

Optical characterization of Se-Te-Sb chalcogenide glass

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The chalcogenide glasses of $\text{Se}_{85-x}\text{Te}_{15}\text{Sb}_x$ ($x = 2, 4, 6, 8$ and 10) material were prepared by melt quenching technique. Then films of these materials were deposited by flash evaporation technique. Absorption spectra of these films were used to calculate energy band gap of these materials. It is observed that energy band gap of the material is changing with the composition of different samples and this difference may be attributed to the change in the structure of the material, which occurred during preparation of thin films.

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1. Introduction

An extraordinary evolution has recently taken place in our understanding of the structure semi-conducting chalcogenide glasses from the viewpoint of their wide range of applications as solid-state devices both in scientific and technological fields. One can investigate these glasses by analyzing their various physical properties [1, 2] and another approach is to investigate these glasses is related with their stability [3].

The Glass Forming Ability (GFA) of chalcogens or pseudo chalcogen combinations has been known for several decades but compared to oxide glasses, especially silicate, this class of vitreous materials is just emerging from its infancy [4]. The main attention paid to these materials relies on their large optical window extending in the mid-infrared and covering usually two atmospheric windows lying from 3 to 5 μm and 8 to 12 μm . These low-phonon materials have to be considered as heavy-anion glasses since S, Se and even Te are the main constituents of their compositions. This situation leads to fundamental vibrational modes shifted far in the IR, and rendering these glasses interesting for the fabrication of thermal imaging systems [5]. It must be noticed that these chalcogenide glasses also exhibit unique properties, such as photo-darkening [6], giant photo-expansion as well as photo-fluidity [7] when irradiated by appropriate light.

High field conduction studies on amorphous Se-Te-Sb thin films [8] have shown that the dominant mechanism of conduction is of Poole-Frenkel type.

In this context an effort has been made to determine optical band gap of these materials in thin film form using spectrophotometer with absorption spectra in the wavelength region between 500 to 800 nm.

2. Experimental

High purity (99.999%) Se, Te and Sb in appropriate atomic weight percentage proportions were taken to prepare the glassy powder of the materials and their nature was confirmed by XRD [9,10]. Thin films of these glassy materials were prepared by vacuum flash evaporation technique. The absorption spectra were taken using spectrophotometer in the wavelength range between 500 to 800 nm. Fig. 1 shows the absorption spectra of $\text{Se}_{75}\text{Te}_{15}\text{Sb}_{10}$ glass as a representative case.

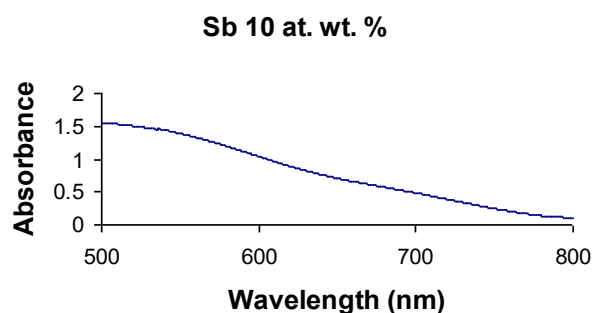


Fig. 1. Absorption spectra of $\text{Se}_{75}\text{Te}_{15}\text{Sb}_{10}$.

3. Results

Typical absorption spectra of these materials were recorded in the wavelength range 500 to 800 nm. The variation of $[(\alpha - \alpha_0)h\nu]^2$ has been plotted with energy ($h\nu$) for the samples. This variation for $\text{Se}_{81}\text{Te}_{15}\text{Sb}_4$ glass sample is shown in Fig. 2 as a representative case. Optical band gap (E_g) for samples containing Sb 2, 4, 6, 8 and 10 at. wt. % are listed in Table 1.

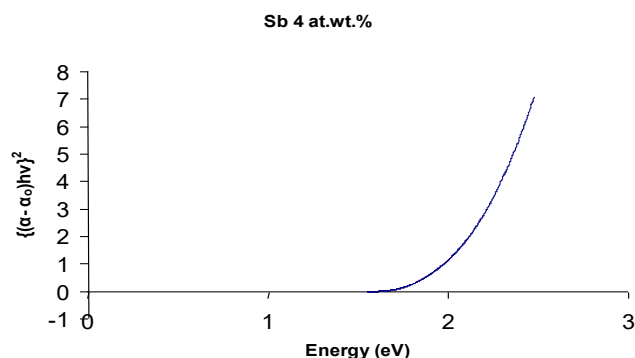


Fig. 2. Calculation of band gap for $\text{Se}_{81}\text{Te}_{15}\text{Sb}_4$.

Table 1. Band gap of glassy samples.

Composition	E_g (eV)
$\text{Se}_{83}\text{Te}_{15}\text{Sb}_2$	2.108
$\text{Se}_{81}\text{Te}_{15}\text{Sb}_4$	2.043
$\text{Se}_{79}\text{Te}_{15}\text{Sb}_6$	1.7
$\text{Se}_{77}\text{Te}_{15}\text{Sb}_8$	1.65
$\text{Se}_{75}\text{Te}_{15}\text{Sb}_{10}$	1.91

4. Discussion

It is clear from the table that value of E_g is decreasing with the increase in Sb content in the sample. There is a drastic decrement in E_g as we go beyond the Sb 4 at wt % in the sample. This might be due to the formation of either Sb_2Se_3 or SeTe with the segregation of Sb depending upon the concentration of Sb in the ternary alloy. Keeping this in view, now we concentrate our discussion of results in three different composition regions of the present series.

It is generally accepted fact that in Se containing alloys, there is a tendency to form polymerized network glasses and homopolar bond is qualitatively suppressed. The structure of Se-Te system prepared by melt quenching is regarded as a mixture of Se_8 member rings, Se_6Te_2 mixed rings and SeTe chains [11]. A strong covalent bond [12] exists between the atoms in the ring, whereas between the chains only van der Waals forces are dominant.

In our first composition range (Sb 2-4 at wt %); for lower percentage of Sb the system contains $\text{SbSe}_{4/2}$ tetrahedral units dissolved in a matrix composed of Se chains supported by infrared transmission spectra [13]. With the increase of Sb content, Se-Se bond of lower energy (205.8 kJ/mol) will be replaced by Sb-Se higher energy (214.2 kJ/mol) bonds. The decrement in band gap is in good agreement with the results reported elsewhere [3].

Many workers [14, 15] have established that the inclusion of Sb in Se reduces its GFA tremendously. Te

which has a similar structure to that of Se, can also be incorporated in Se only up to a maximum of 30 at wt %. Thus it is not surprising that Sb, which has quite a different structure, leads to a decrease in GFA of Se-Te system. One possibility for this is that Sb is responsible for reducing SeTe ring concentration and is acting as a via media to change that weak bonding between the linear polymeric chains to relatively strong covalent bonds. It has been observed from the present investigations that the band gap decreases with the increase of Sb concentration in Se-Te-Sb system except for 10 at wt % of Sb. This trend is in quite good agreement with the reported [16] results in similar systems. It is important to note here that the pellets of glassy materials of a given stoichiometry with different concentrations of Sb in it have been used for the deposition of films. The structural changes and the change in stoichiometry have not been detected in the samples of the films and therefore these changes may bring the inconsistent behaviour of band gap for different concentrations of Sb with the changed stoichiometry of the films.

There is a sharp decrease in band gap of samples containing Sb 4 at wt % and 6 at wt %. This can be attributed to the formation of Sb_2Se_3 configuration in the sample. Systematic study of Sb_2Se_3 has revealed that the formation of localized amorphous structure is responsible for the decrease of band gap to 1.6 eV [17]. One can look into the formation of localized amorphous Sb_2Se_3 molecular structure [18] in the following manner: if two Sb atoms suitably replace two Se atoms substitutionally on two nearby Se chains and the threefold coordination requirement of Sb makes it convenient for an amorphous Se atom to become bonded to both these Sb atoms and thereby to join two chains, then a further lone-pair bond can be formed between one of these Sb atoms and its nearest Se atom on the other chain. If there are few such structures distributed throughout the system, we may expect to have a decrease in value of band gap to drop to a value close to the value of the band gap for amorphous Sb_2Se_3 system i.e. 1.6 eV. It is quite clear that as Sb exceeds from 4 at wt % to 6 at wt % in the parent system, E_g decreases from 2.04 eV to 1.7 eV. Moreover, it is very difficult to estimate the optimum concentration of Sb in the system, the composition of the sample at which the probability of the formation of Sb_2Se_3 localized structures is sufficiently high. Our results revealed that Sb_2Se_3 structures apparently begin to form as the Sb concentration exceeds 4 at wt % or so.

As it has been established [13, 14] that Sb decreases the GFA of Se. So when the Sb content goes up to 10 at wt %, it reduces the possibility for the formation of glass. In our case, Sb appears to be segregated and the value of E_g comes out 1.91 eV, which is close to that of Se. The other possibility is of the formation of SeTe , which has some lower value of E_g than that of Se (1.99 eV).

5. Conclusions

At the lower percentage of Sb i.e. 2 and 4 at wt %, value of E_g is 2.108 eV and 2.043 eV. As the Sb content exceeds 4 at wt % in the sample at the cost of Se, there is a possibility of the formation of Sb_2Se_3 localized amorphous structures in the material. E_g for Sb 6 at wt % and 8 at wt % is 1.7 eV and 1.65 eV, respectively, nearer to band gap of Sb_2Se_3 i.e. 1.6 eV [16]. The value of band gap at Sb 10 at wt % in the sample is suggestive of the fact that there is a formation of SeTe and Sb might have been segregated out.

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