

Thermoelectric Phenomena in TlInSse Single Crystals

S.R. Al-harbi

Department of Physics, Faculty of Girls Education, King Abdul Aziz University, Jeddah, Saudi Arabia
sr_alharbi@yahoo.com

Abstract: Thallium indium sulphur selenide crystals were grown and identified with X-ray analysis. Measurements of thermoelectric power were carried out in a special high vacuum-tight calorimeter when the direction of temperature gradient is perpendicular to the cleavage plane. The measurements covered a temperature range extending from 175K to 450K. The results indicate P-type conductivity for our investigated samples. At room temperature the value of thermoelectric power was 10 μ V/deg. The electron to hole mobilities ratio was found to be 2.56. The effective mass of holes at room temperature was evaluated as 4.219×10^{-24} kg, while for electrons was equal to 2.23×10^{-28} kg. The relaxation time of majority and minority carriers was estimated as $\tau_p = 1.81 \times 10^{-8}$ sec and $\tau_n = 2.439 \times 10^{-12}$ sec respectively. Also the diffusion coefficient of holes and electrons at room temperature was calculated and found to be 177.78 cm²/sec and 453.25 cm²/sec respectively. The diffusion length of holes and electrons are found to be $L_p = 1.79 \times 10^{-5}$ cm and $L_n = 3.3 \times 10^{-5}$ cm. The efficiency of the thermoelectric elements was evaluated. This studies yields an appreciable amount of information about the actual behavior and are essential to the understanding of the materials and consequently of their practical application.

[S.R. Al-harbi **Thermoelectric Phenomena in TlInSse Single Crystals**. Journal of American Science 2011; 7(9): 919-922]. (ISSN: 1545-1003). <http://www.americanscience.org>.

Keywords: thermoelectric power, effective mass, diffusion coefficient, relaxation time, TlInSse.

1. Introduction

Most of the developments in the field of materials for thermoelectric application have been rather empirical, that is, various materials were tested for the properties of interest in this application, and the best available material was then chosen and adjusted for best results. As the field progresses, it becomes increasingly evident that new materials will have to be found to realize fully the possibilities of thermoelectric power production. Interest, in the field of thermoelectric power, increased recently for, at least, two reasons. In the first place motivation has come about through the greatly increase number of technological problems-in particular, thermoelectric conversion requiring new materials with as yet unknown thermoelectrical properties. Secondly, recent work for replacing power produced from petroleum and nuclear sources with other new sources of power. The study of thermoelectric properties of semiconductors have been an active area in solid state physics. The thermoelectric properties may be applied in more than one way in the development of power.

The electrical [1], photoelectrical [2], optical [3], luminescent [4], structure [5], thermally stimulated current [6], Raman scattering [7] and other properties of TlInSse single crystal have been studied [8,9] comparatively with much thoroughness. Their thermoelectrical properties however have not been studied at all. Investigations of the thermoelectric properties for TlInSse have been stimulated by the growing needs for such materials in many scientific

applications. Since published literature gives no values for the thermoelectric properties of TlInSse, this give us the chance to report this work. To our knowledge, this might be the first study on the thermoelectric properties of this compound. This paper reports on a preliminary attempt at a prior design of materials for thermoelectric power production.

2. Experimental Arrangement

2.1. Sample preparation.

Details of the experimental equipment for crystal growth by modified Bridgman method are described elsewhere [10]. The prepared crystal samples were obtained by direct fusion of the constituents in stoichiometric proportion:

23.7509 g thallium representing 47.5017%, 13.3395 g indium representing 26.6791%, 3.7299 g sulphur representing 7.4599% and 9.1797 g selenium representing 18.3593% were used as starting material in the growth experiment. The purity of the starting materials can be stated as being 99.9999% (Aldrich Mark). Special technique and precautions were adapted to avoid difficulties in preparing such systems containing sulphur. The mixture was enclosed in quartz ampoules internally coated with a thin layer of carbon to prevent contamination of the charge. The charged ampoule was sealed off at a pressure of approximately 10^{-6} Torr. Firstly the composition was kept at a temperature higher than the melting point for several hours, in order to obtain uniform material throughout. After direct fusion, the

ampoule was shaken in order to complete the reaction of the whole content, and then it was allowed to enter the other zones of the furnace. The ampoule was moved in the furnace zones between the temperatures 1053K and 703K for about 17 days. The recorded velocity of the molten zone was almost 1.6 mm/h. When the ampoule with its contents enters the third zone, in which the temperature is less than the melting point, the crystallization proceed till the contents solidify. The product crystal was obtained with 1.5 cm diameter and 25cm length. The samples obtained were single crystals of good quality and they were red in colour, showing a layer structure with monoclinic structure as confirmed by X-ray diffraction chart and the diffraction data did not show the presence of any secondary phases. The obtained crystal showed good optical quality and the freshly cleaved surfaces were mirror-like. Also we can observe the resulting ingots without no cracks and voids on the surface. The investigated sample was cleaved gently from the obtained ingot. To minimize the effect of radiation, the cylindrical shaped specimens were made and the length of the sample was chosen to be as short as possible, whereas the cross section area was large enough. The surface of the sample was flat and parallel.

2.2. Measurement technique.

After preparing the sample with the required dimensions as mentioned before, it was supported vertically by two holders one of which (the lower one) acts as a heat source, while the other serves as a heat sink, and introduced inside a high vacuum tight calorimeter designed [11] specially for this purpose. The sample was insulated from the holders by thin sheets of mica. The temperature of the crystal was considered to be the average of those at its two ends. As an attempt to increase accuracy, simultaneous measurements of temperature and potential difference were carried out. In the present work, a compensation method was used for measuring voltage without drawing appreciable current using a tensity potentiometer (UJ33E). It was necessary to have the temperature equally distributed, therefore we placed contact of silver past across the ends of the specimen uniformly. A two part holder was used for making the temperature difference along the crystal in a direction perpendicular to the natural cleavage plane. Details about apparatus and experimental method for measuring α have been described in previous paper [12]. To avoid the effect of water vapour condensation in the low temperature range and the effect of oxidation in the high temperature range, the measurements were carried under vacuum. Measurements were carried out, during this investigation in a wide range of temperature

extending from 175K up to 450K.

3. Results and Discussion

The variation of the differential thermoelectric power (α) of TlInSSe single crystal as a function of temperature is illustrated in fig.1. 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 its smallest value 0.125 μ v/deg at 269K. This may be due to the presence of some crystal defects or trapping centres in the direction of the carrier flow. (3) Above room temperature, with further rise of temperature, α increases rapidly till reaching its maximum value (318.75 μ v/deg) corresponding to 445K. (4) In the middle zone in which α has nearly a constant value, this can be regarded as a result of the rate of generation of carriers equal to the rate of recombination. In the intrinsic region, we can apply the following formula [13].

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

Where K is the Boltzmann constant, μ_n and μ_p are the electron and hole mobilities, m_n^* and m_p^* are effective masses of electrons and holes, and ΔE_g 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 figure 2. The measured thermoelectric power in conjunction with the obtained value of ΔE_g 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 $\mu_n/\mu_p=2.56$ and $m_n^*/m_p^*=5 \times 10^{-5}$ Since $\mu_p=6864.25$ cm²/v.sec, then we can evaluate $\mu_n=1.75 \times 10^4$ cm²/v.sec. The diffusion coefficient for both majority and minority carriers at room temperature could be evaluated and is found to be $D_p=177.78$ cm²/sec and $D_n=453.25$ cm²/sec respectively. The relationship between α and $\ln T$ is illustrated in fig 3. Calculation of the thermoelectric in the impurity region yields the following results [14]

$$\alpha = \frac{k}{e} \left[2 - \ln \frac{p h^3}{2(2m_p^* kT)^{3/2}} \right]$$

This relation represents a straight line relation in the low temperature region. A sharp drop of thermoelectric power is observed in the impurity region as the temperature increases. In the extrinsic region the effective mass of hole can be determined as $m_p^*=4.219 \times 10^{-24}$ 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 carriers $m_n^* = 2.23 \times 10^{-28}$ 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 1.81×10^{-8} sec, whereas the relaxation time for electrons equals to 2.439×10^{-12} sec. It is noticed that the diffusion constant is inversely proportional to the effective mass of carriers, this is logical because the hole effective mass is larger than that of the electrons. Also the results indicate that 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 $L_p = 1.79 \times 10^{-3}$ cm and $L_n = 3.3 \times 10^{-5}$ cm for holes and electrons respectively. Fig 4 represents the dependence of thermoelectric power α on the carrier density. The thermoelectric power decreases gradually and linearly with the carrier concentration. The same behaviour of the latter curve is observed when we plot the relation α vs. σ as shown in fig 5. The choice of materials for thermocouples, thermoelectric generators and refrigerators is based on the efficiency parameter Z, defined by the relation $Z = \alpha^2 \sigma / k$. 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 of the material. For our best TlInSse samples, the figure of merit $Z = 1.895 \times 10^{-11}$. The value of Z for TlInSse permits the practical application as thermoelectric element. However those parameters are found to be sufficient to give complete information about the general physical behaviour of the TlInSse to use in practical application.

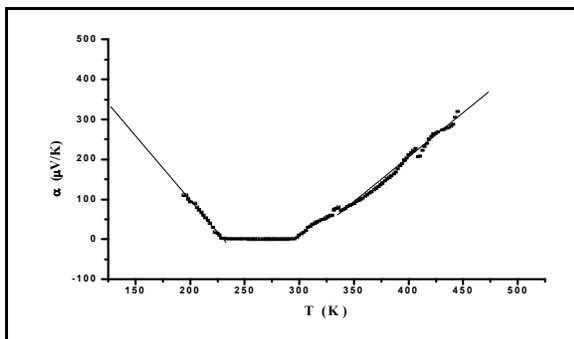


Fig.1- The temperature dependence of the thermoelectric power for TlInSse single crystal

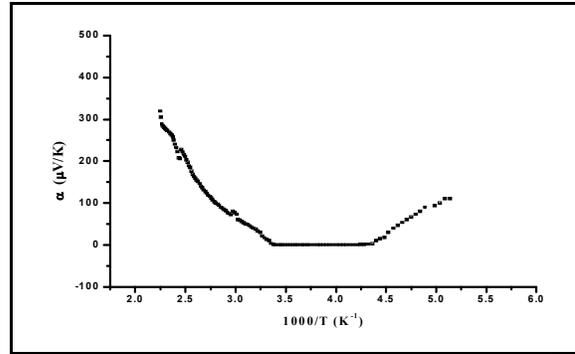


Fig. 2- Plot of the thermoelectric power versus $10^3/T$ for TlInSse single crystal

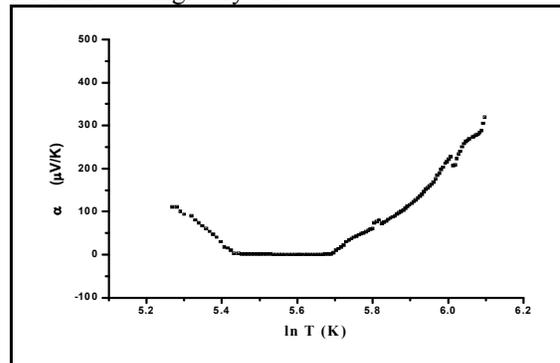


Fig. 3 Relation between thermoelectric power and $\ln T$ for TlInSse single crystal

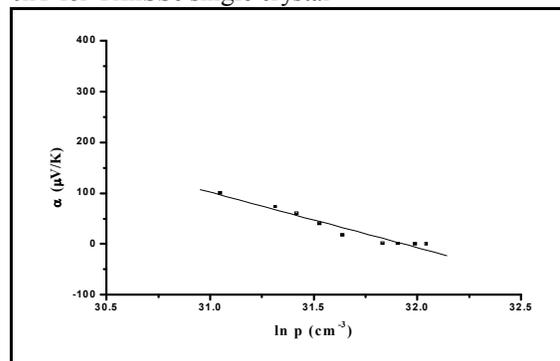


Fig. 4 Dependence of the thermoelectric power of TlInSse carrier concentration

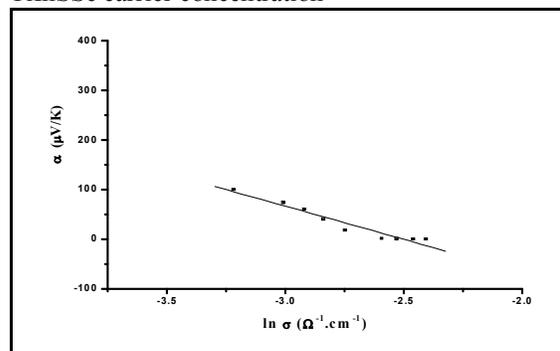


Fig. 5 Variation of thermoelectric power of TlInSse single crystals with the electrical conductivity.

Corresponding author

S.R. Al-harbi

Department of Physics, Faculty of Girls Education,
King Abdul Aziz University, Jeddah, Saudi Arabia
sr_alharbi@yahoo.com

References

1. Ibrahimove J. D. and I. T. Aslanov (2000) Sol. Stat. Commun., 123:664.
2. Uchiki H., D. Kanazawa, N. Mamedov and S. Lida (2000) J. Lumin., 87: 664.
3. Akhmedov A. M., A. E. Bakhyshov, A. A. Lebedev and M. A. Yakobson (1978) Sov. Pysys. Semicond., 12: 299.
4. Gasanly N. M., A. Aydinli and N. S. Yuksek (2002) J. Phys. Condens. Matter., 14: 13685.
5. Gasanly N. M. and I. Guler (2008) J.PHYS. Condens Matter., 22: 3931.
6. Guler I. and N.M. Gasanly(2009) J. Alloys and Compounds, 496: 41.
7. Bakhyshov N. A, N. M. Gasanly, B. M. Dzhavadov, V. I. Tagirov and S. M. Efendiev(1979) Phys. Stat. Sol. 91: 1.
8. Gasanly N. A. (2010) Cryst. Res. Technol., 45: 525.
9. Samedov S. R., O. Boykan and A. Gulubayov. (2004) International J. of Infrared and Millimeter Waves, 25: 735.
10. Hussein S. A. and A. T. Nagat. (1989) Cryst. Res. Technol., 24: 283.
11. Hussein S. A., A. T. Nagat, Y. H. Gameel and A.E. Belal(1988) Egyp. J. Sol., 10: 45.
12. Nagat A. T., S. A.Hussein, Y. H. Gameel and A. E. Belal(1988) Egyp. J. Sol., 11: 60.
13. Johnson V. A and K. Lark Horovity(1953) Phys. Rev., 92: 226.
14. Chaltov V. K(1969). Introduction to Semiconductor. Izd, Mir, Moscow in Russian

9/18/2011