Crystallization and Thermoelectric power of Tl_2GaInS_4 layered compound

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Abstract: The investigation covers a temperature range from 193 to 600K. Thermoelectric power of single crystals Tl_2GaInS_4 prepared by a special modified Bridgman technique, showed that the samples under investigation have a positive TEP in all temperature ranges, indicating p-type conductivity for Tl_2GaInS_4 crystals. The ratio of electron and hole mobilities is $\mu_n/\mu_p = 1.82$. The effective mass of holes m_p^* is found to be $1.37x10^{-33}$kg while for electrons $m_n^* = 3.206x10^{-39}$kg. The diffusion coefficient for both carriers (holes and electrons) is evaluated to be 358.3cm^2/s and 425.338cm^2/s respectively. The relaxation time for both majority and minority carriers were estimated to be $\tau_p = 1.189x10^{-17}$s and $\tau_n = 2.294x10^{-23}$s. Also the diffusion length for holes and electrons were found to be $L_p = 6.528x10^{-8}$cm and $L_n = 9.877x10^{-11}$cm respectively. In addition to these pronounced parameters, the efficiency of the thermoelectric element (figure of merit) was evaluated, which leads to better application in the field of energy conversation technique.

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1. Introduction

The appearance and vigorous development of many modern branches of technology stimulate continuous searching for new promising materials possessing a wider spectrum of properties than the already known and partially tested materials. The study of thermoelectric properties of semiconductors has been an active area in solid state physics. Thallium compounds have recently attracted interest as promising thermoelectric materials[1]. There are two reasons for this. Firstly, Thallium is similar in crystal chemical behaviour to some of the alkali metals. It preferentially forms compounds in oxidation state +1 and its ionic radius is very close to the ionic radius of potassium, however, the electronegativity is higher. Replacement of potassium by thallium may increase the electrical conductivity of compounds, as a result of substantial reduction of the ionicity of the chemical bonds. Secondly, thallium is a heavy element and its introduction into a semiconductor will lead to a decrease of the thermal conductivity. One of the trends in semiconductor materials science is developing new functional materials is the increasing complexity of the investigated systems and of the compounds that form in these systems. Determination of the application potential for new semiconducting materials in solid state physics requires the growth and examination of physical properties of the materials. One of the methods for modifying their physical properties is the production of solid solutions of these semiconductors. The experimental studies carried out on $TlGaS_2$ and $TlInS_2$ demonstrate that investigations for the physical properties of the $TlGaS_2$ -$TlInS_2$ system, should be rewarding in view of the production a new candidate material for thermoelectric generation devices. Tl_2GaInS_4 semiconducting compound crystallises in a layered structure with $TlGaS_2$ and $TlInS_2$ components having the ratio 1:1. In spite of its importance in technological applications as a candidate material for optical devices and also for the understanding of its basic physics, so far very little information on the physical properties, for example photoconductivity (PC) data[2] , thermally stimulated[3] current (TSC), optical properties and crystal structure [4], Photoluminescence [5], optical constant and interband transitions[6], is a variable. However, the thermoelectrical properties of the new semiconductor compound Tl_2GaInS_4 crystals have not been studied at all. So the present investigation was done to be the first study in the literatures, in addition to complete our plan concerning investigation of the thermoelectrical properties of different semiconductor materials.

2. Experimental Set Up

2.1 Material and sample preparation

Tl_2GaInS_4 single crystals were grown using modified Bridgman method from $TlGaS_2$ and $TlInS_2$ polycrystalline compounds having stoichiometric starting materials. The purity of the materials used 99.9999%. Stoichiometric quantities of the constituent elements 30.2099gm Tl, 10.3015gm Ga and 9.4886gm S, were used as starting materials for $TlGaS_2$, also 26.6562gm Tl, 14.9713gm In and

8.3725gm S for $TlInS_2$. The appropriate amounts were first sealed in evacuated quartz ampoule.

Tl_2GaInS_4 single crystals were grown 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[7]. 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 1.7mm/h through the stationary furnace. The movement of the ampoule was very gently and slow with the aid of the hydraulic mechanical system. At least two weeks growth are needed to obtain Tl_2GaInS_4 single crystal. The resulting ingots (yellow-green in color) showed easily cleavage along the layer plane. The single crystallinity of this material was verified by means of x-ray diffraction technique (figure1).

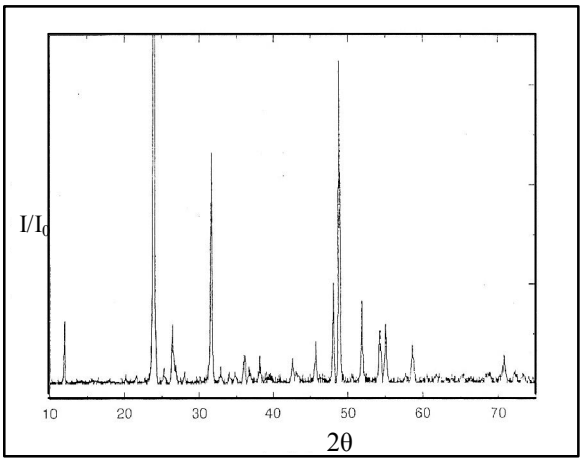

Fig. 1 x-ray diffraction pattern for Tl_2GaInS_4 single crystal.

2.2 Thermoelectric power Measurements

For TEP measurements, we utilized the prepared crystal after removing it from the ampoule because it had a cylindrical shape. Parallel–sided specimens were used through our measurements with dimensions 1.5mm thickness and 14mm diameter. The sample thickness allows the creation of uniform temperature gradient. Contacts were placed uniformly a cross the ends of the used samples to ensure uniform temperature distribution. Silver paste contacts were used and found to be ohmic. The sample was supported between two holders, the lower one acting as a heat source and the upper one as a heat sink. Two copper constantan thermocouples were used for temperature measurements across the two ends and the thermo-EMF in the sample was measured from one of their arms. The thermocouples were made in contact with the upper and lower ends of the crystal sample and were electrically insulated. The measurements were carried out by the compensation method with a high sensitivity potentiometer (UJ33E type). A special high- vacuum-tight apparatus was designed for thermoelectric measurements. The construction of the measuring apparatus was found to be very convenient during the experiment. The obtained results were of 0.1% accuracy. Details about the apparatus and method of measurements are outlined elsewhere[8,9]. The direction of the temperature gradient was perpendicular to the natural cleavage planes. In addition, we considered the following: 1- The specimen surfaces were very smooth with two parallel ends. 2- The temperature of the crystal was considered to be the average of those at its two ends. 3- Finally, it must be mentioned that ten minutes were needed to establish the temperature equilibrium state along the crystal for each observation.

3. Analysis and Discussion of The Results

The results revealing the effect of temperature on the generated thermoelectric power are presented. The temperature dependence of thermoelectric power (TEP) of Tl_2GaInS_4 single crystals at 193K-600K are given in figure 2. The variation of TEP(α) with temperature T can be divided into four different stages. At the beginning of the curve TEP decreases gradually and slowly with temperature.

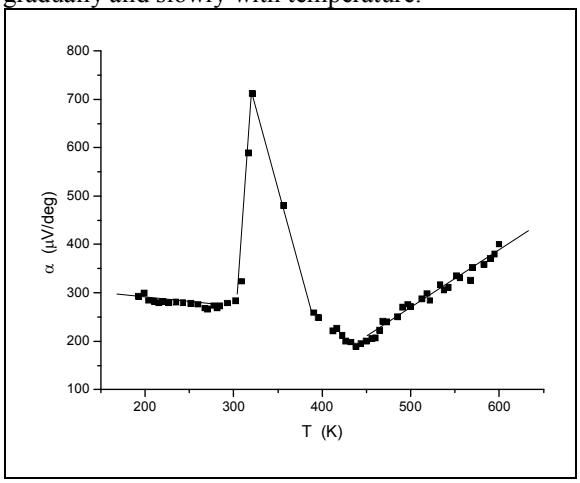

Fig. 2. The temperature dependence of TEP (α) for Tl_2GaInS_4 layered single crystal.

This indicate that the effect of trapping center in this temperature range has a marked effect leading to a decreases of α with T in this stage. The second stage α increases sharply reaching a higher value 711.2μV/K at a temperature of about 320K. In our opinion the reason of these high values of α in this temperature part, is the effect of thermal excitation of the impurity ionization in this extrinsic range. after passing this maximum, which corresponds to the

onset of a mixed conduction, α decreases with increasing temperature. The third stage of variation of α against T in curve 1 is characterized by the sharp diminution in α magnitude till α reaches its smallest value in the temperature range (320K-430K), this is acceptable because in this relative high temperature range the Fermi energy decreases with increasing temperature in the intrinsic conduction region (according to the relation between the Fermi energy, the effective number of states in the valance band and the acceptor concentration). In the fourth stage α increases slightly with temperature, this is due to the thermal generation of the carriers with increasing temperature which occurs in the intrinsic conduction part. The observed positive thermoelectric power in the entire temperature range investigated may be considered as the consequence of hole concentration being greater than that of electron, indicated that the material is always found to be p-type, which is in good agreement with the published data[5]. Now we come to the utilization of the TEP behaviour 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[10]

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

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 relationship shows that a plot of α in the intrinsic range as a function of reciprocal of absolute temperature is a straight line as shown in figure 3, according to the predictions of the above relation.

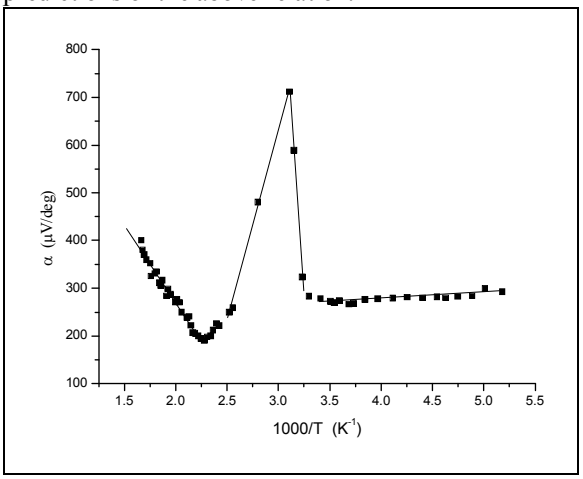

Fig. 3. The dependence of α against 1000/T for Tl_2GaInS_4 compound.

Previous Hall effect data and measuring values of α enable us for the determination of electron to hole mobility ratio and the ratio of charge carrier effective masses. The slopes of the linear part of this dependence are used to estimate the ratio of the electron and hole mobilities. Taking ΔE_g=2.2eV, the ratio $b=\mu_n/\mu_p$ is found to be 1.821. Hence by using the value of $\mu_p=1.38\times10^4 cm^2/V.s$, the electron mobility can be deduced and its value is found to be $1.64\times10^4 cm^2/V.s$. Another important parameter can be deduced with the aid of the obtained value of μ_p and μ_n using the Einstein relation that is the diffusion coefficient for both carriers (holes and electrons) can be evaluated to be $358.33 cm^2/s$ and $425.338\ cm^2/s$ 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 $m_n^*/m_p^* = 1.625\times10^{-6}$, and assume that this ratio does not vary with temperature. Another useful formula[11] was temperature suggested to described the relation between α and lnT in the impurity region for determination many physical parameters.

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

Where p is the majority of charge carriers concentration at room temperature. Plotting the relation between α and lnT as shown in figure 4, a straight line is observed in the extrinsic region. From the slope we computed the value of m_p^* as $1.375\times10^{-33}kg$, then $m_n^* = 2.235\times10^{-39}kg$. Accordingly the mean free time τ_p for holes and τ_n for electrons were obtained to be $1.189\times10^{-17}s$ and $2.294\times10^{-23}s$ respectively. The availability of both the mean free time and the diffusion coefficient enables us to deduced the diffusion length of both carriers types. The diffusion length for holes L_p was found to be $6.528\times10^{-8}cm$, whereas for electrons $L_n = 9.877\times10^{-11}cm$. For more definite understanding of the behaviour of TEP we used our electrical conductivity and Hall effect data.

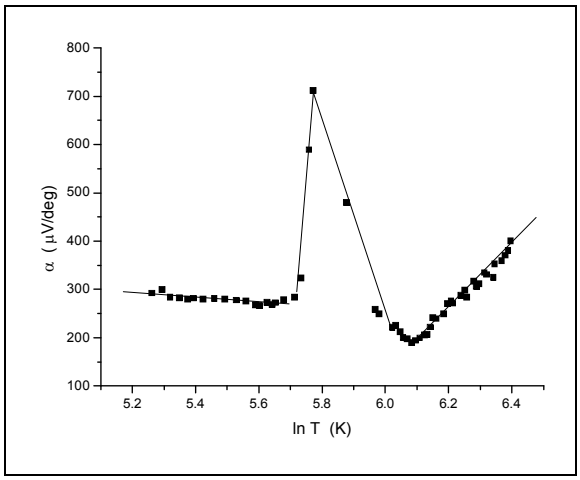

Fig. 4. Plot of α against lnT for Tl_2GaInS_4 compound.

The behaviour of the differential thermoelectric power α against the carrier concentration is presented graphically in figure 5, this graph shows the dependence of TEP on carrier density for a given Tl_2GaInS_4 sample. The general behaviour is that α decreases linearly with the increase of carriers concentration. From this behaviour we realize the effect of charge carrier density is a strong factor governing the variation of α.

Figure 6 illustrates the relationship between TEP and electrical conductivity σ. The following relation can be applied[12]

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

It is seen 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 behaviour of α against lnp. The similarity between the behaviour 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.

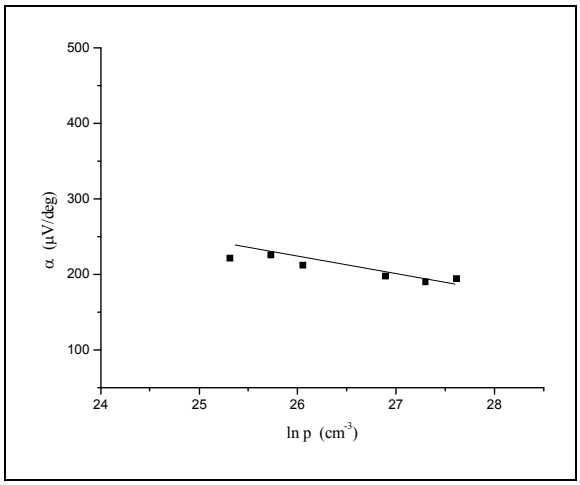

Fig. 5. The relation between the thermoelectric power and concentration of holes for for Tl_2GaInS_4 single crystal.

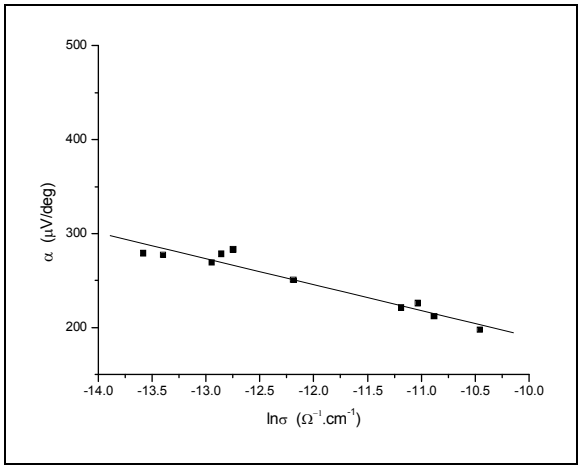

Fig. 6. Thermoelectric power TEP as a function of electrical conductivity for Tl_2GaInS_4 compound.

The choice of materials for thermoelectric generators and refrigerators is based on the efficiency parameter $Z=\alpha^2\sigma/\kappa$, where κ is the thermal conductivity of a semiconductor and σ is the electrical conductivity. This parameter was found to be $3.34x10^{-11}K^{-1}$. Indicating the efficiency of the material for conversion of thermal energy to electrical energy. The proposed treatments of the experimental data sheds new light on the main physical parameters in Tl_2GaInS_4 single crystal. Those parameters are found to be sufficient to give a complete information about the general behaviour for our best compound.

4.Conclusion

In the present work Tl_2GaInS_4 crystals were grown by a modified Bridgman technique. Measurement of TEP were carried out between 193-600K, when the direction of the temperature gradient was perpendicular to the cleavage planes. Throughout

these measurements, various physical parameters such as carrier mobilities, effective masses of charge carriers, diffusion coefficient, relaxation time and the diffusion length for both majority and minority carriers were estimated. In conjunction with the electrical conductivity and the charge carrier concentration, the thermoelectric power is discussed. The present investigation might be the first study on the thermoelectric properties of the Tl_2GaInS_4 compound and reveal the general behaviour of this semiconductor.

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