Photosensitivity of semiconducting SeTeSb glasses

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Abstract. Photo-electrical measurements are done on thin films of SeTeSb to see the influence of Sb additive on the light-induced conduction of binary Se80Te20 alloy. The ratio of electrical conductivity under dark to light conditions has been measured for measuring the photosensitivity of the samples. The activation energies of conduction for dark and light conditions (ΔEph) are also determined. The results reveal that both σph / σd and ΔEph are reduced with an increase in Sb concentration. This indicates that density of defect states (DDS) is increased with an increase in the concentration of foreign element (i.e., Antimony) in thin films of these glassy systems. The cause of the increase in defects is also discussed.

1. Introduction
After the noteworthy finding of the light-induced phase-transformation in chalcogenide glasses (CGs) by Ovshinsky et al in 1971 [1-3], the wide-ranging studies have been reported on photo-induced phenomena in CGs [4-7]. At least seven distinct photo-induced phenomena are observed in amorphous chalcogenides but not usually in crystalline chalcogenides [8-10]. Due to observations of various kinds of striking and interesting photo-induced phenomena, ChGs received a great impulse in the optoelectronic industry for the development of solid-state devices [8-13]. The light-induced phenomena detected in CGs may be categorized into two classes [8-13]. The first class is related to ostensible heat-mode phenomena. In this class, the atomic structural changes are triggered by the heat that is created when the photo-excited carriers recombine in non-radiative way. The ostensible photon-mode is the second class which is responsible for the atomic structural changes induced directly due to the photo-electronic excitation. On the basis of the above photo-induced phenomena, various studies have been reported by different research groups for CGs of 16th group elements Se and Te [11-13] keeping in mind the applications in optoelectronics. Different researchers have employed the foreign atoms in the Se-Te system as chemical modifiers to alter the devitrification rate and the photoconductive properties of these materials [11]. Usually, the photosensitivity parameter (Σ) is calculated by dividing the experimentally determined value of σph by σd. Here, the symbols σph by σd denote the photoconductivity and dark conductivity respectively.
CGs, when irradiated by electromagnetic radiation in the visible range (i.e., white light), then they experience numerous modifications in their electrical and photo-electrical properties. The alteration in such properties is probably linked with the formation of two kinds of defect centres: (i) charged (D⁺ and D⁻) centres, and (ii) neutral (Do) centres. The characteristic feature of CGs is the occurrence of localized energy levels in the mobility gap because of the non-appearance of ordered structuring in addition to numerous intrinsic structural defects. In CGs, the experiment of electrical conductivity in the dark and light conditions is a significant approach to acquire valuable evidence concerning the formation of defect centres. Such studies are also useful for searching their suitable applications because this kind of experiment examines the applicability of a specific material for solar panels and other optoelectronic applications. In this script, the correlation between the electrical conduction and the structural defects density for some CGs of SeTeSb system

2. Material preparation and Experimental

The samples of Se₈₀₋ₓTe₂₀Sbₓ CGs were obtained by rapid-cooling of their melts. The elements of a very high purity were used that were sealed in cylindrical quartz tubes after weighing. Sealing was done in the inert atmosphere. Each tube was reserved in a furnace at a suitable temperature. In the chamber of this furnace, the temperature was increasing at a rate of 5 kelvin per minute. Each tube was rocked regularly for a long time (~ 15 hrs) to confirm the melt homogeneity. Chilled ice-water was used for the rapid-cooling the glassy character of each sample was confirmed by XRD technique.

Thin-films of present samples systems were obtained by thermal evaporation method under high vacuum. The substrates made of corning glass were used for this purpose. First the indium was evaporated for making the electrodes on these substrates and then the thin-films of each sample were deposited. The thickness of the thin-films was uniform for each sample (see Figure 1).

![Figure 1 Co-planar structure of thin film](image)

Thin-film samples were placed in a specifically planned vacuum chamber having a see-through window to expose the samples by white light for the electrical measurements under identical conditions (i.e., constant vacuum and temperature) that were achieved using a heating element and a vacuum pump. Temperature measurements were done by employing a standardised copper-constantan thermocouple that was located very close to the substrate. An electric bulb having tungsten filament was employed as light source. The electrical conductivity with and without light was determined by measuring the electric current.

Knowing the values of electrical resistance R and geometrical parameters (i.e., the cross-sectional area A and the thickness l) of the pellets, we calculated the conductivity (σ) by using the following relation:

\[ \sigma = l/(R.A) \quad -(1) \]

The electrical conductivity was measured in presence of light as well as in dark. The subtraction of these two values gave the value of photoconductivity.

3. Results and discussion
In the case of chalcogenide glasses, it is reported that the conductivity ($\sigma$) varies exponentially with the absolute temperature ($T$). This relation is known as the Arrhenius relation: $\sigma = \sigma_0 \exp\left(-\frac{\Delta E_{\text{d}}}{kT}\right)$. Here, $\sigma_0$ is a pre-exponential factor, $\Delta E_{\text{d}}$ is the activation energy comprised in the corresponding conduction mechanism. The symbol $k$ represents the Boltzmann constant. From this relation, we can plot a graph between $\ln \sigma$ versus reciprocal of the absolute temperature. Such plots of $\ln \sigma$ versus $1000/T$ are the straight lines. This confirms the validity of the Arrhenian temperature dependence of dc conduction in the present samples. When we plotted the graphs between $\ln \sigma_0$ and $\Delta E_{\text{dc}}$ for the present samples we have found a straight line as shown in Figure 2. This shows that the pre-factor of electrical conduction varies exponentially with the activation energy.

![MNR plot for dark conductivity](image1.png)

Figure 2 Meyer-Neldel plots for electrical conduction in thin films of a-SeTeSb

The ratio $\sigma_{\text{ph}}/\sigma_{\text{d}}$ is the direct measure of $\Sigma$ in the conductivity measurements in the dark and light conditions. It is a crucial parameter for a specific material that elects the usage of the specimen material in the opto-electronics. We have, therefore, calculated the values $\sigma_{\text{ph}}$ and $\sigma_{\text{d}}$ at ambient condition. The variation of $\Sigma$ is shown in Figure 3 for thin films of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ systems.

![Composition dependence of $\sigma_{\text{ph}}/\sigma_{\text{d}}$ in thin films of a-SeTeSb](image2.png)

Figure 3 Composition dependence of $\sigma_{\text{ph}}/\sigma_{\text{d}}$ in thin films of a-SeTeSb

It is clear from Figure 3 that $\Sigma$ is reduced with a rise in the concentration of Sb in the parent glass. The decrease in $\Sigma$ can be understood by considering the role of the charged defects. The levels of such defects appear because of the occurrence of dangling bonds in the glassy network of the CGs [14]. The source of the creation of the chemical bonding in the form of such defects was proposed by Kastner et al [15]. This group characterised the charged states as $C^-_1$ and $C^+_3$, $C$ stands for chalcogenide and
subscript designates the atomic coordination. \( C_3^0 \) is labelled as uncharged centre. Further, this group reveal that an additional electron is located on \( C_3^+ \) that is common between the three bonds of the atom.

Consequently, this state is 3-fold coordinated. The reduction in \( \Sigma \) after the entering of Sb atoms in parent sample indicate the rise in the DDS of ternary samples. Such an upsurge in the DDS after adding the chemical modifier is explained if we consider the electron affinity of the constituent elements of the samples [16]. The chalcogens (i.e., Se and Te) belong to the identical group of the periodic table. Consequently, most of Te atoms are undoubtedly assorted in long polymeric chains of Se atoms. However, some of Te atoms behave like the ionized impurities because their electron affinity (1.97 eV) is lower than the atoms of Se (2.02 eV). Consequently, Te atoms play the role of the positively charged localized states. Correspondingly, the inclusion of Sb atoms having less electron affinity (1.07 eV) can persuade more positively charged localized states. These circumstances can be expressed mathematically by amending the model established by Kastner et al [15]. Keeping in mind the case of pure Se, the structural defects (e.g., dangling atoms) appear due to the amorphous or glassy character of Se. Such structural defects are unstable in the normal situations. They are fairly steady when polarized to positively and negatively charged defect states. The DDS of these inherent charged defects can be determined by employing the mass action law in addition with the Kastner’s notations:

\[
2C_3^0 \rightarrow C_3^+ + C_1^-
\]

or

\[
K = \frac{[C_3^+][C_1^-]}{[C_3^0]^2}
\]

or

\[
K[C_3^0]^2 = [C_3^+][C_1^-]
\]

or

\[
K' = [C_3^+][C_1^-] --- (2)
\]

Where \( K' = K[C_3^0]^2 \), because \( [C_3^0] \) is a constant.

The neutral condition is

\[
[C_3^+] = [C_1^-] --- (3)
\]

These structural defects are supposed to be responsible for the formation of the localized energy states in the bandgap of Selenium rich CGs.

In the present work (i.e., the case of Se-Te alloy with Sb as chemical modifier), some Te behaves like the positively charged impurities and metallic Sb atoms also behaves like the positively charged impurities. Consequently, the Eq. (3) takes the form

\[
[C_3^+] + [Te^+] + [Sb^+] = [C_1^-] --- (4)
\]

By inserting Eq. (4) into Eq. (2), one gets

\[
K' = [C_3^+][[C_3^+] + [Te^+] + [Sb^+]]
\]

or

\[
[C_3^+]^2 + ([C_1^-] + [Te^+] + [Sb^+]) - K' = 0
\]

or

\[
[C_3^+]^2 + ([Te^+] + [Sb^+]) [C_3^+]- K' = 0 --- (5)
\]

This is a quadratic equation in \([C_3^+]\), whose solution is

\[
[C_3^+] = \frac{\sqrt{([Te^+]+[In^+])^2 + 4K' - ([Te^+] + [Sb^+])}}{2}
\]

Now eliminating \([C_3^+]\) from Eq. (4) and Eq. (2), we have

\[
K' = [C_1^-][[C_1^-] - [Te^+] - [Sb^+]]
\]
or \[ |C_1^-|[(C_1^-)-[Te^+]-[Sb^+]] - K' = 0 \]

or \[ |C_1^-|^2 - \{[Te^+] + [Sb^+]\}[C_1^-] - K' = 0 \] --- (7)

This is a quadratic equation in \([C_1^-]\), whose solution is

\[ |C_1^-| = \frac{\sqrt{\{[Te^+] + [Sb^+]\}^2 + 4K' + \{[Te^+] + [Sb^+]\}^2}}{2} \] --- (8)

From Eqs. (6) and (8), it is revealed that DDS is increased after the addition of Sb in parent SeTe glass. The decrease in \(\Sigma\), therefore, be explained by considering the rise in DDS, which is, further, understood by the electron affinities of impurity element (i.e., Sb in the present study).

### 3.1.1. Conclusion

The electrical conductivity measurements in absence and the presence of light are made in some ChGs of SeTeSb system. For this, thin films of these alloys are achieved by thermal evaporation method. The detailed analysis confirms that the conduction is thermally activated and it follows compensation rule. Further, the photosensitivity \(\Sigma\) is reduced with the rise in the Sb content. This specifies the rise in DDS after incorporation of Sb additive as expected by modified version of Kastner’s model.

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