Comparative Study on Structural and Electrical Properties of Se-Zn-In and Se-Zn-Te-In Chalcogenide Glasses

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Abstract
Chalcogenide glasses or amorphous semiconducting materials have been frequently used as memory devices. A comparative understanding concerning electrical properties of recent developed materials Se-Zn-In and Se-Zn-Te-In could be helpful to outline their potential applications. Therefore it is worth describing a relative variation in X-ray photoelectron spectroscopy core energy levels \([\text{Se}_{98-x}\text{Zn}_2\text{In}_x (x = 0, 4 \text{ and } 6)] \) and \([\text{Se}_{93-x}\text{Zn}_2\text{Te}_5\text{In}_x (x = 0, 4 \text{ and } 6)] \), Raman bands, I-V characteristics, electrical conductivity and ln(I) vs \(V^{1/2} \) characteristics for the Se\(_{98-x}\text{Zn}_2\text{In}_x (0 \leq x \leq 10) \) and Se\(_{93-x}\text{Zn}_2\text{Te}_5\text{In}_x (0 \leq x \leq 10) \) chalcogenide glasses. Obtained outcome demonstrates that the incorporation of fixed amount of Te with increasing In concentration as cost of Se affects the core energy levels, Raman bands, structural units values and electrical properties. The electrical properties of the described materials have been obtained higher corresponding to their structural thresholds units values.

Keywords
Chalcogenide Glass; XPS; Raman Spectra; Electrical Conductivity; Structural Unit

Introduction
Chalcogenide glasses or amorphous semiconductors are the applicable materials (Lin & Lucas 2011, Desevedavy et al 2010, Bulla et al 2009, Abrutis et al 2008, Person et al 2008) which have been used more than three decades in optoelectronics technologies. Such applicable materials exhibit switching memory like properties during the performances (Stehlik et al 2009). Electrical properties of these materials can extensively influence the structural units (Angell 1985, Hutchinson 1998, Tatsumisago et al 1990, Adam & Gibbs 1965). Meanwhile, the ingredients of alloying composition widely affect the structural units values. Consequently, the applicability in infrared transmission and detection (Boudebs et al 2004), threshold and memory switching (Stehlik et al 2009), optical fibers (Shportko et al 2008, Milliron et al 2007, Bowden et al 2009) functional elements in integrated-optic circuits (Pelusi et al 2009) non-linear optics (Dudley & Taylor 2009), holographic & memory storage media (Vassilev et al 2009, Wuttig & Yamada 2007), chemical and bio-sensors (Schubert et al 2001, Anne et al 2009) and infrared photovoltaics (Sargent 2009) etc, is also affected.

It is well known that the chalcogenides glasses have a few significant drawbacks; like low thermal stability, low crystallization temperature and aging effect. Specifically, inferior electrical parameter value and thermal instability are the major issue in such materials. In order to resolve these shortcomings of chalcogenide glasses, several investigators have proposed improved work such as the metal containing alloy; like, Se-Te-Cu, Se-Te-Ag, Ag-Se-Ge, Cu-As-Se, Se-Te-Cd, W-Co-Se, Se-Te-Zn, Se-Sb-Ag, Fe-Se-Ge-Sb, As-Se-Tl etc (Sharma & Kumar 2010, Faheem et al 2010, Ohara et al 2010, Rahim et al 2010, Lee et al, 2007, Srivastava et al 2008, Bindra et al 2007, Marco et al 2002, Ho et al 1997). The metallic chalcogen materials have a scientific superiority over the non-metallic compositions. Thus, the addition of metallic or semi-metallic elements in a glassy configuration can partially overcome difficulties in chalcogenide alloys.

In recent years, electrical properties of chalcogenide glasses have attracted much attention due to solid state technical applications advantages. The electrical properties of vitreous Se based materials have exhibited large Fermi level shift and a high order photovoltaic effect (Watanabe & Yamamoto 1985, Sato et al 1987). The I-V characteristics and consequent field effect in such materials have been reported by the investigators (El-Kady 1999). These characteristics in these materials can be explained by the different existing models and theories, such as, Pool-Frankel effect (Hill 1971), Small Polaron Conduction (Emin et al 1972), Hopping Conduction (Bagley et al 1970),
Tunneling Conduction (Stubb et al 1972) and Space Charge Limited conduction (Lampert & Mark 1970).

To achieve improved electrical properties and higher thermal stability in the present glasses, we had demonstrated the thermal, electrical & dialectical and optical properties of Se$_{98-x}$Zn$_2$In$_x$ ($0 \leq x \leq 10$) and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($0 \leq x \leq 10$) chalcogenide glasses, in our past studies (Singh et al 2009, 2009, 2009, 2009, 2010, 2009, 2010, 2009). Outcome of these studies revealed that the elemental alloying concentration can play an important role in physical property variation. In order to examine the collective effect of the variable In and fixed amount of Te concentration on the elemental X-ray photoelectron spectroscopy (XPS) core energy levels [Se$_{98-x}$Zn$_2$In$_x$ ($x = 0, 4$ and $6$) and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($x = 0, 4$ and $6$)], Raman vibration bands and electrical properties of the Se$_{98-x}$Zn$_2$In$_x$ ($0 \leq x \leq 10$) and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($0 \leq x \leq 10$) glasses, additional work is required. Therefore, an effort is made to describe the comparative structural changes and structural units dependence I-V characteristics, electrical conductivity ($\sigma$) and ln(I) vs V$^{1/2}$ characteristics for Se$_{98-x}$Zn$_2$In$_x$ ($0 \leq x \leq 10$) and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($0 \leq x \leq 10$) chalcogenide glasses.

**Material Preparation and Characterizations**

Bulk glassy materials were prepared by conventional melt quenched technique. High purity (99.999) elements Selenium, Zinc and Indium were used. The required amount of elements was weighed by electronic balance. The properly weighed elements were kept inside the clean quartz ampoules. The material containing quartz ampoules were evacuated and sealed under at a vacuum of $10^{-5}$ Torr. The material sealing process needs to evacuate clean quartz ampoules due to the reactive nature of materials with oxygen at high temperature. Bunch of sealed ampoules were heated in electric furnace, where the furnace temperature was raised at a rate of 5-6 K (min)$^{-1}$ upto 1173 K and held at that temperature for 10-11 h. To ensure the homogeneity of molten materials, were ampoules frequently rocked during the heating process. After achieving heating time, molten materials ampoules were rapidly quenched into ice cooled water. The prepared ingots of glassy materials were taken-out from the ampoules.

The X-ray photoelectron spectroscopy (XPS) core energy level and valence band spectra of the materials were obtained by the High energy resolution AXIS ULTRA-165 instrument. For this Al K$\alpha$ X-ray (1486.6 eV) was used, whereas the base vacuum was $3\times10^{-7}$ Pa. However, Raman spectroscopic characterization was performed from the LabRAM HR equipment in the wave number range from 100 to 700 cm$^{-1}$, whereas the 325 nm wave length Argon LASER was used, the charge coupled detector (CCD) in backscattering geometry. The spectra were recorded with the resolution 0.5 cm$^{-1}$.

The well prepared glassy materials cursed into fine powder to make its pellet (12 mm dia and ~ 2 mm thickness) under a 5 tons load. I-V measurements were performed across the plane surface of prepared pellet samples by Keithely 2400 source measure unit under fixed bias (V), in the voltage range 10 to 200 V at normal room temperature. To ensure the homogeneity of experimental data, each observation was performed 3 to 4 times. The schematic circuit diagram of I-V measurement is given in FIG. 1.
Results and Discussion

XPS Interpetation

To describe the existence of the alloying elements and effect of the foreign element (In) on the core energy levels of the Se$_{98-x}$Zn$_2$In$_x$ ($0 \leq x \leq 10$) and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($0 \leq x \leq 10$) materials, the XPS measurement has been performed for the Se$_{98-x}$Zn$_2$In$_x$ ($x = 0, 4$ and $6$) and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($x = 0, 4$ and $6$) (Singh & Singh 2009, Singh & Singh 2010) compositions glasses. The obtained outcome is given in FIG. 2 (A, B, C, D).

These materials have exhibited element Se 3d $5/2$ core energy level peaks in the binding energy range from 52 to 59 eV (See FIG. 2 (A)); which is generally related to the binding energy range of the Se. It has been observed that Se 3d $5/2$ core energy level peak shifted toward the lower binding energy side due to incorporation of the In content in Se$_{98-x}$Zn$_2$In$_x$ and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ materials. The incorporation of the Te in the SeZn matrix has also affected the core binding energy level of the Se 3d $5/2$ by showing the lower value for the Se$_{93}$Zn$_2$Te$_5$ (54 eV) in comparison to Se$_{98}$Zn$_2$ (57 eV) composition. Further FIG. 2 (B) shows XPS core energy levels signal in the range from 1015 ev to 1064, for the element Zn. Although in some compositions Zn peak at ~ 1021 eV has not appaered due to the very low compositional amount, they were attributed to the XPS signals in the range. This revealed the presence of the element Zn in the alloying compositions.

The in indium core level energy peak for the Se$_{98-x}$Zn$_2$In$_x$ ($x = 4$ and $6$) and Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($x = 4$ and $6$) is given in FIG. 2 (C). The little indium core binding energy peak shift toward lower energy side has been observed for the Se$_{93}$Zn$_2$In$_4$ & Se$_{89}$Zn$_2$Te$_5$In$_4$ in comparison to Se$_{87}$Zn$_2$Te$_5$In$_6$ & Se$_{86}$Zn$_2$Te$_5$In$_6$ compositions. Moreover the core binding energy peak of the element Te for the Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($x = 0, 4$ and $6$) compositions is exhibited in FIG. 2 (D). Almost negligible Te core binding energy shift has been observed in these glasses.

Raman Interpetation

Raman spectroscopic analysis can also describe the materials amorphous (or disordered) or crystalline behaviour. Raman spectra of the amorphous materials are analogous to the crystalline materials with a distinguishable difference in their relative peak broadening. The broader peak broadening in Raman spectra is generally related to the disorder structure of the materials (Cardona, 1982). The Raman spectra for the Se$_{98-x}$Zn$_2$In$_x$ ($0 \leq x \leq 10$) glasses is given in FIG. 3 (A). The most intense SeZn and SeZnIn Raman peaks are between the 200 to 300 cm$^{-1}$ wave number range.
Along with a few very low intensity peaks at 131, 142, 203 and 207 cm$^{-1}$, this Raman spectroscopic outcome also provides an additional information regarding the enhancement in the main peak broadening with the incorporation of the indium content and it seems to be maximum for the optimum In = 6 composition glass.

While the Raman spectra of the Se$_{93-x}$Zn$_2$Te$_5$In$_x$ (0 $\leq$ x $\leq$ 10) glasses have exhibited (See FIG. 3 (B)) relatively broader peaks in the wave number range from 165 to 260 cm$^{-1}$. With a noticeable feature, two partially separated peaks were at 188 cm$^{-1}$ and 223 cm$^{-1}$. The existence of these partially separated peaks in the broad peak range revealed that materials have unseparated two phasic intrinsic structure within the homogeneous amorphous structure. Alongwith, this outcome also has a distinguishable feature, that is, the intensity of the second peak seems to be in a decreasing order upto the threshold composition (In = 6), afterward increases for the In = 10 composition glass. Meanwhile, the incorporation of indium content in the Se$_{93-x}$Zn$_2$Te$_5$In$_x$ configurations prevails to form a single phasic amorphous material upto threshold composition; after that, In = 10 composition material approaches toward the phase separation due to enhancement in the crystallinity.

**Electrical Properties**

Comparative I-V characteristics of Se$_92$Zn$_2$In$_6$ and Se$_87$Zn$_2$Te$_5$In$_6$ (Singh & Singh 2009, Singh & Singh 2010) glasses in the common voltage range from 50 to 200 V is given in FIG. 4, which is recorded at room temperature. In previous studies (Singh et al 2009, 2009) it was demonstrated that below 120 volt these glasses exhibited nearly linear current growths, therefore, here electronic conduction at lower voltages is not entertaining. The exhibited results revealed that the switching like behaviour (or abrupt current
growth) initiated in the 120 V and higher for Te containing glasses. Relative current growths with structural units of Se_{98-x}Zn_{2}In_{x} (0 \leq x \leq 10) and Se_{93-x}Zn_{2}Te_{5}In_{x} (0 \leq x \leq 10) glasses at the maximum applied voltage 200 V (the equipment experimental limit) are given in FIG. 5. Outcomes reveal that the structurally thresholds glasses have high order current growths at the maximum applied voltage (200 V). At the utmost applied voltage, the linear and abrupt current growths show the ohmic to non-ohmic transition behavior.

The electrical conductivity can be calculated from the given relation;

\[ \sigma_{DC} = \frac{1}{\rho_{DC}} = \frac{1}{R} \frac{L}{A} \]  

(1)

Here R is the resistance of the sample, L is the thickness of the sample, A is the cross-sectional area of the sample and \( \sigma_{DC} \) is the resistivity of the materials. The plots of average electrical conductivity vs structural units of the alloys over the entire voltage (10-200 V) range is given in FIG. 6. It has been observed that the sudden rise in average electrical conductivity corresponding to structural units values lies between 2.08 to 2.1; beyond that a sharp decline noticed for the 2.12 to 2.15 compositions. Further, the electrical conductivity variation with structural units at the maximum applied voltage 200 V is also given in FIG. 7. The rapid rise in electrical conductivity (in comparison to threshold voltage 120 V) i.e, rapid drop in resistivity in the particular voltage range might arise due to complex glassy structures.

It is well accepted in chalcogenide glasses that the electrical conduction can take place by two parallel processes namely band conduction and hopping conduction. The band conduction occurs when the carriers excited beyond the mobility edges into a non-localized states. The excitations of the carriers into localized states at the band edge cause hopping conduction (Mott&Davis 1979). Thus the total electrical conductivity of the system can be expressed as;

\[ \sigma = \sigma_i + \sigma_h \]  

(2)

Here \( \sigma_i \) is the intrinsic conductivity and \( \sigma_h \) is the hopping conductivity.

Due to increasing voltage, the thermal effects may decrease the electrical resistance; thus allowing more current to flow through the sample. As a consequence, I-V characteristics changes the behaviour toward non-ohmic conduction at higher voltages.

To describe the non-ohmic conduction behaviour at high voltages, Jonscher and Hill (Jonscher & Hill 1975) have proposed the following relationship between current and the applied voltage;

\[ I = I_{PF} \exp \left( \frac{\beta V^{1/2}}{KT} \right) \]  

(3)

Here \( \beta = \frac{e^2}{4\pi \varepsilon \varepsilon_0 d} \) \( \varepsilon_0 \) is the permittivity of the space, \( \varepsilon \) is the relative permittivity of the sample, \( d \) is the spacing between filled and empty sites (jump distance) and \( I_{PF} \) is given as (at V=0)

\[ I_{PF} = I_0 \exp \left( \frac{\phi}{KT} \right) \]  

(4)

Here \( \phi \) is the trap depth

\[ I_0 = Aned\nu \]

A is the electrode area, n is the carrier concentration, e is the electronic charge and \( \nu \) is the phonon frequency, here it can be considered constant \( (10^{13}/s) \) (El-Hassan 2001).

With the help of Equation (3), one has obtained the
relationship between $\ln(I)$ and $V^{1/2}$ in the applied voltage range. Comparative plots of $\ln(I)$ vs $V^{1/2}$; in the common voltage range 50-200 V, for the two most electrically efficient alloys ($\text{Se}_{92}\text{Zn}_2\text{In}_6$ and $\text{Se}_{87}\text{Zn}_2\text{Te}_5\text{In}_6$) are given in Fig. 8. A vast number of past studies (Saraswat et al 2006) on chalcogenides have demonstrated that such glasses usually have exhibited a linear relationship between $\ln(I)$ vs $V^{1/2}$ at room temperature. While the present glasses (except $X = 0, 2$) have a sharp increment at higher voltage followed with a slightly discarded values at $-120V$, and comparatively high for the Te containing Se-Zn-In composition. The deviation from the linearity at some places arises due to structural inhomogeneity in glassy configurations (Singh & Singh 2011, Singh 2012).

Hence, the non-linearity has been obtained in $I-V$ curves for these glasses at higher voltages. According to the Pool-Frenkel (Abdel Latif 1998) demonstration, such type of conduction mechanism is observed in those materials; where electrons and traps generated due to defects and/or impurities are involved in conduction process. The structural defects in the material cause formation of additional energy close to the band edge called traps. The traps restricts the current flow; to capture and emission process: thereby becoming the dominant current mechanism.

The structural units of these materials extensively vary with alloying network (Saffarini 2006). Many approaches have been proposed to explain the structural units/ or composition dependence physical properties of such materials (Lucovsky et al 1977, 1977, Betts 1970, Lucovsky et al 1974); in which the formation of heteropolar bonds is favored over the formation of homopolar bonds. These models demonstrated that the glass structure is assumed to be composed of cross-linked structural units of the stable chemical compounds (heteropolar bonds) of the system and excess of the elements (homopolar bonds). Due to the occurrence of chemical ordering feature, a variety of physical properties have been exhibited at the so-called tie line or stoichiometric compositions at which the glass structure is made up of cross-linked structural unit consisting of heteropolar bonds only. At the tie line compositions features have been seen chemical origin; referred to as a chemical threshold for the system (Phillips 1983, Phillips & Thorpe 1985).

The values of structural units are varying between 2.04 and 2.15. Structural thresholds occur at 2.10 and 2.11 for the 6 percent indium concentration. This has followed the well known concept of chalcogenide glasses; and 2D structure can be formed for the structurally threshold compositions. Beyond the compositional structural thresholds, electrical properties of these materials have drastically decreased; owing to 2D$\rightarrow$3D configuration network transformation. Therefore, the addition of a fixed amount of the concentration in Se-Zn-In configuration has enhanced the values of structural units. Subsequently variable and fixed amounts of In & Te concentrations create the high order steric hindrance in alloys stoichiometry. This kind of structural fluctuations could be responsible for enhanced values of $I-V$ characteristics, electrical conductivity and Pool-Frenkel relationship in Se-Zn-Te-In glasses.

**Conclusions**

In conclusive remarks; the author has presented a comparative study on Se-Zn-In and Se-Zn-Te-In chalcogenide glasses. The XPS core energy levels peak shift of the Se and In in presence of the Te and Zn, has revealed the intrinsic structural changes within the materials. Subsequently the Raman spectroscopic analysis of these materials has demonstrated the overall amorphous structure. With a distinguishable difference, Te containing materials have broader unseparated two phasic behaviour compared to single phasic non Te containing materials. Therefore, Raman spectroscopic outcome demonstrated that the Te containing materials have a superior tendency to form an amorphous structure compared to the non Te containing materials. Additionally, the structural units dependent electrical properties of these materials
revealed; the electrical properties of the materials have drastically changed to the values of the structural units. The addition of a fixed amount of Te and variable In concentration in Se-Zn stoichiometry has enhanced the value of the structural units, I-V characteristics, electrical conductivities (σ) and Pool-Frenkel relationship compared to ternary glasses. It has been found that the structural thresholds in Se-Zn-In and Se-Zn-Te-In glasses occur corresponding to 2.10 and 2.11 structural units values. The higher value of the electrical parameters has been achieved corresponding to Te containing glass structural threshold unit; owing to the existence of a large number of heteronuclear bonds cross linking density in localized state.

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