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Optical properties of $Ge_{40-x}Sb_xSe_{60}$ glasses

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The optical properties of $Ge_{40-x}Sb_xSe_{60}$ glasses have been studied in the infrared spectral region and also in the short wavelength region. The spectral dependence of the absorption coefficient in the region of multiphonon absorption, optical gap and average gap was discussed in relation to the chemical composition. It is supposed that the structure of these glasses is complicated due to structural units containing mainly Ge–Se, Sb–Se and also Ge–Ge, Ge–Sb and Sb–Sb bonds.

1. Introduction

Ge–Sb–Se glasses are used for the development of passive infrared (IR) optical elements owing to their transparency especially in the 8 to 13 μm spectral region. Although considerable attention has been paid to the preparation and physical properties of these glasses (see, e.g., [1–3] and references therein), the study of relation property-chemical composition in the Ge–Sb–Se system is still of interest [4, 5], especially the possibility of improving optical transmission in long wavelength cutoff by changing the chemical composition. It has been shown [1] that a decrease of Ge–Se bond density in regular $GeSe_4$ tetrahedra leads to the improvement of IR transmission if the chemical composition changes from $Ge_{19}Sb_{17}Se_{64}$ to $Ge_{28}Sb_{12}Se_{60}$ and $Ge_{23.5}Sb_{18}Se_{58.5}$.

Some physical properties of $Ge_{40-x}Sb_xSe_{60}$ glasses, including composition trends of the softening temperature and d.c. electrical conductivity, have been reported recently [5]. Here we give some results of our optical property study in the region of multiphonon absorption and also in the short wavelength region of $Ge_{40-x}Sb_xSe_{60}$ glasses.

2. Experimental Procedure

Glasses $Ge_{40-x}Sb_xSe_{60}$, for $x = 0, 4, 8, 12, 16, 20, 24, 28$, were prepared by the usual procedure (way 1) from elements of 5 N purity (total weight 8 g) in evacuated ($p \sim 10^{-3}$ Pa) quartz ampoules (0.8 cm i.d., 1.0 cm o.d.). Prior to filling, the quartz ampoules were baked for 4 h at 1000° C under vacuum ($p \sim 10^{-3}$ Pa) to remove adsorbed water. Synthesis was carried out in a rotary furnace. After annealing (550° C for 4 h) and homogenization (900° C for 18 h) had taken place, the ampoules were cooled in air (composition with $x = 0$ in ice water). To suppress oxygen contamination of glasses deoxidized selenium was used for synthesis (way 2). Selenium was first heated for 3 h at 200° C and $p \sim 10^{-3}$ Pa and then distilled to germanium and antimony. The oxidizer (50 p.p.m. aluminium) was also added. Plane-parallel samples for the optical measurements were prepared by cutting from the bulk and polishing to optical quality with a suspension of Al_2O_3 powder in water-free ethanol.

IR transmission and reflectivity measurements between 4000 and 300 cm^{-1} were made using a Perkin–Elmer 684 spectrophotometer. The densities of prepared glasses were determined by a hydrostatic method. At ambient temperature the densities of $Ge_{40-x}Sb_xSe_{60}$ glasses were $x = 0$, $\varrho = 4.39\,\mathrm{g\,cm^{-3}}$; $x = 4$, $\varrho = 4.49\,\mathrm{g\,cm^{-3}}$; $x = 8$, $\varrho = 4.59\,\mathrm{g\,cm^{-3}}$; $x = 12$, $\varrho = 4.67\,\mathrm{g\,cm^{-3}}$; $x = 16$, $\varrho = 4.77\,\mathrm{g\,cm^{-3}}$; $x = 20$, $\varrho = 4.89\,\mathrm{g\,cm^{-3}}$; $x = 24$, $\varrho = 5.01\,\mathrm{g\,cm^{-3}}$; $x = 28$, $\varrho = 5.13\,\mathrm{g\,cm^{-3}}$.

3. Results and discussion

3.1. The long wavelength cutoff

The long wavelength IR cutoff of Ge–Sb–Se glasses is determined by multiphonon absorption. However, it can also be modified by extrinsic absorption originating from oxygen impurities like GeO_2, SeO_2, SiO_2, Sb_2O_3, Sb_2O_5 [2, 6, 7]. Typical IR spectra for $Ge_{28}Sb_{12}Se_{60}$ and $Ge_{20}Sb_{20}Se_{60}$ glasses are shown in Fig. 1. There are two characteristic features: (i) the long wavelength cutoff with the onset around 680 cm^{-1} and (ii) strong absorption band (AB) around 780 cm^{-1} in sample 1 prepared in way 1. This AB (due to the Ge–O stretching [7]) can be depressed by improving the method of sample preparation, see IR spectra of samples 2, 3, respectively, which were prepared in way 2. Nevertheless the IR transmission still decreases below 960 cm^{-1}. This decrease of transmission can be associated with both the traces of oxygen (of the order of less than 1 p.p.m.) incorporated in the form of ≡Ge–O–Ge≡ bridges in the glassy matrix and with the third-order absorption process associated with the Ge–Se fundamental vibrational mode. A similar conclusion concerning the nature of the transmission decrease around 800 cm^{-1} in glassy $Ge_{28}Sb_{12}Se_{60}$ was also supposed [1]. The transmission in the spectral

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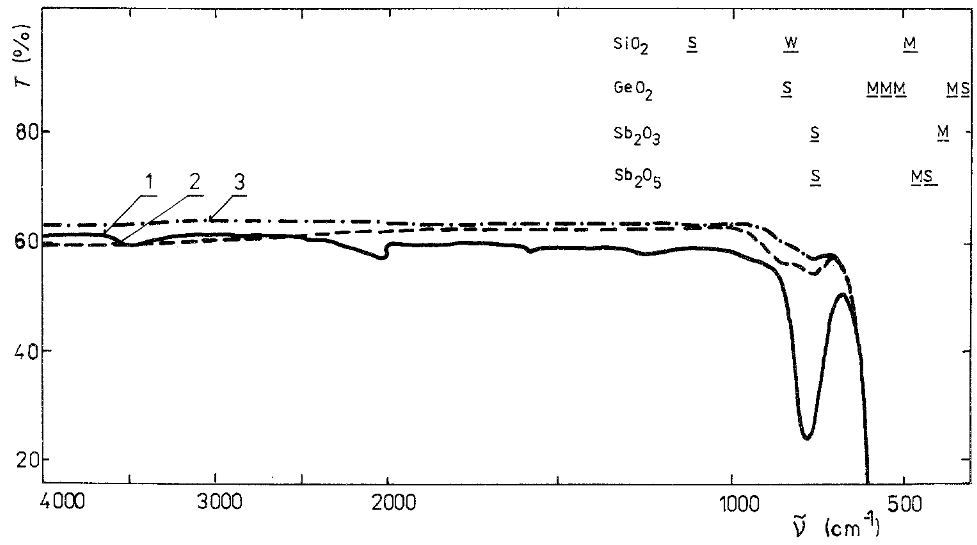

Figure 1 Infrared spectrum of glassy $Ge_{20}Sb_{20}Se_{60}$ prepared by common procedure (1) and spectra of $Ge_{20}Sb_{20}Se_{60}$ (2) and $Ge_{28}Sb_{12}Se_{60}$ (3) glasses prepared by purification procedure. Sample thicknesses are: (1) 4.37 mm, (2) 4.72 mm, (3) 5.69 mm. The upper part shows positions of maxima absorption bands of oxides which can cause extrinsic absorption in Ge–Sb–Se glasses (taken from [8]). Relative intensity of absorption bands is: s strong, m medium, w weak.

region of two-phonon processes was studied for the samples with thicknesses $d \sim 0.8$ to 0.9 mm. The results are summarized in Fig. 2 in α against $\tilde{\nu}$ (wavenumber) coordinates. The absorption coefficient (α) was calculated according to

$$\alpha = d^{-1} \ln (\{(1 - R)^2 + [(1 - R)^4 + 4R^2T^2]^{1/2}\}/2T) \quad (1)$$

where T is the transmission, d the sample thickness and R the reflectivity in the transparent region (at 1000 cm^{-1}). As evident from Fig. 2 there are three main features around 560, 490 and 395 cm^{-1}, respectively. According to Rechtin *et al.* [1] the following assignment of observed AB can be made (i) AB at 560 cm^{-1} to the second-order process associated with Ge–Se bonds (the fundamental vibrational mode for Ge–Se is around 250 cm^{-1}: (245 cm^{-1} [1], 254 cm^{-1} [9], 263 cm^{-1} [10]), (ii) AB at 395 cm^{-1} to the second-order process associated with Sb–Se bonds (the fundamental mode for Sb–Se is 180 cm^{-1} [1], (iii) AB at 490 cm^{-1} to the combination of fundamental Ge–Se and Sb–Se. However, this assignment of AB at 490 cm^{-1} requires further consideration. This AB should have a more complicated origin since this AB also appears in pure $Ge_{40}Se_{60}$ (see Fig. 2). It is observed in glassy $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ [11] and also present in $GeSe_x$ glasses for $1.4 \leqslant x \leqslant 9$ [12]. The compositionally nearly independent intensity of AB at 490 cm^{-1} in $GeSe_x$ glasses [12] can indicate that the AB is of extrinsic origin and can be assigned to the presence of Si–O bonds in SiO_2 which is dissolved into the melt from the inner walls of the silica ampoules used during the synthesis. Although such an origin of AB at 490 cm^{-1} cannot be fully excluded we suppose that contamination of the melt by SiO_2 cannot be the dominant origin of this AB. The above supposition is explained by the following reasons: (i) the most intensive AB indicating the presence of silica contamination should be observed around 1100 cm^{-1} (see Fig. 1 and [1]), where the most intensive feature of SiO_2 exists. No

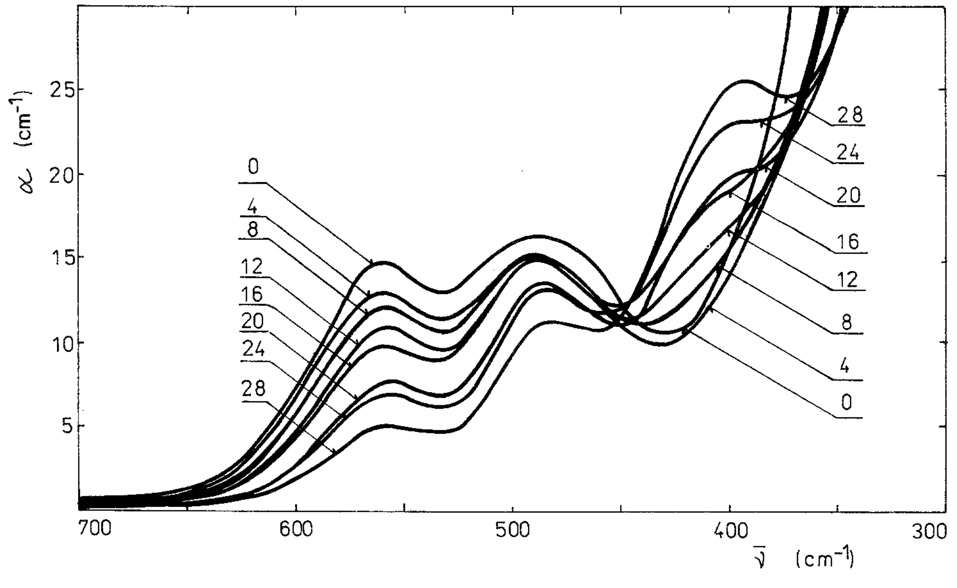

Figure 2 Spectral dependence of absorption coefficient for $Ge_{40-x}Sb_xSe_{60}$ glasses in the region of infrared cutoff. Chemical compositions (x) are marked by numbers.

absorption in this region was observed in our glasses (see Fig. 1). (ii) The absorption in the region around $490\,\mathrm{cm}^{-1}$ has been observed with a tendency of α increase if the chemical composition of Ge–Sb–Se glasses is changed in such a way that the probability of regular $GeSe_4$ tetrahedra formation increases ([1], see Fig. 7). (iii) The AB at $490\,\mathrm{cm}^{-1}$ was observed in $(GeSe_2)_{0.5}(As_2Se_3)_{0.5}$ glass and it was assigned to the two-phonon process originating from combination of the first-order bands in $GeSe_2$ [11]. The empirical selection rule scheme for predicting the multiphonon absorption frequencies according to activity factors (see [13]) was used [11]. In order to discuss, at least quantitatively, the possible origin of AB at $490\,\mathrm{cm}^{-1}$ in our glasses, we refer to our recent letter [5] in which it was shown that within Shimakawa's effective medium theory classification of chalcogenide glasses the $Ge_{40-x}Sb_xSe_{60}$ glasses probably cannot be taken as a solid solution of the two types of clusters composed of $\equiv Se_3\text{–}Ge\text{–}Ge\text{–}Se_3 \equiv$ and $SbSe_3 \equiv$ structural units (s.u.). It means that one cannot exclude in these glasses the existence of Sb–Sb and/or Ge–Sb bonds in e.g. following type of s.u. $= Se_2Sb\text{–}SbSe_2 =$ and/or $\equiv Se_3Ge\text{–}SbSe_2 =$. We noted also that the existence of Ge–Sb or Sb–Sb bonds was supported in Ge–Sb–Se glasses [1]. In such a case we can expect that as the number of Ge–Sb or Sb–Sb bonds increases, the number of Ge–Se bonds in $GeSe_4$ tetrahedra also increases. This of course does not mean that the total density of Ge–Se bonds increases significantly with an increase of x, because the density of Ge–Se bonds is first of all determined by the concentration of germanium atoms and the same time the existence of $Ge\text{–}Ge_2Se_2$ tetrahedra cannot be fully excluded, besides $Ge\text{–}GeSe_3$. Hence we speculate that the origin of the AB at $490\,\mathrm{cm}^{-1}$ can be due to the superposition of the two-phonon processes. The first two-phonon process is associated with Ge–Se fundamental in $GeSe_4$, $Ge\text{–}GeSe_3$ or $Ge\text{–}Ge_2Se_2$ tetrahedra, and the second two-phonon process is associated with the combination of the Ge–Se fundamental and the Sb–Se fundamental modes. The fact that the frequencies of all the multiphonon processes are shifted to higher energies in comparison with strict multiples or combinations of the fundamental ones can be due to the anharmonic nature of these overtones [14]. In Fig. 3 the compositional dependences of absorption coefficients at 590, 490 and $395\,\mathrm{cm}^{-1}$, respectively, are shown. The full lines show the $\alpha(x)_{\text{Ge–Se}}$ calculated from Relation 2 assuming the additivity of absorption coefficients of pure Ge_2Se_3 and Sb_2Se_3 in the spectral region studied and $\alpha_{Sb_2Se_3} \simeq 0$

$$\alpha(x) = f\alpha_{Sb_2Se_3} + (1 - f)\,\alpha_{Ge_2Se_3} \qquad (2)$$

where f is the volume fraction of Sb_2Se_3:

$$f = (XM_1/\varrho_1)/[(XM_1/\varrho_1) + ((1 - X)M_2/\varrho_2)],$$
$$X = x/40$$

where X, M_1, ϱ_1 are the mole fraction, formula weight, and density of Sb_2Se_3 and $(1 - X)$, M_2, and ϱ_2 respectively, is the corresponding quantity for Ge_2Se_3. The value $\varrho_1 = 5.35\,\mathrm{g\,cm}^{-3}$ was taken from [15]. As evident for AB at $560\,\mathrm{cm}^{-1}$, the experimental points are close to the calculated line which indicates that this band is closely associated with Ge–Se bond density. The increase of absorption at $395\,\mathrm{cm}^{-1}$ corresponds to the increase of Sb–Se bond density and thus to an increased intensity of second-order process associated with the Sb–Se fundamental mode. However, the nonlinear dependence $\alpha(x)_{\text{Sb–Se}}$ indicates some structural changes which can be associated with the Ge–Sb and/or Sb–Sb bonding. In Fig. 4 the spectral dependences for $\alpha_{Sb_2Se_3}$ calculated from Relation 2 for $x = 8$, 20 and 28 are shown. In the case of no structural changes

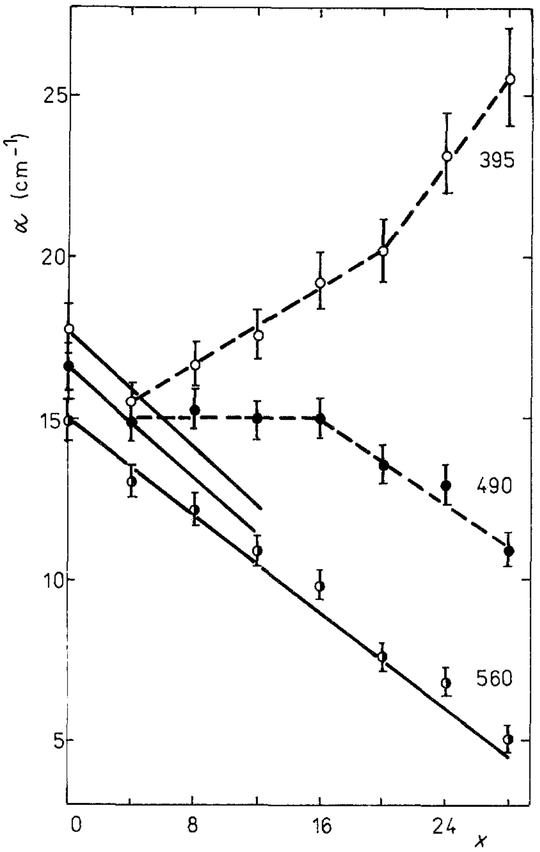

Figure 3 Compositional dependence of absorption coefficient at 560, 490 and $395\,\mathrm{cm}^{-1}$ for $Ge_{40-x}Sb_xSe_{60}$ glasses. The full lines show values of absorption coefficient of glasses assuming $\alpha_{Sb_2Se_3} \simeq 0$. Marked error is ±1% of transmission.

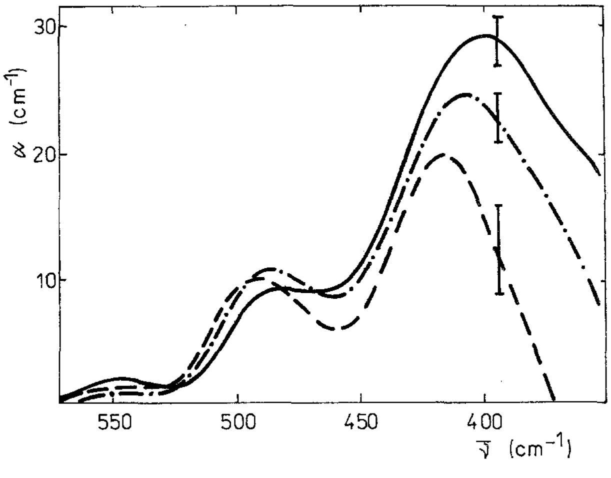

Figure 4 Spectral dependence of absorption coefficient for Sb_2Se_3 calculated from Relation 2 using experimental values of absorption coefficient of Ge_2Se_3 and $Ge_{12}Sb_{28}Se_{60}$ (——), $Ge_{20}Sb_{20}Se_{60}$ (– – –), $Ge_{32}Sb_8Se_{60}$ (—·—), respectively. The bars indicate error of transmission ±1%.

around antimony atoms i.e. for conserved $SbSe_3 \equiv$ pyramids in $Ge_{40-x}Sb_xSe_{60}$ glasses, one would expect that the spectral dependence of $\alpha_{Sb_2Se_3}$ for all the compositions to be nearly identical. However, as evident from Fig. 4 considerable discrepancies are seen for $\alpha_{Sb_2Se_3}$ for various compositions. This fact can indicate some structural changes in $SbSe_3 \equiv$ pyramids. The composition dependence of experimental values of absorption coefficient at 490 cm^{-1} significantly deviates from calculated $\alpha(x)_{Ge\text{-}Se}$ from Relation 2, assuming that $\alpha_{Sb_2Se_3} \simeq 0$ in this spectral region. This indicates that AB at 490 cm^{-1} can result from the superposition of two processes of which one is due to the combination Ge–Se and Sb–Se fundamental. Unfortunately we are not able to calculate $\alpha(x)$ for 490 cm^{-1} since the $\alpha_{Sb\text{-}Se}$, owing to the possible structural changes in $SbSe_3 \equiv$ pyramids, depends on the chemical composition. From the above discussion it seems that the structure of $Ge_{40-x}Sb_xSe_{60}$ glasses can be rather complicated with structural units containing mainly Ge–Se, Sb–Se and also Ge–Ge, Ge–Sb and/or Sb–Sb bonds.

3.2. Optical gaps and average gaps

The compositional dependence of the optical gaps (E_g^{opt}) in $Ge_{40-x}Sb_xSe_{60}$ glasses has been reported previously [4, 5]. In both papers different ways to estimate the E_g^{opt} values were used. While in [4] the E_g^{opt} values were determined from Tauc plots $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ in [5] the energy corresponding to $\alpha = 10^3\,cm^{-1}$ was taken as an optical gap. The reason why those values were used in [5] as E_g^{opt} follows from the fact that optical measurements in the short wavelength region were provided on the samples of thickness ~0.1 to 1.0 mm and the $\alpha(\hbar\omega)$ dependence has been found in the form $\alpha \sim \exp(\hbar\omega/\Delta)$ [5]. It is known that in chalcogenide glasses the Tauc plot can be used for $\alpha > 10^3\,cm^{-1}$ i.e. for thin samples, because for $\alpha < 10^3\,cm^{-1}$ the $\alpha(\hbar\omega)$ dependence takes an exponential form. The results of [4] (see Figs 7 and 8) also show that $\alpha(\hbar\omega)$ takes the form $\alpha \sim \exp(\hbar\omega/\Delta)$ and the fact, that simultaneously $\alpha(\hbar\omega)$ gives straight lines in $(\alpha\hbar\omega)^{1/2}$ plotted against $\hbar\omega$ coordinates can be fortuitous. Hence for comparison of the results of optical measurements in the short wavelength region [4, 5] we use the values of $E_g^{opt} = \hbar\omega_{\alpha=10^3 cm^{-1}}$. In order to relate E_g^{opt} to the chemical composition of $Ge_{40-x}Sb_xSe_{60}$ glasses we use the correlation between average heat of atomization ($\bar{H}_s$) and optical gap, see e.g., [16] and recently [17]. In [17] it is supposed that the optical gap relates to the average bond energy. The ratio $\bar{H}_s/m$ (where m is the mean coordination number) can be taken as a measure of the average bond energy. This ratio for our glasses is given by

$$\bar{H}_s/m = \frac{(40-x)H_s^{Ge} + xH_s^{Sb} + 60H_s^{Se}}{(40-x)N_{Ge} + xN_{Sb} + 60N_{Se}} \qquad (3)$$

The values of the heat of atomization (H_s) are: $H_s^{Ge} = 90$ kcal g atom^{-1}, $H_s^{Sb} = 62$ kcal g atom^{-1}, $H_s^{Se} = 49.4$ kcal g atom^{-1} [17] and the coordination numbers of germanium, antimony and selenium atoms are $N_{Ge} = 4$, $N_{Sb} = 3$, $N_{Se} = 2$, respectively. In Fig. 5 the composition trend of optical gap values taken from [4] (full circles) and from [5] (open circles) is shown. The full curve represents the calculated $\bar{H}_s/m$ dependence plotted against m or x ($x = 280 - 100$ m). As evident the energy optical gap decreases with decreasing average bond energy. Some deviations in the otherwise monotonical decrease of the optical gap are seen around $x = 12$. These deviations can arise from structural changes in the glassy matrix associated with a relative increase of Ge–Se bonds in regular $GeSe_4$ tetrahedra as we speculated in the discussion of the two-phonon absorption process in the studied glasses.

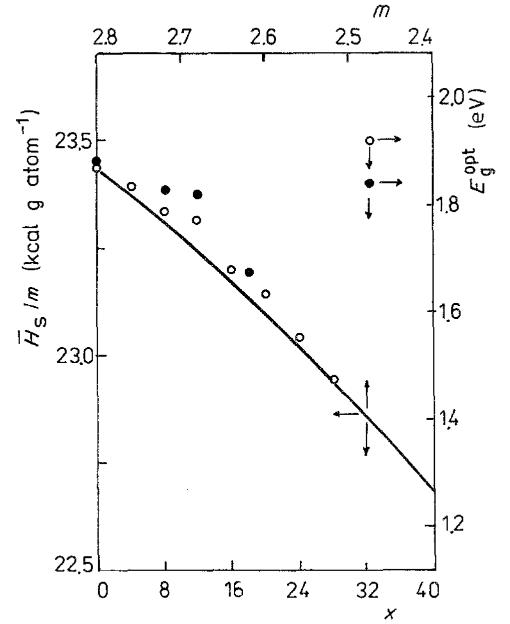

Figure 5 The optical gap E_g^{opt} and the average heats of atomization per single bonds $\bar{H}_s/m$ as a function of the composition parameter x and the average coordination number m, respectively. The full curve shows the computed $\bar{H}_s/m$ as a function of m or x. Values marked by full circles are taken from [4] and recalculated to $E_g^{opt} = \hbar\omega_\alpha = 10^3\,cm^{-1}$.

It was shown by Lucovsky [18] that there exists some correlation between minimum optical gap (E_g^{opt}) and average gap $\bar{E}_g$ for amorphous chalcogenides. The average gap as defined by Penn [19] is given by

$$(\bar{E}_g)^2 = \frac{(\hbar\omega_p)^2}{\varepsilon_1(0) - 1} S \qquad (4)$$

where $\varepsilon_1(0) = \varepsilon_\infty = n^2_{(\omega\to 0)}$ is the real part of the electronic dielectric constant in the limit $\omega \to 0$, $\hbar$ the Planck's constant divided by 2π, ω_p the plasma frequency of the valence band electrons and S can in the first approximation be 1. ε_∞ and $\hbar\omega_p$ can be determined from

$$\varepsilon_\infty = [(1 + \sqrt{R})/(1 - \sqrt{R})]^2 \qquad (5)$$

where R is the reflectivity in the transparent region (see e.g., [18]),

$$(\hbar\omega_p)^2 = 4\pi\hbar^2\bar{N}(x)N_0\frac{\varrho(x)}{\bar{M}(x)}\frac{e^2}{m_e} \qquad (6)$$

where $\bar{N}(x)$ is the average number of electrons participating in optical transitions, N_0 Avogadro's number, $\varrho(x)$ the density, $\bar{M}(x)$ the average atomic mass and e and m_e the electron charge and the free electron mass, respectively. The Penn's average gap is linked by Hoppfields [20] sum rule (E_a) to the dispersion energy (E_d) and the energy of the effective dispersion oscillator

TABLE I The values of real part of electronic dielectric constant (ε_∞), plasma energy ($\hbar\omega_p$), dispersion energy (E_d), effective dispersion oscillator (E_0), "Hoppfields gap" (E_a), average gap ($\bar{E}_g$) and optical gap (E_g^{opt}) for $Ge_{40-x}Sb_xSe_{60}$ glasses

x	ε_∞	$\hbar\omega_p$ (eV)	E_d (eV)	E_0 (eV)	E_a (eV)	$\bar{E}_g$ (eV)	E_g^{opt} (eV)
0	6.15	13.81	20.78	4.03	9.24	6.08	1.87
4	6.33	13.72	20.95	3.93	8.95	5.94	1.83
8	6.55	13.64	21.12	3.80	8.80	5.78	1.78
12	6.81	13.52	21.28	3.66	8.58	5.60	1.77
16	7.12	13.43	21.44	3.50	8.42	5.42	1.68
20	7.61	13.37	21.60	3.26	8.28	5.08	1.63
24	8.17	13.31	21.76	3.03	8.15	4.96	1.54
28	8.76	13.25	21.92	2.82	8.01	4.75	1.47

(E_0) of the Wemple–Di Domenico (WD) [21] single oscillator formula for refractive index dispersion, which in the limit $\omega \to 0$ takes the form

$$\varepsilon_1(0) = 1 + E_d/E_0 \qquad (7)$$

Using Hoppfield's rule

$$\bar{E}_g = E_a E_0 \qquad (8)$$

and consequently

$$(\hbar\omega_p)^2 = E_a E_d \qquad (9)$$

E_d can be evaluated using the simple empirical relation [21]

$$E_d = \beta N_c Z_a N_e \qquad (10)$$

where N_c, Z_a, N_e are the coordination number of the cation nearest neighbour to the anion, formal chemical valency of anion and total number of valence electrons (cores excluded) per anion, respectively, $\beta = 0.37 \pm 0.04$ eV for covalent materials and $\beta = 0.26 \pm 0.03$ eV for ionic materials [21]. To estimate E_0, E_d, $\hbar\omega_p$ and $\bar{E}_g$ for studied $Ge_{40-x}Sb_xSe_{60}$ glasses studied we take (i) $\bar{N}(x) = [4(40 - x) + 3x + 4 \times 60]/100$ i.e. four sp^3 electrons of germanium atoms, three p electrons of antimony atoms and four p electrons of selenium atoms are taken into consideration, which gives for $x = 0$ the same value $\bar{N}(0) = 4$ as used by Lucovsky [18], (ii) $N_e(x) = [4(40 - x) + 5x + 6 \times 60]/100$, $Z_a = 2$, $N_c = 3$ and $\beta \sim 0.4$ eV. The calculated values of ε_∞ from experimental reflectivity in the transparent region (at $1000\,cm^{-1}$) and $\hbar\omega_p$, E_d, E_0, E_a, $\bar{E}_g$ are summarized in Table I.

From Table I it is evident that the values of E_a, $\bar{E}_g$, E_0, E_g^{opt} fulfil the condition [21] $E_a > \bar{E}_g > E_0 > E_g^{opt}$ and the mean value of $E_0/E_g^{opt} \simeq 2.03 \pm 0.12$ and $\bar{E}_g/E_g^{opt} \simeq 3.18 \pm 0.07$ which indicate that the compositional changes of E_g^{opt} follow the changes in $\bar{E}_g(x)$. In [4] the value of E_0/E_g^{opt} for $Ge_{28}Sb_{12}Se_{60}$ (TI 1173) was found to be 2.56 which is a little higher than our result. However, taking into consideration the way we estimated $\hbar\omega_p$ and E_d, this difference seems to be acceptable.

4. Conclusions

Our results can be summarized as follows. (i) The absorption in the long wavelength IR cutoff of $Ge_{40-x}Sb_xSe_{60}$ glasses seems to be mainly influenced by the multiphonon process associated with the Ge–Se fundamental mode. (ii) Some improvements of absorption in this region can be achieved with an increase of the antimony content as recently found in another group of Ge–Sb–Se glasses [1]. (iii) From the compositional dependences of all the absorption coefficients at 500, 490 and $395\,cm^{-1}$, the optical gap and the average gap, it seems that the optical properties of $Ge_{40-x}Sb_xSe_{60}$ glasses are mainly controlled by chemical composition. (iv) It is, however, supposed that the structure of these glasses is complicated due to the existence of Ge–Sb and Sb–Sb bonds in addition to the Ge–Se, Sb–Se and Ge–Ge bonds. Such a bonding arrangement could be responsible for the existence of the complicated structural units in these glasses and it explains some deviations from the expected compositional dependences of α ($395\,cm^{-1}$), α ($490\,cm^{-1}$) and E_g^{opt}, respectively. Further work seems to be necessary to explain the structure of these glasses and its influence on the physical properties.

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