International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 03 Issue: 01 | Jan-2016 www.irjet.net p-ISSN: 2395-0072

Growth and characterization of some ternary chalcopyrite from the group $A^{I}B^{III}C_2^{VI}$ semiconductor compound

Jazi Abdullah Mohammed Abdulwahed

Physics Department, Umm Al-Qura University College in Qunfudah-Female-KSA

Abstract *- $AgGaS_2$ single crystals were grown by modified Bridgman method. The present work is devoted to investigate the electrical and thermoelectric transport properties of $AgGaS_2$. Measurements of electrical conductivity and Hall effect were performed in the temperature range (380-660 K) and (344-690 K) for thermoelectric power. Our investigation showed that our samples are P-type conducting . The forbidden energy gap was calculated and found to be 2.57 eV. The analysis of the temperature dependent of electrical conductivity and carrier concentration reveal that acceptor level is located at 0.5 eV above the valance band of $AgGaS_2$.The combination of the electrical and the thermal measurements in the present investigation makes it possible to find various physical parameters, such as mobilities, effective mass, relaxation time, diffusion coefficient and diffusion lengh, both for majority and for minority carriers. In addition to these pronounced parameters, the efficiency of the thermoelectric elements (figure of merit) was evaluated which leads to better application in the field of energy conversation technique, semiconductor devices and electronic engineering.*

Key words : *$AgGaS_2$, Dc conductivity, Hall effect, thermoelectric power.*

1- Introduction

The chalcopyrite semiconductors have received considerable attention for their different promising practical applications, namely, non-linear optical, light-emitting diodes, photovoltaic optical detectors and solar cell[1] . the ternary compounds type $A^{I}B^{III}C_2^{VI}$ which belong to the family of chalcopyrite semiconductors have received considerable attention in recent years due to their potential applications[2]. Among the ternary semiconducting compounds of chalcopyrite structure belonging to the $A^{I}B^{III}C_2^{VI}$ formily, silver gallium disulphide has been shown to be of interest for nonlinear optical applications[3]. The semiconductor compound $AgGaS_2$ has been extensively studied because of its potential use not only for nonlinear frequency converts but also for photonic devices [4].

The ternary semiconductors of the $A^{I}B^{III}C_2^{VI}$ family. (where A=Cu, Ag ; B=In, Ga, Al and C=Se,S,Te) adopt the tetragonal chalcopyrite structure. They are isoelectronic analogous to the II-III semiconductors having Zinc-blende structure[5]. Silver gallium sulfide ($AgGaS_2$) belong to the category of $A^{I}B^{III}C_2^{VI}$ ternary compound semiconductor that crystallizes in the chalcopyrite structure which belong to the $\overline{14}$ 2d space group and the $\overline{42}$ m point group symmetry[6].

Chalcopyrite $AgGaS_2$ (AGS) crystal transmits light between 0.5 and 12μm and demonstrates a high nonlinear optical coefficient combined with good mechanical properties [7] . The optical properties of silver gallium disulphide $AgGaS_2$ and the optical parametric oscillator was published [4, 7- 11]. Raman scattering was studied [12,13].The effect of laser light was also investigated [14]. Electron paramagnetic resonance measurements were carried out[3,15]. Anew method of synthesis on high-quality $AgGaS_2$ polycrystalline was discussed[16,17]. The structural characterization of $AgGaS_2$ was printed [18]. Theoretical studied of hyperfine structure constants for $AgGaS_2$ and $AgGaSe_2$ crystals was discussed[19]. In spite of all the above reported studied, literature still lacks of the information about Hall properties, the carrier effective masses ,the position of the forbidden gap and the impurity level, mobility of

charge carriers as well as relaxation time, diffusion coefficient, diffusion length and the dominate scattering mechanisms, in $AgGaS_2$ crystal. Thus;

The aim of this work is to report these properties through the electrical conductivity, Hall effect and thermoelectric power measurements. The proposed treatment of the experimental data sheds new light on the main physical parameters of this compound, which lead to better application in many modern physics.

2- Experimental procedures

2-1 Growth technique

For the preparation of $AgGaS_2$ materials,6N Ag, Ga and 5N S elements were used as starting materials. Stoichiometric ratio of the initial materials was used to obtain high quality $AgGaS_2$ single crystals. The materials were supplied from Aldrich and placed in an evacuated (10^{-5} Torr) and sealed quartz capsule which was internally coated with aspecular layer of pyrocarbon to prevent the produced ingots from adhesion with silica tube. The capsule with its charge was introduced in a three zone tube furnace. This furnace is quite suitable for the crystallization process for its unique mechanical system which is used to draw the charge capsule from one zone to another with the required rate. In the first zone of the furnace (T=1100º c) the capsule was held to about 24 h for melt homogenization. During this stage the ampoule was agitated very gently .Then the melt was driven to the middle zone with a constant rate (2mm/h). The temperature of the middle zone of the furnace was 995ºc corresponding to published value[19] of crystallization temperate of $AgGaS_2$. When the ampoule and its contents entered the third zone gradual solidification occurred since the temperature was less than the melting point. Eleven days were required to obtain $AgGaS_2$ single crystal. The observation showed that the $AgGaS_2$ ingot appears as dark yellow material. The ingot was crack-free and free of voids with 6 cm length and 1.5 cm in diameter has been obtained. More details about the apparatus, the electrical system, and the mechanical system were previously published [20]. X-ray diffraction analysis of grown crystals was performed with adiffractometer, using monochnomatic Cu K_α radiation. The results of X-ray analysis confirmed that $AgGaS_2$ is a single crystal of a high-purity single phase of $AgGaS_2$.

2-2 Measuring arrangements

A sample of rectangular cross-section was prepared from the virgin ingot. For the electrical conductivity and Hall effect measurements.

The mean dimensions 7.9 x 2.9 x 2.5 mm^3 after the polishing processes. A mirror-like surface crystal was placed in a Pyrex cryostat designed for the measurements in the meant temperature range. To prevent the oxidation or the water vapour condensation, the cryostat was evacuated to 10^{-3} Torr. Electrical conductivity and Hall effect measurements were performed using the conventional DC potentiometer method. The silver paste was employed for making contacts. The ohmic nature of these contacts was checked by recording the volt-ampere characteristics. Hall measurements were made in a magnetic field of 0.5 Tesla. Details of the experimental arrangements and cryostat were described previously[21]. For measuring the thermoelectric power (TEP), the sample was prepared in a cylindrical shape. The length of the sample should be as short as possible, but the cross sectional area should be as a large as possible. A two parts holder was used for making the temperature difference along the crystal, in a direction perpendicular to the natural cleavage plane for investigation the thermoelectric power. The temperature gradient of about 5-10 K was maintained by two electric heaters. One of them stands at one end of the sample and the other one surrounding the whole sample body. 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. Also these measurements were done under vacuum for preventing oxidation of the sample on water vapour effect. The temperature was measured with the aid of a calibrated thermocouple. Details of the apparatus, working chamber and method of measurements have been published[22,23].

3- Results and discussion

3-1 Temperature dependence of electrical conductivity and Hall effect for $AgGaS_2$

Electrical properties of $AgGaS_2$ in a crystalline form and their temperature dependence were investigated over the wide temperature range extend from 380-660 K. The results were depicted in the fig 1. The curve consists of three regions these curves are quite similar to the semiconductor behavior. The first region lie between 380-535 K ,and represents the extrinsic region. In this region, the conductivity was observed to increase with temperature, indicating that impurity atoms are ionized under the influence of temperature at this stage. From the slope of the curve in this region, the ionization energy was evaluated to be ΔE_a=0.5 eV. The second region lies over the temperature range 535-575 K, and indicates the transition region, in which the σ-T curve passes through an intermediate region. This is the transition from impurity to intrinsic conductivity which depends on the carrier concentration and their mobilities. At temperature above 575 K, the conductivity increases rapidly because both of the carriers being excited from the extended state of the valance band into the conduction band. The third region lies at 575-660 K, is the intrinsic part. From the slope of the curve in this region the width of the forbidden gap can be calculated according to the following relation.

$$\sigma = \sigma_\circ \exp\left(-\Delta E_g / 2KT\right) \qquad (1)$$

Where σ_e is the pre-exponential factors, ΔE_g is the energy gap width, T the absolute temperature and k is the Boltzaman constant.

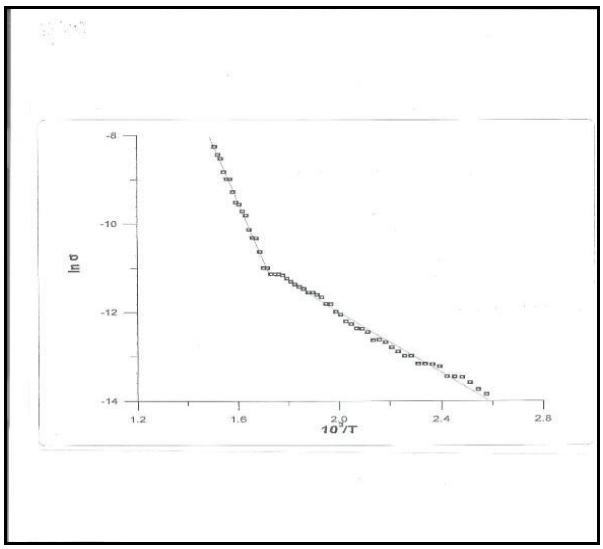

Fig (1) Effect of temperature on the electrical conductivity of $AgGaS_2$

From the above relation the energy gap width can be calculated from the slope of this curve. It is found to be ΔE_g equal to 2.56 eV This value nearly in close to the published value[16]. As for the importance of the Hall effect measurement, the present investigation is extended to cove this phenomenon.

Fig 2 shows the behavior of the Hall coefficient R_H against temperature. The Hall coefficient is positive all over the temperature interval of investigation. This means that the major carriers are holes and hence $AgGaS_2$ is a P-type semiconductor in agreement with that reported previously [18]. Fig 3 shows the relation between R_h $T^{3/2}$ and 10^3/ T. The value of ΔE_g as deduced from this figure is 2.57 eV. This value approximately in good agreement with the conductivity and published value [16]. From the figure, we have also showed three regions of the curve. This agrees with that we observed in fig 1. Also we can observe that the Hall coefficient in the low temperature range is less temperature dependent compared with the high temperature range. Simultaneous measurements of the Hall effect

and the electrical conductivity permit us to study the influence of temperature on the mobility.

Fig 4 depicts the variation of $R_H\sigma$ as a function of temperature. It is clear from the graph that the mobility grows as the temperature rises according to the low $\mu \sim T^{3.6}$ in all temperature range of investigation. Since our material has a wide band gap energy. Such dependence means that phonon scattering mechanism is responsible of this mobility behavior in this temperature range. Also, in this defected semiconductor, the presence of stoichiometric vacancies and creation of defects play an important role in understanding this scattering mechanism. From Hall coefficient data the charge carries concentration was calculated. Fig 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.

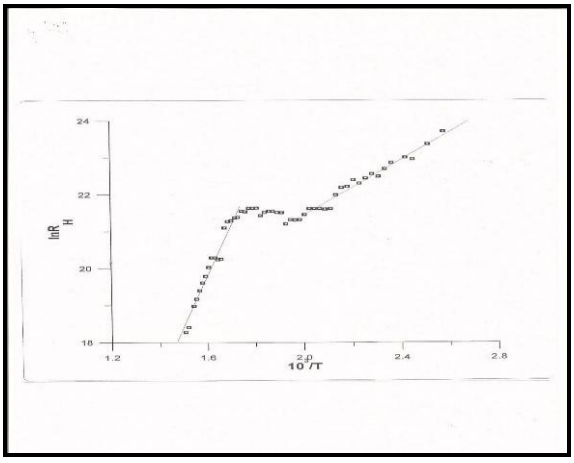

Fig (2) The relation between Hall coefficient and temperature

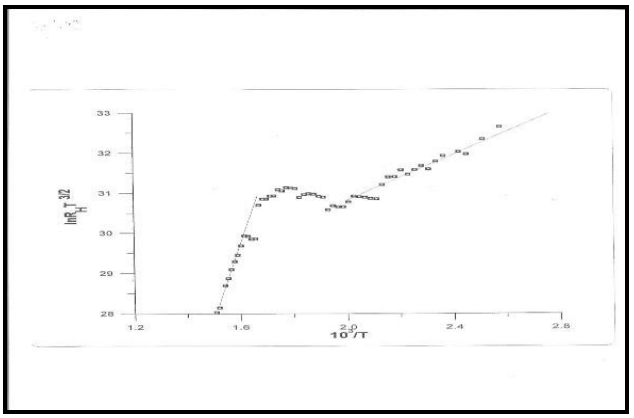

Fig (3) Temperature dependence of $R_HT^{3/2}$ for $AgGaS_2$ crystal

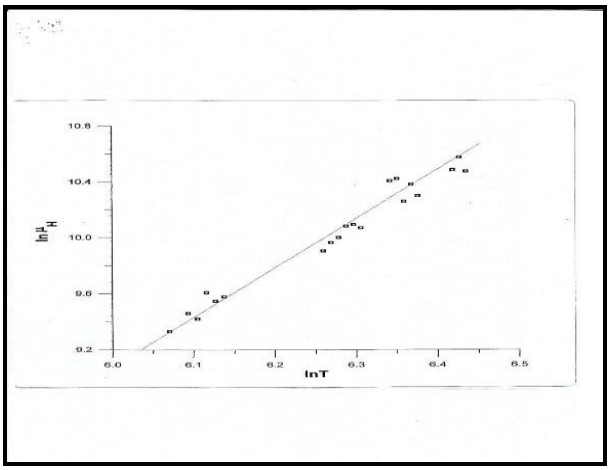

Fig (4) represent the variation of $R_H\sigma$ as a function of temperature

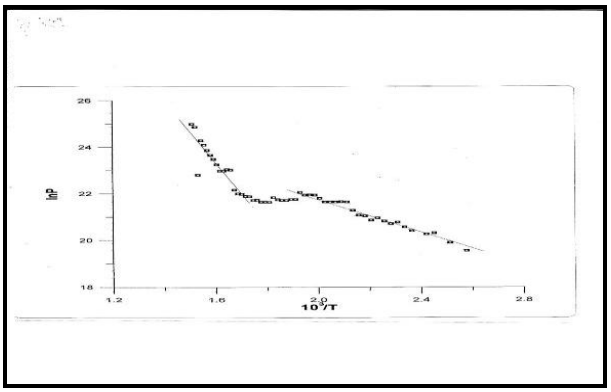

Fig (5) depicts the dependence of charge carrier concentration on temperature

Now; it is well established that, the following relation can be applied to describe the temperature dependence of the charge carrier concentration as follows

$$P_i = (N_c N_v)^{1/2} e^{-\Delta E_g / 2KT} \qquad (2)$$

The energy gap calculated from the slope of this curve in the high temperature range and the activation energy calculated in low temperature range are found in good accordance with data from the electrical curve. Fig 5 is helpful for understanding fig 1.

3-2 Temperature dependence of thermoelectric power for $AgGaS_2$.

In order to have a good idea of the thermal transport properties of the $AgGaS_2$ single crystals, the thermoelectric power (TEP) α, was measured as a function of the environmental temperature. The thermoelectric power (TEP) measurements were carried out as a complementary part to the electrical conductivity and Hall effect. The combination of the electrical and thermoelectric power measurements 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 variation of the differential thermoelectric power α of the $AgGaS_2$ single crystal as a function of temperature is illustrated in fig 6. Results and the figure indicate the following points.

1- Our sample shows P- type conductivity.
2- The figure shows that the value of the thermoelectric power decreases as the temperature rises till reaching small value 66μV/K at 412K. This may be due to the presence of some crystal defects or trapping centres in the direction of the carrier flow.
3- Above 412K , with further rise of temperature α increases rapidly till reaching its maximum value 2300 μV/deg. Corresponding to 525K. Such behavior led to the assumption that more holes are generated and contributed to the increment of α values as the temperature rises.
4- Third region in the same figure is observed where α rapidly falls above 525 K. The decrease of α magnitude is regarded as a result of the compensation process which take place in this temperature region .
5- With further rise of the temperature α increases . Such behavior is expected in this intrinsic range where generation of both carriers (electrons and halls) contributes to the increment of α value. In the intrinsic region, we can apply the following formula (24).

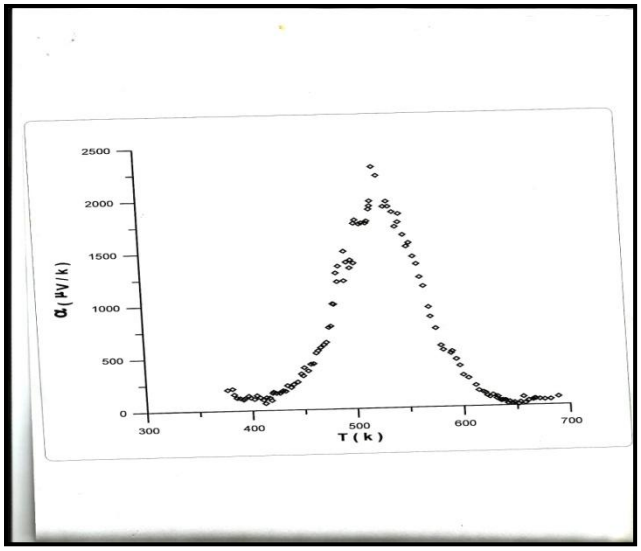

Fig (6) variation of the differential thermoelectric power as a function of temperature

$$\alpha = \frac{-k}{e}\left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p}\left(\frac{\Delta E_g}{2KT} + 2\right) + \frac{3}{4}\ln\frac{m_n^*}{m_p^*}\right] \qquad (3)$$

Where k the Boltzman constant, μn and μp are the electron and hole mobilities, and m_n^* and m_p^* are the effective masses of electrons and holes, and ΔEg is the width of the forbidden energy band. The above equation indicates that the relation between α and 1/ T in the intrinsic region should be a straight line. This is true as seen in fig 7.The measured thermoelectric power in conjuction with the obtained value of ΔEg is used to calculate the carrier effective masses and electron-to –hole mobility ratio.This is done by using the slopes of thermoelectric

power versus 1/ T plot and the intercepts, so we deduce that μn/μp =2.22 and μ*n /μ*p =8.92 x 10^{-6}. Since μp=5541.4cm^2/v.sec,then we can evaluate μn= 12311.3 cm^2/ V.sec. The diffusion coefficient for both majority and minority carriers could be evaluated and is found to be Dp=143.5 cm2/sec and Dn=318.3cm2/sec respectively. For more making use of the phenomena another formula was suggested by wilson(25) to be employed in the extrinsic region that is

$$\alpha = \frac{k}{e}\left[2 - \ln \frac{Ph^3}{2\left(2\pi m_p^* KT\right)^{3/2}}\right] \qquad (4)$$

This formula leads us to represent the relation between α and lnT as seen in fig 8.

This equation represents a straight line relation in the impurity region. A sharp drop of thermoelectric power is observed in the impurity region

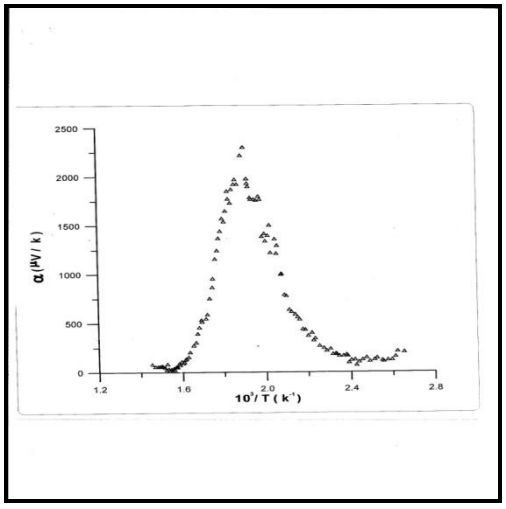

Fig (7) The relation between α and 1/T for $AgGaS_2$

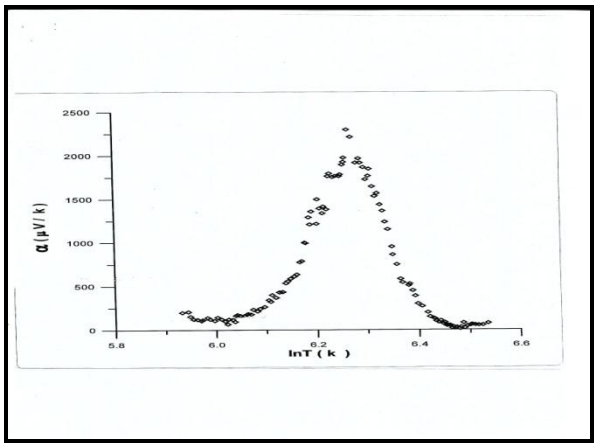

Fig (8) The relation between α and ln T for AgGaS2 crystal

as the temperature increases. In the extrinsic region the effect mass of hole can be determined as m_p^* =1.22 x 10^{-29} Kg. Combining this value with the above mentioned result for the ratio $m_n^*/\ m_p^*$ we obtain the value of the effective mass of the minority carrier m_n^*=1.09x10^{-34} Kg.

Since the effective mass values are available, now the relaxation time for both types of carriers can be determined.

The relaxation time for holes as calculated is 4.24 x 10^{-14} sec, whereas the relaxation time for electrons equals to 8.41 x 10^{-19} sec.

It is noticed that the diffusion coefficient is inversely proportional to the effective mass of carries, this is logical because the hole effective mass is larger than that of electrons. Also, the results indicate the electron mobility is much higher than the hole mobility, this is acceptable since the hole effective mass is much greater than that of electrons. Combining the values of diffusion coefficient and relaxation time one can obtain the diffusion length of free charge carriers L_p = 6.08 x10^{-12} cm and L_n = 1.64 x 10^{-8} cm for holes and electrons respectively.

For a better understanding of the real factors governing the thermoelectric power, the present work has been extended to cover the correlation between α and both ρ (carrier density) and σ (electric conductivity). Fig 9, represents the dependence of thermoelectric power α on the carrier density. We show that α decreases sharply and linearly with the carrier concentration as suggested from the following formula[26]

$$\alpha = \frac{K}{e}\left[A + \ln\frac{2(2\pi m_p^* kT)^{3/2}}{(2\pi h)^3}\right] - \frac{K}{e}\ln p \qquad (5)$$

Fig 10. Show the dependence of the thermoelectric power coefficient on the natural logarithm of the electrical conductivity.

This behavior which govers the relation between the electrical conductivity and TEP is similar to that of α versus p . The similar behaviors of fig 9 and fig 10 predicts that the variation of α is mainly due to the carriers concentration variation with temperature.

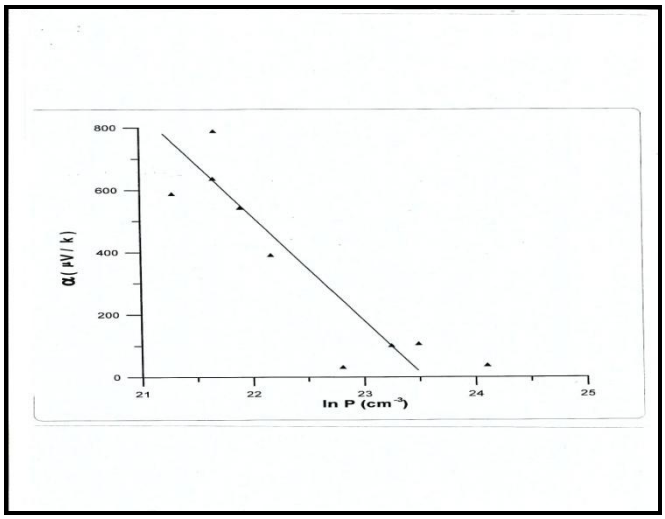

Fig (9) represent the relation between α and carrier density

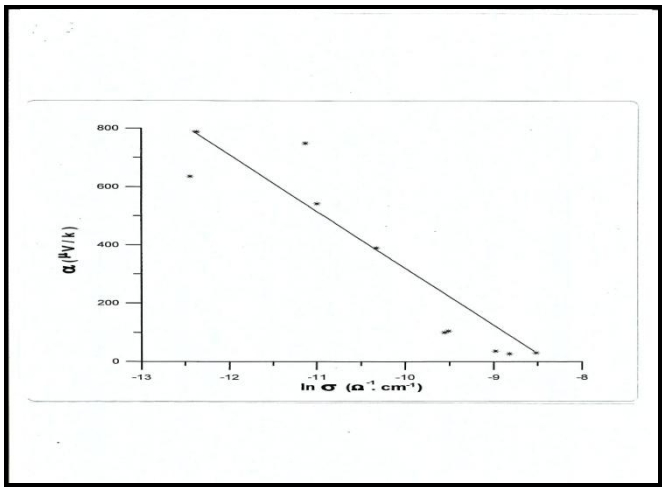

Fig (10) Show the dependence of thermoelectric power on the electrical conductivity

The choice of materials for thermocouples thermoelectric generators and refrigerators is based on the efficiency parameter, Z defined by the relation

$$Z = \frac{\alpha^2\sigma}{k} \qquad (6)$$

Where α,σ,K are TEP, electrical conductivity and thermal conductivity of the compound under test. However, the term figure of merit is a measure of both performance and efficiency of a certain thermoelectric element. Therefore the main technical problem to obtain a good thermoelectric element is to answer the question how to promote the figure of merit Z =1.35 X 10^{-7} K^{-1} permits the practical application as thermoelectric element.

The proposed treatment of the experimental data sheds new light on the main physical parameters of $AgGaS_2$ single crystals. The pronounced parameters obtained from electrical conductivity, Hall effect, and TEP data gave evidence for practical application.

4- Conclusion

In the present work $AgGaS_2$ crystals were grown by a modified Bridgman technique. From the data obtained we can conclude the following :

1- $AgGaS_2$ is a semiconductor with P-type conductivity

2- The forbidden energy gap was calculated and found to be 2.57 eV and the position of the acceptor level was determined
3- The electron and hole mobilities was evaluated
4- The effective mass of holes and electrons was estimated
5- The relaxation time of majority and minority carriers was evaluated
6- The diffusion coefficient as well as the diffusion length of holes and electrons was determined
7- The efficiency of thermoelectric elements was calculated
8- These studied yield an appreciable amount of information about the actual behavior of this compound and reveal the possibities of their practical application especially in the field of energy conversion, semiconductor devices and electronic engineering.

References

1- Mobark M.,Shaban H.T and Elhady A.F.(2008) Electrical and thermoelectric properties of $CnInS_2$ single crystals; Materials chemistry and physics 109:287
2- Bouloufa A., Messous A., Yakushev M.V.,Tomlinson R.D., and Zegadi A.(2003) Optical properties of $CuInTe_2$ single crystals by photoacoustic spectroscopy, J. Electron Devices 2; 34
3- Bardeleben H.J.Von, Goltzene A., and Schwab. C. (1978) EPR characterization of optical-quality AgGaS2 grown from the melt, Appl. Phys. Lett. 32;741
4- Hau H-c., chen H-b., Kuo S-Yi , chang C-S and Hsieh W-F (2002) Effect of annealing on the structural and optical properties of AgGaS2 thin films prepared by pulsed laser deposition, thin solid films 419;237
5- Gonzalez J., Derollez P.,Fouret, R. and Hennion B. (2003) temperature dependence of soft modes in I-III-VI2 chalcopyrite semiconductors Rev. Mex. Fis. 49;172
6- Zhao D-J, Zhu,S-F,Yu F.L.,Li H-Y.,Gao D-Y, and Li Z-H (1998) poly crystalline Synthesis and single crystal growth of $AgGaS_2$ cryst. Res. Technol.33,943
7- Vodopyanov K.L.,Maffetone, J.P.,Zwieback I.and Ruderman W.(1999) $AgGaS_2$ optical parametric oscillator continvously tunable from 3.9 to 11.3 μm, Appl.phys.Lette.75;1204
8- Wang T.J., Zhang H.Z., Wn F.G., Feng, H.Y.,Zang Z.H., Jiang Y. and Gao J.Y.(2009) 3-5 μm $AgGaS_2$ optical parametric oscillator with Prism cavity, solid state and liquid lasers 19;377
9- Wang Tle-Jun, Kang Zhi-Hui, Hong Zhi.Z, Xiong-Yi He, Y:Qu, Feng Z.S., Jiong Yun and Gao J.Y.Andreev Y.M and Gregory V.L.(2006) wide-tunable,high-energy $AgGaS_2$ optical parametric oscillator, optics Express 14;13001
10- Haider S.,I to H. (2002) periodically poled lithium niobate optical parametric oscillator pumped at 0.532 μm and use of its output to produce tunable 4.6-8.3 μm in AgGaS2 crystal, optics communications 202;227
11- Eom.S.H., Kim D.J,Yu Y.M., Choi Y.D.(2005) Temperature-dependence absorption edge in $AgGaS_2$ compound semiconductor, Journal of alloys and compounds 388;190
12- Ockwood D.J.I. and Montgomery H.(1975) Raman spectrum of AgGaS2 , J.D.E.physique 36;183
13- Gonzalez J. Derollez P.Fouret.R. and Hennion B (2003) Temperature dependence of soft modes in I-III-VI2 chalcopyrite semiconductors Materia condensada 49;172
14- Bangmin Z. and Dinghua W.(1991) Second-Harmonic Generation of Tea Co_2 10.6 micrometer laser light in $AgGaS_2$ crystals FTD, 10;339
15- Zheng W.Ch., Dong H.N.,Tang S., and Zi J. (2004) Zero field splitting and local lattice distortion for Fe3+ ions in some Ib-IIb-VI2 semiconductors verlag der Zeitschrift fur Naturforschung 6,100
16- Zhang J., Zhu S., Zhao B., Chen B., He Z.(2010) Anew method of synthesis on high-quality $AgGaS_2$ polycrystalline, current Applied physics 10;544
17- Zhao B.J.,Zhu S.F.,Yu F. L., Li, H.Y.,Gao De-Y.and Li Z.H.(1998) polycrystalline synthesis and single crystal growth of $AgGaS_2$ cryst. Res.Technal 33;903

18- Choi S.H.,Jang J.S.,Shin N. and Lee J.S.(2007) Structural characterization of $AgGaS_2$ – type photocatalysts for hydrogen production from water under visible light, International conf.proc.382;628
19- Chen Z.W.,Shae Wu.,Jun Z.B and Shi Z.Fu.(1999) Theortical studies of the g factors and hyperfine structure constants for Ni+ in $AgGaS_2$ and $AgGaSe_2$ crstals, physica B, Condensed Matter 269;319
20- Hussein S.A., and Nagat A.T (1989) On the preparation and electrical properties of thallium selenide monocrystals, cryst.Res. Technal.24;283
21- Gamal.G.A.,Nassary M.M.,Hussein S.A., and Nagat A.T.(1992) Single crystal growth and electrical properties of Gallium Monotelluride, Cryst.Res.Technal. 27;629
22- Hussein S.A.,Nagat, A.T,Gameel.Y.H. and Belal A.E (1988) Thermal Transport properties of gallium selenide crystals Egypt. J.Solids 10;45
23- Nagat A.T., Hussein S.A.,Gameel Y.H.and Belal A.E (1988) Thermal E.M.F of some phases of In-Se system, Egypt.J. solids 10;60
24- Johnson V.A. and Lark Horovity K.,(1953) Theory of thermoelectric power in semiconductor with application to Germanium, phys.Rev 92;226
25- Wilson A.H.W 1953 Theory of Metals 2nd Edition combridge university press, London
26- Shmid,P.H.E. and Mooser E. (1972) The maximal Kinematical invariance group of the free schrodinger equation, Helv. Phys, Acta,45;870