On the preparation and thermal transport properties of a quaternary thallium dichalcogenides $Tl_2GaInTe_4$ compounds

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Abstract: In the present study high quality single crystal of $Tl_2GaInTe_4$ were grown by a modified Bridgman method. Measurements of thermoelectric power (TEP) were performed in the range (190-590K). From these measurements the conductivity of the crystals was p-type. From the obtained experimental data several physical parameters such as diffusion coefficient, diffusion lengths, effective masses, relaxation time of both free charge 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 especially in the field of energy conversation technique.

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Key words: Crystal growth, $Tl_2InGaTe_4$ thermoelectric power, effective mass, diffusion coefficient, relaxation time.

1. Introduction

The ternary semiconducting chalcogenides with the formula $TlBx_2$ were studies, where Band x represent the metal and chalcogen atoms respectively. They have both layered (TlGaS2, $TlGaSe_2$ and $TlInS_2$) and chain (TlInSe2, $TlInTe_2$ and $TlGaTe_2$) structures[1]. The quaternary $Tl_2GaInTe_4$ crystal belongs to the group of chain semiconductors.

Thallium compounds have recently attracted interest as promising thermoelectric materials[2]. Recently increasing interest has been shown in the physical properties of chain-like structured materials, including crystalline $Tl_2InGaTe_4$. This material is a structural analogue of $TlInTe_2$ ($TlGaTe_2$), in which half the trivalent indium (gallium) atoms are replaced by gallium (indium) atoms[3].

In the lattice of $Tl_2InGaTe_4$, indium (gallium) atoms are each surrounded by four tellurium atoms and form chains along the tetragonal c-axis. These chains are connected to each other by univalent thallium atoms. Some of the structural, electrical and optical properties of the $TlInTe_2$ and $TlGaTe_2$ crystals have been reported[4-12]. The quaternary thallium chalcogenide $Tl_2GaInTe_4$ is formed from $TlInTe_2$ - $TlGaTe_4$ system having the ratio 1:1.In spite of its importance in technological applications as a candidate material for optical devices and also for the information of its basic physical properties. So far very little information on the physical properties of this compound[3,13,14]. Previously[15], we have studied the temperature dependence of DC electrical conductivity and Hall coefficient for this compound. Thermoelectric properties of several quaternary thallium tellurides have also been reported recently[16]. However, to the best of the author's knowledge, no systematic investigation has been carried out on the thermo-electric properties of the new semiconductor compound $Tl_2GaInTe_4$.

In the present paper, we report for the first time an investigation into the thermoelectric power of the $Tl_2GaInTe_4$ compound, to study this material for practical applications, especially in the field of energy conversion. Our aim is to investigate the thermoelectric power (TEP) in wide temperature range extend from 190K to 590K.

2-Experimental arrangement

2-1-Preparation of sample

$Tl_2GaInTe_4$ single crystal ingots have been prepared using a modified Bridgman technique for growing crystal from melt. The purity of the materials used 99.9999% stoichiometric quantities of the constituent element 19.309 gm Tl, 6.584 gm Ga and 24.107 gm Te, were used as starting materials for $TlGaTe_2$, also 17.7925 gm Tl, 9.9930 gm In and 22.2145 gm Te for $TlInTe_2$.The appropriate amounts were first sealed in evacuated quartz ampoule.

$Tl_2GaInTe_4$ single crystals were grown from $TlGaTe_2$ and $TlInTe_2$ polycrystalline by slight freezing in sealed quartz ampoule evacuated to about ($\sim 10^{-6}$ mbar). The method is a modified Bridgman technique as was described in a previous work.[17] The tipped silica tube was internally coated with a specular layer of pyrocarbon before introducing the chemicals. In the first procedure the tube was placed in a three-stage tube furnace in which controlled temperature gradient was maintained. The ampoule is allowed to move with a constant rate of 1.5 mm / h through the stationary furnace. The movement of the ampoule was very gently and slowly with the aid of the hydraulic

mechanical system. At least two weeks growth are needed to obtain $Tl_2GaInTe_4$ single crystal. The resulting ingots (grey-black in color) showed good optical quality. The single crystallinity of this material was verified by means of x-ray diffraction technique. 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 basic 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 facts that the broadenings are functions of the crystal quality.

2-2- Thermoelectric power measurements

For studying the thermoelectric power (TEP)an evacuated calorimeter (10^{-3} m bar) 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) discharge, its heat slowly to the specimen environment. The inner heater (connected to the lower end of the crystal) was used purposely 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). For TEP measurements, we utilized the prepared crystal after removing it from the ampoule because it had a cylindrical shape parallel-sides specimens were used through our measurements with dimensions 1.5 mm thickness and 14 mm diameter. The sample thickness allows the creation of uniform temperature gradient. Contacts were placed uniformly across the ends of the used samples to ensure uniform temperature distribution.Silver paste contacts were used and found to be ohmic. 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 measurements.

Details about the apparatus and method of measurements are outlined elsewhere.[18,19] The sample was supported between two holders, the lower one acting a heat source and the upper as a heat sink. Two copper constantan thermocouples were used for temperature measurement 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. The thermoelectric power of the investigated $Tl_2GaInTe_4$ is measured through out a temperature range from 190-590K.

3. Results and Discussion.

The results of the temperature dependence of thermoelectric power (TEP) of $Tl_2GaInTe_4$ single crystals are given in fig (1). The results in figure indicate the following points:

1- Our sample shows P-type conductivity within the temperature range of investigation which is quantitative agreement with previousdata[15].
2- The room temperature TEP value for $Tl_2GaInTe_4$ mounted to 278μVdeg^{-1}.
3- The figure shown that at the beginning of the curve the value of thermoelectric power decreases gradually and slowly as the temperature rises. This may be due to the presence of some crystals defects or trapping centers in the direction of the carrier flow.
4- With further rise of temperature α increases rapidly till reaching its maximum value (710μV deg^{-1}), corresponding to 335K. Such behavior led to the assumption that, more holes are generated and contribute to the increment of (α) value as the temperature rises.
5- A third region in the same figure is observed where (α) rapidly falls above 335 K reaching a minimum value 194 μ.V deg^{-1} at 444 K. The decrease of (α) magnitude is regarded as a result of the compensation process which takes place in this temperature range.
6- With further rise in the temperature TEPincreases very rapidly, such behavior is expected in this intrinsic range where generation of both carriers (electrons and holes) contribute to the increment of (α) value.

Now we come to the utilization of the TEP behavior against temperature in the determination of the main physical parameters of this crystal. For this purpose, we consider a well – known relationship that governs the variation of α against temperature in the intrinsic part [20]

$$\propto = \frac{K}{e}\left[\frac{b-1}{b+1}\left(\frac{\Delta E_g}{2KT}+2\right)+\frac{1}{2}\ln\left(\frac{m_n^*}{m_p^*}\right)^{3/2}\right]$$

Where K is the Boltzman constant, b is the ratio of the electron to hole mobilities, ΔE_g is the energy gap width and m_n^*, m_p^* are the effective masses of electrons and holes respectively. This formula predicts that a plot of α as function of the reciprocal of the temperature in the intrinsic range should be a straight line with parameters determined by $b=\mu_n/\mu_p$ is found to 3.887. Fig.2 shows a plot of α versus 10^3 / T for p-type $Tl_2GaInTe_4$. This linear relation has negative slope, indicating the increase of TEP with elevating surrounding temperature. Knowing ΔE_g from the Hall data and assuming that (m_n^*/ m_p^*) does not vary with temperature .Hence by using the value of $\mu_p=1.368\text{x}10^4$

cm^2/V.sec, the electron mobility can be deduced and its value is found to be 5.32x10^4 cm^2/V.sec. Another important parameter can be deduced with the aid of the obtained values of μ_n and μ_p using the Einstein relation that is the diffusion coefficient for both carriers (holes and electrons) can be evaluated to be 354 cm^2/sec and 1376.4 cm^2/sec for both carriers respectively. The ratio between the effective masses of both electrons and holes can be evaluated from the intersection of the curve. We evaluate this ratio as m_n^*/ m_p^* =3.41x10^{-7}. This means that the effective mass of holes is much greater than that of an electron.

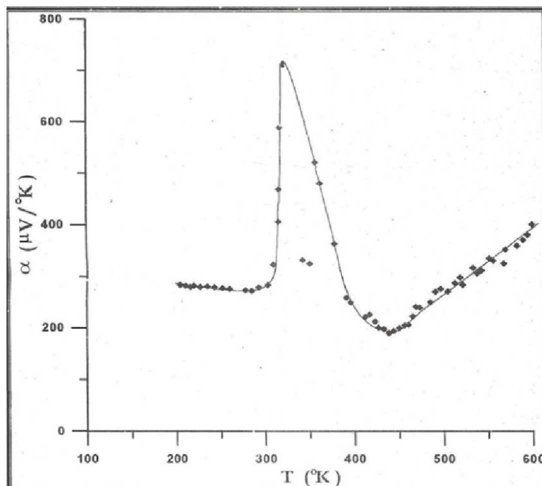

Fig 1. Variation of thermoelectric power coefficient (α) with temperature of Tl_2GInTe_4

Another useful formula [21] was suggested to described the relation between α and lnT in the impurity region for determination many physical parameters

$$\propto = \frac{K}{e}\left[2 - \ln\frac{ph^3}{2\left(2\pi m_p^* KT\right)^{3/2}}\right]$$

Where p is the majority charge carries concentration at room temperature. Plotting the above relation between α and lnT we obtain fig 3. This figure shows. That α decreases linearly with the increase of temperature, in the temperature corresponding to the extrinsic conductivity region. Calculation of the effective mass of holes from the intersection of the curve yields the value m_p^* =1.87x10^{-32} kg. Combining these value with the above mentioned results for the ratiom_n^*/m_p^*, one obtains an effective mass of minority carriers of electronsm_n^* =6.36 x10^{-39} kg. The results indicates 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 value of the effective masses for both minority and majority carrier can be used for the determination of the relaxation time for both current carries. Its value for holes comes to be 1.598 x 10^{-3} sec whereas for the electrons is equals 2.113 x10^{-19} sec. The diffusion length as another important physical parameters, can be deduced using the formula $L=\sqrt{D\tau}$ the value $L_p$and L_n are calculated and they are found to be 7.5 x 10^{-6} cm and 1.7 x10^{-8} cm for holes and electrons respectively.

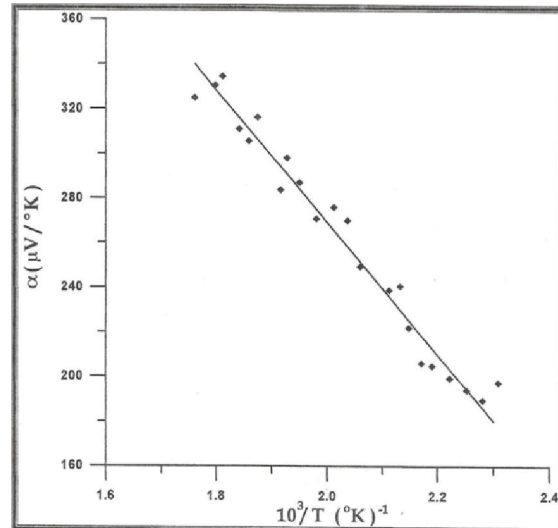

Fig 2. The relation between (α) and 10^3 / T for Tl_2GInTe_4 single crystal

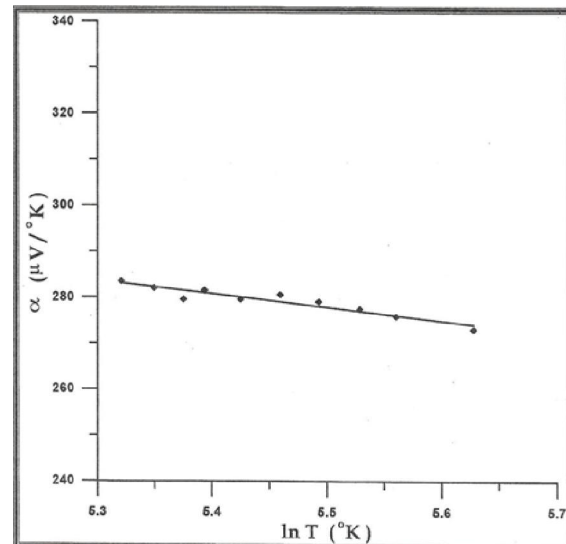

Fig 3. Illustrates the relation between (α) and lnT for Tl_2GInTe_4

For more definite understanding of the behavior of TEP are used our electrical conductivity and Hall effect data.

The behavior of the differential thermoelectric power α against the carrier concentration is presented graphically in fig 4. This graph shows the dependence of TEP on carrier density for a given $Tl_2GaInTe_4$

sample. The general behavior is that α decreases linearly with the increase of carrier concentration. From this behavior we realize the effect of charge carrier density is a strong factor governing the variation of α.

The decrease in the value of α with carrier concentration can be attributed to, as the temperature increase, the carrier density decreases due to recombination processes and trapping centre, this lead to the rate of diffusion of charge carriers decreases. This is the reason for decreasing of α with carrier concentration.

Fig 5 illustrates the relationship between TEP and electrical conductivity σ. The following relation can be applied[22]

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

It is seem from the curve that the TEP decreases gradually and linearly as the electrical conductivity increased. The relation between α and σ is similar to the behavior of α against lnP. The similarity between the behavior of these curves indicates that the mode of α variation against T is governed mainly by σ. But the conductivity is proportional to the carrier concentration and the mobility, so we can conclude that the mobility is the dominant factor that governs α.

The choice of materials for thermoelectric generators and refrigerators is based on the efficiency parameter $z = \alpha^2 \sigma / K$, where K is the thermal conductivity of a semiconductor and σ is the electrical conductivity. However the term figure of merit is a measure of both performance and efficiency of a certain thermoelectric elements. For our best $Tl_2GaInTe_4$ samples the obtained value of $z = 2.3 \times 10^{-8}$ k which permits the practical application as thermoelectric elements.

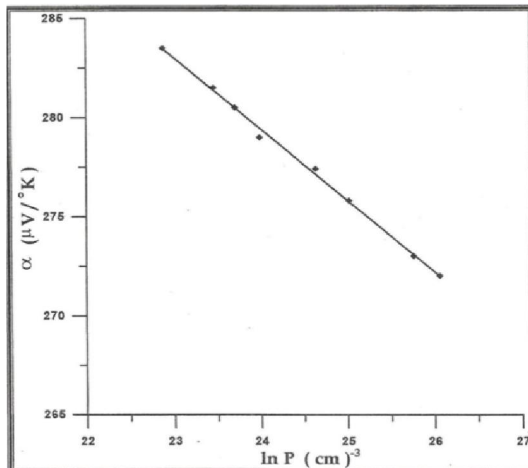

Fig 4. Dependence of TEP (α) on concentration of charge carriers (holes) for Tl_2GInTe_4

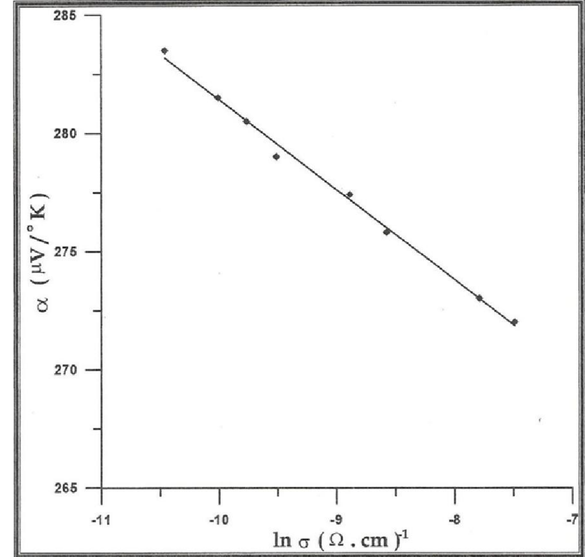

Fig 5. Variation of thermoelectric power with electrical conductivity (σ) of Tl_2GInTe_4

The proposed treatment of the experimental data sheds new light on the main physical parameter in $Tl_2GaInTe_4$ single crystals. However, those parameters are found to be sufficient to gave complete information about the general behavior of the $Tl_2GaInTe_4$ crystals.

This gives the chance of practical application especially in the field of energy conversion.

4. Conclusion.

In the present work we growth high quality single crystal compound $Tl_2GaInTe_4$ by a modified Bridgman technique. Measurements of thermoelectric power in a wide range of temperature for $Tl_2GaInTe_4$ single crystals were reported. The experimental data, give us the chance to determine the following pronounced parameter, such as conductivity type of free charge carriers mobilities, effective masses of charge carriers, diffusive coefficient and diffusion length as well as the relaxation time for Charge carriers, diffusive coefficient and diffusive length as well as the relaxation time for both types of charge carriers. Also the efficiency parameter was deduced. This mode of investigation (crystal growth and thermoelectric properties study), is an ideal way for finding out the possibility of making applications for these semiconductor compound especially in the field of energy conversion, semiconductor devices and electronic engineering. The present investigation might be the first study on the thermoelectric properties of the $Tl_2GaInTe_4$ compound and reveal the general behavior of this new semiconductor compound.

References

1. Guler, I., Gasanly, N. M., (Trapping center parameters in TlInSSe layered single crystals by thermally stimulated currents measurements. J. Alloys and Compound 485 (2009) 41-45
2. kozma, A. A.,Barchtly, I. E. and peresh E. Yu. (phase relations in the Tl_2SnSe_3- Tl_4SnSe_4- $TlBiSe_2$quasiternary system) chem. Mat. Alloys 4 (2011) 94-94.
3. Qasrawi, A. F., and Gasanly, N. M.,(study of trapping and recombination centres in $Tl_2InGaTe_4$ chain crystals by dark electrical conductivity and photoconductivity measurements) .Philosophical Magazine 87(2007)5741-5747.
4. Nagat, A. T., Gamal, G. A., and Hussein S.A., (Growth and characterization of ternary compound $TlGaTe_2$ single crystals) Phys. Stat. Sol.(a) 120 (1990)183-167.
5. Nassary, M. M., Hussein S. A., and Nagat, A. T., (Behaviour of switching phenomena in single crystals of $TlGaTe_2$) cryst. Res. Tech.29 (1994) 869-873.
6. Godzhaev, E. M.,Orudzhev, G. S. and Kafarova D.M.,(Band structure and permittivity of the $TlGaTe_2$ compound) physics of the solid state 46(2004) 833-835.
7. Kurbanov, M. M.,(Thermal expansion and isothermal compressibility of TlGaTe2 Inorganic Materials 41(2005)1277-1279.
8. Gospodinov, M. M., Yanchevs, I. Y. Mandalidis, S., Anagnostopoulos A. N. (Growth and characterization of $TlGaTe_2$) Materials Research Bulletin 30(1995) 981-985.
9. Gojaev, E. M., Allakhyarov, E. A., Nazarov, A. M., Gyul,mamedov,K. D., Khalilovakh. S and Mamedov, E. M.(Acoustophotovoltaic effect in $TlInSe_2$, $TlInTe_2$ and $TlGaTe_2$ single crystals) Inorganic Materials 43 (2007) 1059 - 1064.
10. Wakita, K, Shim Y., Orudzhev, G., Mamedov, N,.Hashimzade,F., (Band stracture and dielectric function of $TlInTe_2$) physica status solidi(a) 203(2006)2841- 2844.
11. Watzke, O., Schneider T., and Martienssen W., (Crisis induced intermittency in the electrical conductivity of $TlInTe_2$) choosSolitons and Fractals11 (2000) 1163-1170.
12. Abay B. Gürbulak B.,Yildirim,M., Efeoglu, H., Tuzumen S., Yogurtu, Y.K. (Electrothermal investigation of the switching effect in P-type $TlInSe_2$,$TlInTe_2$ and $TlGaTe_2$ chain chalcogenide semiconductors) Journal of Electronic Materials 25(1996)1054-1059.
13. Qasrawi, A. F., and Gasanly N.M.(Crystal data and some physical properties of $TlInGaTe_4$) cryst.Res.Technal.42(2007)807-811.
14. Qasrawi, A.F., and Gasanly N.M.,(Thermal lattic scattering mobility and carrier effective mass in intrinsic $Tl_2InGaTe_4$ single crystals, J. Phys. Conden. Matter 19 (2007)156206.
15. Jazi Abdullah Mohammed Abdulwahed (Growth and transport properties of the quaternary chalcogenides $Tl_2GaInTe_4$ compounds) Life. Science Journal 11 (2014) 109-113.
16. Iianxiao Xu, Abdeljalil Assound, Yanjie Cui, Holger Kleinke (Crystal structure, electronic structure and physical properties of a new semiconducting thallium antimony selenide $Tl_{2.35}$ $Sb_{8.65}$ Se_{14}) Solid state Sciences 10(2008) 1159-1165.
17. Hussein S. A. and Nagat, A.T., (On the preparation and electrical properties of thallium selenidemonocrystals) cryst. Res. Technol.24 (1989) 283-
18. Hussein, S. A, Nagat, A. T., Gameel Y. H., and Belal A.E. (Thermal transport properties of Gallium selenide Crystals) Egyp.J.Sol.10 (1988) 45.
19. Nagat, A. T., Hussein S.A., Gameel Y. H. and Belal A. E. (Thermal e.m.f of some phases of In-Se system) Egyp. J. sol. 11(1988)60.
20. Johson V. A. and Lark-Horovitz K., (Theory of thermoelectric power in semiconductors with applications to Germanium) Phys.Rev.92 (1953) 226.
21. Wilson, A.H. (Theory of metals) 2nd ed. Cambridge university press, Cambridge (1953).
22. Shimid P. H. E. and Mooser E. (Thermoelectric power of Thallium-selenide ,Heiv, Phys. Acta 45 (1972) 870.

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