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Electrical transport properties and Mott's parameters of chalcogenide cadmium sulphoselenide bulk glasses



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ABSTRACT

This research article was devoted to study some electrical characteristics of chalcogenide bulk $Cd_{50}S_{50} - {}_xSe_x$ (30% $\le x \le 50\%$) glassy systems. CdSSe Bulk glasses were previously prepared by the mechanical milling technique. The products of the grinding process were pressed as disc-shaped pellets of diameter 12 mm and thickness 1.5 mm by using a compressor of pressure about 6.5 MPa. Two point probe technique was used to measure the electrical resistance and dc-electrical conductivity in the temperature range 293 K–435 K. Conduction mechanism studies reveal that, the transition temperature was detected at around 370 K. Below this temperature, the conduction mechanism was via the variable range hopping conduction near Fermi level according to Mott's model. Above 370 K, the mechanism was hopping conduction via localized states by the activated thermionic emission. The activation energies of bulk CdSSe glasses were found to be decreased by adding more Se. The pre-exponential factors, Mott parameters, and the density of localized states near Fermi level, trapping state energy, the potential barrier energy, were evaluated and studied. The relation between cohesive and activation energies was discussed. All obtained data were strongly dependent upon Se-content in the bulk $Cd_{50}S_{50} - {}_xSe_x$ glassy compositions.

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1. Introduction

In the past few decades, non-crystalline chalcogenide alloys and compounds were subjected to extensive studies because of their unique, interesting properties and the possibility of adjusting and tailoring their properties. What attracted researchers and scientists to these materials is also the ability to modify and control their properties even after their fabrication, just by exposing them to the external and nonmechanical effects, such as Gamma rays, X-rays, laser beam, light and thermal waves [1-4]. Chalcogenide materials can also be engineered to cope with the maximum span of the visible spectrum. Amorphous chalcogenide compositions are widely used in optical DVDs and nonvolatile memory devices (phase-change random-access memory) [5–7], as waveguides and optical fibers and in fabrication of inexpensive solar cells [8–10]. In addition, they are used in advanced opto-electronic applications because they have strong photosensitivity, high infrared transparency, high refractive index, etc. [6–8]. Chalcogenide glasses also show the largest non-resonant third-order nonlinear susceptibility among inorganic glasses [11,12]. Therefore, these glasses are considered to be promising semiconducting materials [13–15]. Cadmium sulphoselenide glassy compositions have an important and great place in this regard [16,17]. These compositions are also characterized by their high photoconductivity, a tunable band gap, and electrical resistivity [17–19]. Therefore, they are commonly used in photovoltaic applications and optical devices, as well as in the field of electronics and infrared optics [20–22]. In addition, they are used as IR photodetectors, photo-electrochemical, phototransistors and electroluminescent devices. CdSSe can be also used as temperature sensors, gas sensors, environmental sensors, piezoelectric devices, light emitting diodes, electron-beam pumped lasers [23–26], spintronics, quantum computing, electro-photography, photo-catalysis, and solar cells [26,27].

On the other hand, bulk glasses of Cd–S–Se systems are like other chalcogenide compositions, exhibit continuous changes in their electrical properties with changing the ratios of their basic ingredients and the doping process [18,21], especially the transport mechanism of charge carriers. The types and concentrations of dopant materials play key roles in the efficiency of the semiconductor thus affecting their practical applications [28]. Therefore, it is very important to study the electrical properties of these glassy chalcogenide materials to know whether they could be used in the different purposes. Where, the electrical conductivity and electrical parameters of materials are considered

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from basic descriptions of the possibility of their usage in the various applications [28,29]. The dependence of electrical conductivity upon the temperature gives good information about the structural defects and the localized state of amorphous chalcogenide alloys [30,31]. However, studying the electrical conductivity of materials provides essential information about the nature of defect centers, which are responsible for the type of conduction in amorphous glassy systems. Generally, the nature of electron transport in chalcogenide glasses still remains under extensive investigation [32]. The density of defect states in the mobility gap controls the electrical properties of chalcogenide glasses. They can be calculated after knowing the type of the conduction mechanism, where there are various models can determine the density of these defect localized states $N(E_F)$. At lower temperatures, Mott's variable range hopping of charge carriers between the localized states can be successfully applied in chalcogenide glasses [30-34]. The density of localized states and some other parameters can be obtained from the linear fitting of the measured experimental data according to Mott's model [33]. In the high temperature region, the dominant mechanism is the band conduction through the extended states. Sometimes this mechanism cannot be inferred or does not occur because the high energy is required for its occurrence or this mechanism may be appeared at higher temperatures and don't reach it. This mechanism is identified with the transition to the intrinsic conduction in semiconductors, so the density of carriers is equal to that of intrinsic carriers [30–35].

Authors have reviewed the previous literature which published through the recent few years. They found that, there are many research articles consecrated to study the optical and electrical properties of crystalline CdSSe thin films only. But they did not find any literature allocated in studying the chalcogenide glassy CdSSe bulk compositions. To our knowledge also, no attention in the previous literature has been devoted to study the bulk CdSSe glasses and their electrical conductivity and Mott's parameters or in general their electrical properties. Therefore, our motivation of this manuscript is to study some of these unstudied topics and issues for the ternary chalcogenide Cd50S50 - xSex bulk glasses. The present study was undertaken in order to discuss and study the thermal and compositional effects on the electrical properties of chalcogenide non-crystalline bulk Cd₅₀S_{50 - x}Se_x systems $(30\% \le x \le 50\%)$. This work complements our previous studies on these bulk glasses. The authors in a previously published paper studied many of the physical properties of these bulk glassy samples which were successfully synthesized by using the mechanical grinding technique [36]. The authors also studied the influence of the addition of more Se on the optical properties and the dispersion parameters of the refractive index for the thermally evaporated thin films of ternary glassy $Cd_{50}S_{50} = {}_{x}Se_{x}$ networks (30% $\leq x \leq 50\%$) [37]. Furthermore, the authors also studied the microstructure parameters and crystal imperfection of the chalcogenide crystalline CdS_xSe_{1-x} (0.0 $\leq x \leq$ 0.4) thermally evaporated thin films [38]. The aim of the present work is also to study the possible conduction mechanisms, determining the preexponential factors and their corresponding activation energies as well as estimating Mott's parameters, the density of localized states, trapping state energies, the potential barrier energies and others. The authors find a difficulty to get similar data to compare our obtained results with them, where there is a dearth in the previous works concerned with the study of the bulk CdSSe glassy systems.

2. Experimental details

2.1. Preparation of the bulk glasses

Chalcogenide bulk $Cd_{50}S_{50} = {}_{x}Se_{x}$ glassy samples were prepared previously by using the mechanical grinding technique. High-purity elemental powders of Cd, S, and Se ($s_{igma-Aldrich}$) were weighted according to their atomic mass ratios in stoichiometric quantities. Mixtures of the input elemental powders of Cd, S, and Se were used to get different compositions ($30\% \le x \le 50\%$). The mixtures were well mechanically

grounded using a tightly closed agate mortar and then placed in an electric mill for 48 h to get a highly homogeneous solid solution of chalcogenide ${\rm Cd_{50}S_{50}}_{-{\rm x}}{\rm Se_x}$ alloys (x = 30, 35, 40, 45 and 50%) [39–41]. Each output composition was pressed using a compressor of pressure about 6.5 MPa to get glassy bulk pellet samples. The details of the used mechanical milling process and the checking of the amorphous nature of bulk ${\rm Cd_{50}S_{50}}_{-{\rm x}}{\rm Se_x}$ pellets were published in a previous work [36].

2.2. Preparation of samples for electrical measurements

The obtained bulk $Cd_{50}S_{50} - {}_{x}Se_{x}$ glasses were pressed in order to have a disc-shaped of a diameter about 12.0 mm. The two opposite faces of each bulk glassy pellet were carefully ground and polished to a thickness about 1.5 mm. A thin layer of silver paste was manually coated above each face of the disc sample. It was found that, the two silver paste electrodes mainly give good contacts, where each face of the investigated samples was connected by a fine Cu-thin wire. Two point probe technique was used to measure the electrical resistance and to determine their dc-electrical conductivity. The resistance of prepared samples was measured by using a digital Keithley electrometer (model 616) and a stabilized power supply. The temperature of the specimens was recorded with a previously calibrated chromel alumel thermocouple which placed in closed thermal contact with the specimen surface. The thermocouple was connected to a digital thermometer to measure the temperature degree of samples. The temperature dependence of the dc-electrical conductivity of the studied bulk glassy CdSSe samples was carried out in the temperature range of 293 K-435 K. Experimental data of the dc-electrical conductivity, σ_{dc} were calculated from the following equation:

$$\sigma_{dc} = \frac{t}{RA} \tag{1}$$

where t is the thickness of the pellet glassy sample (1.5 mm), R (Ω) is the sample resistance, A is the surface area of the disc-shaped glassy samples (4.52 sq mm). Measurements of the electrical resistance, R were repeated more than once to insure the accuracy of the obtained dc-electrical conductivity data. The accuracy of the temperature measurements was better than ± 2 K and the error in the resistance measurements does not exceed ± 5 Ω .

3. Results and discussion

3.1. Thermal and compositional effects on dc-electrical conductivity

The electrical properties of the bulk $Cd_{50}S_{1-x}Se_{x}$ glassy samples were carried out by means of the temperature dependent conductivity. Fig. 1 shows, the variation of the dark dc-electrical conductivity with the absolute temperature for these bulk glasses in the temperature range of 293 K-435 K. It was observed that, dc-electrical conductivity was found to have very similar behavior except the magnitudes over the studied range of the chalcogenide Cd₅₀S₅₀ - _xSe_x glassy compositions (30 at.% \leq x \leq 50 at.%). It was evident also from Fig. 1 that, the dcconductivity increases exponentially with increasing temperature for all CdSSe samples. This indicates that the conduction is through an activated process, which also shows the semiconductor behavior of the glassy bulk CdSSe samples. This consolidates that, the same conduction mechanisms are dominant for all studied bulk Cd₅₀S_{50 - x}Se_x glasses [17,26]. Furthermore, the dc-electrical conductivity (σ_{dc}) was found to be increased slowly by raising the temperature up to about 370 K. This implies that conduction occurs in this region via the variable range hopping of the charge carriers in the localized states near the Fermi level, which is predicted by Mott's variable range hopping model [30,31,42]. At higher temperatures, the electrical conductivity has increased rapidly over the residual temperature range. This indicates that, the conduction

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