I-V measurements of Ge-Se-Sn chalcogenide glassy alloys

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Abstract

Current-voltage characteristics and DC electrical conductivity were studied for $Ge_{30-x}Se_{70}Sn_x$ (x = 8, 11, 14, 17 and 20) glassy thin pellets of diameter 12 mm and thickness 1 mm prepared under a constant load of 5 tons using a well-known melt quenching technique in bulk as a function of composition. The I-V characteristics were recorded at room temperature as well as elevated temperatures up to 300 °C. The experimental data suggests that glass containing 20 at.% of Sn has the minimum resistance allowing maximum current through the sample as compared to other counterparts of the series. Therefore, DC conductivity is found to increase with increasing Sn concentration. Composition dependence of DC conductivity is discussed in terms of the bonding between Se and Sn. Plots between $\ln I$ and $V^{1/2}$ provide linear relationship for both low and high voltage range. These results have been explained through the Pool-Frenkel mechanism. The I-V characteristics show ohmic behaviour in the low voltage range and this behaviour turns to non-ohmic from ohmic in the higher voltage range due to voltage induced temperature effects.

Keywords: chalcogenide glasses, amorphous materials, electrical conductivity, I-V characteristics

I. Introduction

Chalcogenide glasses containing metal atoms form an interesting class of amorphous semiconductor (ASC) because of their potential applications as switching and memory devices. The additions of metals to these glasses increase the average coordination number and, thus, transform the network from one with a soft structure to one which is nearly tetrahedral. Glasses containing Se are known to consist of a mixture of long chains and Se_8 rings [1]. The addition of Ge with Se forms very good covalently bonded glass. The dominant feature of the network is fourfold coordinated Ge [2]. Ge-Se glasses have been particularly studied because of their ready glass formation, easy synthesis requirements and good chemical stability [3].

Experimental results reported by various researchers have shown that the addition of impurity atoms in binary Se-Ge and Se-In systems does change the electrical properties of chalcogenide glasses significantly [4–6]. It has also been found that the effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of doping. Impurity concentration is obviously a critical factor in such cases because all impurities cannot behave in an electrically active manner. Several of the physical properties are found to improve by the addition of certain impurities. Therefore, investigations on the influence of impurities on the properties of chalcogenide glasses are of relevance both from the basic science and application point of view.

Among all chalcogens, Se is one of the most important chalcogen element, as it has applications in electrography. The pure Se has disadvantage due to its short life time and low sensitivity, which can be improved by incorporation of group III, IV, V, and VI elements like Ga, In, Ge, As, Sb, Bi, Te, etc. The work on binary Se-alloys has already been reported [7–9]. Se-Ge has been used as a base material and incorporation of Sn as the third element has been studied [10,11]. The addition of the third element expands the glass forming area, and also, creates compositional and configurational disorder in the system. Generally, the binary alloys are covalent in the nature and the addition of third element creates iono-covalent bonds and as a result the conduction increases.

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Certain efforts were made to enhance the electrical properties by doping binary chalcogenide glasses with some metal additives that can induce conduction in these glasses, to improve their applicability in device fabrication. Fadel *et al.* [12] have investigated the effect of Sn on the electrical and optical properties of $Ge_{1-x}Sn_xSe_3$ ($x = 0, 0.2, 0.4$ and 0.6) glasses. In an effort to give more insight into the effect of metals on the transport properties of Ge-Se glasses, we study the variation of electrical conductivity with composition for a series $Ge_{30-x}Se_{70}Sn_x$ ($x = 8, 11, 14, 17$ and 20) of bulk samples with metal content of Sn. The study includes measurements of X-ray diffraction, scanning electron microscope and DC electrical conductivity at room temperature.

II. Experimental techniques

Bulk sample of $Ge_{30-x}Se_{70}Sn_x$ ($x = 8, 11, 14, 17$ and 20) glasses were synthesized from elements Ge, Se and Sn with high purity (99.999% pure) by the well-established melt-quenching technique. For these particular compositions, the constituent elements were weighed according to their atomic percentages and sealed in quartz ampoules under a vacuum of $\sim 10^{-6}$ Torr. The sealed ampoules were then placed in a microprocessor-controlled programmable furnace, where the temperature was increased at the rate of 3 K per minute up to $925\,°C$ and kept at that temperature for 12–14 h with frequent rocking to ensure the homogenization of the melt. The melt was then rapidly quenched in ice water. Quenched samples were then removed from the ampoules by breaking the quartz ampoules. These ingots were then ground into a fine powder using mortar and pestle.

Amorphous nature of these glasses was confirmed by X-ray diffraction (XRD) patterns. These patterns of X-ray diffraction were made using Bragg-Brentano geometry on a Panalytical X'pert Diffractometer with a Cu K$_\alpha$ radiation source ($1.5406\,Å$). Microstructures of these samples were seen by scanning electron microscope (SEM). SEM photographs are taken in secondary electron emissive mode using Carl Zesis Evo-18 Special Edition scanning electron microscopy. These powders were used to make pellets of dimensions as thickness ~ 1 mm and diameter 12 mm. Measurements of I-V characteristics of $Ge_{30-x}Se_{70}Sn_x$ ($x = 8, 11, 14, 17$ and 20) were performed on Keithley high resistance meter/electrometer 6517A at room temperature as well as elevated temperatures up to $300\,°C$. The electrometer was used to apply the voltage across the sample and to measure the current through the sample as it has an in-built capability of output independent voltage source of $+1000$ V. The indigenously designed sample holder with copper electrodes was used in the circuitry for bulk pellets. The basic circuit diagram, used for this study, is shown in Fig. 1. The electrical conductivity has been calculated from the relation:

$$\sigma_{DC} = \frac{1}{\rho_{DC}} = \frac{L}{R \cdot A} \tag{1}$$

where R is the resistance of the sample, L is the thickness of the sample, A is the cross-sectional area of the sample and ρ_{DC} is the resistivity of the sample under test.
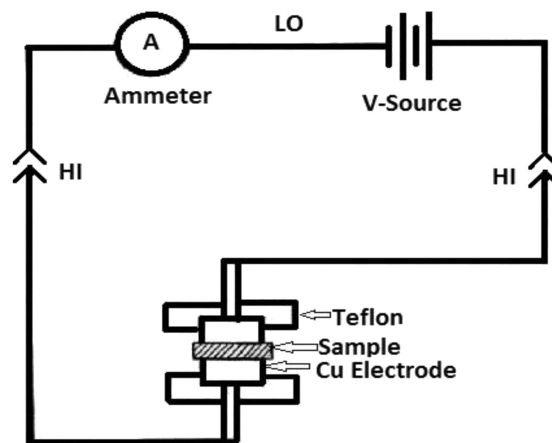

Figure 1. Circuitry used for measurement using electrometer

III. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction patterns give valuable information about the nature and structure of the samples. A Bragg-Brentano geometry on a Panalytical X'pert Diffractometer was employed for studying the structure of as-prepared samples of $Ge_{30-x}Se_{70}Sn_x$ ($x = 8, 11, 14, 17$ and 20) at room temperature. The X-ray diffraction traces, taken at room temperature for as-prepared samples, are shown in Fig. 2. The absence of any sharp
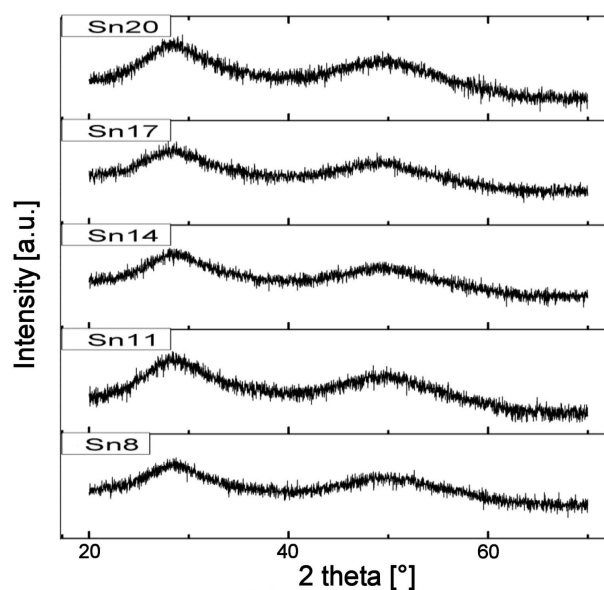

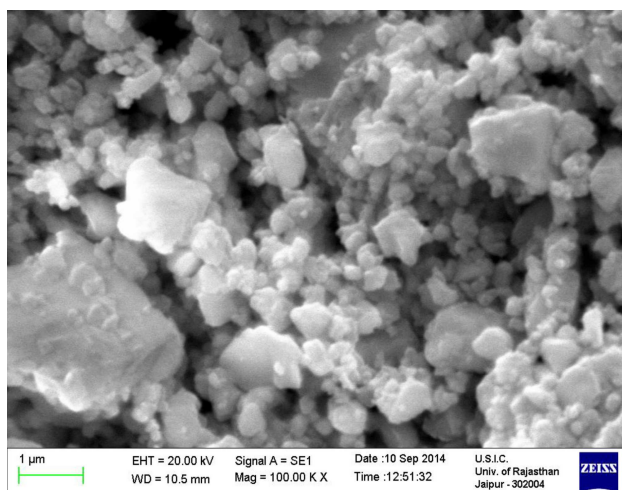**Figure 2. XRD patterns of $Ge_{30-x}Se_{70}Sn_x$ ($x = 8, 11, 14, 17$ and 20) chalcogenide glasses**

Figure 3. SEM image of as-prepared Ge$_{10}$Se$_{70}$Sn$_{20}$ glass

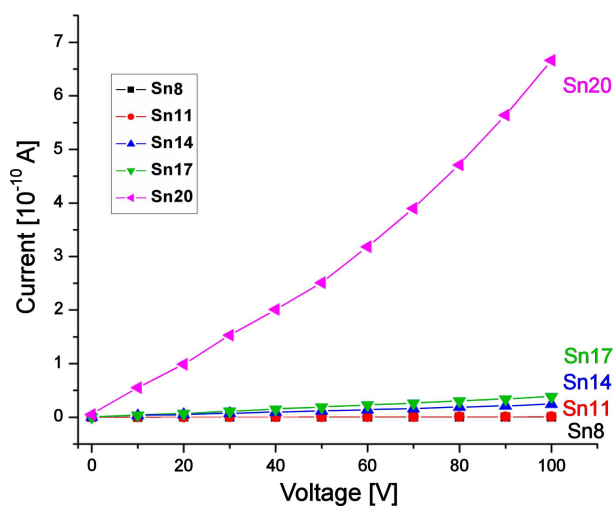**Figure 4. I-V characteristics of Ge$_{30-x}$Se$_{70}$Sn$_x$ (*x* = 8, 11, 14, 17 and 20) glassy pellets at room temperature**

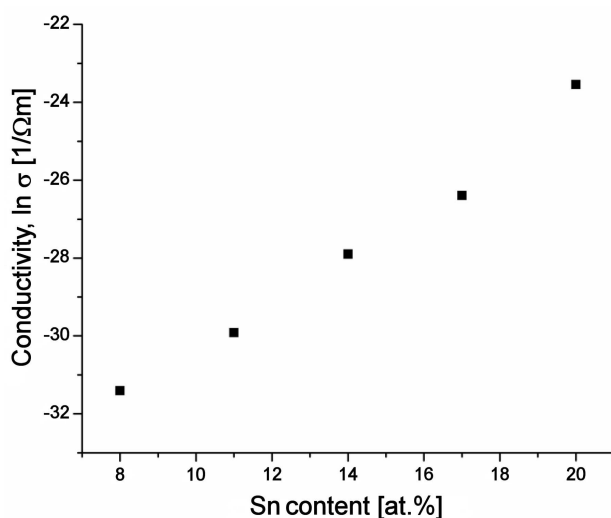**Figure 5. Composition dependence of conductivity of Ge$_{30-x}$Se$_{70}$Sn$_x$ (*x* = 8, 11, 14, 17 and 20) glassy system at room temperature**

structural peaks confirms the amorphous nature of the as-prepared samples.

3.2. Scanning electron microscopy

Surface of these samples has been studied by the scanning electron microscope (SEM) images of these glasses. SEM is a technique which is used to determine the surface morphology and structure of the material. The surface microstructures of amorphous samples at room temperature were examined by means of SEM. Figure 3 shows the SEM images of Ge$_{10}$Se$_{70}$Sn$_{20}$ as representative case in series under study. The irregular edges of the particles are consistent with amorphous nature of these particles.

3.3. DC conductivity

The typical I-V characteristics of Ge$_{30-x}$Se$_{70}$Sn$_x$ (*x* = 8, 11, 14, 17 and 20) chalcogenide glasses, recorded at room temperature in 10–100 V voltage range are shown in Fig. 4. It is clear from Fig. 4 that the five glasses (*x* = 8, 11, 14, 17 and 20) of the present glassy system show linear I-V characteristics as well as non-linear growth of current with increasing voltage. It can be seen from Fig. 4 that current is increasing linearly up to 50 V. For further increment in the applied voltage, current starts increasing faster than lower voltages and loses its linear dependency on voltage. The linear and non-linear current growth behaviour of present glasses indicates that the electrical characteristics tend towards to non-ohmic behaviour from ohmic at higher voltages applied across the sample. The deviation of ohmic behaviour in lower voltage range towards the non-ohmic in higher voltage range is due to the high voltage induced temperature effects in the sample. It is also evident from Fig. 4 that the current is highest for Ge$_{10}$Se$_{70}$Sn$_{20}$ glass as compared to other glasses of Ge$_{30-x}$Se$_{70}$Sn$_x$ (*x* = 8, 11, 14, 17 and 20) system.

The variation of electrical conductivity with Sn composition is shown in Fig. 5. It is observed from this figure that the five glasses Ge$_{30-x}$Se$_{70}$Sn$_x$ (*x* = 8, 11, 14, 17 and 20) exhibit sudden rise in electrical conductivity with increasing Sn percentage. It can be seen that with every increment of *x* value by 3 is showing approximately 10 times increase in conductivity. This has been termed as "sudden rise" in conductivity.

The variation of electrical conductivity of Ge$_{30-x}$Se$_{70}$Sn$_x$ (*x* = 8, 11, 14, 17 and 20) chalcogenide glasses could be explained on the basis of changing structure of these glasses with addition of Sn. Ternary Ge-Se-Sn glasses are particularly important for study because of the structural changes which have been observed to occur as Ge is replaced by Sn [13,14]. The structure of GeSe$_2$ in both its crystalline [15] and glassy [16] states is built up of Ge(Se$_4$)$_{1/2}$ tetrahedra which form corner-sharing chains crosslinked by edge-sharing tetrahedra. In the crystal this structure forms layers which are then stacked in the out-of-plane direction to form an an-isotropic three-dimensional
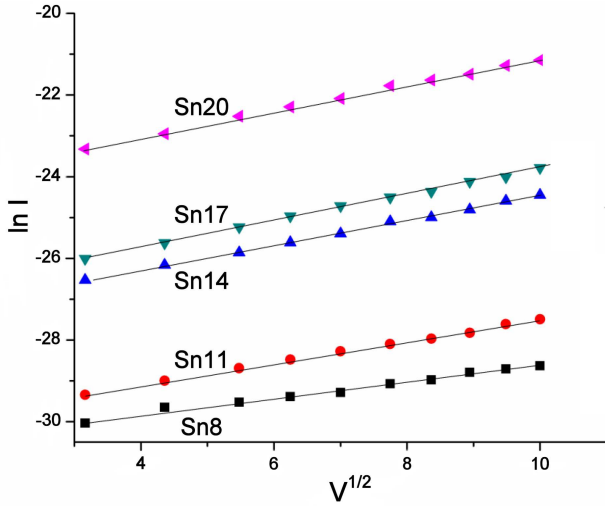
Figure 6. Linear relationship between ln I and $V^{1/2}$ for Ge$_{30-x}$Se$_{70}$Sn$_x$ (x = 8, 11, 14, 17 and 20) at room temperature: Verification of Poole-Frenkel conduction mechanism

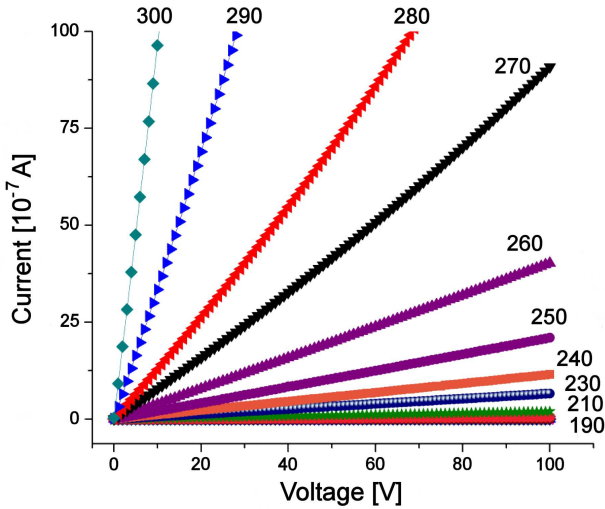**Figure 7. I-V characteristics for Ge$_{13}$Se$_{70}$Sn$_{17}$ glass as representative case in the series at different temperatures (25–300 °C)**

structure. The glassy form is made up of fragments of these layers which form randomly-oriented clusters terminated in the direction of the cross-linking by Se-Se bonds. To maintain the stoichiometry of these clusters by additional units in which Ge-Ge bonds occur, these clusters are slightly Se-rich. The widths of these clusters are variable depending upon the composition of ternary glasses. Ethane-like chains were formed by these Se-rich clusters [17]. In the ternary compounds Sn goes substitutionally into Ge sites in both crystal [18] and glass [17,19], preferentially occupying the sites at the edge of the clusters. As the number of Sn atoms is increased and more edge sites are required to accommodate them, the average size of the clusters within the glass decreases.

A model for the structure of the pseudo binary glass Ge$_{1-x}$Sn$_x$Se$_3$ (0.0 ≤ x ≤ 0.7) was presented by Mikrut and McNeil [20], which can be employed for the system

under study here. They reported that Ge is replaced by Sn in these glasses without changing the basic structure of these glasses, so it is reasonable to adopt a virtual-crystal approach to the shift of the band edge as Sn composition is increased. Therefore, as the Sn content is increased and the virtual cation becomes more Sn-like, the states at the band edges increase maintaining the character of the loosely bound electrons of Sn. It is clear here that Sn atoms bind their valance electrons more loosely than the Ge atoms do. As the number of Sn atoms increases, the number of loosely bound valance electrons increases. The loose valance electrons contribute in current flow resulting in more current. Hence the conductivity of samples enhances more and more with the addition of more and more Sn content in basic Ge-Se structure in the studied series of Ge$_{30-x}$Se$_{70}$Sn$_x$ (x = 8, 11, 14, 17 and 20) chalcogenide glasses as shown in Fig. 4.

Moreover, it is well known for chalcogenide glasses, the electrical conduction can take place by two parallel processes namely band conduction and hopping conduction. The band conduction occurs when the carriers are excited beyond the mobility edges into non-localized states. The excitation of the carriers into localized states at band edge causes hopping conduction [21]. Therefore, the total electrical conductivity of system can be expressed as:

$$\sigma = \sigma_i + \sigma_h \qquad (2)$$

where σ_i is the intrinsic conductivity and σ_h is the hopping conductivity.

As voltage increases, thermal effects may decrease the electrical resistance; thereby allowing more current to flow through the sample. Thus, we can state that I-V characteristics are changing their behaviour towards non-ohmic at higher voltages. For such conditions, the following relationship between current and applied voltage is given by Jonscher and Hill [22]:

$$I = I_{PF} \exp \frac{\beta \cdot V^{1/2}}{k \cdot T} \qquad (3)$$

where

$$\beta = \frac{e^2}{4\pi \cdot \varepsilon \cdot \varepsilon_0 \cdot d} \qquad (4)$$

and ε_0 is the permittivity of the space, ε 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 $V = 0$):

$$I_{PF} = I_0 \exp \frac{\phi}{k \cdot T} \qquad (5)$$

where ϕ is the trap depth, $I_0 = A \cdot n \cdot e \cdot d \cdot \nu$, A is the electrode area, n is the carrier concentration, e is the electronic charge and ν is the phonon frequency, which was considered as constant (10^{13}/sec) [23]. As shown in equation 3, we have obtained the linear relationship between ln I and $V^{1/2}$ in the applied voltage range which suggests that conduction mechanism in these materials

is of Pool-Frenkel type [24]. The plot of ln I versus $V^{1/2}$ of all glassy alloys is shown in Fig. 6. The earlier study [25] on chalcogenides showed that such glasses generally exhibit a linear relation between ln I vs. $V^{1/2}$ and reported that the excess of Sb in Se-Te-Sb system induces changes in conductivity and it has been concluded that 4 at.% of Sb has the maximum electrical conductivity. It is interesting to note that DC electrical conductivity in our study is increasing with Sn content in the composition range $x = 8$ to 20 at.% while Shaheen *et al.* [26] reported that the DC conductivity increases with Sn concentration up to 6 at.% only, after which it decreases due to the formation of $SnSe_{4/2}$ tetrahedral induced by local environmental readjustment which involves the change in the coordination number of Sn. Singh *et al.* [27] studied the I-V characteristics of Se-Zn-In ternary chalcogenide system at room temperature and reported that this system also exhibits both ohmic and non-ohmic behaviour in the studied voltage range.

I-V characteristic measurements at different temperatures of these samples have been done. Figure 7 shows the I-V characteristic for sample $Ge_{13}Se_{70}Sn_{17}$. It is clear from Fig. 7 that current is increasing with applied voltage when temperature is fixed and with temperature when applied voltage is fixed. This behaviour of these samples shows the semiconducting nature of these samples. Relevant materials for these amorphous GeSe materials are crystalline semiconductor materials. Bahl *et al.* [28] reported the resistivity study of crystalline GeTe. Results show that these samples have a low resistivity ($\sim 10^{-4}$ $\Omega \cdot$cm at 300 K) which increases with temperature slowly and nearly linearly in low temperature range (below $\sim$300 K) and rapidly in higher temperature range while in our study these amorphous materials have high resistivity and with increasing temperature this resistivity is decreasing which is clear from Fig. 7. Ge-Sb-Te alloys are also characterized in its amorphous, face-centered-cubic, and hexagonal phases and it is clear that the face-centered-cubic and hexagonal phases are highly conductive [29].

IV. Conclusions

$Ge_{30-x}Se_{70}Sn_x$ ($x = 8, 11, 14, 17$ and 20) chalcogenide glass samples have been prepared by melt quenching technique. The obtained bulk samples are found to be of amorphous state. Following are the conclusions that can be drawn from this study:

- X-ray diffraction patterns of these samples have confirmed the amorphous nature of these glasses.
- The present results show that I-V characteristics of $Ge_{30-x}Se_{70}Sn_x$ ($x = 8, 11, 14, 17$ and 20) chalcogenide glasses exhibit both ohmic (in 0–50 V range) and non-ohmic behaviour (in 50–100 V range).
- The influence of Sn content on DC electrical conductivity of these glassy alloys has also been investigated here. Results show that electrical con-

ductivity increases with increasing Sn content. The value of electrical conductivity is found maximum for $Ge_{10}Se_{70}Sn_{20}$ chalcogenide glass in the series under study.
- The behaviour of the I-V characteristic at different temperatures shows the semiconducting nature of these samples.

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