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The Growth and Characteristic Features of Some Chalcogenides from the Group A^{iii} B^{iii} C_2^{vi} Semiconductor Compounds

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Abstract: In the present paper, the electrical conductivity, Hall effect and thermoelectric power of single crystals prepared by a special modified Bridgman technique have been investigated over the temperature range 228 -553 K for electrical conductivity and Hall effect and in the temperature range 181 – 373 K for thermoelectric power. Our investigation showed that our samples are P- type conducting. The forbidden energy gap was calculated and found to be 0.826 eV, whereas the ionization energy of the impurity level was 0.336 eV, the values of the electrical conductivity, Hall coefficient and carrier concentration at room temperature were 8.55×10^{-4} Ω^{-1} cm^{-1}, 1.11×10^{6} cm^3 C^{-1} and 5.615×10^{12} cm^{-3} respectively. The Hall mobility at room temperature was found to be 9.52×10^{12} cm^2 $V^{-1}s^{-1}$. The combination of the electrical and thermal measurements in the present investigation makes it possible to find various physical parameters such as mobilities, effective mass, relaxation times, diffusion coefficients and diffusion lengths both for majority and for minority carriers. Also figure of merit was determined. This mode of investigation (crystal growth, electrical conductivity, Hall Effect and thermoelectric power) is an ideal way for finding out the possibility of making applications for these semiconductor compounds especially in the field of energy conversion, semiconductor devices and electronic engineering

Key words: $TlGaTe_2$, single crystals, σ, R_H, α,

INTRODUCTION

In the past three decades, significant interest in chalcogenide semiconductor has been shown by various workers because of their interesting physical properties as well as their wide technological applications. $TlMX_2$ (M = Ga, In) chalcogenides (Mehta *et al.* 2009) offer large gage factors, memory switching behavior, and high photosensitivity in the IR through visible spectral region. Of particular interest are compounds with the TlSe structure.

$TlGlTe_2$, $TlInTe_2$ and $TlInSe_2$ are ternary chalcogenides with belong to the group of strongly anisotropic semiconductors (Banys *et al*. 1990) with the general formula $TlAB_2$ where A= Ga, In and B= S, Se and Te_2. The triple compound $TlGlTe_2$ is a semiconductor of TlSe type. This compound is the least (Gurbulak *et al*. 2000) known representative of the triple analogs of thallium selenide. Attention has been given to the crystal structure and thermo dynamical properties of $TlGlTe_2$ have been studied in sufficient detail (Gurbulak *et al*. 2004 and Ibragimov *et al*. 1988). The band gaps of $TlGlTe_2$ was found to differ drastically and amount to be 2.3 eV (Nagat *et al*. 1991), 1.2 eV (Aldzhanov *et al*. 1985) and 0.84 eV (Godzhaev *et al*. 2004). Heat capacity, thermal expansion (Okazaki *et al*. 2001 and Gasanly *et al*. 1980), Also phase transition was observed at 89.5 K. The electrical, photoelectrical and optical properties was published (Shim *et al*. 2011 and Sheleg *et al*. 2011). The anisotropy of electrical properties as well as temperature dependence of dielectric constant was studied (Hussein *et al*. 1989 and Nagat *et al*. 2009). Nevertheless to our best knowledge relatively good data for this semiconductor compound $TlGlTe_2$. In view of the scarcity of the data on the properties of thallium gallium dietelluride, also from the above reported studies, literature still lacks of the information about Hall properties, carrier effective masses, the impurity level, mobility of charge-carriers as well as relaxation time, diffusion coefficient, diffusion length, the dominate scattering mechanisms, and figure of merit of $TlGlTe_2$ crystals. In view of the current interest in this materials and its possible practical application. 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 devices.

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Experimental Details:

The samples we have worked with were $TlGlTe_2$ single crystals. They have been grown from melt by the modified Bridgman technique. The purity of the materials used was as follows Tl, 99.9999%, Ga, 99.9999% and Te, 99.9999%. Stoichiometric mixture of the elements was used as starting material in the growth experiments. At the beginning of the growth run, the ampoule with its charge was held in the hot zone of the furnace at 820 ^{0}c for 10 h. for melt homogenization, the charge was shaken during heating several times to accelerate the diffusion of contaminates through each other. Then the ampoule was moved into the middle zone of the furnace with a temperature of 773 ^{0}c according to the phase diagram at a rate of 0.15 cm/h. Afterwards, the ampoule was cooled down slowly in the third zone of the furnace, then the furnace was switched. Details of the experimental equipment for the crystal growth and of preparation procedures are described elsewhere (Al-Ghamdi *et al.* 2009) X-ray analysis and DTA investigation confirmed that $TlGaTe_2$ is a single crystal. The XRD patterns show that these crystals have tetragonal structure with the lattice parameters of a = 8.43 Å, b = 8.43 Å, c = 7.2 Å and $\alpha = \beta = \gamma = 90$.

Specimens for measurements were prepared for electrical conductivity and Hall Effect in rectangular shape with means dimensions 7.8x2.3x1.1 mm^3. Ohmic contacts were formed on the specimen surfaces by means of silver paste and the ohmic nature of the contact was checked by recording the current voltage characteristic. The dc compensation method was adopted for measuring voltage without drawing appreciable current by using a Tensily UJ33E potentiometer. All measuring were carried out under vacuum with 0.5 tesla magnetic field strength. Details of the experimental arrangements and cryostat were described (Gamal *et al*. 1992) previously. 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 large as possible. A two parts holder was used for making the temperature difference a long 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 accuracy of the measurement was enough because the potential difference and the temperature were measured simultaneously. Also these measurements were done under vacuum for preventing oxidation of the sample on water vapor 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 (Allakhverdiev *et al*. 1989).

RESULTS AND DISCUSSION

1-Temperature dependence of electrical conductivity and Hall Effect for $TlGaTe_2$:

Electrical properties of $TlGaTe_2$ in a crystalline for and their temperature dependence were investigated over the wide temperature rang extend from 228-553 K. Fig.1. Shows the results of electrical conductivity as a function of temperature.

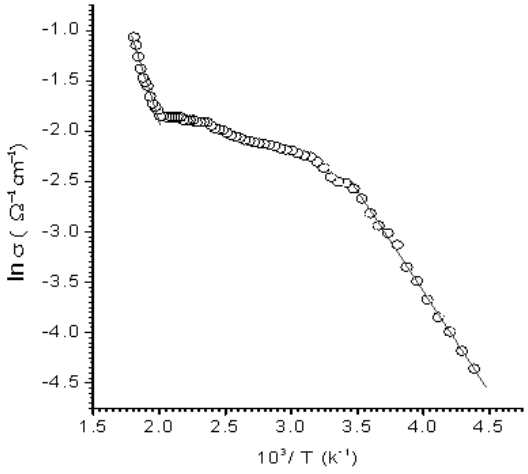

Fig. 1: Electrical conductivity of $TlGaTe_2$ as a function of temperature

The curve consists of three regions. These curves are quite similar to the semiconductor behavior. The first region lies between 228-283 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=0.252eV. The second region lies over the temperature range 283-423 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 423 K, the conductivity increases rapidly because both of the carries being excited from the extended state of the valance band into the conduction band. The third region lies at 425-553 K, is the intrinsic part. From the slope of the curve in this region, the width of the forbidden energy gap can be calculated according to the following relation

$$\sigma = \sigma_0 \exp\left(-\Delta E_g / 2KT\right) \tag{1}$$

Where σ_0 is the pre-exponential factor; ΔE_g is the energy gap width. It is found ΔE_g equal to 0.826 eV. This value in close to the published value (Johnson *et al*. 1953). The room temperature conductivity of this sample is 0.0855 Ω^{-1} cm^{-1}.

Fig.2 shows the behavior of the Hall coefficient R_H against temperature. The Hall coefficient is positive all over the temperature interval investigated. This means that the major carriers are holes and hence $TlGaTe_2$ is a P-type semiconductor. The value of R_H at room temperature equals 11.13x10^5 cm^3/C.

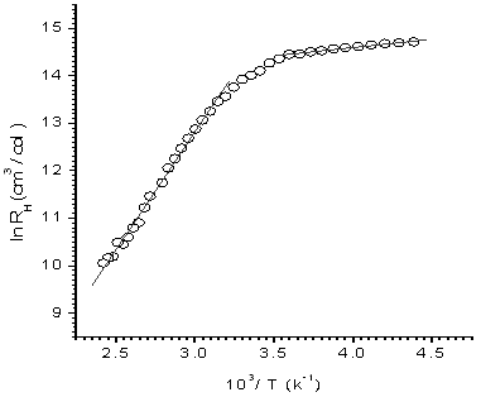

Fig. 2: The dependence of R_H against the temperature for $TlGaTe_2$ single crystal

Fig.3 shows the relation between $R_HT^{3/2}$ and $10^3/T$. The value of ΔE_g as deduced from this figure is 0.826 eV. This value is in good agreement with the conductivity measurements and published value. 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.

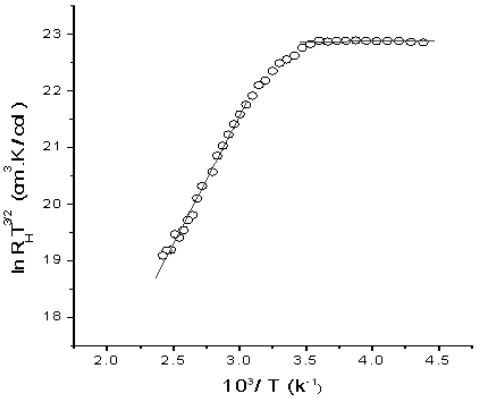

Fig. 3: Variation of $\ln R_HT^{3/2}$ with $10^3/T$ for $TlGaTe_2$ single crystal

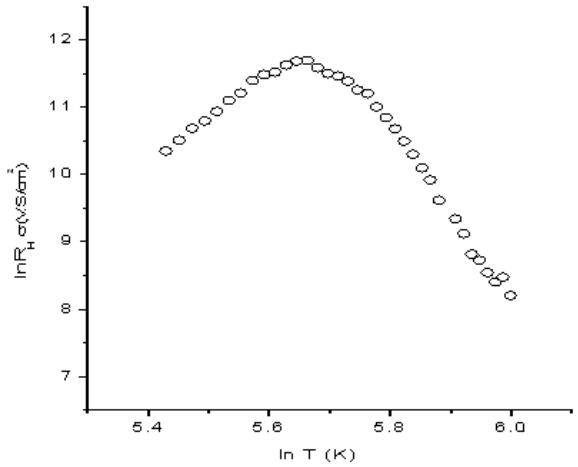

Fig. 4: Hall mobility as a function of temperature for $TlGaTe_2$ single crystal

Fig.4 depicts the variation of R_H σ as a function of temperature. Two regions can be distinguished. At low temperature the mobility seems to increase as the temperature increase reaching a maximum value at 11.69 cm^2 $V^{-1}s^{-1}$ corresponding to 288 K and obeys a power low $\mu \sim T^{7.13}$. The second region of the curve is highest temperature range, in which the mobility decreases according to the low $\mu \sim T^{-12.46}$. The high values of the exponent in the relation $\mu_H \sim T^n$ suggest that the scattering mechanisms of the carriers should differ from that in semiconducting single crystal materials. This behavior is in contradiction compared with that of typical semiconducting material. This anomalous behavior cannot be understood by the usual theory of semiconductor. Hall mobility behavior of the higher resistivity's $TlGaTe_2$ may be due to a change in the transport mechanism between localized state either within the energy gap or in the regions close to the bottom of the conduction band or to the top of the valance band. However there is a need for more work to be carried out on the role of the mobility behavior with temperature before any definite conclusions can be drawn from this type of measurement. The Hall mobility at room temperature has the value 9.52×10^4 cm^2 $V^{-1}s^{-1}$. Clearly charge carrier mobility in our material is much higher among other semiconductor materials from this group of compounds $TlAB_2$.

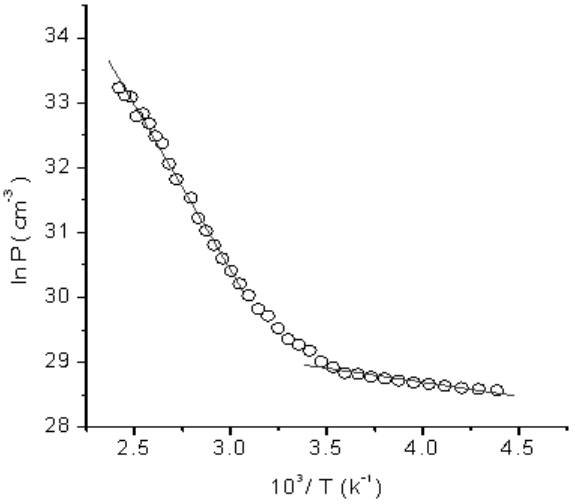

Fig. 5: Behavior of the carrier concentration with temperature

Fig.5 the curve represents the free-carrier concentration as a function of the inverse absolute temperature; Fig. 5 is helpful for understanding Fig.1.

The charge carriers concentration was calculated from Hall coefficient data using the relation ($P=1/R_H$ e) where P is the hole concentration and e is the hole charge. Now, it is well established that, the following relation can be applied to describe the temperature dependence of the charge carrier concentrates as follows

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

This relation facilitates calculation of the energy gap. The value of ΔE_g agrees with that obtained from the conductivity and Hall effect work, and also agrees with the published value (Johnson *et al.* 1953). Furthermore, at room temperature carrier concentration calculated to be 5.615×10^{12} cm^{-3}.

2-Temperature dependence of thermoelectric power for $TlGaTe_2$:

The thermoelectric power for $TlGaTe_2$ was characterized in the temperature range 181-564 K and is shown in fig.6. At the beginning of the curve TEP increases with temperature, reaching a maximum value at α equal to 55 μVK^{-1} at 250 K. A drop of TEP is observed after 250 k until it reaches a minimum value of α equal to 2 μVK^{-1} at 350 K. This decrease in α reveals that the compensation process takes place in this range of temperature. Above 350 K the TEP increases sharply with increasing temperature. The increment of α is interpreted as a result of thermal generation of the charge carriers with increasing temperature. The results show that, the conduction can be regarded as P-type with no polarity charges over whole temperature range, which is in agreement with our pervious data of Hall coefficient. The value of thermoelectric power at room temperature α = 82 μV/K.

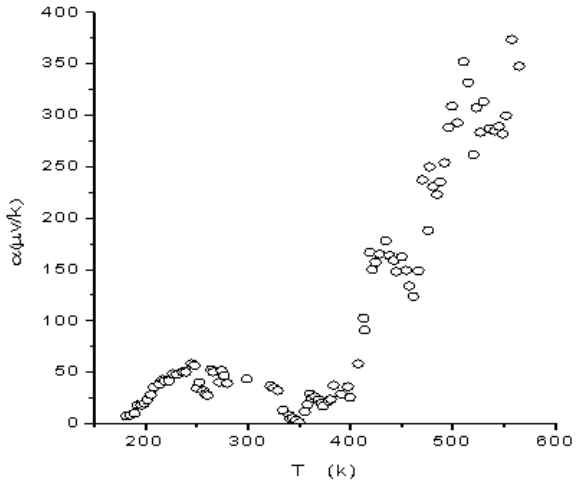

Fig. 6: Temperature dependence of TEP for $TlGaTe_2$ single crystal

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

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

Where b is the ratio of electron and hole mobility, ΔE_g is the energy gap and (m_n^*, m_p^*) are the effective mass of electrons and holes, respectively, K is the Boltzman's constant. The relationship shows 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.7.

The slope of the linear part is used to estimate the ratio of the electron and hole mobility. Taking ΔE_g = 0.826 eV, as obtained from the electrical conductivity and Hall Effect measurements, the ratio $b=\mu_n/\mu_p$ is found to be 8.28. Hence by using the value of $\mu_p = 9.521 \times 10^4$ $cm^2/V.s$. The electron mobility can be deduced and its value is found to be 78.87×10^4 $cm^2/V.s$. Also the ratio (m_n^* / m_p^*) is calculated from the intercept of the curve with α-axis and it was 1.07×10^{-7}. Another important parameter can be deduced with the aid of the obtained values μ_n and μ_p using the famous Einstein relation, that is the diffusion coefficient for both carries (holes and electrons) can be evaluated to be 2.4636×10^3 cm^2/s, and 20.4078×10^3 cm^2/s, respectively. In addition, a formula was suggested for analyzing the data of α in the impurity region as (Wilson. 1953)

$$\propto = \frac{k}{e}\left[2 - l\,\mathrm{n}\frac{ph^3}{2(2\pi m_p^* KT)^{3/2}}\right] \tag{4}$$

Plotting the above relation between α and lnT predicts that TEP increases with temperature increase in the in the temperature range corresponding to the impurity region as shown in Fig.8.

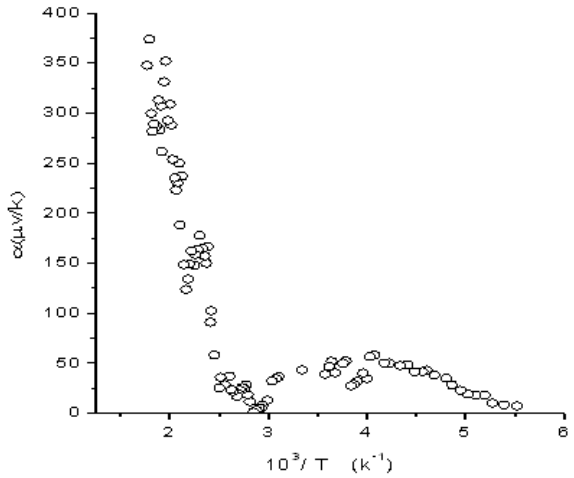

Fig. 7: Plot of α against 10^3/T for $TlGaTe_2$ single crystal

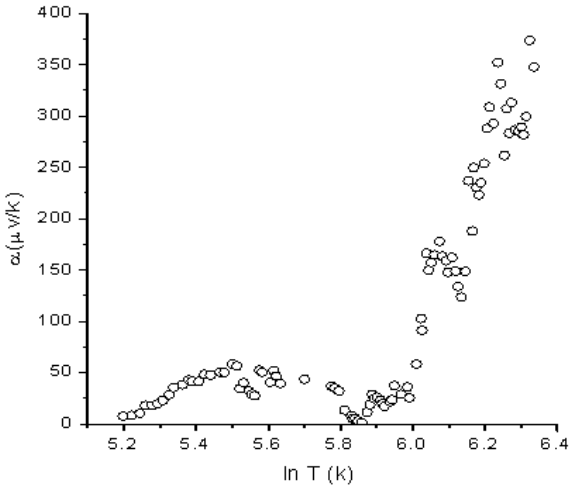

Fig. 8: The relation between α and lnT for for $TlGaTe_2$ single crystal

From the intercept of the line with the α-axis we got $m_p^* = 3.08x10^{-33}$ kg. Combining this value with the above ration (m_n^*, m_p^*) allows us to determine the effective mass of electrons. This value equal $3.29x10^{-40}$ kg.

The calculated values of the effective masses both for minority and for majority carriers can be used for determination of the relaxation time for both current carriers. This value for holes turned out to be $1.83x10^{-13}$ s, whereas for electrons is equals $1.62x10^{-19}$ s. the diffusion constant is inversely proportional to the effective mass of hole and electrons. So this result is quite logical. Another important parameter can be estimated, that is the diffusion length, the values of L_P and L_n were found to be $2.12x10^{-5}$ cm and $5.75x10^{-8}$ cm for hole and electrons respectively.

Fig.9. depicts the dependence of the TEP on the natural logarithm of the charge carrier concentration. The main conclusion from this curve is that α decreases sharply and linearly as the concentration increase as suggested from the following formula

$$\propto = \frac{k}{e}\left[A + l\,\mathrm{n}\frac{2(2\pi m_p^* KT)^{3/2}}{(2\pi h)^3}\right] - \frac{K}{e} InP \tag{5}$$

Fig.10. shows the dependence of the thermoelectric power coefficient on the natural logarithm of the electrical conductivity. The following relation can be applied (Shmid. 1972)

$$\propto = \frac{k}{e}\left[A + l\,\mathrm{n}\frac{2(2\pi m_p^* KT)^{3/2} e\mu}{(2\pi h)^3} - In\sigma\right] \tag{6}$$

This behavior which governs the relation between the electrical conductivity and TEP is similar to that of α versus P. The similar behaviors of Fig. 8 and Fig. 9 predicts that the variation of α is mainly due to the carrier's concentration variation with temperature.

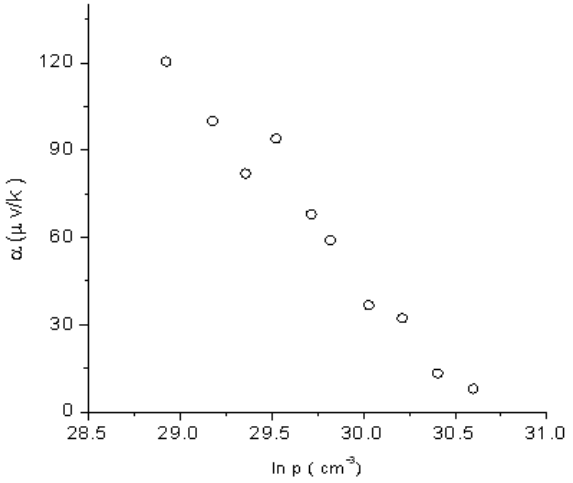

Fig. 9: The dependence of the TEP on the natural logarithm of charge carrier concentration for $TlGaTe_2$ compound

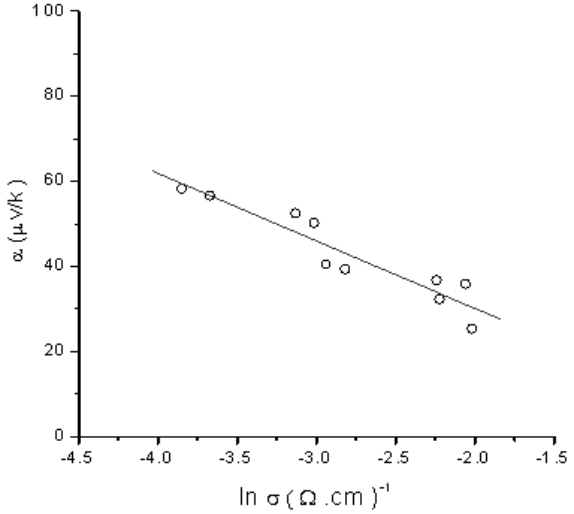

Fig. 10: The dependence of the thermoelectric power coefficient on the natural logarithm of the electrical conductivity for $TlGaTe_2$

The choice of materials for thermoelectric generation refrigerators and thermocouples 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. For our best $TlGaTe_2$ samples the obtained value of $Z= 1.31x10^{-6}\ K^{-1}$ permits the practical application as thermoelectric element.

Conclusion:

High quality of $TlGaTe_2$ single crystals grown by modified Bridgman technique. The electrical conductivity, Hall coefficient and thermoelectric power were measured as a function of temperature. The experimental data, give us the chance to determine the following pronounced parameters: conductivity type, carrier concentration, mobility, effective masses of charge carriers, diffusive coefficient and diffusive length as well as the relaxation time of both types of charge carriers. Also the width of the forbidden gap and position of the acceptor level as well as the figure of merit. This mode of investigation (crystal growth, electrical conductivity, Hall Effect and thermoelectric power) is an ideal way for finding out the possibility of making applications for this semiconductor compound especially in the field of energy conversion, semiconductor devices and electronic engineering.

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