Compositional effect on the spectral dependence of the absorption in $Ge_{40}Te_{60-x}Sb_x$ alloy

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Abstract-

The investigation of composition dependence of various properties of chalcogenide glasses has been increased in recent years. In the present work, the effect on the physical properties viz. average coordination number, optical gap, deviation of stoichiometry and energetic parameter with the variation in Sb content has been studied theoretically for $Ge_{40}Te_{60-x}Sb_x$ (x = 0, 2, 4, 6 and 10) glassy semiconductors. It has been found that almost all the parameters, studied here, except the parameter R, Eg and A were decreased with the increase in Sb content.

Introduction-

Phase-change materials based on chalcogenide alloys are found to be suitable for optical and electrical memories due to its fast crystallization. The operation principle of these devices is based on the ability of the active materials to reversibly transform between amorphous and crystalline phases. Chalcogenide materials, especially those containing Ge and Te, are of importance in modern technology due to the following reasons: -

(1) large change in optical constants between crystalline and amorphous state

(2) rapid phase transition between amorphous and crystalline (two stable states) states.[1]

Modern chalcogenide compounds like Ge-Sb-Te, widely used in rewritable optical disks and PRAM devices, are fragile glass formers; therefore they are able to crystallize in about 100 ns[1-8] Therefore these alloys are used for data recording based on the rapid and reversible amorphous-to-crystalline phase transformation[9-10] that is accompanied by increase in the optical reflectivity and the electrical conductivity. However, uncertainties about the optical band gaps and electronic transport properties of these phases have persisted because of inappropriate interpretation of reported data and the lack of definitive analytical studies.

The optical band gap is the most significant parameters in amorphous semiconducting thin films. The optical behavior of a material is utilized to determine its optical constants. Films are ideal specimens for reflectance and transmittance type measurements. Therefore, an accurate measurement of the optical constants is extremely important.

In the view of the above, here we concerned with the theoretical prediction of the compositional effect on the spectral dependence of the absorption and how to correlate the optical band gap with composition of $Ge_{40}Te_{60-x}Sb_x$ (x = 0, 2, 4, 6 and 10) alloy.

THEORETICAL STUDIES AND DISCUSSION

Bonding Constraints & Average Coordination Number-

Phillips [11] gave the mechanical-constraint counting algorithms to explain glass forming tendencies. Constraints associated with the weaker forces of more distant neighbors must be intrinsically broken leading to the absence of long-range order. The well known Phillips–Thorpe approach [12-13] is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. The bond constraint theory maintains the balance between stressed and floppy materials in terms of arrange number of constraints per atom in the inter-atomic force field space and the number of degree of freedom in real space.

The average coordination number (Z) was calculated using standard method [14-18] for the composition $Ge_{40}Te_{60-x}Sb_x$ (x = 0, 2, 4, 6 and 10) is given by –

$$Z = \frac{x\,N_{Ge} + yN_{Sb} + zN_{Te}}{X + Y + Z}$$

where x, y and z are the at. % of Ge, Sb and Te respectively and $N_{Ge}(4)$, $N_{Sb}(3)$, $N_{Te}(2)$ are their respective coordination number [19]. Fig. - 1 shows values of Z increase from 2.80 to 2.90 with increase in concentration of Sb from 0 to 10 at. % using the calculated values of average coordination number for $Ge_{40}Te_{60-x}Sb_x$ (x = 0, 2, 4, 6 and 10) system.
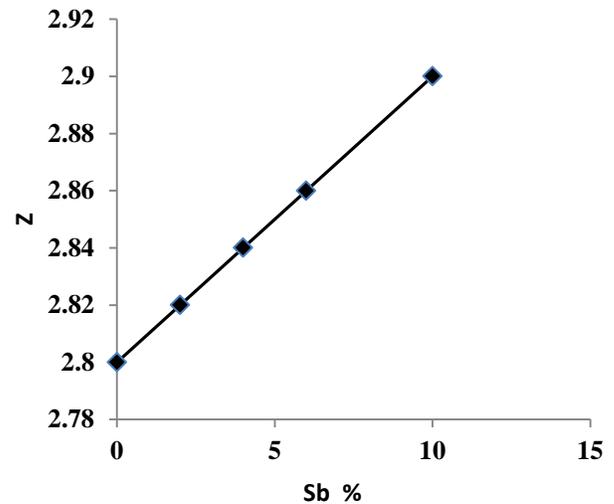

Fig. 1: Variation of Average Coordination Number with Sb at. %

Deviation from the stoichiometery of composition-

The parameter R that determines the deviation from stoichiometry is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For $Ge_{40}Te_{60-x}Sb_x$ (x = 0, 2, 4, 6 and 10) system, the parameter R is given by [20]

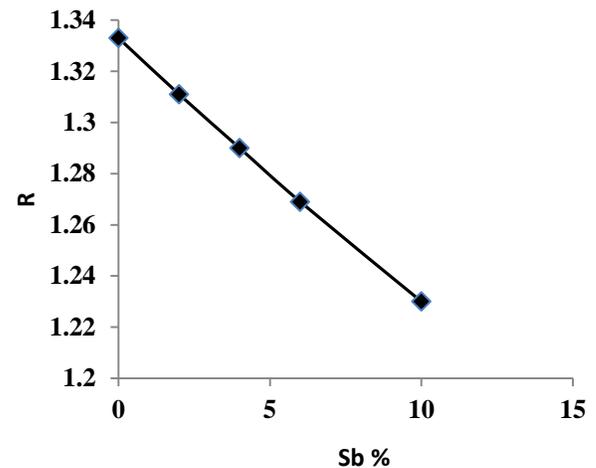$$R = z(CN)Ge \,/\, x(CN)Te + y(CN)Sb$$

Fig.-2 Variation of parameter R with Sb at %

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where x, y, z are atomic frictions of Te, Sb, and Ge respectively. The values of R are mentioned in Table- 1 which shows that R decreases from 1.333 to 1.230 with increase in concentration of Sb from 0 to 10 at. %. The threshold at R=1 (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For R>1, the system is chalcogen rich and for R<1, the system is chalcogen poor. From Fig.-2, it is clear that our system is chalcogen rich and may turn towards chalcogen poor with the increase in content of Sb in the system.

Table-1 Values of Z, R, E_g(eV) and A for the $Ge_{40}Te_{60-x}Sb_x$ system

x	Z	R	E_g(eV)	A x 10^4/Kel
0	2.80	1.333	0.70	0.327
2	2.82	1.311	0.62	0.324
4	2.84	1.290	0.59	0.316
6	2.86	1.269	0.56	0.307
10	2.90	1.230	0.52	0.298

Optical gap and Energetic Parameter-

The value of optical gap for the composition $Ge_{40}Te_{60-x}Sb_x$ (x = 0, 2, 4, 6 and 10) alloy has been tabulated from the published data by S.Kumar et al. [21]. The value of E_g is listed in Table -1. And the variation of Eg with composition x is illustrated in Fig.-3 as-
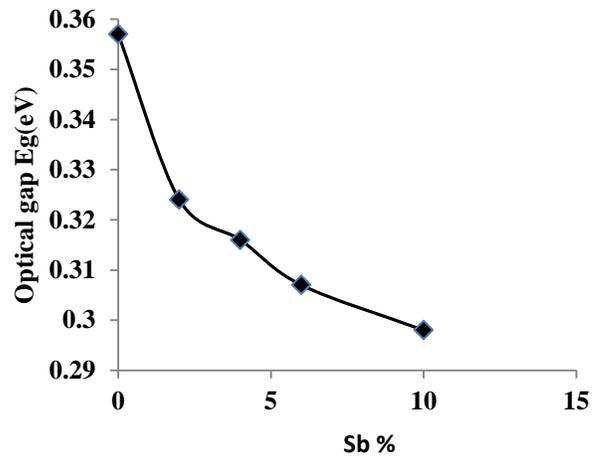

Fig.-3 Variation of optical gap with Sb at %

The spectral dependence of the absorption coefficient indicates an indirect allowed transition. The result is verified by energetic parameter relation Vs. composition. According to Angell proposal [22], the compositional changes in the optical gap is correlated by energetic parameter (A) which is given by the equation-

$$A = Є\Delta E_g/k$$

Where $Є = δ(z-2)$ and k = Boltzmann constant and δ = independent constant.

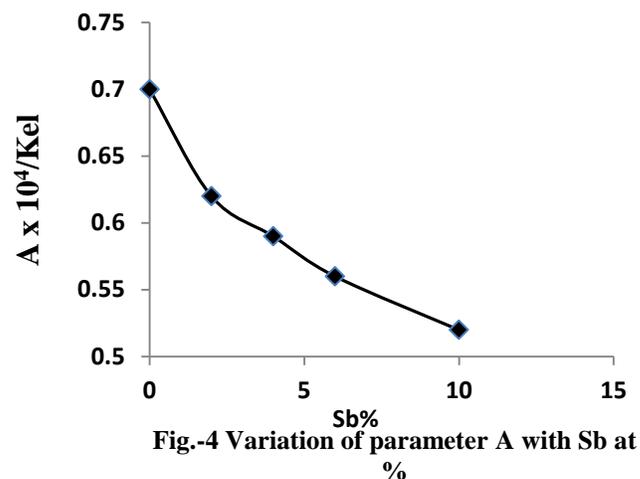The variation of energetic parameter A with composition x is illustrated in Fig.-4 as-

Fig.-4 Variation of parameter A with Sb at %

It is seen from the graphical representation that energetic parameter values decreases with the increase of Sb content. The increase of (A) with Sb content may be due to the formation of weaker bonds in the glass system.

Conclusion-

It is concluded here that the variation in Sb content in Ge-Sb-Te glassy alloys leads to change in the physical properties. As it is clear from various figures and table given that almost all the parameters, except the parameter R, Eg and A decreases with the increase in content of Sb in $Ge_{40}Te_{60-x}Sb_x$ system. It has been found that mean coordination number Z is proportional to composition x and increases with the increase in content of Sb from 0 to 10 at %, resulting in decrease of optical band gap and energetic parameter.

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