

Semiconducting properties of In_3Te_4 crystals: An experimental study

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Abstract

IndiumTelluride In_3Te_4 crystal was characterized for electrical conductivity, Hall mobility, carrier concentration, and thermoelectric power (TEP) as a function of temperature in the range 202–526 K this was done with the aid of liquid nitrogen which enabled us to detect the intrinsic behavior. The crystals were prepared by a modified vertical Bridgman technique. Throughout these measurements various physical parameters, such as effective mass of charge carriers, carrier mobility, diffusion coefficient, and relaxation time for both majority and minority carriers were found.

Key Words: In_3Te_4 , crystal growth, semiconductors, thermoelectric power, electrical conductivity Hall effect

1. Introduction

In the InTe phase diagram reported by Skunk [1], it is evident that it contains phases of In_3Te_4 , InTe, In_2Te_3 , In_3Te_5 , In_2Te_5 and In_9Te_7 . It was believed that In_3Te_4 had a rhombohedral structure with $a = 4.26 \text{ \AA}$ and $c = 40.6 \text{ \AA}$ [2]. But according to Karakostas et al. [3], it is now an established that In_3Te_4 has a tetragonal structure with $a = 6.173 \text{ \AA}$ and $c = 12.438 \text{ \AA}$. Some InTe systems behave like superconductors; it has been reported that In_3Te_4 becomes superconducting at 1.25–1.15 K [2]. Tolutis et al. [4] studied the diffraction data of In_3Te_4 thin films. Recrystallization of In_3Te_4 in thin indiumtellurium films consisting of a mixture of In_2Te_3 and In_3Te_4 was also made by Deksnis and Tolutis [5]. In_3Te_4 formation processes in a polyphase indium tellurium layer were investigated by Deksnis et al. [6]. X-ray studies and microanalysis work were presented by Vesiene et al. [7]. Investigations of the dependence of the electrical and photoelectric properties of films on proportions of the components were already published by Tolutis et al. [8]. In that work the film consists of mixtures of In_2Te_3 and In_3Te_4 and the activation energy of the In_3Te_4 phase was

determined as 1.4 eV. When only the In_3Te_4 phase occurs it has a coarse-grained spherulitic with two activation energies 1.58 eV and 1.62 eV. An optical work concerning absorption edge of In_3Te_4 thin films was performed by Deksnis and Bobonas [9]. The compound has a tetragonal structure with lattice parameters corresponding that obtained by Karakostas et al [3]. U. Schwarz et al did a comparison between the materials In_3Te_4 and In_4Se_3 [10]. Also the crystal structure of the crystals was considered

The aim in this work was to grow In_3Te_4 crystals then investigate the electrical conductivity, Hall effect and TEP properties of In_3Te_4 crystals and hence to obtain the main semiconductors parameters of this compound. A recent work in 2007 was published by the present authors, concerning the Distribution of Dislocation Etch Pits on as Grown Surfaces of In_3Te_4 Crystals [11] The unique properties and promising applications of the In_3Te_4 crystal can be caused by its specific composition, which has a tendency to disorder. A remarkable piezo-photoresistive effect [12 13] and an abnormal temperature dependence of kinetic coefficients [14] were also observed.

2. Experimental procedures

For the present work the chemicals used in preparing the In_3Te_4 sample were 5.755 g of In and 8.53 g of Te (both of purity 99.9999%). The percentages of the charge elements are 40.29% In, and 59.71% Te. The chemicals were obtained from Aldrich. Both indium and tellurium were introduced into a silica tube, which was then evacuated to 10^{-6} Torr and sealed under this vacuum. The ampoule with its charge was supported in its holder inside the furnace (more details about this technique see ref. [15]). According to the phase diagram [1], the ampoule and its charge were exposed to a high enough temperature to melt both In and Te in the first zone of the furnace. In the middle zone where the temperature was adjusted at 649 °C (corresponding to the crystallization point of In_3Te_4 compound), the ampoule was kept for 24 hours. After that the ampoule was translated at a rate of $-3 \text{ mm} \cdot \text{h}^{-1}$. This was enough to obtain high quality crystal. Identification of the product crystal was done by means of X-ray diffraction analysis at the Central Metallurgical Research Development Institute (CMRDI) Egypt. The X-ray results (see Figure 1) for our compound indicate that the crystalline product has the required phase without any secondary phases.

The compound has a tetragonal structure with lattice parameters corresponding to that obtained by Karakostas et al [3]. The length of the grown crystal was 50 mm. With the aid of a polarizing microscopy we determined the crystallographic directions where both the axes a and b lie in the layer plan and c axes is located in a direction normal to the layers.

Plate-like samples were extracted from the ingot so as to conduct electrical conductivity and Hall effect measurements. The sample dimensions were adjusted to be $8.5 \times 2.2 \times 2 \text{ mm}^3$. The specimen length was nearly three times its width according to Isenberg recommendations to avoid the Hall voltage drop [16].

For the thermoelectric measurements the length of the cylindrical product crystal was adjusted to be 5 mm via polishing, while the crystal diameter was 10 mm. This was performed by fine polishing papers (0.5 Leco Mark USA) i.e. without coarse polishing. The cross-section was chosen to be large enough to minimize the effect of heat loss by radiation. Electrical and thermal measurements were conducted using silver conducting paste employed as an ohmic contact and recording the I-V characteristics in both forward and reverse bias directions to check its ohmic nature.

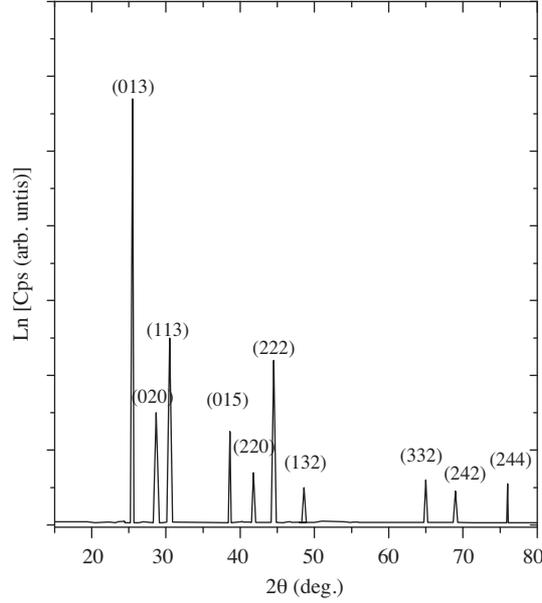


Figure 1. XRD pattern for In_3Te_4 crystals.

3. Analyses of the results

The electrical conductivity behavior against temperature is an important method to understand the electronic transport properties of a semiconductor by compensation method. The temperature dependence of the electrical conductivity σ was carried out along the crystallographic c -axis for In_3Te_4 crystals in a temperature range 222–526 K. This was done with the aid of liquid nitrogen which enabled us to detect the intrinsic behavior. Figure 2 shows this dependence. The curve shows a typical semiconductor behavior. From the curve we can notice that σ increases slowly in the low temperatures (the extrinsic region). But as the temperature rises the conductivity grows very rapidly because of the rapid increase in the current density. In the same curve one can notice an intermediate region appears between 303 K and 462 K. Measured data for $\sigma - T$ as a function of temperature are found to exhibit the following relationships:

1. $\sigma = \sigma_o \exp(-\Delta E_d/2K_B T)$ In the extrinsic region;
2. $\sigma = \sigma_o \exp(-E_g/2K_B T)$ In the intrinsic region.

Here σ_o denotes the preexponential factor, ΔE_d is the impurity (dopant) ionization energy and E_g is the energy gap width.

From the electrical conductivity results, we can sum up the following:

1. The extrinsic conduction appears in the temperature interval 222–303 K. The value of ΔE_d was found to be 0.58 eV. This value suggests that the extrinsic conductivity is due to impurity carriers, as will be confirmed later from the Hall data and this result will be appear in the following
2. The intrinsic conduction became more favorable between 383 K and 498 K. The energy gap width E_g was found to be 1.6 eV. This result agrees with that obtained by Tolutis et al. [8].

We extend our work to cover the effect of temperature on the carrier concentration n , of In_3Te_4 crystals which calculated from the relationship $n = \frac{1}{eR_H}$, this is shown in Figure 3. The figure shows the strong increase of n from $1.77 \times 10^{13} \text{ cm}^{-3}$ at 222 K to $3.94 \times 10^{15} \text{ cm}^{-3}$ at 526 K.

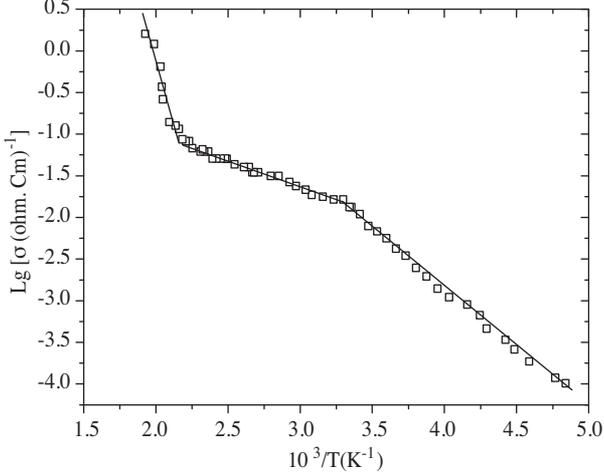


Figure 2. Temperature dependence of electrical conductivity for In_3Te_4 crystal.

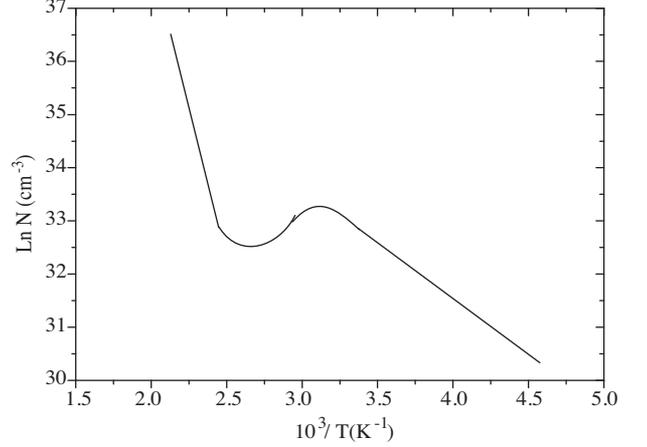


Figure 3. Behavior of carrier concentration versus temperature for In_3Te_4 crystal.

At low temperatures (below 338 K), the number of ionized donors determines the carrier concentration. This is noticed evidently because the slopes of the variation of the carriers are quite slow. In this range we computed the depth of the donor level as 0.61 eV. At high temperatures the crystal is exhibiting an intrinsic behavior. The expected value for the intrinsic concentration could be given as follows:

$$N_i = 2(2\pi K_B/h^2)^{3/2}(m_n^* m_p^*)^{3/4} T^{3/2} \exp(E_g/2K_B T)$$

Here, m_n^* , m_p^* are the effective electron and hole masses respectively. Utilization of this relationship leads to calculation of the energy gap width of In_3Te_4 . It was computed as 1.7 eV. The value of E_g calculated from Hall work deviated slightly from the value obtained from electrical conductivity work, as for this situation we used to consider the average value of E_g as 1.65 eV. Finally the charge carrier concentration at room temperature equals to $1.35 \times 10^{14} \text{ cm}^{-3}$ for In_3Te_4 crystal.

The present work dealt with the effect of temperature on the Hall mobility, which was calculated, from the relationship $\mu = \frac{\sigma}{ne}$. Figure 3 illustrates this dependence for In_3Te_4 sample. The general behavior of μ against T can be divided into three regions:

1. Below $T = 263 \text{ K}$ (the low temperature part) which corresponds to the extrinsic conduction, μ decreases with increasing the temperature.
2. The middle region ($263 \text{ K} < T < 354 \text{ K}$), which corresponds to the transition region, μ increases with increasing the temperature.
3. The high temperatures part ($T > 354 \text{ K}$) where is the intrinsic conduction part, μ decreases with increasing the temperature.

From Figure 4 the value of μ at room temperature equals $1013 \text{ Cm}^2/\text{Vs}$ in comparison with the data from reference [17].

In the low temperatures $\mu(T)$ can be described as $\mu \propto T^{-2.5}$. This indicates the domination of ionized impurity scattering in the low temperature region [18].

The values of Seebeck coefficient α for In_3Te_4 have been calculated by the differential method at different temperatures. The results were carried out over a temperature ranging from 202 K up to 500 K. We measured α when the temperature gradient was produced in a direction perpendicular to the c-axis. Figure 5 shows the relationship between α and $10^3/T$ for In_3Te_4

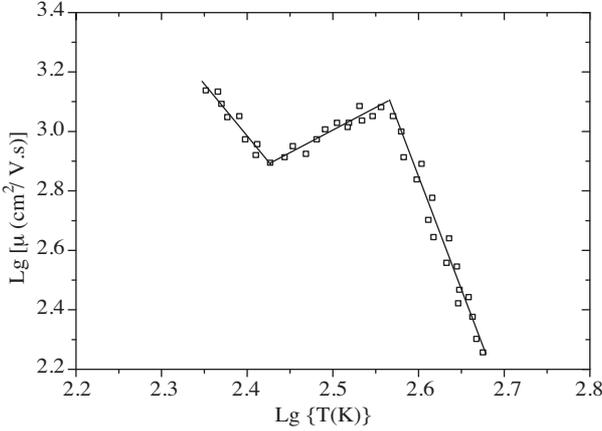


Figure 4. Behavior of the Hall mobility as a function of temperature for In_3Te_4 crystal.

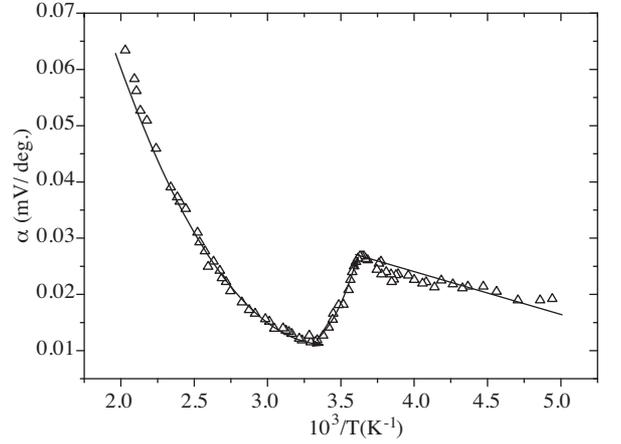


Figure 5. Plot of thermoelectric power versus $10^3/T$ (K^{-1}) for In_3Te_4 crystal.

From the figure we can conclude the following:

- The magnitude of α at room temperature is equal to $(11.6 \mu\text{V deg}^{-1})$.
- The sign of α for In_3Te_4 is negative indicating that the predominate conducting mechanism in these sample is of ntype.
- The value of α is found to increase continuously with increasing temperature in the range from 202 K up to 272 K.
- From 272 K to 303 K α decreases rapidly with increasing temperature.
- Up to 303 K the magnitude of α increases as the temperature increases. The rise of α value is attributed to the thermal activation of the charge carriers in this range.

We can utilize the thermoelectric phenomena and its variation with temperature to estimate some major semiconductor parameters for In_3Te_4 crystals such as: carrier effective mass, electron to Hall mobility ratio, relaxation time of majority and minority carriers, diffusion coefficient and diffusion length. This can be done by make a combination between TEP results, Hall effect and electrical conductivity results. The following relationship will be useful in the high temperature region (intrinsic region) [19]:

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

Here, μ_n, μ_p, m_n^* and m_p^* are the electron mobility, the hole mobility, the electron effective mass and the hole effective mass respectively. Values of E_g and μ_n were used as deduced from the previous Hall effect and the electrical conductivity data at room temperature. From the curve we computed the ratio μ_n/μ_p to be 1.2. This helps us to calculate the value μ_p as $844 \text{ cm}^2/\text{Vs}$. Also the ratio m_p^*/m_n^* was found to be 0.47. For more making use of the phenomena, another relationship was suggested by Wilson [20] to be employed in the extrinsic region (low temperatures) that is:

$$\alpha = \frac{K_B}{e} \left[2 - \text{Ln} \left(\frac{nh^3}{2(2\pi m_n^* K_B T)^{3/2}} \right) \right]$$

This relationship leads us to represent the relation between α and $\ln(T)$ as seen in Figure 5. From the intercept of the line (in the extrinsic range) with α axis we get $m_n^* = 2.84 \times 10^{-32} \text{ Kg}$. Using the ratio $m_p^*/m_n^* = 0.47$ (as obtained previously) from Figure 5 we could evaluate m_p^* as $6.07 \times 10^{-32} \text{ Kg}$. From both the Hall mobility and the carrier effective mass, we could estimate the values of the relaxation time for charge carriers from the following formula: $\tau = \frac{2\mu m^*}{e}$

They are $\tau_n = 3.61 \times 10^{-10} \text{ s}$, and $\tau_p = 6.37 \times 10^{-10} \text{ s}$. Also the diffusion constants for electrons and holes were calculated by using the well-known Einstein relation. They were found to be $D_n = 26.14 \text{ cm}^2/\text{s}$ and $D_p = 21.77 \text{ cm}^2/\text{s}$. The diffusion length, as another important physical parameter, can be deduced. It is for electrons $L_n = 9.5 \times 10^{-5} \text{ cm}$, while it is for holes $L_p = 11.7 \times 10^{-5} \text{ cm}$. It must be mentioned that the last equation (Wilson's formula) can be written in the form:

$$\alpha = \frac{3K_B}{2e} \ln T + \text{Constant}$$

This means that a plot of α against $\ln(T)$, for a given semiconductor, should be a straight line of slope $3K_B/2e$. The last quantity has the numerical value of $129 \mu \text{ V deg}^{-1}$

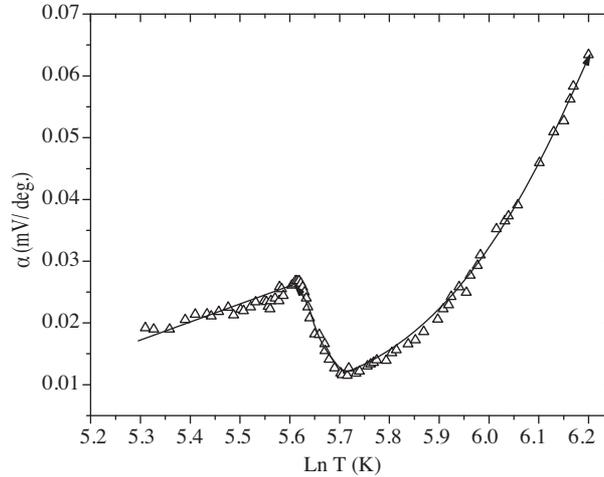


Figure 6. Plot of thermoelectric power versus $\ln T$ (K) for In_3Te_4 crystal.

The slope of the plot in our case (as calculated from Figure 6) was found to be $130 \mu \text{ V} \cdot \text{deg}^{-1}$. This value is in a good agreement with the theoretical predications. This also indicates that the effective masses of the charge carriers in In_3Te_4 crystal are temperature independent.

4. Conclusion

In the present work In_3Te_4 crystals were grown by a modified vertical Bridgman technique. From the data obtained we can conclude the following:

- In_3Te_4 is a semiconductor with ΔE_d equals to 0.6 eV and E_g equals to 1.65 eV.
- Values of Hall coefficient (R_H) and Seebeck coefficient (α) are negative over the temperature range of investigation indicating that In_3Te_4 is ntype semiconductor.
- The mobility follows the relationship $\mu \propto T^{-12}$ (in the high temperatures region) and $\mu \propto T^{-2.5}$ (in the low temperatures region).
- The charge carriers concentration at room temperature equals to $1.35 \times 10^{14} \text{ cm}^{-3}$, the ratio $\mu_n/\mu_p = 1.2$ and the ratio $m_p^*/m_n^* = 0.47$.
- The effective masses of the charge carriers in In_3Te_4 crystal are temperature independent.

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