Abstract: High pure starting materials were used for the preparation of In$_n$S$_n$ crystals in the form of large cylindrical ingots of black and a circular and were identified by X-ray analysis. In$_n$S$_n$ single crystals were grown by a modified Bridgman technique. Measurements of electrical conductivity ($\sigma$), Hall Effect ($R_H$) and thermoelectric power (TEP) were performed over a wide range of temperature. Throughout these measurements, various parameters such as type of conductivity, energy gap width as well as ionization energy, effective mass of charge carriers, carrier mobility, diffusion coefficient, relaxation time and diffusion length for both majority and minority carriers were found. Also the value of figure of merit was calculated. All results were discussed and analyzed. Studies for such samples are very important and necessary in order to understand their use as elements for energy conversation and their use as element in electronic devices.

Key words: hexaindium heptasulfide-semiconductor – single crystal- $\sigma$, $R_H$, $\alpha$

INTRODUCTION

The sulfur indium (In-S) system is a binary system (Zavrazhnov et al. 2007) which consists of one of the most complex system among the A$^{III}$ B$^{VII}$. The majority of 111-V1 materials have been identified as semiconductors, such as In$_n$S$_n$, InS, In$_x$S$_{1-x}$, etc. These semi-conductors have attracted attention because of their applications especially in the photovoltaic domain, in nonlinear optic and optoelectronic devices like infrared detectors (Abdallah et al. 2006).

In particular, in this work we have chosen the In$_n$S$_n$ compound, which possesses many scientifically interesting and technological important properties. It has been identified as a semiconductor, with typical band gap in the range 0.64 - 0.75 eV (Qasrawi et al. 2006 and Gamal, 1997). This semiconductor has attracted much attention because of its potential application in photovoltaic and optoelectronic devices, such as light sources and infrared detectors (Abdallah et al. 2009). Literature concerning the preparation and physical properties of In$_n$S$_n$ crystal is relatively rare due to the difficulty of growing large single crystals (Abdallah et al. 2006). Some of the physical properties of this compound have been investigated. Several experimental studies have been carried out on In$_n$S$_n$ material which permit to determine the absorption band edge, the long-wave optical phonons (Gasanly et al. 1981), infrared reflection spectra and dielectric permittivity (Gasanly et al. 1978), electronic structure (Abdallah et al. 2006), luminescence properties (Gasanly et al. 1976), temperature dependent absorption band edge (Tagirov et al. 1978). With these properties In$_n$S$_n$ monocrystal constitutes a new candidate for technological applications. In spite of the above reported studies, literature still lacks of the information about some physical properties. The purpose of this work is to report these properties for modified Bridgman technique – grown In$_n$S$_n$ single crystal through the electrical conductivity, Hall Effect and thermoelectric power measurements and analysis.

Experimental Techniques:

2-1- Preparation of In$_n$S$_n$ in Single Crystal Form:

The compound In$_n$S$_n$ were prepared by direct melting of the elements taken in stoichiometric ratio and placed in sealed quartz ampoules evacuated to about 10$^{-5}$ Torr. The silica tube has a constricted sharp end at the bottom to facilitate seeding in the growth process. The quartz ampoule is washed with pure alcohol and hot distilled water, and then coated with a thin layer of graphite to prevent contamination of the charge on the internal surface of the ampoule. Stoichiometric quantities of high purity indium and sulfur (99.9999%) were reacted in evacuated sealed silica tubes 37.7143 g. In and 12.2857 g.S representing 75.4286% indium and 24.5714% sulfur were used as starting materials. The reaction was performed in a specially constructed three
zone tube furnace described previously (Hussein et al. 1989) using Bridgman technique. In order to obtain a greater degree of crystallinity, the growth process was carried out at a rate not exceeding 1.2 mm h\(^{-1}\). The tube was kept in the high temperature zone at 980 K for about 24 h. In order to achieve complete reaction of the whole content. During the melting process, the ampoule was frequently agitated in order to intermix the constituents to ensure homogeneity of the melt. The tube was gradually lowered with the required rate through the furnace from the high temperature zone to the zone with temperature corresponding to the crystallization (952 K) according to the phase diagram (Zavrazhnov et al. 2006). Finally the ampoule enters the cooler zone of the furnace, where the temperature is below the melting point. As the ampoule to be interred the low temperature zone, crystallization proceeds until all the contents solidify. The time required for this process is about two weeks. The single crystallinity of the product was verified by means of X-ray diffraction technique. The prepared material showed that it is strongly crystalline as identified with diffraction chart, and the diffraction data did not show the presence of any other phase. The monoclinic crystals of In\(_2\)S \(_2\) appear in the form black and a circular cylindrical ingot.

2-2- Measuring Technique:

For studying the electrical conductivity and Hall Effect, the sample was prepared in a rectangular shape. After polishing processes the sample dimensions were 9.5 x 3.7 x 2 mm\(^3\). This means that the sample has a length of three times its width. This is useful to avoid the Hall voltage drop according to Isenberg recommendation. The electrical conductivity and Hall Effect measurements were measured using a dc four probe method. The sample was placed in an evacuated Pyrex cryostat (10\(^{-3}\) Torr). The cryostat works as a liquid nitrogen container and was supported with electric heaters in cases of low-and high-temperature measurements, respectively. Electrical measurements were made with the aid of silver past contact. The ohmic nature of the contacts was checked by recording the current-voltage characteristics. A study of the Hall Effect was carried out in magnetic field of 0.55 Tesla employing a direct current. In order to avoid thermogalvanomagnetic effects, several measurements were carried out for temperature values, by reversing the direction of both the current and magnetic field. Detail of the experimental Equipment described elsewhere. For the purpose of thermoelectric power measurements we utilized the original shape of the product crystal, i.e., the cylindrical form. Only the length is adjusted to be 5 mm, while the crystal cross section was 10 mm in diameter.

In the TEP measurements, an evacuated calorimeter (10\(^{-3}\) Torr) was used to protect the sample from oxidation and water vapor condensation at high and low temperatures, respectively. The calorimeter has two heaters; the outer heater (the external source) discharges its heat slowly to the specimen environment. The inner heater (connected to the lower end of the crystal) was made purposely to properly control the temperature and its gradient. Along the specimen, the measurements were carried out by the compensation method with a high-sensitivity potentiometer. Simultaneous measurements of temperature and the potential difference were carried out to increase the accuracy of measurements. Details about the apparatus and the method of measurements are outlined elsewhere.

RESULTS AND DISCUSSIONS

The temperature dependence of the electric conductivity in the In\(_2\)S \(_2\) crystals were carried out in the temperature range 188 – 558 K, as shown in Fig (1). The curve shows the typical semiconductor behavior. We can see that \(\sigma\) increases slowly in the low temperatures (the extrinsic region). This is due to liberation of the ionized acceptors from the impurity level. The impurity ionization energy \(\Delta E\) was found to be 0.14 eV. As illustrated in the figure a much less rapid increase in the conductivity is observed in the low temperature range with a linear relation up to 278 K. After this region the electrical conductivity exponentially increase with relatively speed rate in the temperature range extending from 278 up to 300 K, after which \(\sigma\) decrease gradually with a constant rate. The fall in the electrical conductivity was due to a decrease of the mobility, since the carrier density in this temperature region remained practically constant, until the intrinsic region is reached. At temperatures above the transition point, the conductivity rose rapidly. The temperature dependence exhibited a transition from a region of lower slope to one of higher slope. The slopes of the curve increased with increasing temperatures because of the carriers being excited from the extended state of the valence band into the conduction band. The width of the forbidden zone as calculated from the slope of the curve in the high temperature region according to the relation

\[
\sigma = \sigma_0 \exp \left( \frac{-\Delta E_g}{2kT} \right)
\]
This was found to be 0.66 eV. This pattern of change in the electrical properties is due to the appearance of impurity and intrinsic conductivity, and to the variation of the hole mobility and concentration with temperature.

![Graph](image1)

**Fig. 1:** plot of Ln $\sigma$ versus $10^3/T$ for single crystal p – type In$_3$S$_3$.

This work was extended to cover the effect of the temperature of the Hall coefficient $R_n$ in the same temperature range of $\sigma$. Fig (2) shows the relation between $R_n$, $T^{3/2}$ and $10^3/T$. From the curve and data the following facts can be summarized (1) values of $R_n$ are positive in the entire temperature range of investigation. This indicates that the compound In$_3$S$_3$ monocrystal is a brilliant P-type semiconductor (2) The Hall coefficient at room temperature was evaluated as $8.47 \times 10^4$ cm$^2$/c (3) from this figure, we have also showed three regions of the curve, this is in agreement with the observation of the conductivity curves. (4) The forbidden gap width is obtained to be 0.7 eV. Also, we estimated $\Delta E_s$ (from the low temperature part) to be 0.15 eV, these data are approximately in a agreement with those obtained from the electrical conductivity data and agrees with the optically determined band gap (Tagirov et al. 1978).

![Graph](image2)

**Fig. 2:** The relation between $R_n$, $T^{3/2}$ and $10^3/T$ for In$_3$S$_3$ monocrystal
As a result of availability of both σ and R_{H} data, we obtained Hall mobility temperature dependence as shown in Fig (3). The general behavior of µ against T can be divided into two regions, in the low temperature region µ increase with increasing temperature following the low µ ∝ T^{1.35}, such behavior is a characteristic of scattering mechanism of charge carriers with ionized impurities. In high-temperature range which is the intrinsic conduction region, the Hall mobility decrease with increasing temperature according to low µ ∝ T^{−1.9} which indicates that lattice scattering are responsible for scattering processes. At room temperature the Hall mobility 5091.4 Cm² V⁻¹ S⁻¹. The charge carriers’ concentrations were calculated from Hall coefficient date.

![Fig. 3: variation of Ln µ with Ln T for In_{x}S_{1-x} single crystal](image1)

Variation of the carrier density versus reciprocal temperature is depicted in Fig (4). At low temperatures (below 278 K) we computed the depth of the acceptor level to be 0.16 eV. At high temperatures the crystal exhibits the intrinsic behavior and the energy gap width of In_{x}S_{1-x} was found to be 0.7 eV. The value of the hole concentration at room temperature is 7.38x10¹⁷ cm⁻³.

![Fig. 4: dependence of carrier concentration of In_{x}S_{1-x} single crystal](image2)
In the present work measurements of TEP of In$_3$S$_2$ crystal were carried out in the temperature range 182 – 410 K. Fig (5) shows the relation between $\alpha$ and $10^3/T$. It is clear from the graph that the general mode of $\alpha$ variation against $T$, decrease rapidly with temperature, reaching a minimum value at nearly 300 K as a result of the compensation process which takes place in this temperature range. With further rise in temperature, a much increase in the magnitude of $\alpha$ has been observed. Such behavior is expected in this intrinsic range where generation of both carriers contributes to the increases of $\alpha$ value.

![Graph showing the relation between $\alpha$ and $10^3/T$ for In$_3$S$_2$ single crystal](image)

Fig. 5: plot of the thermoelectric power and $10^3/T$ for In$_3$S$_2$ single crystal

Studying the TEP in the intrinsic region yields information about the carrier mobilities, and effective masses of the free charge carriers as described by (Johnson et al. 1953)

$$\alpha = \frac{K}{e} \left[ \frac{b - 1}{b + 1} \left( \frac{\Delta E_p}{2KT} + 2 \right) + \frac{1}{2} \ln \left( \frac{m_{n}^{*}}{m_{p}^{*}} \right) \right]$$

(2)

Where $K$ is Boltzman's constant, $b$ is the ratio of the electron to hole mobilities, $\Delta E_p$ is the energy gap, $m_{n}^{*}$, $m_{p}^{*}$ are the effective mass of both electron and holes, respectively. The ratio of the electron and hole mobilities was determined from the slope of the line, its value was found to be $b = \mu_n / \mu_p = 1.207$. On considering the value of $\mu_p = 5091.4$ Cm$^2$ V$^{-1}$ S$^{-1}$ which was obtained from the Hall measurements data, the value of electron mobility estimated and found to be $\mu_n = 6147.8$ Cm$^2$ V$^{-1}$ S$^{-1}$. Also the ratio between the effective masses of both electrons and holes can be evaluated from the intersection of the curve. This ratio has been evaluated as $m_{n}^{*} / m_{p}^{*} = 0.23$

Another formula has been suggested by Wilson (Wilson et al. 1953) to be employed in the extrinsic region (low temperature) was used

$$\alpha = \frac{K}{e} \left( 2 - \ln \left( \frac{P h^2}{2(2\pi m_{p}^{*} KT)^{3/2}} \right) \right)$$

(3)

This formula leads us to represent the relation between $\alpha$ and InT as shown in Fig (6).

Calculation of the effective mass of holes from the intersection of the curve give the value $m_{p}^{*} = 5.38 \times 10^{-27}$ kg. Using these values with the previously ratio $m_{n}^{*} / m_{p}^{*}$, we have obtained the effective mass of electron $m_{n}^{*} = 1.24 \times 10^{-27}$kg. The calculated values of the effective masses of both minority and majority carriers can be used to determine the relaxation time for both current carriers. Its value for electrons comes to $T_e = 4.76 \times 10^{-14}$ sec and for holes equal to $T_p = 1.71 \times 10^{-16}$ sec. Another important parameter can be deduced
with the aid of the obtained values of $\mu_n$ and $\mu_p$ using the Einstein relation ($D = kT\mu /e$), from which the diffusion coefficient for both carriers (electrons and holes) can be evaluated to be $D_n = 159.07 \text{ cm}^2/\text{sec}$ and $D_p = 131.7 \text{ cm}^2/\text{sec}$.

The diffusion length, as another important physical parameter, can be deduced by using the formula ($L = \sqrt{D_t}$). The diffusion length for electrons $L_n = 2.8\times10^{-7} \text{ cm}$, while for holes $L_p = 1.5\times10^{-7} \text{ cm}$. We can notice the following remarks. (1) The diffusion constant as noticed is inversely proportional to the effective mass of hole and electron. (2) The electron mobility as calculated is higher than the hole mobility, this result is acceptable since the holes effective mass is greater than that of the electrons. The effectiveness of a material for thermoelectric application is determined by the dimensionless figure of merit $Z_T$ (Kuroski et al. 2003), where $T$ is the absolute temperature and $Z = \frac{\alpha^2\sigma}{k}$ ( $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $k$ is the thermal conductivity ). However the term figure of merit is a measure of both performance and efficiency of a certain thermoelectric element. For our best In$_x$S$_{1-x}$ samples the obtained value of $Z = 4.7\times10^{-11}$ which permits the practical application as thermoelectric element. Fig (7) represents the dependence of TEP on the natural logarithm of electrical conductivity according to the relation (Shmida et al. 1972).

$$\alpha = \frac{K}{e} \left[ 4 + \frac{\ln (2\pi m_i^* k T)^{3/2}}{(2\pi k)^{3/2}} \right] \frac{K}{e} \ln \sigma$$

$\alpha$ decreases as the electrical conductivity increases, the decrease of TEP with the electrical conductivity may be due to the decrease of the carrier density.

Fig. 6: relation between thermoelectric power and Ln $T$ for In$_x$S$_{1-x}$ single crystal

The same behavior is observed when we plot $\alpha$ versus carrier density for the In$_x$S$_{1-x}$ sample, as shown in Fig (8).

**Conclusion:**

We have grown In$_x$S$_{1-x}$ single crystals by using the modified Bridgman technique, and have investigated the electrical conductivity, Hall Effect and TEP measurements. The In$_x$S$_{1-x}$ is a semiconductor with $\Delta E_g = 0.135 \text{ eV}$ and $\Delta E_i$ equal to 0.7 eV. The Hall coefficient $R_H$ and Seebeck coefficient $\alpha$ are positive over the temperature
range of investigation, indicating that In\textsubscript{5}S\textsubscript{7} is a p-type semiconductor. The behavior of the carrier density and Hall mobility with temperature was analyzed, and the scattering mechanism was checked. Various semiconducting parameters, such as effective mass of a charge carriers, carrier mobilities, diffusion coefficient, and relaxation time, diffusion length for both majority and minority carriers have been found. Also determination of figure of merit Z, indicated that the possibility of practical application our crystal in the field of energy conversion. The proposed treatment of the physical data sheds new light on the main physical parameters of In\textsubscript{5}S\textsubscript{7}, single crystals.

![Graph](image1)

**Fig. 7:** variation of thermoelectric power of In\textsubscript{5}S\textsubscript{7}, single crystal with the electrical conductivity.

![Graph](image2)

**Fig. 8:** dependence of thermoelectric power of In\textsubscript{5}S\textsubscript{7} on carrier concentration

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