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STUDY THE EFFECTS OF Te ADDITION ON PHYSICAL AND OPTICAL ENERGY GAP OF Ge-Se-Te THIN FILMS

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The study aims to present the physical characteristics and optical energy gap of the $Ge_{10}Se_{90-x}Te_x$ thin films (where $0 \leq x \leq 70$ at. %). Thermal evaporation technique is utilized for the preparation of amorphous thin films from the bulk of glasses. In the paper, the researchers have examined the density, molar volume, compactness, cohesive energy and distribution of the chemical bonds of the amorphous thin films theoretically. Within the spectral range from 400 to 1000 nm, the optical absorption spectra of as-prepared films have been evaluated. Furthermore, the study calculated absorption coefficient of thin films by using the absorption spectra to get the values of the optical energy gap and Urbach energy. It has been observed that the energy gap decreases from 1.88 to 1.17 eV due to the increase in Te content from 0 to 70 at. %. The outcomes of the study were found to be consistent with each other and are discussed thoroughly by using the chemical bond approach. It has been noticed that the terms due to $GeSe_2$ and SeTe are present in stoichiometric composition ($Ge_{10}Se_{55}Te_{35}$), whereas in the case of non-stoichiometric compositions, excess Se or Te causes additional term that comes into effect.

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1. Introduction

Chalcogenide glasses which are composed of Te- and Se hold significance due to their use in many technical applications. The wide use of these glasses is due to their effective physical and optical properties which are good to use for the transparency in the IR region [1-3]. The vital properties of these glasses make them suitable to be used for the manufacturing of many technological advance devices including IR detectors, phase change memory, optical switches and electronic devices [4-6].

The elements of chalcogenide glasses, Te and Se lie in the VIth column of the periodic table where Te is found to be isovalent to Se. The properties of these atoms include 2-fold local coordination with two of the 4 valence p-electrons that enter into σ bonds with nearest neighbor atoms whereas the remaining 2 electrons form non-bonding lone-pair. As per the study, it has been determined that Te as an additive in a Se glass that can replace Se to form a flexible chainlike structure out of its non-crystalline form [7].

The formation of Ge–Se–Te glasses are obtained by the substitution of Se atom by Te atom within the system of Ge–Se. This is because this substitution does not cause any drastic change in the fundamental structure of the glass. Structure and composition are correlated and showing the dependency of several properties in the chalcogenide glasses [8-10]. The performance of solid-state devices is enhanced by composing them with Te- and Se-based properties. The purpose is usually achieved by introducing variations while composing complex chalcogenides.

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This helps in altering the physical composition of glasses in order to fulfil the requirements. The results are produced due to the formation of various Te- and Se-based compositions [11-14].

It has been observed during the phenomenon of chemical bonding that different kinds of atoms combine more favorably as compared to the atoms of similar properties. Atomic bonding continues to occur until all the valences decreased to come at the saturating point. Hence the chemical bond approach [15] helps in explaining and understanding the composition and dependency of the physical and optical properties of $Ge_{10}Se_{90-x}Te_x$ (where $0 \leq x \leq 70$ at. %) glasses. The study shows that Te and Se show divalent bonding while Ge bonds tetravalently for the purpose of achieving Mott "8−N" rule [16].

The study aims to present the formation and preparation of bulk glasses and thin films of $Ge_{10}Se_{90-x}Te_x$ (where $0 \leq x \leq 70$ at. %), in addition to this the study also aims to determine the impact on the density, molar volume, compactness, optical energy gap and Urbach energy due to the addition of the element Te. Throughout the paper, the study provides detailed insights about the cohesive energy and the distribution of the chemical bonding for the specified systems.

2. Experimental details

Melt quenching method was utilized for the synthesis of bulk glasses with the composition of $Ge_{10}Se_{90-x}Te_x$ (where $0 \leq x \leq 70$ at. %). The preparation of glasses was started by weighing the components of high purity (i.e. Sigma–Aldrich at 99.999% purity) in the pre-cleaned silica tubes. The tubes were then sealed under vacuume of about 5×10^{-6} Torr. The heating rate of 20 K/h was used for heating the ampoules up to 1225 K then the temperature was maintained constatnt over the time period of 24 hours. For maintaining the homogeneity of the ingots, ampoules were shaken with consistency for complete 24 hours. The next step was to quench the ampoules in the ice-cold water for attaining the amorphous specimens.

At room temperature, the thin films were placed upon the glass substrates which were unheated and vacuumed by thermal evaporation coater Edward 306A at 2×10^{-6} Torr. Edward FTM5 monitor was used for measuring the thickness of the film and monitoring the evaporation rate for the purpose of controlling the thickness of glass. The thickness was maintained within the range of 800-850 nm and deposition rate at 0.1 nm/s remained constant. For obtaining the uniformity in the thickness of films, the substrates of films were rotated at ≈30 rpm during the process of deposition.

To identify the chemical composition of glass films, energy dispersive x-ray spectroscopy was used which assured the close correlation and association of elemental ratio and the nominal composition. In addition to this, x-ray diffraction, Shimadzu XRD 6000 diffractometer was used to check the amorphism of the thin films and Jasco V-630 spectrophotometer measured absorption spectra, in the range 400 to 1000 nm wavelength.

3. Results and discussion

The physical outcomes of the study were analyzed by the parameters of density (ρ), molar volume (V_m) and compactness (δ). Archimedes technique was used to measure the density of bulk glasses, using toluene as a buoyant liquid from equation [10, 17]:

$$\rho = \frac{W_{air}}{W_{air} - W_{tol}} \ \rho_{tol} \tag{1}$$

where ρ_{tol} density of toluene,
W_{air} is the weight of the sample in air and
W_{tol} is the weight of the sample in toluene,

Measurement of the density was taken five times per glass in order to acquire the average value.

V_m of the studied glasses was calculated using the relation [10]:

$$V_m = \rho^{-1} \sum_i c_i A_i \tag{2}$$

where c_i and A_i are the atomic fraction and the atomic weight of the i^{th} element of the glass. δ of the glassy structure was estimated by the formula [18-20]:

$$\delta = \frac{\sum_i c_i A_i \rho_i^{-1}}{\sum_i c_i A_i \rho^{-1}} - 1 \tag{3}$$

In this equation ρ_i denotes the atomic density of the i^{th} element of the glass. whereas the error in the calculation of density then in molar volume and compactness was measured to be less than 1%.

Fig. 1 shows the correspondence of measured density and calculated values of the molar volume and compactness for the $Ge_{10}Se_{90-x}Te_x$ glasses. The figure illustrates that with the increase in Te content, the density, molar volume and compactness also increase in the glass. It can be concluded from the previous research that density can be identified as the replacement of less dense Se (4.28 g/cm^3) with denser Te (5.67 g/cm^3) atoms [21] . The study also determined that the atomic radius of Te is 1.43 A° which is large in comparison to the atomic radius of Se which is 1.16 A° [22]. For this reason, it is justified to conclude that the increase of the molar volume is proportional to that of tellurium and selenium atomic radii ($R_{Te}/R_{Se} \approx 1.23$).

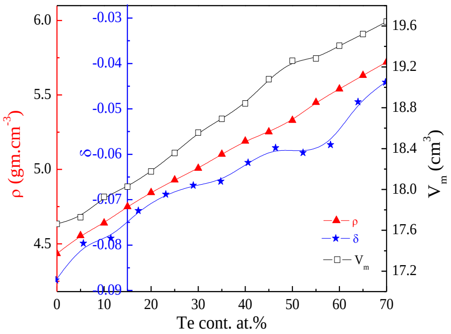

Fig. 1. Compositional dependence of the glass density (ρ), molar volume (V_m) and compactness (δ) for the $Ge_{10}Se_{90-x}Te_x$ (where $0 \leq x \leq 70$ at. %) glasses.

Equation 3 shows that the normalized changes in the mean atomic volume, caused by chemical interactions of the constituent elements, are defined as the compactness of the network of the glass and hence is said to be linked with the network flexibility and free volume [20]. Fig. 1 illustrates that all the values of compactness are in negative that determines the fact that glasses have the property of having large free volume and flexibility.

Fig. 2 illustrates the absorbance as a function of wavelength for the $Ge_{10}Se_{90-x}Te_x$ (where $0 \leq x \leq 70$ at. %) thin films. As shown in this figure the absorption edge has shifted towards the higher wavelength, i.e. red shift, with the increasing the ratio of Te content. If the thickness (t) of the films is known, then it is easy to evaluate the absorption coefficient (α) via the knowing of the absorbance (A) by using the equation: $A = \exp(\alpha t)$, or $\alpha = (\ln A)/t$.

In accordance with Tauc's relationship [23, 24] of the allowed non-direct transitions, the variation of α as a function of hν is obtained by use of the relation:

$$(\alpha h\nu)^{1/2} = B\,(h\nu - E_g) \tag{4}$$

where B is constant and
E_g is the optical energy gap.

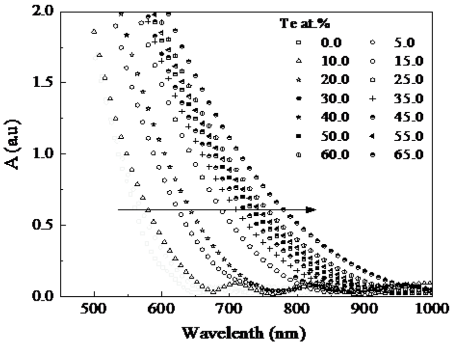

Fig. 2. Spectral dependence of the absorbance (A) for the $Ge_{10}Se_{90-x}Te_x$ (where $0 \le x \le 70$ at. %) thin films.

Fig. 3 demonstrates the variation of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ thin films. E_g may be obtained from the intercepts at hν = 0.

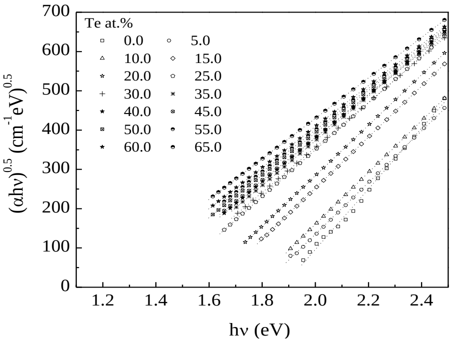

Fig. 3. Plots of $(\alpha h\nu)^{0.5}$ vs. hν for the $Ge_{10}Se_{90-x}Te_x$ (where $0 \le x \le 70$ at. %) thin films.

For $\alpha \le 10^4$ cm^{-1}, α shows an exponential variation with hν according to the Urbach relation [25]:

$$\ln(\alpha) = \ln(\alpha_0) + (h\nu / E_e) \tag{5}$$

where α_0 is a constant and
E_e is the Urbach energy.

E_e is a vital parameter for describing the amorphous semiconductors where it is used to express the degree of tailing of either the conduction or valence bands. The characterization of non-crystalline semiconductors is done by the imperative factor i.e. E_e. The plots for the $Ge_{10}Se_{90-x}Te_x$ thin films of ln(α) versus hν can be seen in Fig. 4.

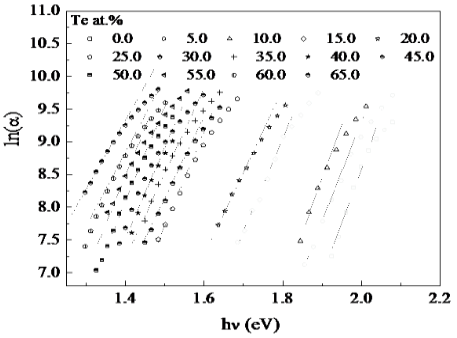

Fig. 4. Plots of ln(α) versus hν for the $Ge_{10}Se_{90-x}Te_x$ (where $0 \le x \le 70$ at. %) thin films.

Fig. 5 shows the compositional decency of E_g and E_e values. From the figure, it is evident that according to Mott and Davies model [26], the values of E_g is indirectly proportional to E_e. According to Mott and Davies Model, when the Urbach energy increases the width of the band gap decreases and therefore it is evident that in the study E_e values are leading to decrease the E_g. Moreover, it is also determined that the incorporation of isoelectronic atom Te into a-Se causes an increase in the density of defect states [27]. However, the structural defect model argues that due to the low electronegativity value of Te as compared to Se, Te generates the impurities with positive charge [27]. Moreover, Te is with a band-gap width of 0.34 eV, which is narrower than that of Se (1.74 eV) [28]. Hence, E_g of $Ge_{10}Se_{90-x}Te_x$ thin films decreases with an increase of Te content.

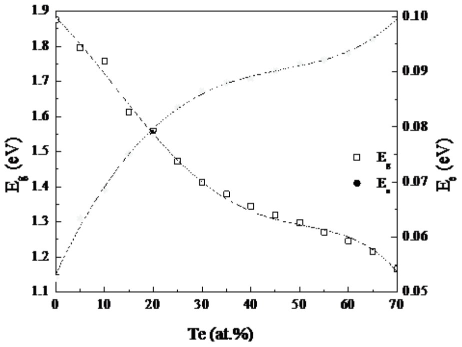

Fig. 5. Compositional dependence of E_g *and* E_e *for the* $Ge_{10}Se_{90-x}Te_x$ *(where* $0 \leq x \leq 70$ *at. %) thin films.*

Chemical bond energies are helpful in explaining the modification in the Ge–Se-Te system. Different types of energies are observed on various bonds including Ge-Ge (37.6 kcal/mol), Se-Se (44.0 kcal/mol), Te-Te (33.0 kcal/mol), Ge-Se (49.1 kcal/mol), Se-Te (40.6 kcal/mol) and Ge-Te (37.4 kcal/mol) [21, 29]. Moreover, results are interpreted on the basis of the chemical bonding approach [15]. This model may be satisfied for Ge-Se-Te glasses. As per the depending bond energy (De), the probability function $e^{De/Kt}$ calculated the relative probability of the formation of that bond [30].

Fig. 6 illustrates the theoretical results which were obtained by the calculation of the distribution of the chemical bonds in the studied glasses. It is to be noted in the figure that there are only four types of chemical bonds present that are Ge-Se, Se-Te, Se-Se and Te-Te are present. As the Te concentration increases up to 35 at. % (stoichiometric composition), the Se-Se bonds are replaced with Se-Te bonds. For further introduction of Te above 35 at. % the Se-Te bonds are replaced with Te-Te bonds. The pattern of linear increase is observed in the Se-Te bond concentration up to x=35 at. % which gradually decrease in a similar pattern while increasing the value of x above 35 at. %. The bonds between like atoms such as Se-Se and Te-Te disappear at x=35 at. % (stoichiometric composition).

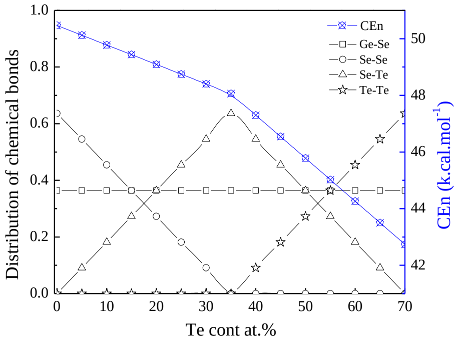

Fig. 6. Distribution of chemical bonds and cohesive energy (CEn) for the $Ge_{10}Se_{90-x}Te_x$ *(where* $0 \leq x \leq 70$ *at. %) glasses.*

The cohesive energy (CEn) or the average stabilization energy of any composition is the total sum of the products of the number of probable formed bonds times their energies, hence it can be computed from the following formula [31]:

$$CE = \sum_i \frac{N_i De_i}{100} \tag{6}$$

where N_i denotes the number of expected formed bonds,
De_i denotes the energy of that bond.

The calculated values of CEn for the $Ge_{10}Se_{90-x}Te_x$ (where $0 \leq x \leq 70$ at. %) glasses are represented in Fig. 6. With the illustration, it is justified to say that if Te content increases it decreases the values of CEn. This occurs because of the replacement of Se-Se (44.0 kcal/mol) by the Se-Te (40.6 kcal/mol) bonds for x < 35 at. % and due to the replacement of Se-Te (40.6 kcal/mol) by Te-Te (33.0 kcal/mol) bonds for x > 35 at. %.

4. Conclusions

All in all, the paper observed the effects of Te addition on the physical properties and optical energy gap of different compositions of $Ge_{10}Se_{90-x}Te_x$ (where $0 \leq x \leq 70$ at. %) thin films. The estimation of the absorption coefficient was based on the measurement of absorbance of thin films. The study also concludes that glass density, molar volume, and compactness increase while the cohesive energy decreases when the content of Te is increased in the $Ge_{10}Se_{90-x}Te_x$ glasses. Moreover, when the Te content is increased it causes a decrease in the optical band gap while causing an increase in the Urbach energy for the $Ge_{10}Se_{90-x}Te_x$ thin films. When the bond energy was analyzed and relative probability of formation of various bonds was calculated, it was revealed that only the bonds Ge-Se, Se-Te, Se-Se and Te-Te are present in the studied glasses.

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