of GeS_4 tetrahedra and BiS_3 pyramids connected in a three-dimensional network via bridging S atoms. Nevertheless, in some papers also the co-ordination number of Bi of 6 was proposed, at least for Ge–Bi–Se glasses [6]. The glass-forming region in the Ge–Bi–S system extends mainly into the S-rich region, where according to the chemically ordered structural network (COSN) model S–S bonds should be formed inside the glass network, whereas the extension into the low-S region with metal–metal bonds is very small (Fig. 1).

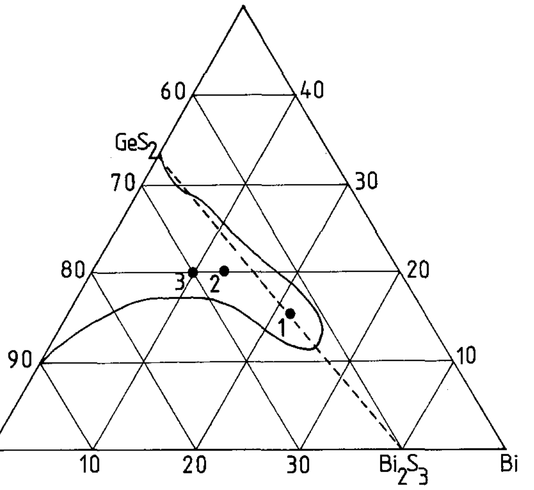

Figure 1 Glass-forming region of the Ge–Bi–S system (according to [6]). (●) Glassy samples studied: 1, $(GeS_2)_{0.6}(Bi_2S_3)_{0.4}$; 2, $Ge_{20}Bi_{13}S_{67}$; and 3, $Ge_{20}Bi_{10}S_{70}$.

As Raman spectroscopy proved to be a useful tool for obtaining an information on the types of basic structural units in similar ternary chalcogenide glasses of the Ge–Sb–S [7, 8] and Ge–As–S [9] systems, we tried to measure the Raman spectra of Ge–Bi–S glasses for the study of bonding in these glasses. Previous attempts to measure the Raman spectra of dark Ge–Bi–S glasses failed due to the high absorption of excitation Ar or He–Ne lasers radiation in these black glasses with short-wavelength absorption edge shifted into the near-infrared region. Therefore, only the application of long-wavelength excitation laser radiation with the combination of the Fourier-transformed Raman technique made it possible to obtain these spectra.

Ge–Bi–S glasses were prepared by direct synthesis from Ge and Bi of 99.999% purity and S (Mark DAB-6) purified by the process described in [10]. The elements were put in stoichiometric amounts into quartz ampoules (total batch 7 g), which were evacuated and sealed. After synthesis and homogenization at 1200 K for 8 h, the ampoules were quenched in ice-water. The absence of crystallinity was also checked by X-ray diffraction. Three glass compositions with a relatively high Bi content were prepared: $Ge_{20}Bi_{10}S_{70}$ and $Ge_{20}Bi_{13}S_{67}$ from the S-rich region and $(GeS_2)_{0.6}(Bi_2S_3)_{0.4}$ glass, which corresponds to the $Ge_{15.8}Bi_{21}S_{63.2}$ composition (their positions inside the glass-forming region are shown in Fig. 1).

Raman spectra were measured at room temperature on a Bruker IFS-66 Fourier-transform infrared spectrometer equipped with the Raman module FRA 106. Raman spectra were excited by a Nd:YAG laser with energy 40 mW at the sample. The spectral resolution was 4 cm^{-1} and 25 scans were accumulated for each spectrum. The obtained interferograms were transformed using the program RAMANSK.

The obtained Raman spectra of the three Ge–Bi–S glasses investigated are shown in Fig. 2, together with the spectrum of their "mother" GeS_2 glass. In the Raman spectra of Ge–Bi–S glasses

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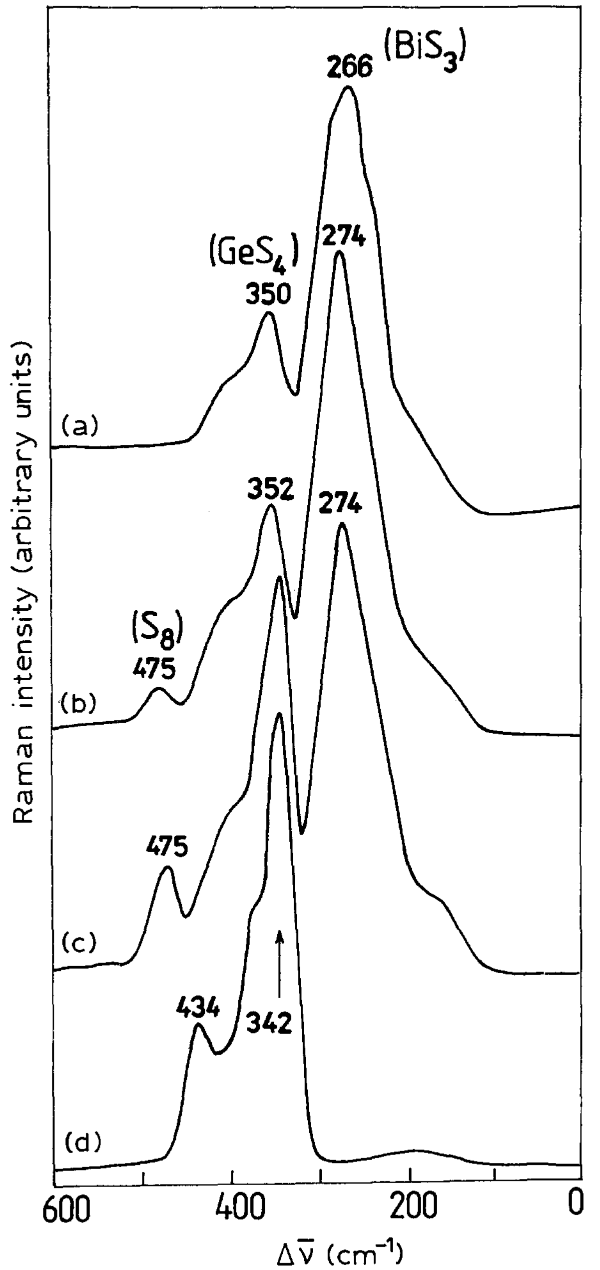

Figure 2 Raman spectra of $Ge_xBi_yS_z$ glasses: (a) $Ge_{15.8}Bi_{21}S_{63.2}$, (b) $Ge_{20}Bi_{13}S_{67}$, (c) $Ge_{20}Bi_{10}S_{70}$ and (d) GeS_2.

there is a dominant band at 274 cm^{-1} for the $Ge_{20}Bi_{10}S_{70}$ and $Ge_{20}Bi_{13}S_{67}$ glasses and at 266 cm^{-1} for the $Ge_{15.8}Bi_{21}S_{63.2}$ glass. Its relative intensity increases with increasing Bi content, and therefore we assume that it can be assigned to the vibrations of structural units formed by Bi atoms.

The sharp band at 342 cm^{-1} dominant in the Raman spectrum of GeS_2 glass shifts its position in the Ge–Bi–S glasses up to 350–352 cm^{-1} and its relative strength decreases. In accordance with previous work [5] we suppose that the structural network of Ge–Bi–S glasses is composed of GeS_4 tetrahedra and BiS_3 pyramids interconnected via S bridging atoms. The vibrational band at 342–352 cm^{-1} can thus be ascribed to the symmetric stretching vibration of GeS_4 units as in similar Ge–S-based ternary chalcogenide glasses [7–9].

The vibrational frequency of BiS_3 pyramidal units is not easy to calculate accurately, due to the lack of knowledge of the magnitude of the force constant k_{Bi-S} and the valence angles in the BiS_3 pyramids. We can only suppose that its structure will be similar to that of the $BiCl_3$ molecule and calculate an approximate value of its symmetrical stretching vibration (which gives the strongest response in the Raman spectra) by the scaling method used in [8].

For the estimation of the $\nu_1(A_1)$ vibrational frequency of the BiS_3 pyramid from that of the $BiCl_3$ molecule [11] we used the scaling factor derived from the relation of similar structural units of SbS_3 [12] and $SbCl_3$ [11], as $f = \nu_1(SbS_3)/\nu_1(SbCl_3) = \nu_1(BiS_3)/\nu_1(BiCl_3) = 0.76$. In this way we obtained the value $\nu_1(BiS_3) = 260\ \mathrm{cm}^{-1}$. Due to the approximate character of this estimated value, the experimentally observed position of the dominant band at 266–274 cm^{-1} in the Ge–Bi–S glasses seems to be reasonable for assignment to the stretching vibration of BiS_3 units.

In the Raman spectrum of glasses with 10 and 13 at % Bi, respectively, there is an additional band at 475 cm^{-1}, the strength of which was greater for the glass with higher S content. In ternary chalcogenide glasses with a surplus of S this band is characteristic of the presence of S_8 molecules in the structural network [7, 9]. Its absence in the Raman spectrum of the $(GeS_2)_{0.6}(Bi_2S_3)_{0.4}$ glass shows that at this composition in the structure of Ge–Bi–S glasses there are only Ge–S and Bi–S bonds, in agreement with the COSN model.

Therefore, we can conclude that the analysis of the Raman spectra of Ge–Bi–S glasses confirmed that their structural network is composed of GeS_4 and BiS_3 structural units. These units are manifested in the Raman spectra by vibrational bands at 342–352 cm^{-1} (GeS_4) and 266–274 cm^{-1} (BiS_3). The maxima of both of these bands shift slightly with composition, giving evidence for some vibrational coupling of the structural units via S bridging atoms. In the S-rich part of the glass-forming region, Ge–Bi–S glasses also contain S_8 molecules incorporated in the structural network.

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