Electrical and Thermal Transport Properties of TlGaSe$_2$ Single Crystals

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Abstract. The electrical conductivity (σ) and Hall coefficient (R$_H$) of single crystals prepared by a special modified Bridgman technique have been investigated over the temperature range 245-495 K. Our investigation showed that our samples are p-type conducting. The dependence of the Hall mobility on temperature was presented graphically. The forbidden energy gap was calculated and found to be 2.1 eV whereas the ionization energy of the impurity level was 0.36 eV. The values of the electrical conductivity, Hall coefficient and carrier concentration at room temperature were 1.87×10^{-6} Ω^{-1} cm^{-1}, 3.98×10^9 cm^3 C^{-1} and 1.57×10^9 cm^{-3} respectively. The Hall mobility at room temperature (μ$_H$) was found to be 7.46×10^3 cm^2 V^{-1}s^{-1}. Also, the thermoelectric power (TEP) was investigated in the temperature range 271-493 K. 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. These parameters reveal the general behavior of this semiconductor.

Keyword: Hall coefficient, TlGaSe$_2$, mobility, thermal properties, electrical properties.

1. Introduction

The ternary semiconducting chalcogenide with the formula ABX$_2$ (A, B represent metal atoms, X represents chalcogen atoms) have been studied intensively in recent years. Recently ternary thallium chalcogenides

received a great deal of attention due to their optical and electrical properties, in view of possible optoelectronic device application[1,2]. The ternary compound TlGaSe$_2$ belong to the class of III-III-VI$_2$ type semiconductors and have potential application[3,4]. Due to this applicability there is a need for studying its detailed physical properties. Much interest has recently pointed on ternary chalcogenide TlGaSe$_2$ compound, which possesses both ferroelectric and semiconductor properties[5,6]. TlGaSe$_2$ crystallizes in monoclinic system and belongs to a space group of c_{2h}^6 at room temperature. The interest of these materials is simulated not only by their fundamental properties but also by possible practical application[7]. The photoconductivity of TlGaSe$_2$ single crystal was investigated in the temperature range 78-300 K[8]. The photoluminescence (PL) spectra of III-III-VI$_2$ single crystals (*e.g.*, TlGaSe$_2$, TlGaS$_2$, TlInS$_2$) was studied[9-11]. Also the spectral dependence of photoconductivity and the near band edge absorption were reported[12]. The thermal expansion properties have been studied[13]. Moreover, gamma irradiation effect on the electrical properties[14] and the behavior of TlGaSe$_2$ crystals near phase transition in static electric field have also been reported[15]. The low temperature photoluminescence (PL) and infrared (IR) spectra of TlGaSe$_2$ crystals were published[11,16]. Ramman spectra of TlGaSe$_2$ crystal at different temperatures were discussed[17]. The optical properties of layered single crystals of TlGaSe$_2$ have been studied[18]. The dielectric characteristic of TlGaSe$_2$ was reported[19]. In spite of all the above reported studies, literature still lacks information about Hall properties, the carrier effective masses, the impurity level, mobility of charge carriers as well as relaxation time, diffusion coefficient, diffusion length, and the dominant scattering mechanisms in TlGaSe$_2$ crystals. Thus the aim of this work is to report these properties through the electrical conductivity, Hall effect and thermoelectric power measurements.

2. Experimental Details

The TlGaSe$_2$ compounds were synthesized by fusing initial components consisting of extra pure elements (purity 99.999%). The crystal was synthesized and grown in evacuated quartz ampoules. The silica ampoule was evacuated to 10^{-6} Torr and sealed under vacuum. The ampoule, with its charge, was placed in a three-zone tube furnace which

was designed and constructed in our laboratories. More details about the apparatus, the electrical system and the mechanical system were previously published[20]. 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[21]. In the final stage as the ampoule began to enter the third zone, the solidification process was achieved, since the temperature inside this zone was below the crystallization temperature. The duration for obtaining $TlGaSe_2$ in single crystal form was about fourteen days. X-ray analysis and DTA investigation confirmed that $TlGaSe_2$ is a single crystal. The XRD patterns show that these crystals have monoclinic structure with the lattice parameters of a = 10.756ºA, b = 10.1730ºA, c = 15.596ºA and β = 99.92ºA specimens for measurements were prepared for electrical conductivity and Hall effect in rectangular shape with mean dimensions $7 \times 2.2 \times 1$ 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 Tensely UJ33E potentiometer As to the sensitivity of our potentiometer the error limits are not exceeding 1%. All measurements were carried out under vacuum with 0.5 tesla magnetic field strength. The magnetic field was oriented parallel to the cleavage plane, *i.e*, H ⊥ C (where the C-axis is perpendicular to the cleavage plane)[3]. Details of the experimental arrangements and cryostat was described previously[22]. For measuring the thermoelectric power (TEP), the sample was prepared in a cylindrical shape. The length of 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 along the crystal, in a direction perpendicular to the natural cleavage plane, for investigation the thermoelectric power. The sample (5.6 mm length) was supported between the two holders. A temperature gradient of about 5-10K 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 or 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[23-24].

3. Results and Discussion

Typical data presented in Fig. 1 show the conductivity as a function of temperature in the range 245-495 K. The curve is quite similar to the simple semiconductor behavior. It should be noted that in the curve in Fig. 1, three regions can be distinguished. Beginning from the low temperature, the electrical conductivity (σ) increased slowly with temperature, and this is due to the fact that the carrier concentration in this region is determined by the number of ionized acceptors liberated from
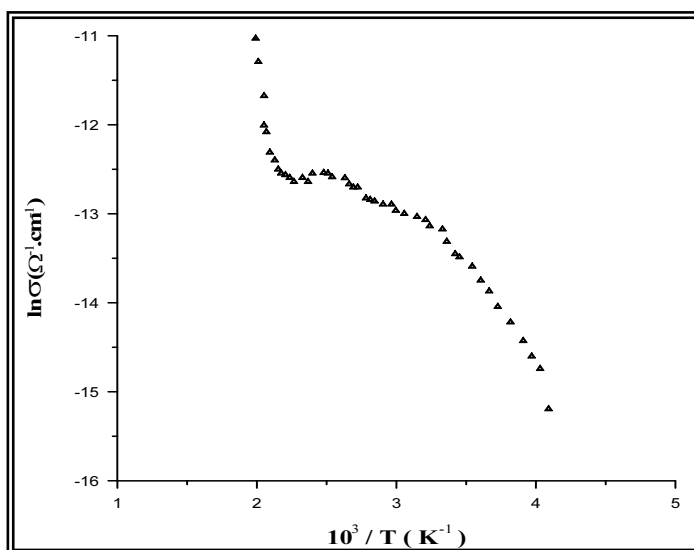

Fig. 1. The temperature dependence of electrical conductivity (σ) for TlGaSe₂ single crystal.

the impurity level. From this region the ionization energy was calculated, indicating that the acceptor level lies 0.36 eV above the top of the valance band. The σ-T curve passes through an intermediate region, 309-441. This is the transition from impurity to intrinsic conductivity which depends on the carrier concentration and their mobilities (this will be clear if one observes both Fig. 3 & 4 in that temperature range 1). At temperature above 441 K, the conductivity increases rapidly because of the carrier being excited from the extended state of the valance band into

the conduction band. So the width of the forbidden energy gap can be calculated. It is found to be 2.1 eV. From Fig. 1 the value of σ, at room temperature equals 1.87×10^{-6} $(\Omega.\text{cm})^{-1}$. Since Hall measurements are important, Fig. 2 is constructed in the temperature range 248-484 K. Figure 2 shows the dependence of $R_H T^{3/2}$ against the temperature. The positive sign of R_H indicates that the majority carriers are holes. It can be seen from Fig. 2 that the Hall coefficient decreases with the rise in temperature, but above 400 K it decreases very rapidly. Determination of the energy gap from Hall data is possible from this relation. The band width of the energy gap calculated from the slope of the curve in the intrinsic region was found to be 2.1 eV. The values of the Hall coefficient and carrier concentration at room temperature are 3.98×10^{9} cm³ C⁻¹ and 1.57×10^{9} cm⁻³ respectively. The temperature dependence of the Hall mobility for TlGaSe₂ is shown in Fig. 3. It was found that the exponent n
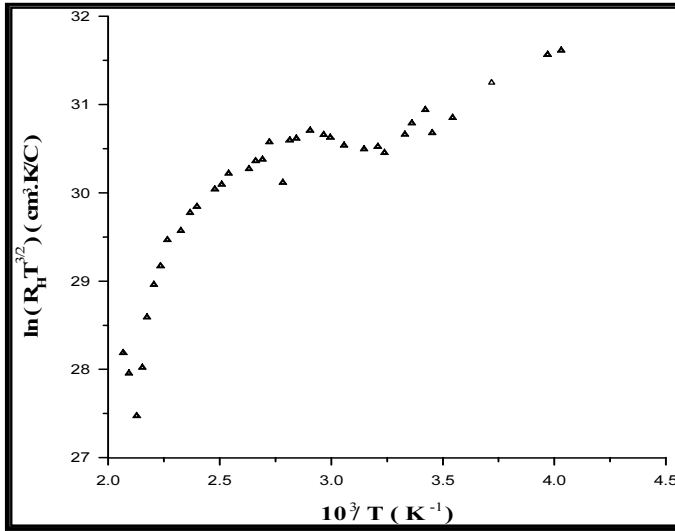

Fig. 2. The dependence of $R_H T^{3/2}$ against the temperature for TlGaSe₂ single crystal.

in the relation $\mu_H \propto T^n$ (below 330 K) is 1.5 indicating that the scattering of the carriers is influenced by the impurities, *i.e.*, the impurities play an important role in this range of temperature. We will be able to say that the mobility increases with temperature. As temperature decreases, the mobility due to impurity ion scattering decreases too. In the high temperature range (T > 330 K), the carrier scattering mechanism is the

scattering on thermal lattice vibration, which causes the mobility to decrease with the temperature increase. The mobility decreases according to the law $\mu_H \, \alpha \, T^{-7.2}$. This leads to the assumption that phonon scattering is dominant. At room temperature the Hall mobility is $\mu_H = 7.46 \times 10^3$ cm^2 V^{-1}s^{-1}. Figure 4 illustrates the variation of the current carrier density against the temperature. Figure 4 is helpful for understanding Fig. 1. Also from the basis of the relation $P_i = (N_c \, N_v)^{1/2} \, e^{-\Delta Eg/\,2KT} = ce^{-\Delta Eg/\,2KT}$. Thus the energy gap ($\Delta E_g$) can be calculated from the slope of the curve in the intrinsic region which is good agreement with the value obtained from the conductivity and Hall effect work and also agrees with value in[3,25]. The result for the temperature dependence of TEP of single crystal of TlGaSe$_2$ in the temperature range 271-493 K is presented in Fig. 5. At the beginning of the curve TEP increases as the temperature rises, reaching a maximum value at α equal to 563 μVK^{-1} at T = 307. A sharp drop of TEP is observed until it reaches 24 μVK^{-1} at 343 K. The decrease of α values, at temperature higher than 307 K, is regarded as a result of the compensation processes. Above 343 K the TEP increases with increasing temperature. The observed positive thermoelectric power value in the
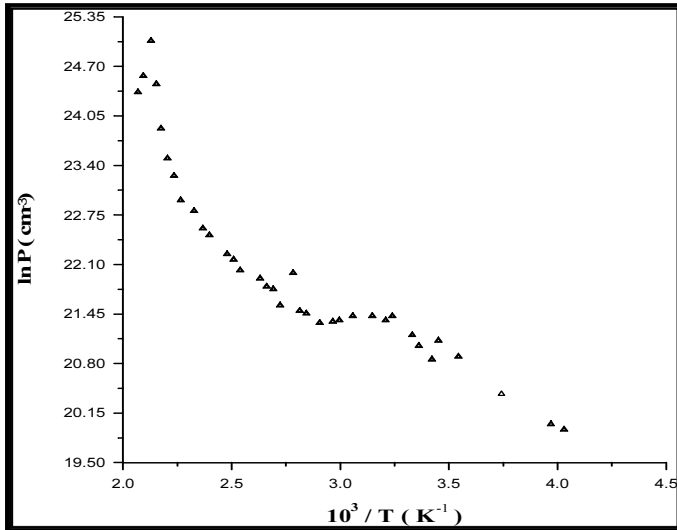

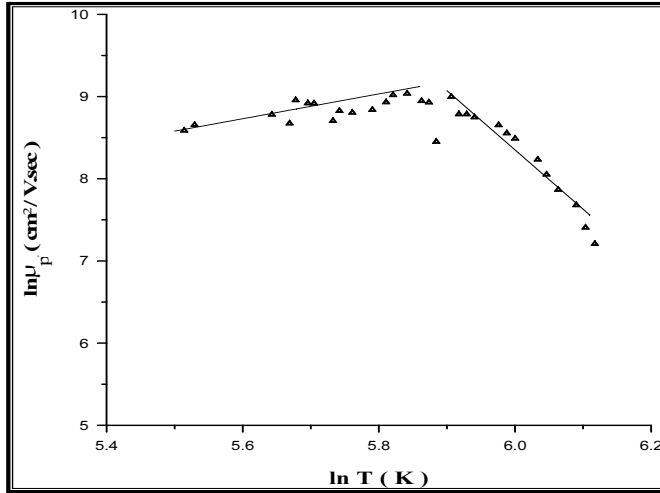**Fig. 3. Variation of ln p with ln T for a TlGaSe$_2$ single crystal.**

Fig. 4. Hall mobility as a function of temperature for TlGaSe₂ single crystal.

entire temperature range investigated result from the fact that the hole concentration is greater than that of electrons, that is, the material is P-type. This Agrees with result obtained from Hall effect data and published data[3,25]. In the intrinsic region the TEP can be described by the following relation[26]

$$\alpha = \frac{-K}{e}\left[\frac{b-1}{b+1}\left(\frac{\Delta E_g}{2\,K\,T} + 2\right) + \frac{3}{4}\,\ln\left(\frac{m_n^*}{m_p^*}\right)\right]$$
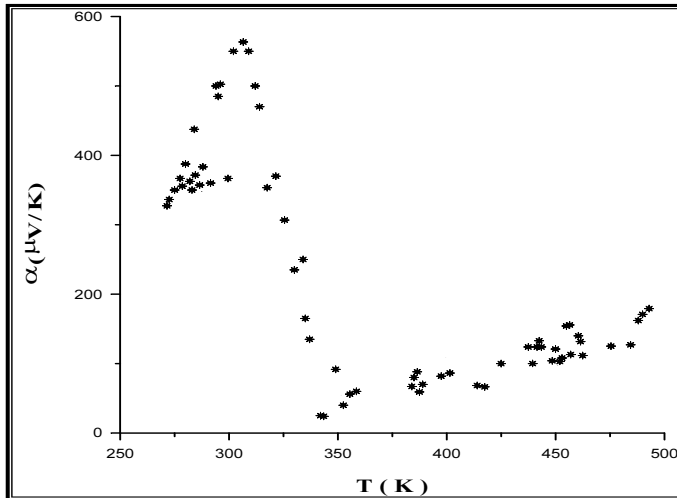

Fig. 5. Temperature dependence of TEP for TlGaSe₂ single crystal.

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. This formula predicts that a plot of α as a function of the reciprocal of the temperature in the intrinsic range should be a straight line. The plot of the thermoelectric power (α) as a function of the reciprocal of the temperature is shown in Fig. 6. 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 $\mu_p = 7.46 \times 10^3$ cm^{2}V^{-1}s^{-1} at room temperature means that $\mu_n = 9.85 \times 10^3$ cm^{2}V^{-1}s^{-1}. The ratio of electron and hole effective masses m_n^*/m_p^* are evaluated from the intercept of the curve with the α-axis and it was found to be $m_n^*/m_p^* = 8.49 \times 10^{-4}$. It is known that the thermoelectric power of a semiconductor, when one type of carriers dominates, is given by the following relation[27]

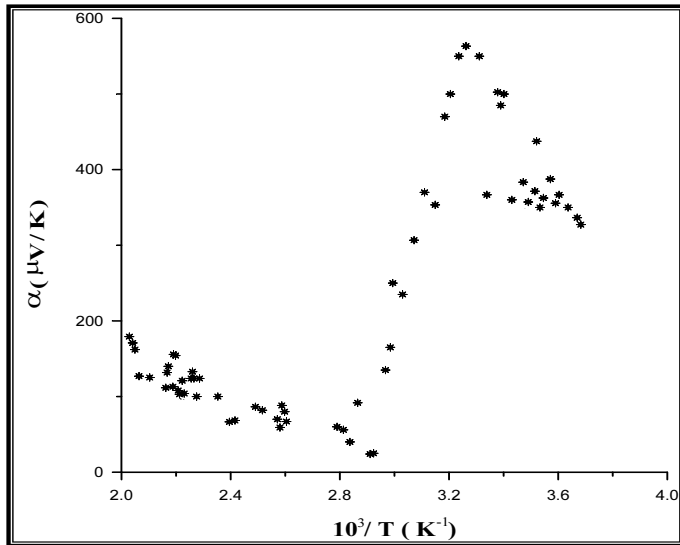$$\alpha = \frac{K}{e} \left[2 - \ln\left(\frac{ph^3}{2\,(2\pi\,m_p^*\,K\,T)^{3/2}} \right) \right]$$

Fig. 6. Plot of (α) against 10³/T for TlGaSe₂ single crystal.

Plotting the above relation between α and ln T predicts that TEP increases with temperature in the temperature range corresponding to the impurity region as shown in Fig. 7. From the intercept of the line (in the impurity region) with the α axis we got $m_p^* = 2.647 \times 10^{-31}\,\text{kg}$. Combining this value with the above ratio m_n^*/m_p^* allows us to determine the effective mass of the electrons. This value equals $2.247 \times 10^{-34}\,\text{kg}$. 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 turns out to be 1.23×10^{-12} s, whereas for electrons is equal to 1.38×10^{-15} s. The diffusion coefficients for holes and electrons can be deduced to be $D_p = 193.02\ \text{cm}^2\text{s}^{-1}$ and $D_n = 254.79\ \text{cm}^2\text{s}^{-1}$ respectively. 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 1.54×10^{-5} cm and 5.93×10^{-7} cm for hole and electrons respectively. Figure 8 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.
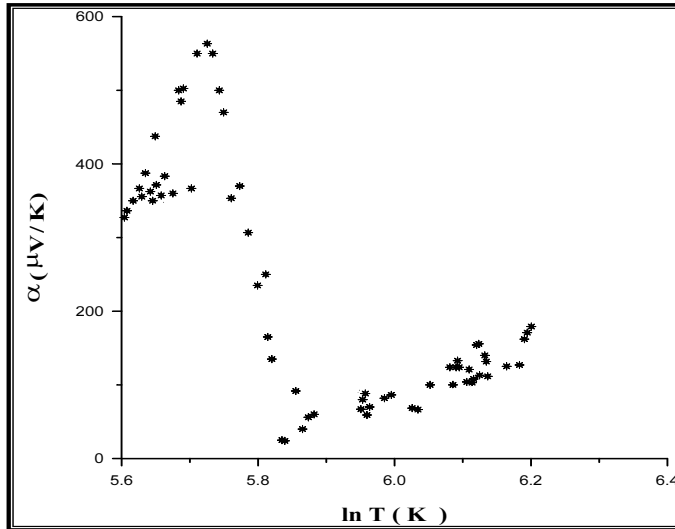

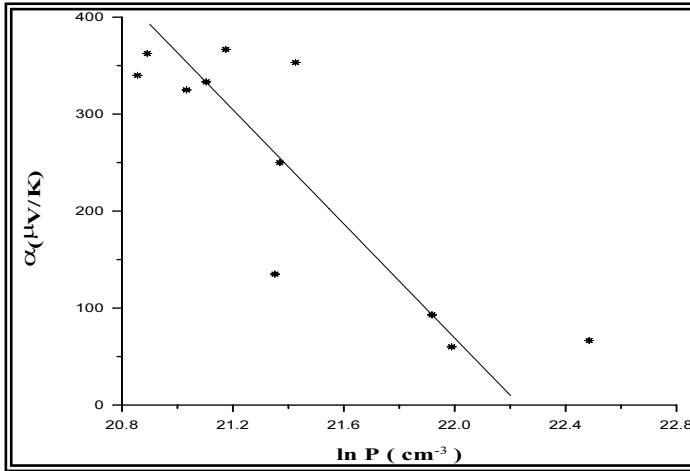**Fig. 7. The relation between (α) and ln T for TlGaSe₂ single crystal.**

Fig. 8. The dependence of the TEP on the natural logarithm of the charge carrier concentration for TlGaSe₂ single crystal.

Figure 9 shows the dependence of the thermoelectric power coefficient on the natural logarithm of the electrical conductivity. The following relation can be applied

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

This behavior which governs the relation between the electrical conductivity and the TEP is similar to that of α versus p.
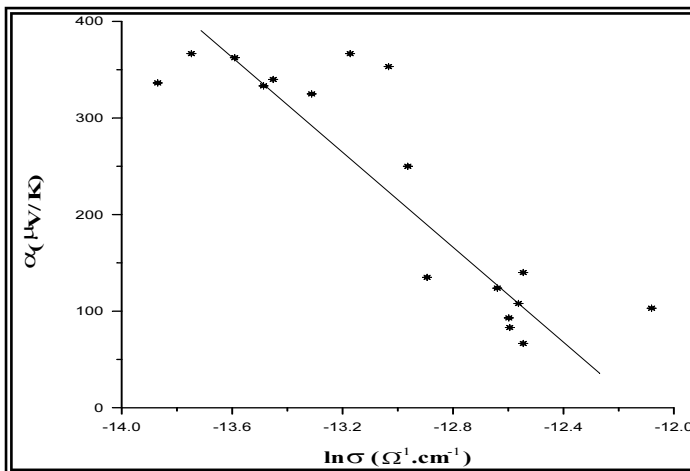

Fig. 9. The dependence of the thermoelectric power coefficient on the natural logarithm of the electrical conductivity for TlGaSe₂ single crystal.

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.

4. Conclusion

In the present paper, the electrical conductivity, Hall effect and thermoelectric power of TlGaSe$_2$ were reported. This work revealed that crystalline thallium-gallium-diselenide has a semiconducting nature with a P-type conductivity. It has an energy gap of 2.1 eV and activation energy of acceptors of 0.36 eV. Combination of the electrical conductivity, Hall effect and thermoelectric power data allows us to deduce many important physical parameters such as the mobilities, effective masses, diffusion coefficient, diffusion length, as well as relaxation time for the majority and the minority carriers. The scattering mechanism of the charge carriers was discussed in the present study. The efficiency of thermoelectric power conversion, also was investigated through determination of figure of merit Z.

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الخواص الحرارية الانتقالية والكهربائية للبلورة النقية لثلاثي الشالكوجنيدي ثاليوم–جاليوم–ثنائي السيلينيوم

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المستخلص. تعتبر المركبات من النظام الثلاثي $A^{111}B^{111}C_2^{VI}$ مـن أشباه الموصلات الواعدة في مجال صـناعة الـدوائر المتكاملـة وكمحولات للطاقة، وفي العديد من التطبيقات الضوئية والحراريـة والكهربائية. كما تعتبر المركبات الثلاثية الشالكوجنيدية المحتويـة على الثاليوم ذات أهمية خاصة، ليس فقط نتيجة خواصها الفيزيائية المتميزة، بل أيضًا في إمكانية التطبيقات العملية لها.

تم تحضير المركب الثلاثي الشالكوجنيدي ثاليوم–جاليوم–ثنائي السيلينيوم في صورة بلورية نقية، عن طريق الاسـتعانة بتـصميم خاص للإنماء البلوري من المصهور اعتمادًا على تقنية بريجمان. تـم قيـاس الموصـلية الكهربائيـة، ومعامـل هـول، والقـدرة الكهروحرارية في مدى واسع من درجات الحرارة، وتحت تفريـغ مناسب، وأظهرت نتائج القياس أن المركب يـسلك سـلوك أشـباه الموصلات، وأن له موصلية من النوع الموجب. كما أمكن تعيـين اتساع النطاق المحظور، وموضع مستوى الشوائب المكتسبة، وتـم أيضا تعيين تركيز حوامل التيار الحرة، والقدرة الكهروحراريـة، ودُرس تأثرها بدرجة الحرارة. كما تم تقدير حركية حوامل التيـار

الحرة والكتلة الفعالة، ومعامل انتشار حوامل التيار، وطول مـــسار الانتشار، وزمن الاسترخاء لكل من حوامل التيار الأغلبية والأقلية. كما أمكن حساب كفاءة المادة كعنصر كهروحراري. وهذه العناصر التي أمكن تقديرها تعطي الضوء على الخواص الفيزيائيـــة لهـــذا المركب وتحدد المسار التطبيقي المناسب له.