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Electrical conductivity, dielectric properties and structure of $GeSe_3Sb_2Se_3$-ZnSe thin films

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ABSTRACT

Electrical conductivity and dielectric properties of the chalcogenides $GeSe_3$, Sb_2Se_3, ZnSe, $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ and $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ thin films are investigated. The effect of ZnSe incorporation with both $GeSe_3$, Sb_2Se_3 results in amorphous $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ composition as obtained from the X-ray diffraction analysis. The estimated DC activation energy, ΔE_{DC}, in the temperature range from 300 to 373 K is found to decrease from 0.72 eV for $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ to 0.65 eV for $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$. However, the estimated AC activation energy, ΔE_{AC}, over the same temperature range and a frequency range from 0.6 to 1000 kHz, exhibits an opposite trend as its values increase for $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ as compared with that of $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ composition. Dielectric constant, ε_1, and dielectric loss, ε_2, behaviour are investigated as well over the same ranges of temperature and frequency.

1. Introduction

In recent years, considerable attention has been focused on amorphous semiconductors, especially these known as chalcogenide glasses due to their wide application [1] besides their unique physical properties [2,3]. Chalcogenide semiconductors have truly emerged as multipurpose materials and have been used to fabricate technologically important devices such as IR detectors [4], electronic and optical switching [5,6] and optical recording media [7]. In addition, some promises physical phenomena like photo-induced structural transformations [8] and photo darkening bleaching [9].

Measurements of AC and DC conductivity of amorphous semiconductors are of particular importance, not only from the application point of view but also from the fundamental point of view, as these composites are essentially good dielectrics [10,11]. Moreover, some additions of metallic element to the chalcogenide cause an enhancement in the conductivity followed by producing a significant decrease in the activation energy for conduction making them more suitable for IC device applications.

The interest towards some of these chalcogenide semiconductors is devoted to the binary $GeSe_2$, Sb_2Se_3 compositions due to their high glass-forming ability in obtaining the pseudo binary composition $GeSe_2$-Sb_2Se_3 [12] where the homogenous amorphous phase covers regions from 0 to 70 mol% Sb_2Se_3. On the other hand, ZnSe is a highly pure crystalline composition and has solubility in $GeSe_2$-Sb_2Se_3 glasses system up to 25 mol% [12,13]. The partial incorporation of ZnSe with $GeSe_2$-Sb_2Se_3 to form the pseudo ternary composition $GeSe_2$-Sb_2Se_3-ZnSe gives a high potential for the resulting composition to be studied as an amorphous one, with different physical properties from that of the pseudo binary composition. The present study was undertaken in order to investigate the influence of ZnSe on some physical properties such as X-ray diffraction, DC and AC electrical properties when partially incorporated with both $GeSe_3$ and Sb_2Se_3 to form $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ glasses composition.

2. Experimental technique

Bulk chalcogenide glassy samples of $GeSe_3$ and Sb_2Se_3 were prepared from their components of high purity (99.999%) by the usual melt quench technique. However, ZnSe composition was supplied by Aldrich Chemical Company Inc., in powder form with purity (99.99%). The source composition of pseudo binary $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ and pseudo ternary $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ samples were prepared in bulk form from the base binaries $GeSe_3$-Sb_2Se_3 and $GeSe_3$-Sb_2Se_3-ZnSe, respectively, also by melt quenching. Thin films of ZnSe, $GeSe_3$, Sb_2Se_3, $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ and $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ with average thickness of ≈500 nm were deposited onto cleaned glass substrates using a single source thermal evaporator (Edwards-306E). Thermal evaporation of the bulk samples was carried under a vacuum of 5.3×10^{-3} Pa and the substrate temperature was held constant at room-temperature ≈298 K during the deposition process of ZnSe, $GeSe_3$, Sb_2Se_3 and $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ compositions. However, the thin film of $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ composition was prepared successfully by raising up the substrate temperature to about 345 K using an electrical heater during the thermal evaporation process. The

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prepared samples were checked out compositionally in both bulk and thin film forms using the energy dispersive X-ray (EDX) analyzer attached to a scanning electron microscope (JEOL-JSM-5400) with an EDX detector of OXFORD Link ISIS system. The difference in the EDX measurement between the starting bulk and thin film is about ±2 at.%. The thermal behaviour of the bulk samples was investigated using a differential thermal analysis (DTA) of Shimadzu DTA-50. The transition temperatures for these samples were investigated in temperature range from room temperature up to 650 °C and with heating rate of 10 °C/min. DTA measurements were carried out in nitrogen atmosphere to prevent oxidation of the samples and a powder of α-Al_2O_3 in Al-cell was taken as a reference material.

The structural phase of the prepared films was investigated using the X-ray diffraction (XRD) analysis with equipment of Bruker-D8 computerized X-ray diffractometer. The X-ray tube was operated at 45 kV and 9 mA. The diffraction patterns were collected using θ–2θ configuration in the angle inverted $5° \leq 2\theta \geq 90°$ with steps of size $\Delta(2\theta) = 0.05°$. For electrical measurements, the gold electrodes of the film sample were electrically connected to two probes of silver. DC conductivity measurements of thin film samples were carried out in the temperature range from 300 to 373 K. The sample temperature was measured using a thermocouple placed very close to the sample. A Keithley-617 digital electrometer was used for measuring resistance of the samples at the different temperatures within the range. For AC conductivity measurement $\sigma_{AC}(\omega)$, the LCR bridge model Hioki 3532 was used in measuring the film impedance Z and the phase angle Φ between the applied AC voltage and the resulting current in the film. The frequency and the temperature ranges were from 0.6 to 1000 kHz and from 300 to 373 K, respectively.

3. Results and discussion

3.1. Differential thermal analysis (DTA)

The recorded data from the DTA analysis of the prepared bulk samples in powdered form are shown in Fig. 1, indicating the existence of three characteristic phenomena in the studied temperature region. The first one corresponds to the glass transition temperature, T_g, which is considered as the temperature corresponding to the intersection of the two linear portions of transition below the DTA trace, the second is the maximum peak temperature of the crystallization, T_c, while the third is the minimum peak of the melting temperature, T_m, and the values of these temperatures are listed in Table 1. For ZnSe composition, neither T_g nor T_c is recorded for this purely crystalline composition, also its melting point is not recorded in the studied temperature range from 27 °C to 650 °C. For Sb_2Se_3 composition, both T_g and T_c are recorded as well as its melting point T_m. However, for $GeSe_3$, $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ and $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ samples, the only recorded temperature corresponds to T_g. The absence of crystallization temperatures, for these samples, could be attributed to their high amorphicity, and their melting temperatures are above the measured temperature range. On the other hand, the recorded values of their T_g are found to decrease in sequence starting from $GeSe_3$ and followed by $(GeSe_3)_{80}(Sb_2Se_3)_{20}$ and $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$, respectively, as given in Table 1. This decrease in T_g value may be attributed to the rigidity of the glass network. In other words, the value of T_g is associated with the bond energy between the atoms [14]; therefore, the decrease in T_g could be attributed to the decrease in the cohesive energy, CE, which are calculated according to method mentioned in [15] and given in Table 1. From Table 1, it can be observed that CE follow the same trend as that for T_g, and thereby the lower the T_g value of the composition, the sooner the softening occurs corresponding to the accessibility of a new configurational energy or degrees of freedom.

3.2. X-ray diffraction (XRD)

X-ray diffractograms of the prepared films are shown in Fig. 2. For ZnSe film, the diffractograms exhibit a sharp line at $2\theta = 27°$, which corresponds to the ZnSe crystalline origin according to the ICDD card no. 37-1463 (cubic system). The lattice parameters of this phase are $a = b = c = 5.67$ Å and $\alpha = \beta = \gamma = 90°$. This peak is surmounted on a broad hump indicating that there is a crystallite centre, i.e., the sample is a mixture of amorphous and minority crystalline phase, which may be attributed to the preparation from a highly pure crystalline powder source. On the other hand, pure amorphous nature is observed for

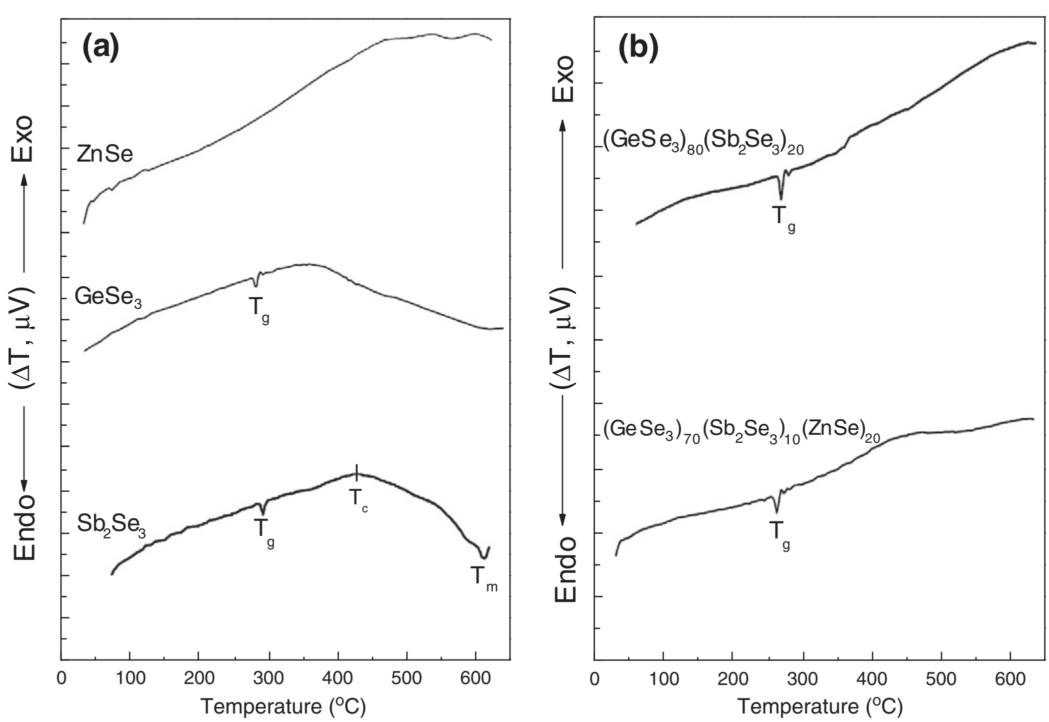

Fig. 1. DTA thermogram of (a) ZnSe, $GeSe_3$, Sb_2Se_3 and (b) $(GeSe_3)_{80}(Sb_2Se_3)_{20}$, $(GeSe_3)_{70}(Sb_2Se_3)_{10}(ZnSe)_{20}$ in powdered form at heating rate of 10 °C/min.