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The composition dependence of the optical band gap in Ge doped Se-Te glassy alloy

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Abstract

Bulk glasses with the chemical composition $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) have been prepared from high purity constituent elements. Fragments of the bulk glasses are used to deposit thin films by vacuum thermal evaporation and compositional dependence of the optical and physical properties have been studied. It has been found that optical absorption is due to indirect transition and the optical band gap E_g increases with increasing Ge content in Se-Te glassy alloy. The relationship between the E_g and chemical composition is discussed in terms of cohesive energy and co-ordination number.

Key Words: Chalcogenides, thin films, optical band gap, Se-Te-Ge

1. Introduction

Optical properties and their experimental measurements represent one of the most important scientific endeavors in the field of materials research. The most common applications of glasses are based on their optical properties. Application of glasses for making optical instruments and lenses are based on properties like refractive index and its dispersion, which can be varied by varying chemical composition [1]. One of the most important applications based on optical properties of glass today is in the field of information technology through the use of glass fibers. Additionally, the absence of long-range order allows the modification of their optical properties to a specific technological application by continuously changing their chemical composition [2]. The use of chalcogenide glasses offers notable advantages such as remarkable optical properties like a wide transmission window (1–20 μm), high refractive indices, making them suitable for sensitive detection of clinical or environmental changes [3–12]. Chalcogenide optical waveguides also play a significant role in the development of optical biosensors [13]. Amorphous films are known to have properties that are sometimes different from their bulk glass counterparts.

However, the calculation of the key parameter, $\langle r \rangle$, requires knowledge of the coordination numbers (CN) of all the constituents of the alloy. For the system under investigation, the CN(Ge), CN(Te) and CN(Se) respect the “8- N ” rule [14], where N is the number of outer shell electrons. The 8- N rule proposed by Mott

conjectured that every atom in an amorphous solid should be incorporated with its preferred chemical valency. This rule implies the complete absence of topological constraints in a random covalent network [15].

Selenium and its derivatives in thin film form have been used in a multi-billion dollar photocopying industry and this glass must be regarded as the single most important chalcogenide in terms of commercial exploitation [16]. The commercial importance of amorphous selenium (a -Se) and its various alloys at present lies in their use as vidicon photoconductor materials (e.g., Se-Te alloys) and as x-ray photoconductors in x-ray imaging [17]. Mixed Se-Te glasses are suitable for optical component applications in the middle and far infrared. Work in the literature [18] suggested that selenide and telluride glasses are compatible and that it would be possible to make high quality stable mixed Se-Te melts. Therefore it was considered that work on mixed Se-Te glasses offered the most useful approach to extending the range of optical properties of the basic selenide glasses for 3–5 μm and 8–12 μm applications.

In the present work, we report and discuss the composition dependence of the optical band gap with germanium content in Se-Te glass films prepared by vacuum thermal evaporation, using a novel data-processing method, based only on their optical transmission spectra at normal incidence. The addition of dopant [Ge] can modify the lattice perfection and optical properties, which play a major role in device preparation. Thus the optical absorption properties of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ glassy alloys are interesting to study in detail from basic as well as application point of view. The study of optical absorption has proved to be very useful for elucidation of the electronic structure to determine direct and indirect transition occurring in band gap of materials by optical absorption spectra [19–20].

2. Experimental procedure

Glassy alloys of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) were prepared by melt quenching technique. Sample under investigation were prepared from highly pure Se, Te and Ge (99.999%) elements. The constituents were weighed according to their atomic percentage and sealed in quartz ampoule in vacuum of $\sim 10^{-5}$ mbar. The ampoules containing the material are heated to 1000 °C and held at highest temperature for 12 h. The ampoules were frequently rocked during heating to make the melt homogeneous. The quenching was done in ice water. Quenched samples were obtained by breaking the quartz ampoules. The amorphous nature of these alloys was verified by X-ray diffraction (X-Pert PRO) as no prominent peak was observed in the spectra.

Thin film samples were deposited by vacuum evaporation technique (using a Hind High Vacuum (HHV) Model 12A4D vacuum coating system) onto thoroughly cleaned microscope glass substrates. A vacuum of the order of 10^{-5} mbar was maintained during the evaporation process. The films were kept inside the deposition chamber for 24 h to achieve the metastable equilibrium. The normal incidence transmission spectra in the transmission range 500–2500 nm of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films were obtained by UV-Vis-NIR spectrophotometer [Perkin Elmer Lamda-750]. All the measurements were performed at room temperature (300 K).

3. Result and discussion

The normal incidence transmission spectra of represented amorphous Se-Te-Ge thin film samples under study are plotted in Figure 1. The Tauc model [21] has been used as a standard model whereby the optical gap

of an amorphous semiconductor may be determined. In this model, it is assumed that the disorder characteristic of amorphous semiconductors relaxes the momentum conservation rules. Assuming square-root distribution of conduction band and valence band states, and assuming that the momentum matrix element is independent of $h\nu$, Tauc et al. [21] assumed that an extrapolation of the essentially linear functional dependence of $(\alpha h\nu)^{0.5}$, observed in amorphous semiconductors at a sufficiently large $h\nu$, allows an empirical optical energy gap to be defined. The optical band gap E_g for Se-Te-Ge films can be calculated from the quadratic equation [22–23], which is often called Tauc law,

$$\alpha h\nu = B(h\nu - E_g)^m, \quad (1)$$

where B^{-1} is the band edge parameter, and m is an exponent that may take values 1, 2 or 3 as found for various amorphous semiconductors. In the case of amorphous chalcogenides, the transitions are known to be indirect ones, and hence the exponent m is found to be 1–2. The exponent $m=1/2$ is for allowed direct transition, while $m=2$ for allowed indirect transition. In the present work, the plots of $(\alpha h\nu)^{0.5}$ versus $h\nu$ for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ films, depicted in Figure 2, show good linearity over a wide range of photon energies indicating the allowed indirect transition. By extrapolating the linear portion of the curves to zero absorption, the energy gaps are determined. The values of optical band gap E_g obtained for indirect allowed transition for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ thin films by making $(\alpha h\nu)^{0.5} \rightarrow 0$ are given in the Table 1.

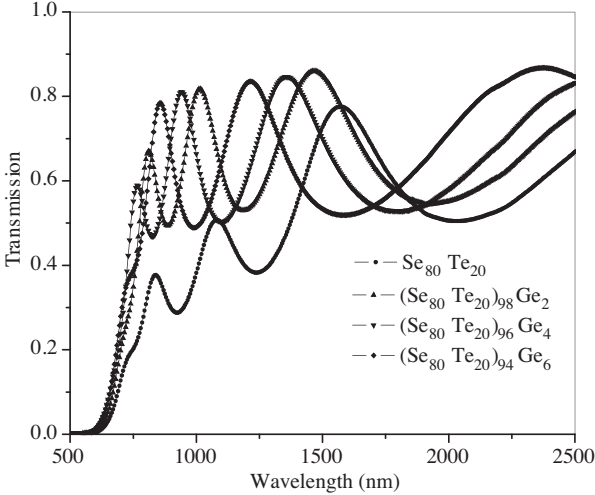


Figure 1. Transmission spectra of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films.

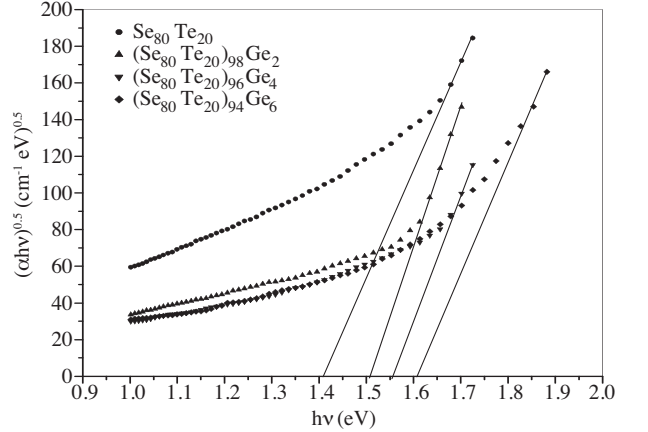


Figure 2. Plots of $(\alpha h\nu)^{0.5}$ versus $h\nu$ for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ films.

Table 1. Values of co-ordination number $\langle r \rangle$, excess of Se-Se bond, cohesive energy (CE) and optical band gap of the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system.

x (at%)	$\langle r \rangle$	Excess of Se-Se bonds	CE (kcal/mol)	E_g (eV)
0	2	120	43.12	1.41
2	2.04	110	43.39	1.51
4	2.08	99	43.69	1.56
6	2.12	89	43.99	1.61

The variation of E_g with covalent coordination number $\langle r \rangle$ is shown in Figure 3 where E_g increases with increase in coordination number. Ioffe and Regel [24] have suggested that the bonding character in the nearest neighbor region, i.e. the coordination number $\langle r \rangle$, characterizes the electronic properties of semiconducting materials. The average coordination number $\langle r \rangle$ in ternary compounds $\text{Se}_x\text{Te}_y\text{Ge}_z$ ($x + y + z = 1$) is generalized as [25]

$$\langle r \rangle = (x\text{CN}(\text{Se}) + y\text{CN}(\text{Te}) + z\text{CN}(\text{Ge})). \quad (2)$$

Calculated data of $\langle r \rangle$ for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system, using the values of coordination numbers, 2 for Se, 2 for Te and 4 for Ge, are listed in Table 1. It can be seen that $\langle r \rangle$ increases with increasing Ge content.

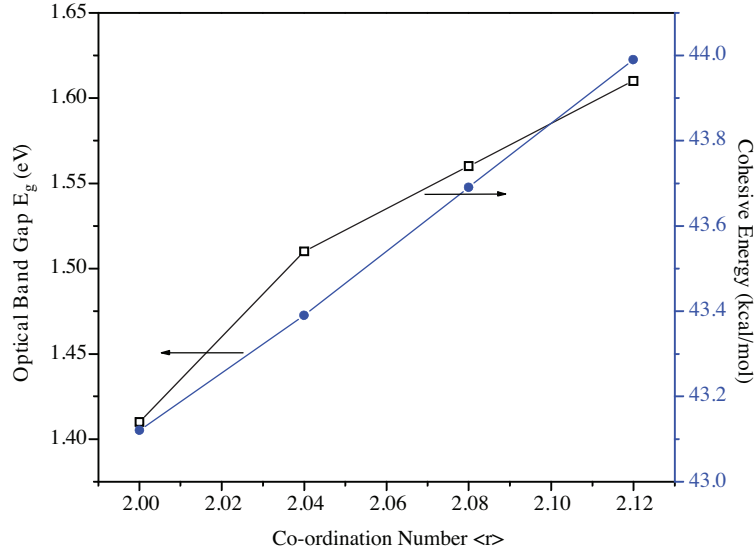


Figure 3. Variation of CE (kcal mol^{-1}) and optical band gap (in eV) with co-ordination number $\langle r \rangle$ for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$.

In chalcogenide glasses, the valence band (σ -bonding) originates from lone-pair (LP) electron states whereas the conduction band arises from anti-bonding (σ^*) states [26]. The variation of E_g with $\langle r \rangle$ is mainly determined by the composition dependence of three major factors, namely, the bond strengths, the network connectedness and density. From a chemical approach [26], an increase in the bond strengths causes a larger splitting between σ and σ^* bands which results in an increase in E_g . In a multi-component glass like Se-Te-Ge the position of conduction and valence band edges and thus the energy gap largely depends on the relative number of various possible bonds in the system and the average bond energy. The bond energies have been estimated by the method suggested by Pauling [27]. Pauling proposed that single covalent bond energy of heteronuclear bonds $D(A-B)$ can be estimated from the single covalent bond energy of homonuclear bonds $D(A-A)$ and $D(B-B)$ [28] and the electronegativity [29]. The bond energies $D(A-B)$ for the heteronuclear bonds can be calculated using the relation [24]:

$$D(A-B) = [D(A-A) \times D(B-B)]^{1/2} + 30(\chi_A - \chi_B)^2 \quad (3)$$

The various possible bonds possible in the Se-Te-Ge system are Ge-Se, Se-Se, Ge-Ge, Se-Te, Ge-Te, and Te-Te. The bond energies are 231.11, 189.22, 187.57, 205.57, 172.08 and 142.35 kJ/mol, respectively. The CON model

suggests that heteronuclear bonds favored over homonuclear bonds. The Ge atoms strongly bond to Se. The Se atoms also fill the available valences of Te. When all these bonds are formed, there are still unsatisfied Se valences, which much is satisfied by the formation of Se-Se bonds. The number of excess bonds of Se-Se for each composition of the Se-Te-Ge system is given in Table 1. It can be seen that the excess Se-Se bonds decrease with Ge content, so one can expect a decrease in energy gap values because Se possesses a higher energy gap than Ge or Te, i.e. the average bond strength of the compound decreases, leading to increase in the optical band gap. Considering that the strong Ge-Se bonds are energetically favored compared to a random mixture of bonding configurations, it is possible to consider the glasses studied as either chalcogen rich or Ge rich in the order of increasing $\langle r \rangle$. E_g is more sensitive to the variation of the chemical bonding nature and the average bond energy.

To this end, it would be interesting to calculate the cohesive energy (CE). Knowing the bond energies, the cohesive energy can now be estimated, i.e. the stabilization energy of an infinitely large cluster of the material per atom, by summing the bond energies over all bonds expected in the system under test. The results for CE are listed in Table 1. It was observed that CE increases with increased Ge content, in agreement with increasing energy gap values. The increase of CE of the Se-Te-Ge system tends to increase the energy of the conduction band edge causing a larger splitting between σ and σ^* orbitals and thus resulting in the observed increase in E_g .

3.1. Ionic character

The ionicity introduces a tendency towards ordering because of the non-directional character. In selenide in which the ionic character is no more than 10% are all good glass formers. Ionicity of a bond is calculated using the Pauling formula [27]

$$I = 1 - \exp\left(-\frac{\Delta x^2}{4}\right), \quad (4)$$

where $\Delta x = \chi_A - \chi_B$ is the difference in the electronegativities of atoms A and B. That there should be a direct connection between bond strength and the glass formations was recognized by a number of investigators [1]. A bond energy criterion for glass formation was suggested by Sun (1947) [30]. High value of bond strength increases the glass forming tendency. The calculated values of ionicity are given in the Table 2.

Table 2. Calculated ionicity and covalent character of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ glassy alloy.

Ionicity	Bond Type	Covalent character (%)
5.54	Se-Te	97.8
5.48	Se-Ge	91.4
5.43	Ge-Te	97.8
5.37	-	-

Since chalcogenide glasses are made from materials such as sulfur, selenium, arsenic, germanium, and tellurium, which have predominantly covalent bonds, the degree of covalency in the bond of amorphous glass under investigation can be calculated by using the Pauling relationship as [27]

$$\text{Amount of covalent character} = e^{\frac{-(\chi_A - \chi_B)^2}{4}} \times 100\% \quad (5)$$

The calculated values are listed in Table 2.

4. Conclusion

The optical characterization of thermally evaporated amorphous $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ films has been carried out, using the transmittance spectra at normal incidence. The optical band gap has been determined in terms of transmittance spectra in the strong absorption region of the investigated films. The optical band gap is appropriately fitted to the indirect transition model proposed by Tauc. In terms of the chemical bond approach, cohesive energy and co-ordination number has been applied to interpret the increase in the glass optical band gap with increasing Ge content. The results indicate that the value of E_g increases with increasing amount of Ge in Se-Te glassy alloy.

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