Synthesis and thermoelectric power measurements of $TlGaSe_2$ single crystals

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Abstract. $TlGaSe_2$single crystals were grown by modified Bridgman method. Thermoelectric power measurement were carried out in a brass working chamber designed for this purpose, allow measurements in a wide range of temperature under vacuum. The experimental results indicates that $TlGaSe_2$ is of p-type conductivity. Throughout these measurements, various parameters such as effective mass of charge carriers, carrier mobility, diffusion coefficient, relaxation time and diffusion length for both majority and minority carriers were found. In addition to these pronounced parameters, the efficiency of the thermoelectric element (figure of merit) was evaluated, which leads to better application in many fields.
[A. T. Nagat, S. A. Hussein, S. E. Al Garni. **Synthesis and thermoelectric power measurements of $TlGaSe_2$ single crystals.** *Life Sci J* 2014;11(8):418-422]. (ISSN:1097-8135). http://www.lifesciencesite.com. 54

Key words: $TlGaSe_2$ Single Crystal, Thermoelectric Power, Electrical Conductivity.

1- Introduction

Nowadays semiconductor compounds play an important role in technological development because of their attractive characteristics. Number of semiconductor compounds from the group $A^{III}B^{III}C_2^{VI}$ have been the subject of intensive investigations in recent years as materials having promising properties. So they call the attention of many physicists to explore more and more of their hidden secrets. Among of these materials chalcogenides have been devoted a particular attention .

$TlGaSe_2$ is semiconductor from $A^{III}B^{III}C_2^{VI}$ group which have been shown to be new materials with attractive characteristics . These materials were chosen as the subject for investigation in our laboratory.

Our investigation aimed to preparation of $TlGaSe_2$ and collecting much more information about the semiconductor parameters of this compound. In the present work, single crystals of $TlGaSe_2$ were grown by the modified Bridgeman technique. According to this technique, the samples have been prepared by the direct melting of the starting materials and then placed in quartz ampoules sealed under vacuum of about 10^{-5}Torr.Double-walled silica glass ampoules with the external part evacuated were used to minimize convection effects. The silica ampoule and its charge were mounted in the first zone of a three-zone tube furnace, where the temperature was higher than the melting point and was kept 24 h for mixing the starting materials. The temperature of the middle zone of the furnace was 1093K corresponding to the crystallization temperature of $TlGaSe_2$[1]. When the ampoule and its contents entered the third zone, gradual solidification occurred since the temperature was less than the melting point.

X-ray diffraction analysis confirmed that $TlGaSe_2$ crystals, by using a very high purity materials. The product ingots were identified with X-ray analysis and differential thermal analysis DTA.

For the last few years there has been considerable interest in the investigation of the physical properties of layered ternary crystal with chemical formula $TlBX_2$, where B=Ga or In and X=S or Se[2,3]. Many studies concerned with electrical, optical and photoelectrical properties of $TlGaSe_2$ have been published[4-7]. The optical properties of layered single crystals of $TlGaSe_2$ have been studied[8]. The dielectric characteristic of $TlGaSe_2$ was reported[9]. The Rammanspectra of $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$ have been investigated[10,11]. Optical, photolumi-nescence spectra and photoelectric properties of $TlGaSe_2$ were studied by many authors[12-14].

This paper presents new data on the thermoelectric power of $TlGaSe_2$ single crystals. This study in a timely one is view of the recent interest in this compound. This investigation is considered as a part of the running research work in our laboratory on ternary chalcogenides compounds.

2- Experimental procedure

The materials were supplied from Aldrich with a purity of 99.999% for Tl, Ga, and Se, 23.6519g of thallium (47.3038%), 8.0653g of gallium (16.1306%) and 18.2828g of selenium (36.5656%) were used as starting materials in the experiment. The thallium and gallium were placed at the opposite end from selenium in a quartz tube. The crystals were grown by modified Bridgman method. The silica tube was

kept for 10 h in the first zone, where the temperature was higher than the crystallization temperature. The melt was shaken during heating several times. Then the ampoule was drawn with a rate of 2 mm/h and allowed to enter the second zone in which the temperature was corresponding to the crystallization temperature. The ampoule with its charge was introduced into a three zone tube furnace[15]. Via a very slow rate of movement, the ampoule with its charge was made to enter the second zone of the furnace where the temperature equals that of the crystallization point[16]. Finally solidification occurs in the third zone. Such processes need about 14 days for one to have single crystals of the $TlGaSe_2$ compound. The resultingingot did not have cracks and voids on their surface.

The product ingots were identified with x-ray and DTA analysis. X-ray diffraction patterns show that these crystals have monoclinic structure with the lattice parameters a=10.756°A, b=10.1730°A, c=15.596°A and β=99.92.X-ray diffraction pattern for $TlGaSe_2$ compound is given in Fig.

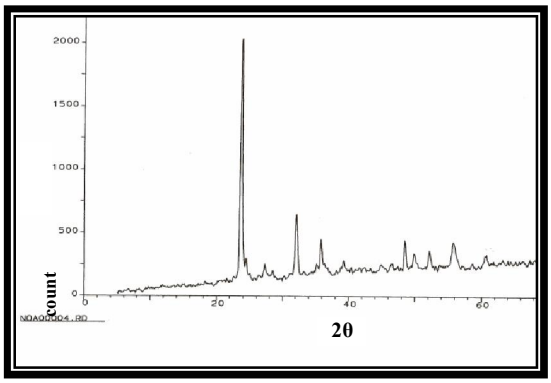

Fig. 1. X-ray diffraction pattern for $TlGaSe_2$ single crystal

The thermoelectric power (TEP) of bulk specimen at different temperature was measured. The used sample holder was of pressure contact type. A vacuum working chamber was locally constructed for the present work and was designed[17,18], in a way that, it allows measurements at a wide range of temperature. The sample freshly cleaved from a large ingot with good optical surfaces was placed inside a copper cylinder chamber for temperature control and electrostatic shielding, and the chamber was evacuated in order to reduce contamination from the atmosphere. A temperature gradient of about 10°C was maintained and controlled by two electric heater, one of them at one end of the sample stand and the other surround the whole sample body. In this work, a compensation method is used for measuring voltages without drawing an appreciable current using a tensely potentiometer type (UJ33E). The potentiometer is used for measuring the thermo-e.m.f., while $T_1$and T_2 are measured using digital multimeter model HC-5010.Measurements were taken under vacuum conditions, and consequently neglect losses of heat by convection. The thermal e.m.f of $TlGaSe_2$ crystals was performed when the direction of temperature gradient is perpendicular to the cleavage plane. Details about the apparatus, method of measurement and the designed working chamber have been described earlier[19].

3- Results and discussion

The investigated range of temperature was between 271-493 K. The results of the temperature dependence of thermoelectric power (TEP) of TlGaSe2 single crystals are given in Fig.2. The value of α increase with increasing of T reaching a maximum value of 563μV/K at 307 K. Such behavior led to the assumption that, more holes are generated and contribute to the increment of (α) values as the temperature rises. a second region in the same figure is observed where (α) rapidly falls above 343K. The decrease of (α) magnitude is regarded as a result of the compensation process which takes place in this temperature range, with further rise of the temperature, α increases very rapidly. Such behavior is expected in this intrinsic range where generation of both carriers (electron and holes) contributes to the increment of (α) value. The discussion of the results could be divided into two regions: the intrinsic and the extrinsic region. This enables us to estimate many physical parameters. In the intrinsic range of a semiconductor, the following expression is usually applied[20]:

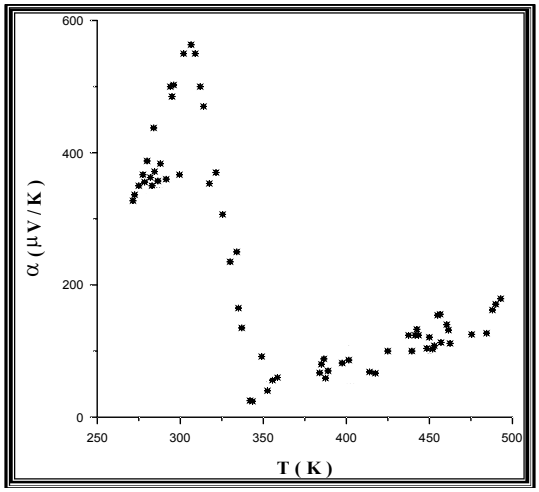

Fig. 2. Variation of thermoelectric power coefficient (α) with temperature of $TlGaSe_2$

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

where K is Boltzmann's constant, b the ratio of mobilities, ΔE_g the width of the forbidden gap and m_n^* and m_p^* are the effective masses of electrons and holes respectively.

Fig. 3 illustrate the variation of α as a function of reciprocal of absolute temperature 10^3T^{-1} for p-type $TlGaSe_2$. The liner relationships of α and inverse temperature 1/T indicate the intrinsic-like characteristic Since ΔE_g equals 2.1 eV from Hall data and we are assuming that m_n^*/m_p^* dose not vary with temperature, it was found that $b = \mu_n/\mu_p = 1.32$ .Thus, using $\mu_p = 7.46\times10^3$ $cm^2V^{-1}s^{-1}$ at room temperature means that $\mu_n = 9.85\times10^3$ $cm^2V^{-1}s^{-1}$.The ratio of electron and hole effective masses m_n^*/m_p^* evaluated from the intercept of the curve with the α-axis and it was found to be $m_n^*/m_p^* = 8.49\times10^{-4}$. It is known that the thermoelectric power of a semiconductor, when one type of carriers dominates, is given by the following relation[21]

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

Poltting the above relation between α and lnT, we obtain fig.4. This figure shows that α increases linearly with the increase of temperature in the temperature range corresponding to the extrinsic conductivity region. From the intercept of the line (in the impurity region) with the α axis we got $m_p^* = 2.647\times10^{-31}kg$. Combining this value with the above-mentioned result for the ratio m_n^*/m_p^*, one obtain an effective mass of minority carriers of the value $m_n^* = 2.247\times10^{-34}kg$. The relaxation time for both current carriers value for holes comes to τ_p=1.23×10^{-12}s, whereas for the electron it equals τ_n=1.38×10^{-15}s.

The diffusion constant is related to the mobility of charge carriers, its value for holes and electrons can be deduced as D_p=193.02cm^2/sec and D_n=254.79cm^2/sec, respectively.

Fig. 5 shows the dependence of α on the nature logarithm of the electrical conductivity according to the following expression [21]:

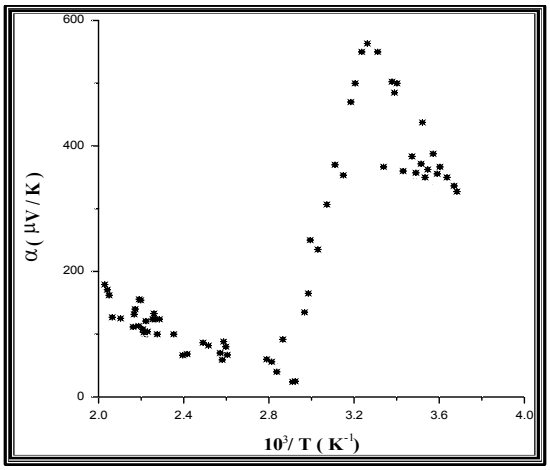

Fig. 3. Temperature dependence of the thermoelectric power for$TlGaSe_2$

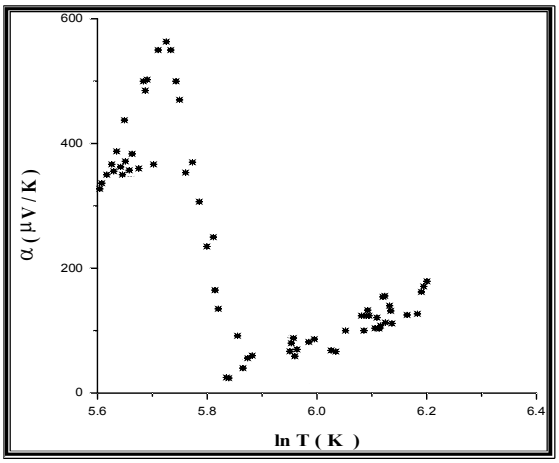

Fig. 4. Relation between thermoelectric power and ln T for $TlGaSe_2$ single crystal

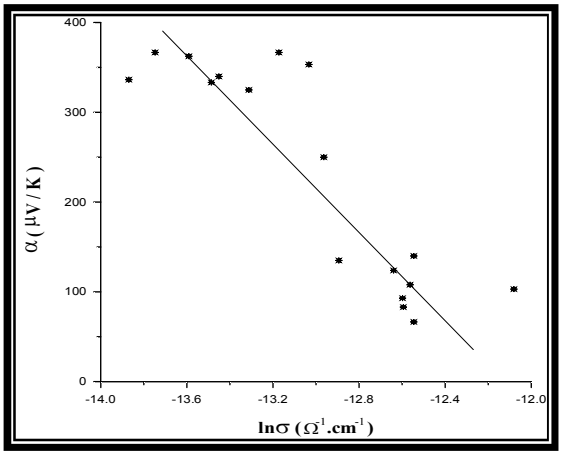

Fig. 5. TEP as a function of the carrier concentration for $TlGaSe_2$

$$\alpha = \frac{K}{e}\left[A + \frac{ln2\,(2\,\pi\,m_p^*\,K\,T)^{3/2}\mu}{(2\,\pi\,h)^2}\right] - \frac{K}{e}\,ln\,\sigma$$

where σ is the electrical conductivity.

The same behavior is observed when we plot α versus carrier density for the $TlGaS_2$ sample, as shown in fig.(6).

By using the results of measurements of the electrical conductivity σ, seebeck coefficient α and published value[28] of thermal conductivity K, the figure of merit (Z) for $TlGaSe_2$ at room temperature is calculated to be 9.62×10^{-12} K^{-1} . This indicated that our best sample $TlGaSe_2$can be used as high efficiency thermoelectric element.

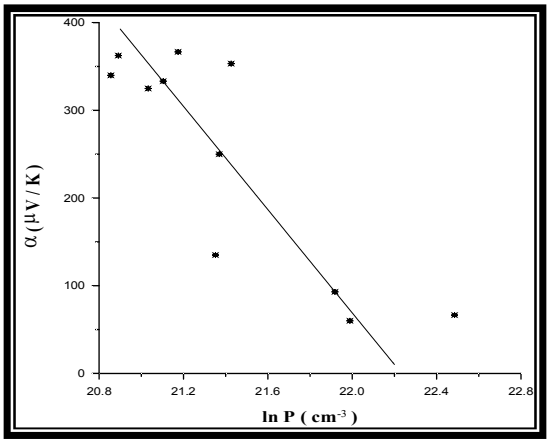

Fig. 6. Dependence of TEP a on the natural logarithm of electrical conductivity for $TlGaSe_2$ single crystal

Conclusion remarks

The temperature dependence of the thermal e.m.f in the temperature range extends from 271-493 K was measured. X-ray diffraction analysis confirmed that $TlGaSe_2$ compounds have a tetragonal structure with single phase.$TlGaSe_2$ is a semiconductor of p-type conductivity as observed from the positive sign of α over the entire investigated temperature range. The energy gap was found 2. 1 eV which confirms the possibility of utilizing such single crystal as a solar energy converter. and activation energy of acceptors of 0.36 eV. We deduce many important physical parameters such as the mobilities, effective masses, diffusion coefficient, as well as relaxation time for the majority and the minority carriers. The efficiency of thermoelectric power conversion, also was investigated through determination of figure of merit Z.

Acknowledgement:

We would like to thank Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, for their kind help and providing the necessary facilities for the preparation of the paper. This work would not have been possible without the generous assistance of DSR.

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5/6/2014