JKAU: Sci., **Vol. 23** No. 2, pp: 31-44 (2011 A.D./1432 A.H.)
DOI: 10.4197 / Sci. 23-2.3

Growth and Transport Properties of some Gallium Chalcogenides from the Group $M_2^{III} X_3^{VI}$ Semiconductor Compounds

A.T. Nagat, F.S. Bahabri, R.H. Orainy, M. Abou Zied[1], S.E. Al-Garni and **W.S.Al-Ghamdi**

Physics Department, Faculty of Sciences for Girls, King Abdulaziz University, Jeddah, Saudi Arabia
[1] Physics Department, Faculty of Science, South Valley University, Qena, Egypt

Abstract. High quality α – $Ga_2 S_3$ single crystal were grown by a modified Bridgman method. The crystals were identified by X-ray diffraction. Measurements of electrical conductivity and Hall effect were performed in the range [278 – 563K] and [158 – 496K] for thermoelectric power (TEP). From these measurements the conductivity of the crystals was p-type. The electrical conductivity, Hall mobility, and hole concentration at 300K were found to be about $2.5x10^{-5}$ Ω^{-1} cm^{-1} , $1.67x10^{4}$ cm^2 v^{-1} s^{-1} and $9.58x10^{9}$ cm^{-3} respectively. The energy gap was found to be 1.75 eV. From the obtained experimental data several physical parameters such as diffusion coefficient, diffusion lengths, effective masses, relaxation time of carriers were estimated. In addition to these pronounced parameters, the efficiency of the thermoelectric element [figure of merit] was evaluated which leads to better application in the field of energy conversion technique.

Keywords: gallium sesquisulphide, single crystals, DC conductivity, Hall Effect, thermoelectric power.

1. Introduction

$M_2 X_3$ compounds (where M = Ga, In, TI and X = S, Se or Te) are the simplest [1] examples of materials whose structure is based on the tetrahedral atomic coordination as in the zincblende (ZB) structure, but in

which some atomic sites are empty. In the case of $M_2 X_3$ compounds one – third of the cation sites of the (ZB) or wurtzite structures available to group III atoms is vacant. It is apparent from the chemical formula that the valences are satisfied. In some of these compounds, the vacancies can be ordered to form a super lattice between certain temperatures. Although many recent papers have dealt with $M_2^{III} X_3^{VI}$ - type compounds, their properties remain rather confusing. The reason for this is that the compounds of this type are defective in respect of their metal atoms: only two – third, of all cationic positions are occupied and every third site in the cation sub - lattice remains vacant. Consequently, the presence of these large number of intrinsic defects strongly affects the motion and scattering of current carriers and phonons, causing their thermal and electrical properties. Studies of $M_2^{III} X_3^{VI}$ compound have attracted the attention of researchers [2] because of their importance in photovoltaic applications. Moreover, these compounds have also reliable properties for applications in electro- thermal devices, such as solid solution electrodes. $Ga_2 S_3$ is a member for the above family and have very interesting electrical, photoelectric, thermoelectric and optical properties[3-7]. The $Ga_2 S_3$ compound is a very promising material for blue – green light emitting devices[8] for having wide direct band gap.A description of the phase diagram for Ga–S has been reported[9-10]. Two types of compounds are found[1] "$Ga_2 S_3$" occurs in four forms and[2] two varieties of GaS are found. Several works[11-14] on the crystal structure have been reported, photoluminescence properties of $Ga_2 S_3$ have been reported[15]. The effect of doping of transition – metal and rare – earth impurities on the physical properties of Ga_2S_3 have been studied[16-19]. There is considerable scientific and practical value in studying the transport properties. It is very essential to have a knowledge of the transport properties of semiconductor in order to understand their use in solid state energy conversion devices, and other application in microelectronics. The basic transport properties of a material are the electrical conductivity, Hall coefficient and Seebeck coefficient.

Very little work has been done on the $Ga_2 S_3$ crystals. Only a few reports are found in the literature relating to the study of some transport properties of $Ga_2 S_3$. This gives us the opportunity to report this work.

The object of the present investigation is to study the electrical conductivity, Hall Effect and thermoelectric power, and to determine the temperature variation in these properties.

2- Sample Preparation and Measurements

2-1. Crystal Growth

High efficiency, low cost, simple and local design was used for crystal growth. Three zone tube furnace based on Bridgman technique was used in our laboratory. Special technique and precautions were adapted to avoid difficulties in preparing such system containing sulphur. A silica tube was filled with 29.6132 g of gallium (59.2263% of the compound) and 20.3868g of sulphur (40.7737% of the compound). The purity of the starting materials can be stated as being 99.9999%. The silica tube was coated internally with a thin layer of carbon and then sealed under vacuum of 10^{-6} mm Hg.

The ampoule, with its charge was mounted in the first zone of the furnace, where the temperature was higher than the melting point and kept for a suitable time. The melt was driven to the second zone and its temperature was adjusted according to the phase diagram[9, 10] to be equal to the melting point. When the ampoule with its contents enters the third zone, gradual solidification occurs since the temperature is less than the melting point. The movement of the ampoule was very gently and slow (2mm/h) with the aid of the hydraulic mechanical system.

The growth method and the experimental apparatus have been described in detail elsewhere[19]. The single crystalinity of this material was verified by means of x-ray diffraction technique. The resulting single crystals had typical dimensions of 15 mm length and 4.5 mm in diameter, and showed a transparent yellowish-color. The X-ray diffraction analysis showed that these crystals have hexagonal structure with α-phase, which agrees with literature[15]. As usual in case of crystals examinations, the XRD is very useful not only for crystal identification but also for having an idea about the crystal quality. We did conclude the high quality on the basis of the following reasons:

- Firstly, X-ray diagram showed different peaks (corresponding to JCPDS cards) without extra peaks.
- Secondly, the peaks are very sharp and not broad. It is an established fact that the broadenings are functions of the crystal quality.

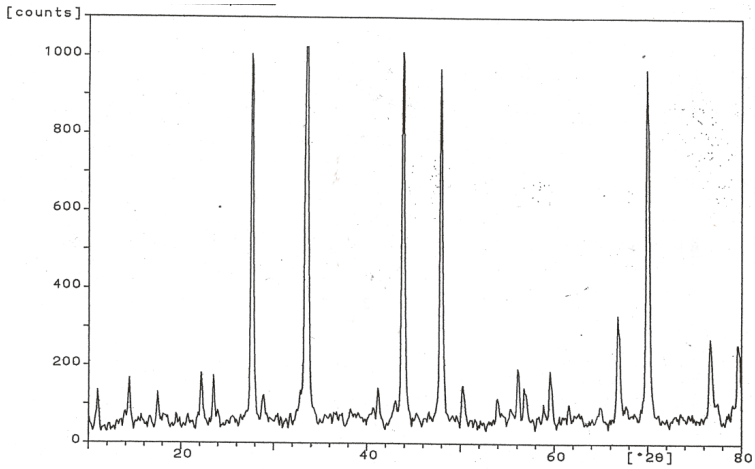

Fig. 1. Shows the X-ray diffraction pattern of α-Ga_2S_3 single crystal.

2-2 Electrical Conductivity and Hall Effect Measurements

Both electrical and Hall measurements were carried out in an evacuated Pyrex cryostat designed locally for this purpose[20]. The cryostat is used as a holder, evacuated container for liquid nitrogen (for low-temperature measurements) and as a support to the electric heater (for high-temperature measurements). For reliable electrical measurements, the electrical contacts were made by painting the sample with high-purity silver paste masks. The ohmic nature of the contacts was checked by recording the I-V characteristics. It was found to be linear and independent of the reversal current. The conductivity and Hall coefficient were measured by a compensation method with conventional dc type measuring system by using a Tinsly UJ33E potentiometer in a magnetic field of 0.5 T. The temperature range of investigation was extended from 278 up to 563 K. All measurements were carried out under vacuum condition of about 10^{-3} Torr.

2- 3 Thermoelectric Power Measurements

For studying the thermoelectric power (TEP) an evacuated calorimeter (10^{-3} Torr) was used to protect the sample from oxidation and water vapor condensation at high and low temperature 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 used purposedly to properly control the temperature and its gradient along the specimen. The

measurement of thermoelectric power was made by establishing a temperature gradient between the two ends of the specimen (not more 5K).

In case of thermoelectric power measurements the investigated crystal was adjusted to be 10 mm in diameter and 5mm in length.

The measurements were carried out by the compensation method with a high-sensitivity potentiometer (UJ33E type). Simultaneous measurements of temperature and the potential difference were carried out to increase the accuracy of the measurements.

Details about the apparatus and method of measurements are outlined elsewhere[21,22]. The sample was supported between two holders, the lower one acting as a heat source and the upper as a heat sink. Two copper constantan thermocouples were used for temperature measurements across the two ends and the thermo EMF in the sample was measured relative to the copper. The thermocouples were made in contact with the upper and lower ends of the crystal sample and were electrically insulated.

3- Results and Discussion

3- 1 Electrical Conductivity and Hall Coefficient.

The temperature dependence of electrical conductivity of α- Ga_2S_3 single crystal sample was studied over temperature range from 278 to 563K. The results were depicted in Fig 2. This curve is quite similar to the semiconductor behavior. From this figure three regions are obtained. The first region (278-358k) represents the extrinsic region, in this region the electrical conductivity increases slowly with temperature and this is due to the fact that the carrier concentration, in this region is determined by the number of ionized acceptors liberated from the impurity level. From the slope of the curve in this region. The impurity ionization energy ΔEa was found to be ≈ 0.3 eV.

The second region from 358 to 473 K represents the transition region. The electrical conductivity increases very slowly with temperature increase. The behavior of σ here is governed mainly by the behavior of both charge carrion concentration and their mobility. The

third region which lies between 473-563 K represents the intrinsic region, where σ increases rapidly.

The excitation of the carriers from the valance band to the conduction band is responsible for this rise of the conductivity where the temperature is high enough. The dependence in this temperature range follows the relation.

$$\sigma = \sigma_0 \exp(-\Delta E_g/2KT) \quad (1)$$

Where σ_0 is constant, ΔE_g the energy gap width. T the absolute temperature and K is the Boltzmann constant. From the above relation the energy gap can be calculated from the slope of this curve. It is found to be 1.98 eV. The room temperature conductivity of this sample is 2.5×10^{-5} Ω^{-1} cm^{-1}.

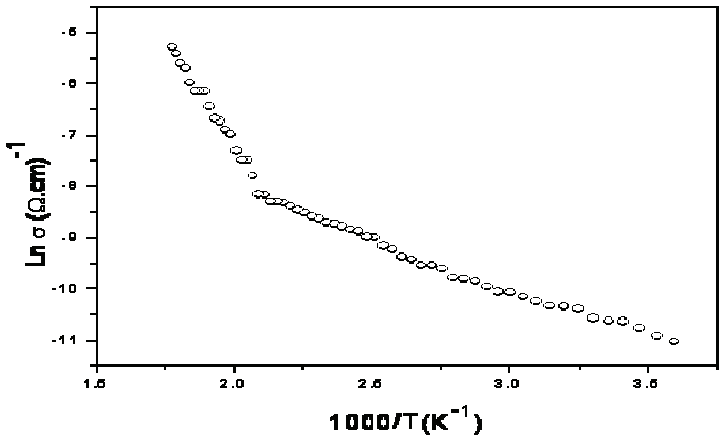

Fig. 2. Electrical conductivity of α- Ga_2S_3 as a function of temperature.

Fig.3 represents the relation between $R_H T^{3/2}$ and $10^3/T$. From the results we can conclude the following:

1- The positive sign of R_H indicates p-type conductivity.

2- This curve consists of three regions, the first region in the temperature range from 278-358K represents the extrinsic region. From the slope of this part, the activation energy is calculated to be $\Delta E_a \approx 0.3$ eV. The second region in the temperature range from 358-473 K, represents the transition region. The third region at high temperature represents the intrinsic region from the slope of this part, the energy gap

is calculated to be $\Delta Eg = 2.0$ eV. This value is in a good agreement with the conductivity measurements. The value of R_H at room temperature equal to 6.52×10^8 cm^3 C^{-1}. A combination of the Hall measurements and electrical conductivity data was used to study the temperature dependence of the mobility of the charge carriers.

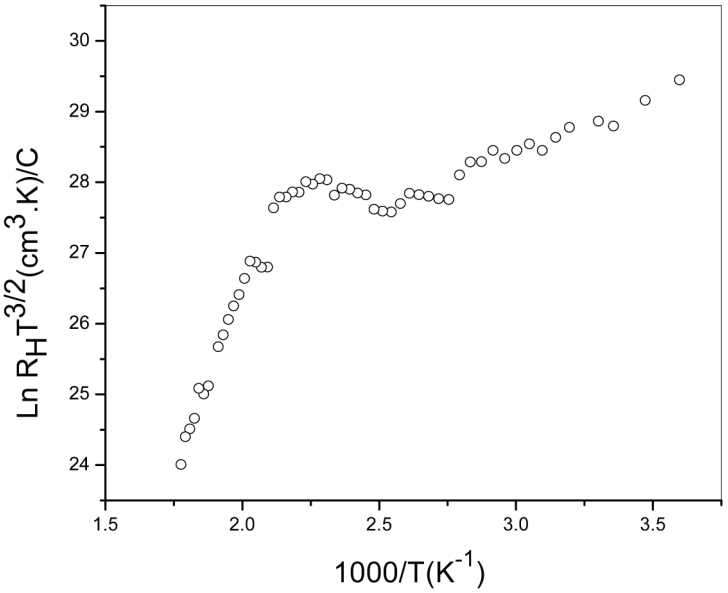

Fig. 3. Relation between $R_H T^{3/2}$ and 10^3/T.

Figure. 4 depicts the variation of μ_H as a function of temperature. The relation $\mu_H \alpha T^n$, governs the variation of the Hall mobility against temperature. The variation of μ_H with temperature can be divided into two regions. In the first region at low temperature, μ_H increases with temperature obeying $\mu_H \alpha T^5$. This behavior agrees with semiconductor behavior. This behavior is characteristic of a scattering mechanism of the charge carriers on ionized impurities. In the second region the Hall mobility decreases with temperature by relation $\mu_H \alpha T^{-3.37}$, which indicates that stoichiometric vacancies and certain defects are responsible for scattering processes. At room temperature the Hall mobility $\mu_H = 1.67 \times 10^4$ cm^2/V. sec. the charge carriers concentration was calculated from Hall coefficient using the relation $P = 1/R_H e$, where p is the hole concentration and e is the electron charge.

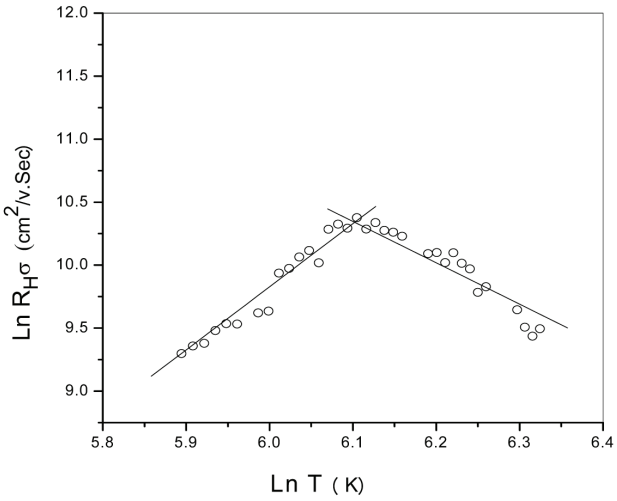

Fig. 4. Behavior of Hall mobility as a function of temperature.

Figure.5 represents the dependence of charge carrier concentration on temperature. From this figure we notice that the concentration of carriers in the extrinsic region increases slowly with increasing temperature, while it increases rapidly with temperature in the intrinsic region. The energy gap calculated from the slope of this curve in the high temperature range is found to be ΔE_g=2.0 eV and the activation energy calculated in the low temperature range is equal to $\Delta E_a \approx 0.3$ eV. The hole concentration at room temperature is equal to $p = 9.58\times10^9$ cm^{-3}.

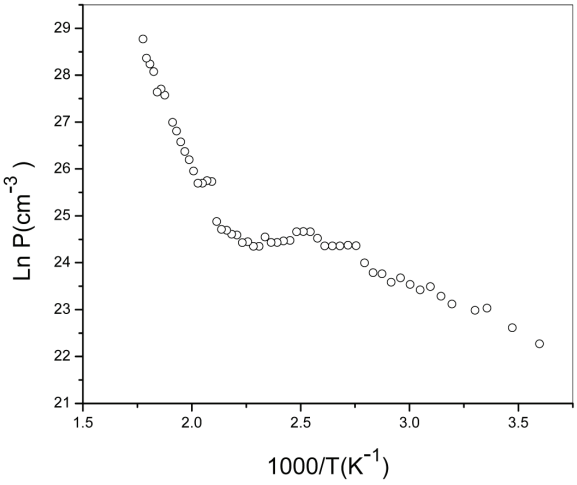

Fig. 5. Variation of carrier concentration with temperature.

3-2 Temperature Dependence of Thermoelectric Power of. α – Ga_2S_3

The thermoelectric power TEP measurements were performed as complementary part to the electrical conductivity and Hall Effect. The combination of the electrical and thermoelectric power measurement in the present investigation makes it possible to find various physical parameters such as carrier mobilities, effective masses of free charge carriers, diffusion coefficients and diffusion lengths as well as the relaxation time. The thermoelectric power α as a function of 10^3/T of α-Ga_2S_3 single crystal is shown in Fig.6.

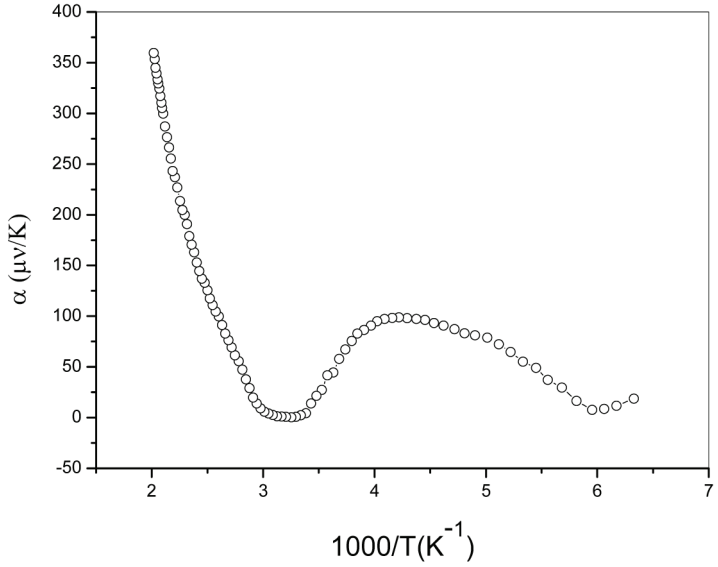

Fig. 6. Relation between α and 10^3/T for α- Ga_2S_3 single crystal.

The value of α decreases slightly with temperature up to 169.5K. Afterwards α increases also slightly with temperature reaching a maximum value α =99 μ V/K at T= 250 K, this may be due to the rate of thermal generation of free charge carrier greater than the rate of recombination effect. After this α falls rapidly as the temperature increases till 294 K, reaching a minimum value α = 0.4 μV/K as a result of compensation process which takes place in this temperature range. With further rise in temperature a much increase in the magnitude of α has been observed α reached a maximum value 360 μV/K at 496 K, such behavior is expected in this intrinsic range where generation of both carriers contributes to the increases of α value. It is evident from these

measurements that α has a positive sign in the whole temperature range of investigation. This is in agreement with results obtained from Hall data.

The behavior of thermoelectric power with temperature in the intrinsic region can be described by the equation given by Lauc[23].

$$\alpha = \frac{K}{e}\left[\frac{b-1}{b+1}\left(\frac{\Delta \mathrm{Eg}}{2KT} + 2\right) + \frac{1}{2} Ln \left(\frac{m_n^*}{m_p^*}\right)^{3/2}\right] \quad (2)$$

Where b is the ratio of electron to hole mobilities, ΔE_g the energy gap, K the Boltzmann constant and m_n^* , m_p^* are the effective mass of both electron and hole respectively.

The relationship (2) shown that a plot of α in the intrinsic range as a function of the reciprocal of absolute temperature is straight line as shown in Fig.6.

The slope of the linear part is used to estimate the ratio of the electron to hole mobilities. Taking into consideration the value of ΔE_g as obtained from the electrical conductivity and Hall effect measurements in the same range of T, the ratio $b=\mu_n/\mu_p$ is found to be 2.273. Hence by using the value of $\mu_p=1.67\times10^4$ cm^2/ V.s, the electron mobility can be deduced and its value is found to be 3.797×10^4 cm^2/V.s. Another important parameter can be deduced with the aid of the obtained values of μ_n and μ_p using the Einstein relation, from which the diffusion coefficient for both carriers (holes and electrons) can be evaluated to be 432.6 and 983.3 cm^2/s, respectively.

From the intersection of the curve, the ratio between the effective masses of the electrons and holes can be estimated to be m_n^* / m_p^* $=63.3\times10^{-2}$ assuming that this ratio does not vary with temperature. In the impurity region the following equation can be applied.

$$\alpha = \frac{K}{e}\left[2 - Ln \frac{Ph^3}{2(2\pi m_p^* KT)^{3/2}}\right] \quad (3)$$

This formula has been suggested by Wilson [24] for analyzing the data of α and ln T. This relation is illustrated in Fig.7.

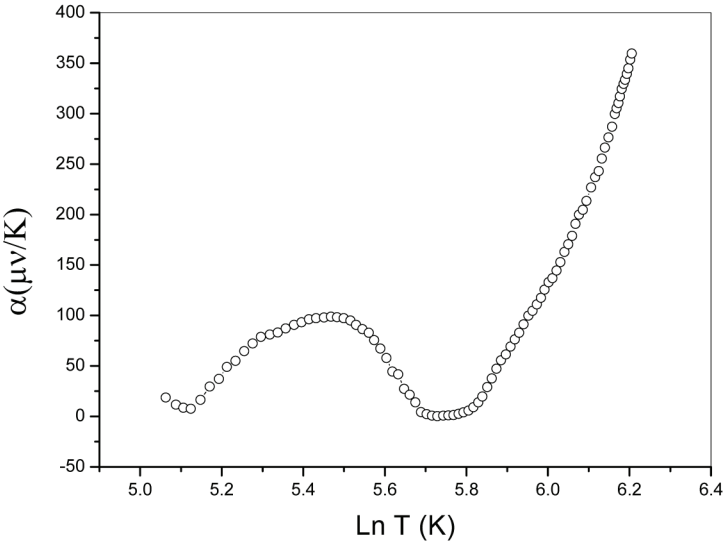

Fig. 7. Dependence of TEP on Ln T for α- Ga_2S_3 single crystal.

Calculation of the effective mass of holes from the intersection of the curve yields the value m_p^*=5.3×10^{-32} kg. Combining these values with the above mentioned results for the ratio m_n^* , m_p^*, one obtains an effective mass of the electrons m_n^* =3.36×10^{-32}kg.

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.

The calculated values of the effective masses for both minority and majority carriers can be used for the determination of the relaxation time for both current carriers. Its value for holes comes to be 5.54×10^{-20} s. whereas for electrons comes to be 7.97×10^{-20}s. The diffusion length as another important physical parameter can be deduced using the formula L= $\sqrt{D\,\tau}$ the values of L_p and L_n are calculated and they are found to be 1.41×10^{-8} cm, and 1.47×10^{-9} cm for holes and electrons, respectively.

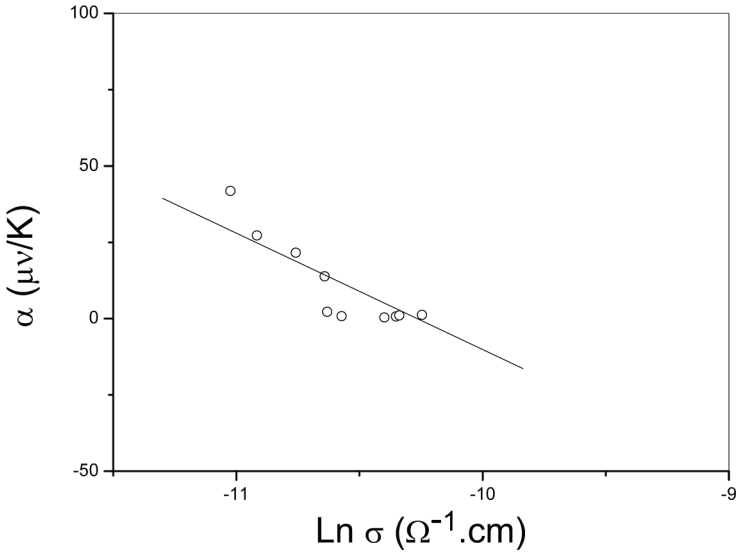

Fig. 8. Variation of TEP with Ln σ of α- Ga_2S_3 single crystal.

Figure.8 shows the dependence of α on the natural logarithm of electrical conductivity according to[25].

$$\alpha = \frac{K}{e}\left[A + \frac{2(2\pi m_p^* KT)^{3/2}\, e\, \mu}{(2\pi h)^3} \right] - \frac{K}{e}\, Ln\, \sigma \qquad (4)$$

It seems that the TEP increased with decreasing conductivity.

Since the efficiency of thermoelectric element can be monitored in terms of the figure of merit. The figure of merit for a certain TEP element was defined by:

$$z = \frac{\alpha^2\, \sigma}{K} = 3.5 \times 10^{-4}\, K^{-1}$$

Indicates that our best material α- Ga_2S_3 have a good value for z and they are within the possibility range of thermoelectric application in the field of energy conversion.

4- Conclusion

High quality α- Ga_2S_3 single crystal was grown by special, simple and cheap local design based on Bridgman technique. The electrical

conductivity, Hall coefficient, and thermoelectric power were measured as a function of temperature. The measurements cover a wide range of temperature under vacuum, from those measurements many physical parameters were estimated. The energy gap was found to be 2.0 eV. α-Ga_2S_3 conductivity type was found to be p-type as concluded from Hall coefficient and thermoelectric power measurements. The combination of the electrical and thermal 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. Also an important physical parameter was evaluated, that is the figure of merit.

References

[1] **Nagat, A.T., Nassary, M.M.** and **El-Shaik, H.A.** (1991) *Semicond. Sci. Technol.,* **6**: 979.
[2] **Bekheet, A.E.** (2008) *Physica* B **403**: 4342.
[3] **Bekheet, A.E.** (2008) *J. Electron Mater*, **37**: 540.
[4] **Afifi, M.A., Bekheet, A.E., El-Shair, H.T.** and **Zedan, I.T.** (2003) *Physica* B **325**: 308.
[5] **Belal, A.E., El-Shaikh, H.A.** and **Ashraf, T.A.** (1994) *Cryst, Res. Technol.,* **28**: 92.
[6] **El-Shaikh, H.A., Abdal-Rahman, M., Belal, A.E.** and **Ashraf, I.M.** (1996) *J. Phys. D: Appl. Phys.* **29**: 466.
[7] **Elshaikh, H.A.** and **Gamal, G.A.** (1995) *Semicond Sci. Technol.,* **10**: 1034.
[8] **Askerov, I.M.** (2007) *J. Magnetism and Magnetic Materials,* **312**: 280.
[9] **Pardo, M.P., Cruittard, M., Chilouet, A.** and **Tomas, A.** (1993) *J. Sol. Stat. Chemist,* **102**: 423.
[10] **Lieth, R.M., Heijligers, H.J.M.** and **Heijden, C.W.M.** (1960) *J. Electrochemical Society,* **113**: 796.
[11] **Goodyear, J.** and **Steigman, G.A.** (1963) *Acta Cryst,* **16**: 946.
[12] **Tomas, A., Pardo, M.P., Guittard, M.** and **Cruymont, M.** (1987) *Mat. Res. Bull.* **22**: 1549.
[13] **Pardo, M.P., Tomas, A.** and **Guittard, M.** (1987) *Mat. Res. Bull.* **22**: 1677.
[14] **Tomas, A., Cruymot, M., Pardo, M.P., Cruittard, M.** and **Flahout, J.** (1988) *Phys. Stat. Sol.* (a) **107**: 775.
[15] **Lee, J.S., Won, I.H., Kim, H.N., Kim, C.D.** and **Kim, W.T.** (1996) *Sol. Stat. Commun,* **97**: 1101.
[16] **Askerov, I.M., Kobelev, V.F., Masterov, V.F., Tagiev, O.B., Shlemakh, K.F.** and **Likholit, L.F.** (1989) *Sov. Phys. Semicond.* **23**: 814.
[17] **Askerov, I.M., Masterov, V.F., Romanov, V.V.** and **Shtelmath, K.F.** (1989) *Sov. Phys. Semicond.* **23**: 813.
[18] **Askerov, I.M., Mekhrokov, A.O., Alanov, G.K., Tagiev, B.G.** and **Nakhmetov, S.M.** (1988) *Phys. Status solidi* (a) **105**: 151.
[19] **Hussein, S.A.** and **Nagat, A.T.** (1989) *Cryst, Res, Technol.* **24**: 283.
[20] **Nagat, A.T., Gamal, G.A.** and **Hussein, S.A.** (1991) *Cryst, Res. Technol.* **26**: 19.
[21] **Nagat, A.T., Hussein, S.A., Gameel, Y.H.** and **Belal, A.E.** (1988) *Egypt. J. Solids* **11**: 60.
[22] **Hussein, S.A., Nagat, A.T., Gameel, Y.H.** and **Belal, A.S.** (1988) *Egypt. J. Solids* **10**: 45.
[23] **Lauc, J.** (1954) *J. phys. Rev.* **95**: 1397.
[24] **Wilson, A.H.** (1953) *Theory of Metals,* Second Ed. Cambridge University Press, Cambridge.
[25] **Schmid, P.H.E.** and **Mooser, E.** (1972) *Helv. Phys. Acta,* **45**: 870.

إنماء و دراسة الخواص الانتقالية لبعض مركبات الجاليوم الشالكوجيندية شبه الموصلة من المجموعة $M_2^{III}X_3^{VI}$

نجات توفيق عباس، و فاطمة باهبري، و رقية العريني، و محمد علي أبوزيد[1]، و صباح القرني، و وفاء الغامدي

كلية العلوم للبنات، قسم الفيزياء، جامعة الملك عبدالعزيز
جدة، المملكة العربية السعودية

[1] *كلية العلوم بقنا، قسم الفيزياء، جامعة جنوب الوادي، مصر*

المستخلص. استخدم تصميم محلي عالي الكفاءة قليل التكلفة بسيطًا وسهل التشغيل لإنماء بلورات أحادية من المركب ألفا ثنائي الجاليوم ثلاثي الكبريت فائقة الجودة اعتمادًا على تقنية بريجمان الشهيرة في الإنماء البلوري من المصهور، وتم التأكد من جودة المنتج ووجوده في طور واحد عن طريق مخطط حيود الأشعة السينية.

تم قياس الموصلية الكهربائية المستمرة وظاهرة هول والقدرة الكهروحرارية في مدى واسع من درجات الحرارة تحت تفريغ مناسب.

تم التعرف على نوعية التوصيل الحادث واتساع النطاق المحظور باستخدام قياسات الموصلية الكهربائية وظاهرة هول، وتم الربط بين نتائج تلك القياسات والنتائج التي توصلنا اليها من قياسات القدرة الكهروحرارية، أمكن تعيين مجموعة من الثوابت الفيزيائية الهامة مثل الحركية والكتلة الفعالة ومعامل الانتشار وطول مسار الانتشار وزمن الاسترخاء لحوامل التيار الحرة من ثقوب والكترونات . كما تم تحديد عنصر فيزيائي هام يحدد إمكانية استخدام هذا المركب في تحويل الطاقة الحرارية إلى طاقة كهربائية فيما يعرف باسم كفاءة التحويل والتي يعبر عنها بالاستحقاق الكهروحراري ووجد أن قيمتها تقع في المدى الذي يسمح باستعمالها كعنصر كهروحراري جيد.