A Contribution of Thermoelectric Properties of the Quaternary Chalcogenide Compound $Tl_2GaInSe_4$ Crystal

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Thermoelectric transport measurements were made on single crystal samples of $Tl_2GaInSe_4$. The crystal was prepared by a special design based on the Bridgman technique. Measurements of thermoelectric power were carried out in a special high vacuum-tight calorimeter when the direction of temperature gradient is perpendicular to the cleavage plane. The measurements covered a temperature range extending from 300 to 725 K. The results indicate P-type conductivity for our investigated samples. At room temperature the value of thermoelectric power was 735 μV/deg. The electron to hole mobility ratio was found to be 1.35. The effective mass of holes at room temperature was evaluated as 4.635×10^{-29} kg, while for electron was equal to 8.468×10^{-31} kg. The relaxation time of majority and minority carriers was estimated as $\tau_p = 2.968\times10^{-10}$ s and $\tau_n = 7.326\times10^{-12}$ s, respectively. Also, the diffusion coefficient of holes and electrons at room temperature was calculated and found to be 265.132 cm^2/s and 358.139 cm^2/s, respectively. The diffusion length of holes and electrons are found to be $L_p = 2.805\times10^{-4}$ cm and $L_n = 5.122\times10^{-5}$ cm. In addition to these pronounced parameters, the efficiency of thermoelectric element (figure of merit) was evaluated which leads to better applications in many fields.

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1. Introduction

Most of the developments in the field of materials for thermoelectric application have been rather empirical, that is, various materials were tested for the properties of interest in this application, and the best available material was then chosen and adjusted for best results. As the field progresses, it becomes increasingly evident that new materials will have to be found to realize fully the possibilities of thermoelectric power production. Interest in the field of thermoelectric power increased recently for, at least, two reasons. In the first place motivation has come about through the great increase of number of technological problems — in particular, thermoelectric conversion requiring new materials with as yet unknown thermoelectrical properties. Secondly, recent work for replacing power produced from petroleum and nuclear sources with other new sources of power needed to investigate [TEM].

The study of thermoelectric properties of semiconductors has been an active area in solid state physics. The thermoelectric properties may be applied in more than one way in the development of power. The room temperature crystal data and the optical properties of $Tl_2GaInSe_4$ crystals are reported [1], the effect of temperature on the optical energy gap [2] for $Tl_2GaInSe_4$ layered crystals were investigated in the temperature range of 10–330 K. Photoluminescence (PL) spectra of $Tl_2GaInSe_4$ layered single crystals were published [3, 4]. The crystal structure and some transport properties of this compound were studied [5]. Published literature gives no values for the thermoelectric properties of $Tl_2GaInSe_4$. This gives us the chance to report this work. Investigations of thermoelectric properties for $Tl_2GaInSe_4$ have been stimulated by the growing needs for such materials in many scientific applications. To our knowledge, this might be the first study on the thermoelectric properties of this compound. This paper reports on a preliminary attempt at a prior design of materials for thermoelectric power production.

2. Experimental procedures

2.1. Sample preparation

Details of the experimental equipment for crystal growth by modified Bridgman method are described elsewhere [6]. The purity of the starting materials can be stated as being 99.9999% (Aldrich Mark). Before loading initial material in the ampoule, the ampoule had been cleaned by several steps to be sure that there were no contamination in it. Care was taken when heating the ingot to control the Se vapor pressure and the exothermic reaction between Se and In. The charged ampoule was sealed off at a pressure of approximately 10^{-5} Torr. The lower end of the ampoule was trapered in order to favor crystal growth at a single point. Silica ampoule was coated internally with a thin layer of carbon to prevent contamination of the charge. A prolonged period of time is necessary for the growth needed to obtain $Tl_2GaInSe_4$ single crystals. The crystal thus grown had good morphology, and displayed easy basal cleavage. The ruby-red colored ingot exhibits good optical quality and yields large platelets when cleaved perpendicular to the optical c-axis. The samples were identified by means of X-ray analysis. No further polishing and cleaning treatments were required because of the natural mirror-like cleavage faces. The investigated sample was cleaved gently

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from the obtained ingot. To minimize the effect of radiation, the cylindrical shaped specimens were made and the length of the sample was chosen to be as short as possible, whereas the cross-section area was large enough. The surface of the sample was flat and parallel.

2.2. Measurements techniques

After preparing the sample with the required dimensions 12.2 mm (diameter) and 3.2 mm (thickness), it was supported vertically by two holders one of which (the lower one) acts as a heat source, while the other serves as heat sink, and introduced inside a high vacuum tight calorimeter designed [7] specially for this purpose. The sample was insulated from the holders by thin sheet of mica. The temperature of the crystal was considered to be the average of those at its two ends. As an attempt to increase the accuracy, simultaneous measurements of temperature and potential difference were carried out.

In the present work, a compensation method was used for measuring voltage without drawing appreciable current using a tense potentiometer (UJ33E). It was necessary to have the temperature equally distributed; therefore we placed contact of silver past across the ends of the specimen uniformly. A two part holder was used for making the temperature difference along the crystal in a direction perpendicular to the natural cleavage plane.

Details about apparatus and experimental method for measuring α have been described in previous paper [8]. To avoid the effect of water vapor condensation in the low temperature range and the effect of oxidation in the high temperature range, the measurements were carried under vacuum. Measurements were carried out, during this investigation in a wide range of temperature extending from 300 to 725 K.

3. Results and discussion

The variation of the differential thermoelectric power α of the $Tl_2GaInSe_4$ single crystal as a function of temperature is illustrated in Fig. 1. Results and the figure indicate the following points:

1. Our sample shows P-type conductivity.
2. The figure shows that the value of the thermoelectric power decreases as the temperature rises till reaching small value 110 μV/K at 414 K. This may be due to the presence of some crystal defects or trapping centres in the direction of the carrier flow.
3. Above 414 K, with further rise of temperature α increases rapidly till reaching its maximum value 2220 μV/deg corresponding to 519 K. Such behavior led to the assumption that more holes are generated and contributed to the increment of α values as the temperature rises.
4. Third region in the same figure is observed where α rapidly falls above 519 K. The decrease of α magnitude is regarded as a result of the compensation process which takes place in this temperature region.
5. With further rise of the temperature, α increases rapidly. Such behavior is expected in this intrinsic range where generation of both carriers (electrons and holes) contributes to the increment of α value.

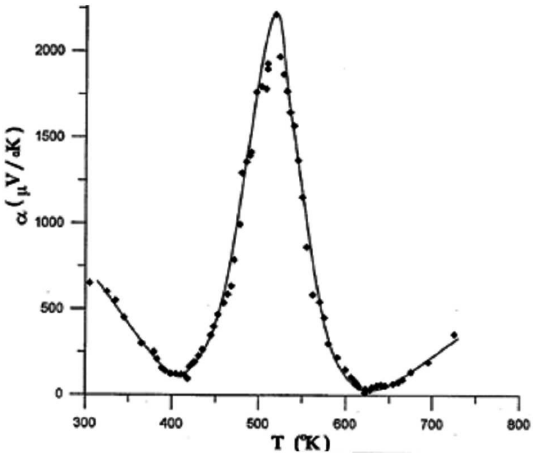

Fig. 1. The variation of the differential thermoelectric power α of the $Tl_2GaInSe_4$ single crystal as a function of T.

As follows from the expression of electromagnetic force (EMF) of a semiconductor in the intrinsic region is given by [9]:

$$\alpha = -\frac{k}{e}\left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p}\left(\frac{\Delta E_g}{2kT} + 2\right) + \frac{3}{4}\ln\frac{m_n^*}{m_p^*}\right], \qquad (1)$$

where k is the Boltzmann constant, μ_n and μ_p are the electron and hole mobilities, m_n^* and m_p^* are the effective masses of electrons and holes, ΔE_g is the width of forbidden energy gap.

The above equation indicates that the relation between α and $1/T$ in the intrinsic region should be a straight line. This is true as seen in Fig. 2.

The measured thermoelectric power in conjunction with the obtained value of ΔE_g is used to calculate the carrier effective masses and electron to hole mobility ratio. This is done by using the slopes of thermoelectric power versus $1/T$ plot and the intercepts, so we deduce that $\mu_n/\mu_p = 1.35$ and $m_n^*/m_p^* = 1.827 \times 10^{-2}$. Since $\mu_p = 10.246 \times 10^3$ cm^2/(V s), then we can evaluate $\mu_n = 13.84 \times 10^3$ cm^2/(V s). The diffusion coefficient for both majority and minority carriers at room temperature could be evaluated and is found to be $D_p = 265.132$ cm^2/s and $D_n = 358.14$ cm^2/s, respectively. For more making use of the phenomena another formula was suggested by Wilson [10] to be employed in the extrinsic region that is

$$\alpha = \frac{k}{e}\left[2 - \ln\frac{Ph^3}{2(2\pi kTm_p^*)^{\frac{3}{2}}}\right]. \qquad (2)$$

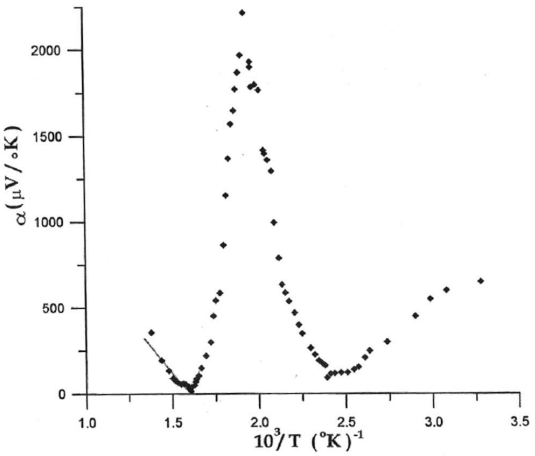

Fig. 2. The relation between α and $1/T$ in the intrinsic region for $Tl_2GaInSe_4$.

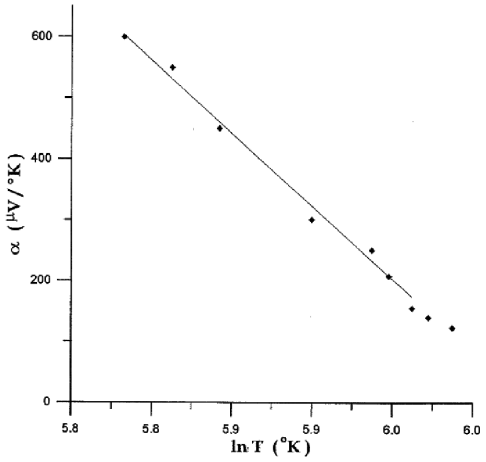

Fig. 3. The relation between α and $1/T$ in the impurity region for $Tl_2GaInSe_4$.

This formula leads us to represent the relation between α and $\ln T$ as seen in Fig. 3. This relation represents a straight line relation in the impurity region. A sharp drop of thermoelectric power is observed in the impurity region as the temperature increases. From the intercept of the line (in the extrinsic range) with α axis we get $m_p^* = 4.635 \times 10^{-29}$ kg combining this value with the above mentioned result for the ratio m_n^*/m_p^*, we obtain the value of the effective mass of the minority carrier $m_n^* = 8.468 \times 10^{-31}$ kg. Since the effective mass values are available, now the relaxation time for both types of carriers can be determined. The relaxation time for holes, as calculated is 2.96×10^{-10} s, whereas the relaxation time for electrons equals to 7.32×10^{-12} s.

It is noticed that the diffusion coefficient is inversely proportional to the effective mass of carriers, this is logical because the hole effective mass is larger than that of electrons. Also, the results indicate that the electron mobility is much higher that the hole mobility, this is acceptable, since the hole effective mass is much greater than that of electrons. Combining the values of diffusion coefficient and relaxation time, one can obtain the diffusion length of free charge carriers $L_p = 2.8 \times 10^{-4}$ cm and $L_n = 5.12 \times 10^{-5}$ cm for holes and electrons, respectively. For a better understanding of the real factors governing the thermoelectric power, the present work has been extended to cover the correlation between α and both P (carrier density) and σ (electric conductivity).

Figure 4 represents the dependence of the thermoelectric α on the carrier density. We show that α decreases sharply at beginning of the curve, and reaches a minimum value, after which the value of thermoelectric power increases exponentially with the carrier concentration.

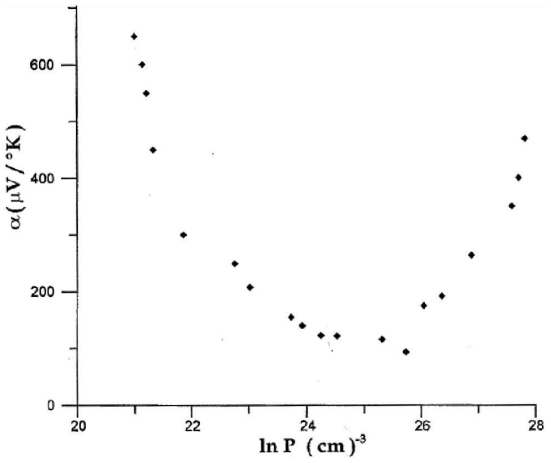

Fig. 4. The dependence of the thermoelectric α on the carrier density for $Tl_2GaInSe_4$.

From this behavior we realize that the effect of the charge carriers is a strong factor governing the variation of α. The same behavior was observed when we plotted α versus $\ln\sigma$ for $Tl_2GaInSe_4$ sample in Fig. 5. The following relation [11] may help us to understand that behavior:

$$\alpha = \frac{k}{e}\left[A + \ln\frac{2(2\pi kTm_p^*)^{\frac{3}{2}}}{(2\pi h)^3}\right] - \frac{k}{e}\ln\sigma, \qquad (3)$$

where A is a constant, m_p^* is the hole effective mass and h is the Planck constant. The decrease of the thermoelectric power with electric conductivity may be due to the decrease of the carrier density in the temperature range $T < 408$ K. Higher than 410 K it seems that thermoelectric power (TEP) increases with electric conductivity. From Figs. 4 and 5, we can deduce that the variation of α with the environmental temperature is not a mobility effect, but is dependent on the variation of the concentration. The choice of materials for thermocouples, thermoelectric generators and refrigerators is based on the efficiency parameter Z, defined by the relation $Z = \alpha^2\sigma/K$, where α, σ, K are TEP, electric conductivity, and thermal conductivity of the compound under test.

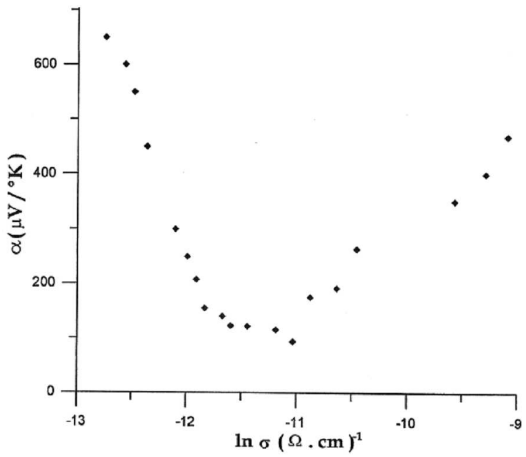

Fig. 5. The relation between α and $\ln\sigma$ for $Tl_2GaInSe_4$.

However, the term figure of merit is a measure of both performance and efficiency of a certain thermoelectric element. Therefore the main technical problem to obtain a good thermoelectric element is to answer the question how to promote the figure of merit of the material. For our best $Tl_2GaInSe_4$ samples, the figure of merit $Z = 9.1 \times 10^{-7}$. The proposed treatment of the experimental data sheds new light on the main physical parameters of $Tl_2GaInSe_4$ single crystals. The pronounced parameters obtained from TEP data gave evidence for practical applications.

4. Conclusion

In the present work $Tl_2GaInSe_4$ crystals were grown by a modified Bridgman technique. From the data obtained we can conclude the following:

1. $Tl_2GaInSe_4$ is a semiconductor with P-type conductivity.
2. The electron to hole mobilities was found.
3. The effective mass of holes and electrons was estimated.
4. The relaxation time of majority and minority carriers was evaluated.
5. The diffusion coefficient as well as the diffusion length of holes and electrons was determined.
6. The efficiency of thermoelectric element was calculated.
7. These studies yield an appreciable amount of information about the actual behavior and reveal the possibilities of their practical application.

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