

## Optical band gap in relation to the average coordination number in Ge–S–Bi thin films

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Chalcogenide glasses belonging to the  $\text{Ge}_x\text{S}_{94-x}\text{Bi}_6$  system ( $14 \leq x \leq 28.33$  at%) have been prepared from high purity constituent elements. Thin films of the same materials have been deposited by vacuum thermal evaporation. Optical absorbance measurements have been performed on the as-deposited films. The allowed optical transition is found to be indirect and the corresponding optical gaps,  $E_g$ , are determined. The variation of  $E_g$  with the average coordination number,  $\langle r \rangle$ , is also investigated. The observed  $E_g - \langle r \rangle$  dependence is discussed on the basis of the chemical bonding between the constituents and the rigidity percolation threshold behavior of the network.

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### 1 Introduction

Amorphous chalcogenides are very well known semiconductor materials. Due to their high transmittance in the IR spectral region and other interesting optical properties, they are used in the fabrication of a great number of optical devices [1]. In general these materials are often preferred to crystalline compounds with similar properties because of their favorable mechanical and interfacing properties. Furthermore, the lack of long-range-order (LRO) makes it possible to modify their optical properties to a specific technological application by changing their chemical composition. Consequently, the investigation of the compositional dependence of their optical properties is important to get a better understanding of the mechanisms underlying these phenomena and also to improve their interesting technological applications.

The Ge–S–Bi is a prototypical chalcogenide system. The first paper that dealt with the addition of bismuth in a chalcogenide matrix was published by Bowman and Schottmiller [2] in 1968. The goal was the preparation of new infrared photodetectors. At the same time, it was discovered that a small amount of Bi atoms incorporated in a selenium matrix changes the electrical conductivity from p to n type [3]. More recently, the possibility of making an all chalcogenide glass p–n junction based on the ability of Bi to change the conductivity type was demonstrated [4, 5]. Since the results of Schottmiller et al., many studies were performed to propose an explanation for the origin of this specific property that the Bi atom seems to possess. Different atomic configurations were proposed. Most of these works were recently discussed in a review paper of Vautier [6]. In regard to this last paper, one of the conclusions was that after more than 30 years of researches and debates, the origins of this specific property are not yet completely elucidated. In fact, one of the main problems is the lack of direct structural investigations of the atomic Bi surrounding. In consequence we have performed Ge K-edge and Bi L<sub>III</sub>-edge extended X-ray absorption fine structure (EXAFS) measurements on these glasses and EXAFS measurements from Bi L<sub>III</sub>-edge on crystalline Bi<sub>2</sub>S<sub>3</sub> [7]. In this latter work we have shown that Ge and Bi atoms in these glasses

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are uniquely coordinated with S atoms with a coordination number (CN) equal to four. This result of the CN of Bi in the glasses coupled with the results obtained from crystalline  $\text{Bi}_2\text{S}_3$  allows us to exclude the presence of  $\text{Bi}_2\text{S}_3$  microcrystalline inclusions and to conclude that these glasses are homogeneous at the microscopic level.

Earlier, we also reported the compositional dependence of the mean atomic volume and packing density of these glasses [8] as well as X-ray photoelectron spectroscopy (XPS) measurements on  $\text{Ge}_{20}\text{S}_{64}\text{Bi}_{16}$  glass [9]. From XPS results, we concluded that Bi enters the parent glass matrix,  $\text{Ge}_{20}\text{S}_{80}$ , as a positive charge centre.

To follow up our investigations we report and discuss in the present work the compositional dependence of the optical band gap of ternary Ge–S–Bi chalcogenide thin films. This work is of particular interest given the scarcity of literature on the optical band gaps of these films.

## 2 Experimental details

Glasses with the general formula  $\text{Ge}_x\text{S}_{94-x}\text{Bi}_6$  were prepared from high purity (99.999%) elemental Ge, S, and Bi. Immediately before use the germanium chunks were broken between filter papers in an air atmosphere to allow their entry into the silica glass tubes, and the Bi pellets and S pieces were used as supplied. Each tube was then evacuated to  $10^{-5}$  Torr and outgassed by a prolonged heating of the exterior of the tube with an oxyhydrogen torch. After cooling under vacuum, each tube was repeatedly flushed with argon, removed from the vacuum system and loaded with the desired amounts of the constituent elements. The tube was then sealed under a vacuum of  $10^{-5}$  Torr using the oxyhydrogen torch and placed in an electric furnace. The furnace was programmed up to 900 °C and the tube was kept in the furnace for 72 h. During this time, the tube was continuously agitated to homogenise the melt. Eventually, the glass was obtained by quenching the tube to 0 °C in an ice–water mixture.

Amorphous Ge–S–Bi films were prepared by standard vacuum thermal evaporation of Ge–S–Bi bulk glasses from an open tungsten boat onto ultrasonically cleaned glass substrates (microscope slides). Bulk glasses with a composition identical to the one of the thin films were used. The source–substrate distance was 0.1 m. The film deposition rate was about 50 nm/s and the deposition time was 3 s. The films were about 150 nm thick and were measured using a multiple beam interferometer [10]. The evaporation was performed inside a standard vacuum installation at a pressure of approximately  $10^{-5}$  Torr. The substrates were kept at room temperature during the deposition.

X-ray diffraction (XRD) measurements with Mo  $K_\alpha$  radiation ( $\lambda = 0.71069$  Å) were carried out on the prepared materials. The XRD patterns depicted diffused haloes with no sharp diffraction lines thus confirming the amorphous nature of the prepared materials.

The chemical compositions of the films were checked by X-ray photoelectron spectroscopy and were found to be very close (within  $\pm 1\%$ ) to those of the starting materials. The measurements were performed using an ESCA spectrometer of Physical Electronics (Perkin–Elmer, PHI 5600 Ci) with 180° hemispherical analyzer and using monochromatized Al  $K_\alpha$  radiation ( $h\nu = 1486.6$  eV).

The absorbance spectra of the thin films at normal incidence and at room temperature were obtained using a double beam recording UV-Vis-NIR spectrophotometer (Hitachi, Model U – 3501) with automatic computer data acquisition. The wavelength range analyzed was between 250 and 3000 nm. The spectrophotometer plots the results as  $\alpha t$  versus wavelength, where  $\alpha$  is the absorption coefficient and  $t$  the thickness of the film. The absorption coefficient  $\alpha$  can be calculated from optical absorption spectra using the relation

$$\alpha = 2.303 \log(I_0/I)/t, \quad (1)$$

where  $I_0$  and  $I$  are the intensities of the incident and transmitted beams, respectively. The absorption measurements were carried out against a virgin ultrasonically cleaned glass substrate which was taken as a reference. They were done in various parts of the films, scanning the entire sample, and excellent reproducibility of the spectra was generally achieved.

### 3 Results and discussion

In the high absorption region, which involves optical transitions between the valence and conduction bands, the absorption coefficient ( $\alpha$ ) of amorphous semiconductors takes the form [11–14]

$$\alpha = B(h\nu - E_g)^n/h\nu, \quad (2)$$

where  $h\nu$  is the photon energy,  $E_g$  is the optical gap,  $B$  is a constant which depends on the electronic transition probability, and  $n$  is a parameter depending on the type of the transition. The parameter  $n$  assumes values of 1/2, 3/2, 2, and 3 corresponding to allowed direct, forbidden direct, allowed indirect, and forbidden indirect transitions, respectively.

The dependence of  $(\alpha h\nu)^{1/n}$  on  $h\nu$  was plotted for different values of  $n$ . The best fit was obtained for  $n = 2$  as shown in Fig. 1. This result indicates that the indirect transition is the most plausible mechanism. The values of  $E_g$  of the indirect transitions for different compositions can be obtained from the intercept with the abscissa of the  $(\alpha h\nu)^{1/2}$  vs  $h\nu$  plots, as shown in Fig. 1. The obtained values of  $E_g$  are listed in Table 1. The dependence of  $E_g$  on the average coordination number  $\langle r \rangle$  is depicted in Fig. 2.

Lately, the average coordination number has been widely used for the description of the structure of network glasses [15–18]. It is defined as the average number of bonded neighbors per atom in the structure. For the  $\text{Ge}_x\text{S}_y\text{Bi}_z$  system under consideration,  $\langle r \rangle$  is given by

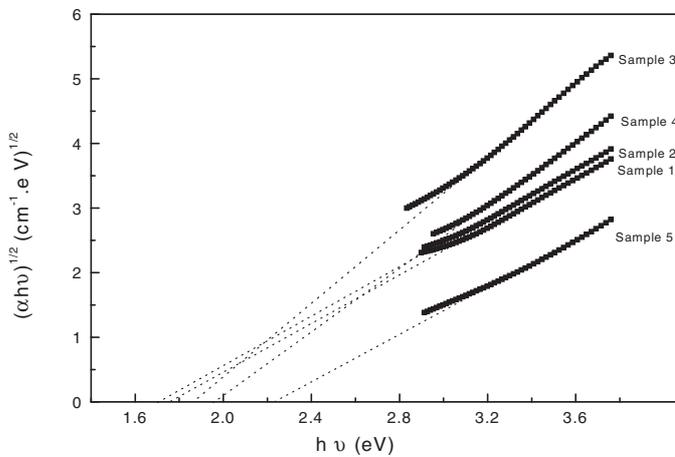
$$\langle r \rangle = x\text{CN}(\text{Ge}) + y\text{CN}(\text{S}) + z\text{CN}(\text{Bi}), \quad (3)$$

where  $x$ ,  $y$ , and  $z$  are the respective atomic concentrations of Ge, S, and Bi and  $\text{CN}(\text{Ge})$ ,  $\text{CN}(\text{S})$ , and  $\text{CN}(\text{Bi})$  are the coordination numbers of Ge, S, and Bi, respectively.

The evaluation of  $\langle r \rangle$  requires the knowledge of the coordination numbers of the individual atoms in the amorphous alloy. As mentioned in the introduction, we have undertaken an extended X-ray absorption fine structure (EXAFS) study on these alloys to obtain values of the coordination numbers of Ge and Bi. It is found that, in these amorphous alloys, Ge and Bi atoms are uniquely coordinated with S atoms with a value for their coordination number equal to four.

It is well known that the coordination number of S atoms in S-containing alloys conforms with the Mott (8- $V$ ) rule [19] where  $V$  is the number of valence electrons. Therefore, coordinations of 4, 2, and 4 for Ge, S, and Bi atoms, respectively, are used for the evaluation of  $\langle r \rangle$  and Eq. (3) for  $\text{Ge}_x\text{S}_{94-x}\text{Bi}_6$  alloys reduces to the formula

$$\langle r \rangle = 2.12 + 0.02x. \quad (4)$$



**Fig. 1** Determination of the optical band gaps in terms of the Tauc plots for  $\text{Ge}_x\text{S}_{94-x}\text{Bi}_6$  thin films.

**Table 1** Optical band gaps and the average coordination numbers in  $\text{Ge}_x\text{S}_{94-x}\text{Bi}_6$  thin films.

sample number	$x$	$E_g$ (eV)	$\langle r \rangle$
1	14	1.76	2.40
2	17	1.69	2.46
3	20	1.86	2.52
4	22	1.97	2.56
5	28.33	2.23	2.69

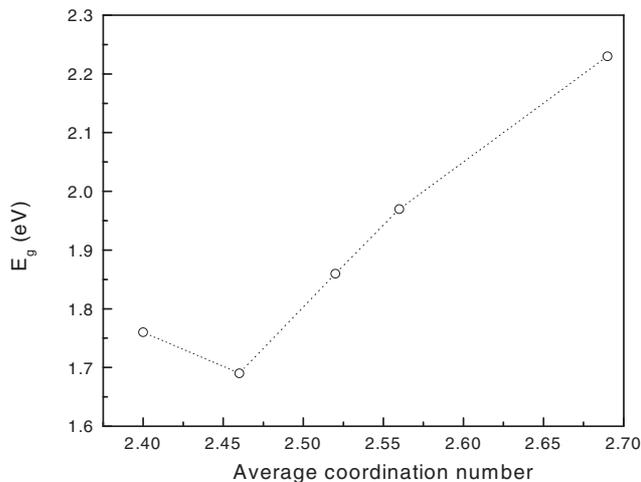
The values of  $\langle r \rangle$  for the investigated compositions are listed in Table 1 and cover a range between 2.40 and 2.69.

As can be seen from Fig. 2, the  $E_g - \langle r \rangle$  dependence displays a minimum at  $\langle r \rangle = 2.46$ . The maximum packing density and minimum mean atomic volume have been observed for this composition [8]. These observations have been associated with a sudden change in the average coordination number of the material where a transformation from an under-cross-linked (or floppy) to a constrained (or rigid) network takes place. In chalcogenide materials, the valence band ( $\sigma$ -bonding) originates from lone-pair (LP) electron states whereas the conduction band arises from antibonding ( $\sigma^*$ ) states [20]. It appears that for the composition with  $\langle r \rangle = 2.46$ , the conduction band is broadened. This broadening is a consequence of short-range-order (SRO) effects which accompany the contraction of the mean atomic volume. The broadening of the conduction band leads to the observed minimum of  $E_g$  at  $\langle r \rangle = 2.46$ . The increase of  $\langle r \rangle$  beyond 2.46 can lead to an increased interaction between the atomic species, which in turn can widen the separation between  $\sigma$  and  $\sigma^*$  bands. The aforementioned increase of  $E_g$  with the increase of  $\langle r \rangle$  can also be interpreted by using the chemically ordered network (CON) model (sometimes also called chain crossing model) as described below.

It is known that the optical gap of amorphous semiconductor alloys strongly depends on the average bond energy [21]. According to the CON model and in chalcogen rich alloys, as in our case, the relative fraction of Ge–S, Bi–S, and S–S bonds, expected to exist in the structure of  $\text{Ge}_x\text{S}_y\text{Bi}_z$  alloys, are given [22, 23] by

$$f_{\text{Ge-S}} = 8x/N, \quad f_{\text{Bi-S}} = 8z/N, \quad f_{\text{S-S}} = (2y - 4x - 4z)/N, \quad (5)$$

where  $N = 4x + 2y + 4z$ . The relative fraction of the bonds is summarized in Table 2. It is seen from this table that the fraction of Bi–S bonds remains almost constant while the fraction of Ge–S bonds increases and the one corresponding to S–S bonds decreases. The heteropolar bond energy  $E_{\text{A-B}}$  for a covalent

**Fig. 2** Variation of  $E_g$  with the average coordination number in  $\text{Ge}_x\text{S}_{94-x}\text{Bi}_6$  thin films.

**Table 2** Relative fraction of the bonds and the average bond energies in Ge<sub>x</sub>S<sub>94-x</sub>Bi<sub>6</sub> thin films.

sample number	$x$	Ge-S	Bi-S	S-S	average bond energy (kcal/mole)
1	14	0.467	0.200	0.333	53.54
2	17	0.553	0.195	0.252	54.21
3	20	0.635	0.190	0.175	54.85
4	22	0.688	0.187	0.125	55.27
5	28.33	0.843	0.178	–	57.55

bond between atoms A and B is estimated from the Pauling formula [24]

$$E_{A-B} = (E_{A-A}E_{B-B})^{1/2} + 30(x_A - x_B)^2, \quad (6)$$

where  $E_{A-A}$  and  $E_{B-B}$  are the single bond energies for atoms A and B in kcal/mole, respectively, and  $x_A$  and  $x_B$  are their corresponding electronegativities. The single bond energies, in kcal/mole, are 37.6 for Ge, 50.9 for S and 25.0 for Bi [24]. Using electronegativity values of 1.8, 2.5, and 1.9 for Ge, S, and Bi, respectively, the bond energies  $E_{Ge-S}$  and  $E_{Bi-S}$  are calculated. The values obtained for  $E_{Ge-S}$  and  $E_{Bi-S}$ , in kcal/mole, are 58.45 and 46.47, respectively. The average bond energies for the different compositions are then evaluated by summing the bond energies of the bonds present in the alloy structure in their relative proportions. These values are listed in Table 2. It is seen from this table that the average bond energy increases with the increase of  $\langle r \rangle$ . This increase of the average bond energy of the system tends to increase the energy of the conduction band edge, causing a larger splitting between  $\sigma$  and  $\sigma^*$  band and thus resulting in the observed increase in the band gap.

## 4 Conclusions

The optical band gap of Ge<sub>x</sub>S<sub>94-x</sub>Bi<sub>6</sub> thin films exhibits allowed indirect transition. The  $E_g - \langle r \rangle$  dependence displays a minimum at  $\langle r \rangle = 2.46$  which is associated with short-range-order effects accompanying the contraction of the mean atomic volume and the floppy-to-rigid transformation of the network. The afterward increase of  $E_g$  with  $\langle r \rangle$  is attributed to the increase of the average bond energy of the system.

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