# Transport Properties of $GaInSe_2$ Crystals

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**Abstract:** High quality of $GaInSe_2$ crystals were prepared by modified Bridgman technique, the transport properties were investigated. The dependence of electrical conductivity, Hall effect, Hall mobility and charge carriers concentration on temperatures was performed in the temperature range (203 K - 443 K) while thermoelectric power measurements were carried out in the temperature range (280 K - 495 K). From these measurements the conductivity of the crystals was found to be p – type, the electrical conductivity, Hall coefficient and hole concentration at 300 K were found to be 2.92 x $10^{-6}\Omega^{-1}$ $cm^{-1}$, 4.18 x $10^{9}cm^{3}/C$ and 1.49 x $10^{9}$ $cm^{-3}$ respectively. The Hall mobility was found to be 12.19 x $10^{3}$ $cm^{2}V^{-1}s^{-1}$. The energy gap was evaluated to be 1.8 eV. Throughout joining the electrical with thermoelectric power measurements many physical parameters were estimated. The effective mass of holes and electrons were determined at room temperature to be 1.95 X $10^{-32}$ kg, and 7.01 X $10^{-39}$ kg respectively. The hole and electron diffusion coefficient were found to be 315.4 $cm^2/s$ and 782.94 $cm^2/s$ respectively. The relaxation times for holes and electrons were calculated and yields the values 1.49 x $10^{-16}$ s and 1.33 x $10^{-22}$ s respectively. Also the diffusion length for holes and electrons were obtained as 2.17 x $10^{-7}$ cm 3.22 x $10^{-10}$ cm respectively. In addition to these pronounced parameters the efficiency of the thermoelectric elements was evaluated which leads to better application in the field of energy conversation technique.
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## 1. Introduction

The $A^{III}B^{III}C_2^{VI}$ ternary sulfide and selenide semiconductors have long been investigated due to their potential applications as nonlinear materials in the infrared wavelength range [1-3]. Among them $GaInSe_2$ is a layered compound and the interesting this materials stimulated not only by its fundamental properties, but also by possible practical applications [4]. Furthermore, it could be easily intercalated with foreign ions, atoms and molecules, thus offering the realistic prerequisites for producing controllable superlattices based on it.

Although the ternary semiconducting chalcogenides have been investigated extensively in recent years [5], very few investigations have been performed on $GaInSe_2$ [6 – 8]. The crystal structure of this compound was reported [9].

In this paper we perform the preparation and characterization (dc electrical conductivity, Hall coefficient, carrier concentration, charge carrier mobility and thermoelectric properties) of $GaInSe_2$ crystals. These investigation are essential for the understanding of the materials and consequently open up also new possible of practical applications.

## 2. Experimental

Crystals of $GaInSe_2$ were grown from a melt using a modified Bridgman technique. The silica glass ampoules were cleaned and then weighted with high-purity (6 N) elements: gallium (23.474 %), indium (26.256%) and selenium (50.268%). The ampoule is coated internally with a thin layer of pyrocarbon to prevent the produced ingot from adhesion with silca tube. The ampoule was evacuated to a pressure of less than$10^{-6}$ Torr and sealed off. Care was taken when heating the ingot to control the high Se vapor pressure and the exothermic reaction between Se and In. The mixture was slowly heated (1.5 $^{o}C$ $min^{-1}$) over a temperature range of 200 – 250 $^{o}C$ to minimize the risk of cracking the ampoule. The temperature was kept at 950 $^{o}C$ for two days to homogenize the melt [9]. The crucible was then lowered to the cold side at 300 $^{o}C$ at a speed of 1.6 $mmh^{-1}$. The growth method and the experimental apparatus have been discussed in details elsewhere [10].The producing ingot has black single crystals with metallic luster as that obtained by other author [9].

X - ray pattern proves that there is no any other phases except $InGaSe_2$ and our x – ray powder diffraction (XRD) data have shown a good agreement with standard international center for powder diffraction data JCPDS No. 77 – 1921.

The platelet was cleaved for the electrical conductivity and Hall measurements, the sample dimension was adjusted to be 1.03 x 0.34 x 0.26 $cm^3$

by gentle cleavage. For the purpose of thermoelectric measurements the length was adjusted to be 5 mm, while the crystal cross-section was 8 mm in diameter. Both electrical and Hall effect measurements were carried out in an evacuated Pyrex cryostat designed for this purpose [11]. For studying the thermoelectric power an evacuated calorimeter was used to protect the sample from oxidation and water vapor condensation at high and low temperature respectively. The calorimeter has tow heaters. The outer heater (the external source) discharge, its heat slowly to the specimen environment. The inter heater (connected to the lower end of the specimen) was used purposely to properly control the temperature and its gradient along the specimen. Details about the apparatus and method of measurements are outlined elsewhere [12, 13].

The silver conducting paste contacts were soldered on the $GaInSe_2$ to carry out the electrical conductivity, Hall effect and thermoelectric measurements. The ohmic nature of the contacts was verified by recording the current – voltage characteristics for forward and reverse directions. From the current – voltage characteristics, the ohmicity coefficient has the nearest value to 1.

## 3. Results & Discussions

### 3.1 Electrical Properties for $GaInSe_2$

The present electrical conductivity work was carried out in a temperature range extending from 203 K up to 443 K. Fig. 1 shows the electrical conductivity $\sigma$ *vs.* $10^3/T$ for $GaInSe_2$ crystals. As shown, in the investigated temperature range, the logarithm of the conductivity showed a linear dependence on the temperatures with two modes of conduction in addition to the transition region that appeared between them. From the relationships between the conductivity and the temperature, the energy gap is deduced to be 1.8 eV while the ionization energy is 0.15 eV, these results agreed with the previous literature data [7]. The increase of $\sigma$ in the intrinsic part (above 368 K) is regarded as a result of excitation of the carriers from the valence band to the conduction band. However in the extrinsic part (below 263 K), $\sigma$ increment is regarded as a result of ionization of impurity atoms.

The transition region (263 – 368 K) is characterized by a slight increase of $\sigma$ as the temperature increases. This is due to the dominant charge carrier concentration effect in this range. At room temperature, $\sigma$ has the value $2.92 \times 10^{-6}\ \Omega^{-1}\ cm^{-1.}$

The Hall effect measurements were performed in the same temperature range. The sign of $R_H$ indicates that $GaInSe_2$ behaves as a p – type semiconductor. The relationship between $R_H T^{3/2}$ and $10^3/T$ was plotted in Fig. 2. From the figure the forbidden gap width is obtained to be 1.8 eV. Whereas the ionization energy as calculated from the same curve (at low temperature) is 0.15 eV.

Simultaneous measurements of the electrical conductivity and Hall effect permit us to investigate the influence of temperature on Hall mobility. This is typically presented in Fig. 3. The work of the Hall mobility enabled us to gain a good interpretation to the scattering mechanism of the charge carriers. From the results we noted that: -

1- The relationship between μ and T in the extrinsic region of temperature justifies the following relationship $\mu \alpha T^{3.3}$. Such dependence leads to the assumption that the scattering mechanism is due to the ionized impurities in this range.
2- In high temperature range (intrinsic), the mobility obeys the power law $\mu \alpha T^{20}$. Based on this, we consider that the effect of the scattering optical phonon is the main reason for the scattering mechanism in this range.

Fig. 4 depicts the results of charge carrier density *vs.* reciprocal temperature. There are three regions of this curve, namely the extrinsic (low temperature side 203 - 263 K), the transition (263 – 368 K) and the intrinsic region (above 368 K). We calculated the energy gap width from the slope of of the curve in the intrinsic region. It is found to be 1.82 eV close to that deduced from $R_H T^{3/2}$ curve. Also the calculation in the extrinsic region showed an acceptor level of impurities at 0.15eV. The room temperature hole concentration is $1.49 \times 10^9\ cm^{-3}$.

### 3.2 Thermoelectric Properties for $GaInSe_2$

We measured the thermoelectric power in a wide temperature range from 280 K up to 495 K. Fig 5 shows the relationship between $\alpha$ and T for $GaInSe_2$. From the figure we can find that the sign of $\alpha$ is positive indicating that $GaInSe_2$ is P – type semiconductor. The value of $\alpha$ is found to decrease continuously with increasing temperature in the range from 280 K up to 345 K. This leads to the assumption of presence of trapping centers or some crystal defects in the direction of the carrier flow. Up to 375 K $\alpha$ is increased with temperature. This is attributed to the thermal activation of the charge carriers in this range, where generation of both carriers contribute to the increases of $\alpha$ value. The value of $\alpha$ at room temperature is $(75\ \mu V\ K^{-1})$.

For more understanding of the behavior of TEP we used our electrical conductivity and Hall effect data to construct Figs. 6 and 7. From Figs. 6, 7 and their comparison with Fig. 5 we can conclude that the concentration of the charge carriers is the dominant factor that governs $\alpha$ .

### 3.3 Transport Parameters for $GaInSe_2$

Some major semiconductor parameters for $GaInSe_2$ crystals, such as the carrier effective mass, electron – to - Hall – mobility ratio, relaxation time of majority and minority carriers, diffusion coefficient and diffusion length can be estimated by using the formulas suggested in refs. [14, 15]. So we plot Figs. 8, 9 to show the relation between $\alpha$ and $10^3$ / T, $\alpha$ and Ln (T) respectively. The effective mass for $GaInSe_2$ crystals is $m^*_p = 1.95 \times 10^{-32}$ kg, where $m^*_n = 7.01 \times 10^{-39}$ kg. The value of ratio $\mu_n/\mu_p$ is found to be 2.4. hence by using the value of $\mu_p$ , the electron mobility can be deduced and its value is found to be $30.28 \times 10^3$ $cm^2$/V.s. The results indicate that the electron mobility is higher than the hole mobility. This is acceptable since the hole effective mass is greater than that of electrons.

Also the values of the relaxation time were calculated to be $\tau_p = 1.49 \times 10^{-16}$ s and $\tau_n = 1.33 \times 10^{-22}$ s, for holes and electrons respectively.

The diffusion constants for electrons and holes were calculated to be $D_p = 315.4$ $cm^2$/s and $D_n = 782.94$ $cm^2$/s. The diffusion length for holes is $L_p = 2.17 \times 10^{-7}$ cm, while for electrons is $L_n = 3.22 \times 10^{-10}$ cm. The data for estimated parameters was different compared to those published [6, 7]. The possible reasons for this discrepancy are detrapping of charge carriers and non-uniformity of an electric field [16, 17].

In addition to these pronounced parameters the efficiency of the thermoelectric element was evaluated to be $3.4 \times 10^{-8}$ $K^{-1}$.

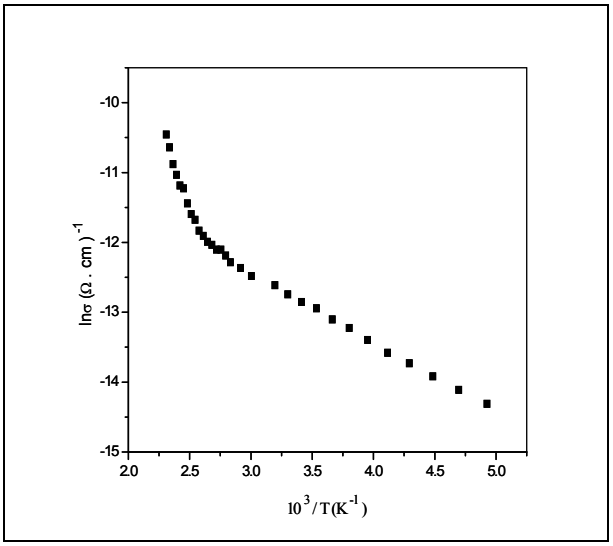


**Fig. 1:** Temperature dependence of electrical conductivity for $GaInSe_2$ crystals.

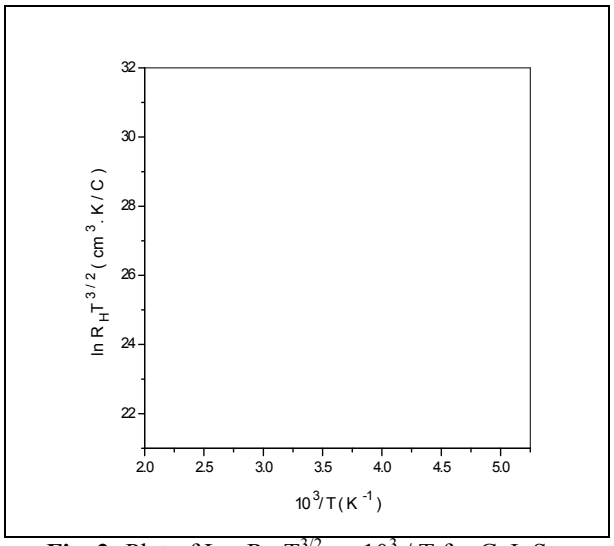


**Fig. 2:** Plot of Ln. $R_H T^{3/2}$ *vs.* $10^3$ / T for $GaInSe_2$ crystals.

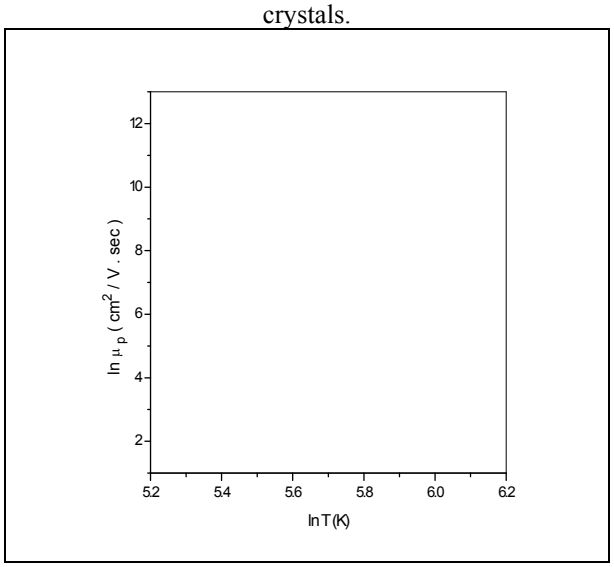


**Fig. 3:** Hall mobility as a function of temperature for $GaInSe_2$ crystals.

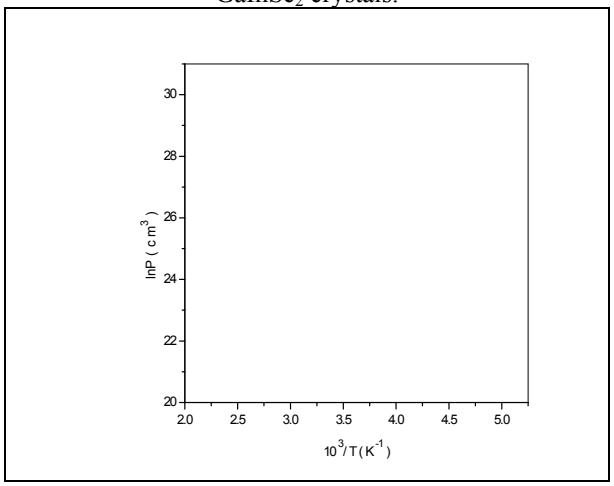


**Fig. 4:** Variation of the carrier density versus reciprocal temperature.

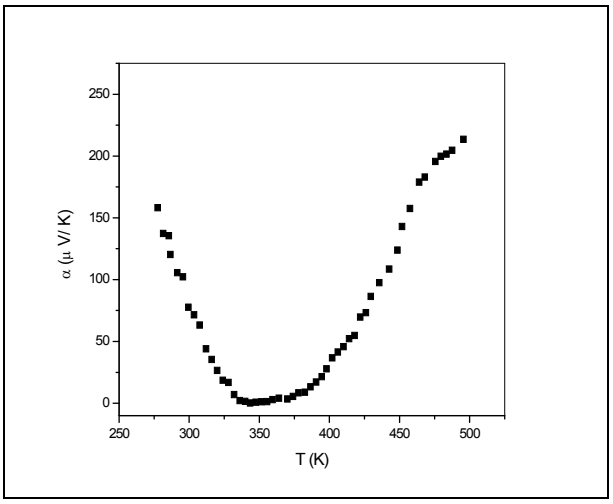


**Fig. 5:** Plot of thermoelectric power and (T)

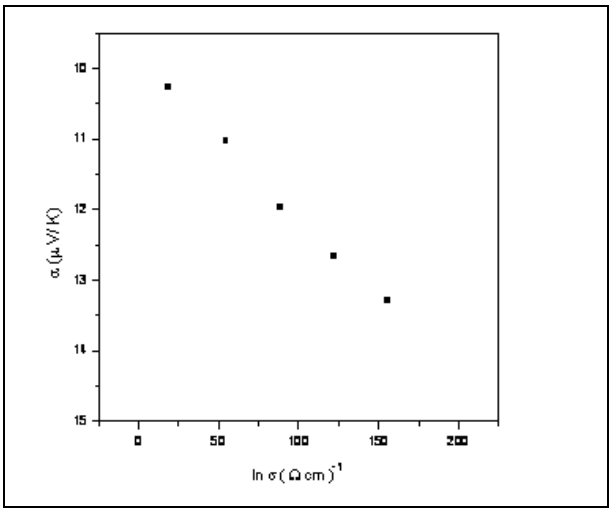


**Fig. 6:** Relation between thermoelectric power and electrical conductivity.

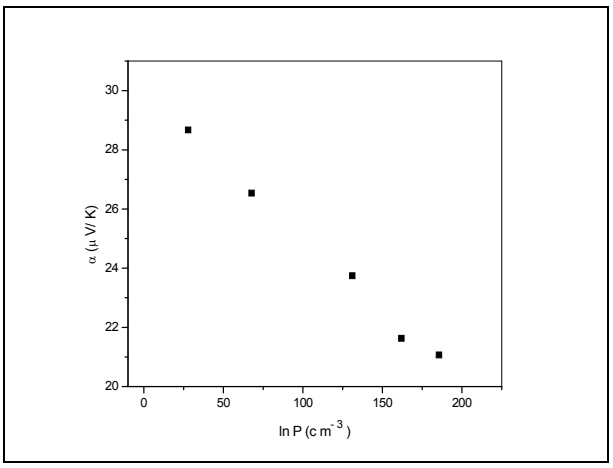


**Fig. 7:** Relation between thermoelectric power and charge carrier density.

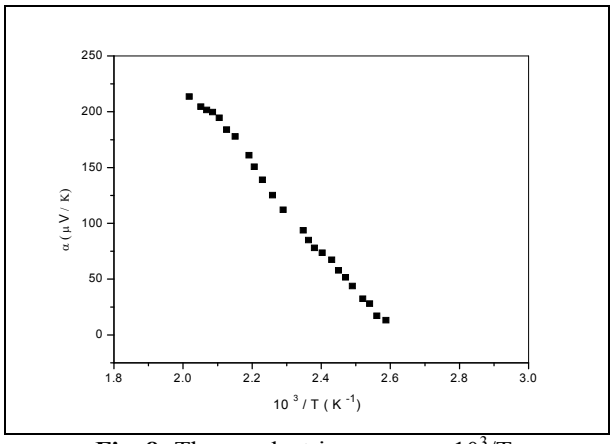


**Fig. 8:** Thermoelectric power *vs.* $10^3$/T.

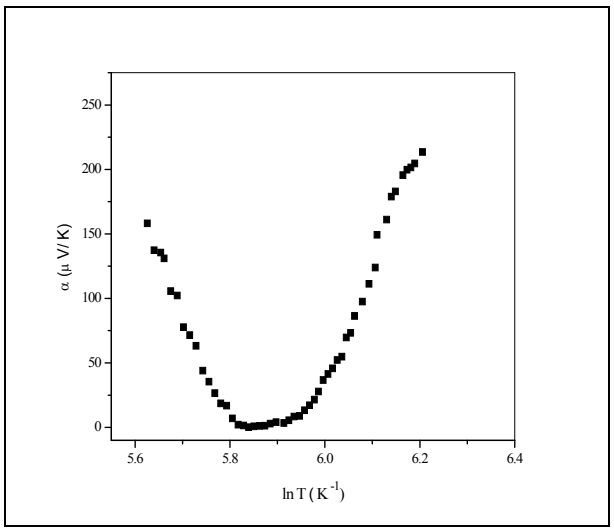


**Fig. 9:** Plot of thermoelectric power and Ln (T).

**Conclusion**

- In the present work $GaInSe_2$ crystals were grown by modified Bridgman technique.
- The electrical conductivity at room temperature has the value $2.92 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$. The energy gap is deduced to be 1.8 eV while the ionization energy is 0.15 eV.
- The sign of $R_H$ indicates that $GaInSe_2$ behaves as a p – type semiconductor. The room temperature hole concentration is $1.49 \times 10^9$ $cm^{-3}$.
- The scattering mechanism in low temperature range is due to the impurities. While in high temperature range (intrinsic), the effect of scattering optical phonon is the main reason for the scattering mechanism.
- The sign of $\alpha$ for $GaInSe_2$ is positive indicating that the conducting mechanism in this sample is of P – type. The value of $\alpha$ at room temperature is (75 μV $K^{-1}$).

- The combination of electrical and thermoelectric power (EMF) measurements makes it possible to deduce a lot of physical parameters such as mobility's ratio, effective masses, relaxation times, diffusion lengths and diffusion coefficient for majority and minority carriers at room temperature.
- The obtained parameters indicates that $GaInSe_2$ have the possibility for different applications.

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