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Electric Characterization of Hexaindium Heptaselenide Single Crystals

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Abstract. The electrical conductivity (σ) and Hall coefficient (R_H) of monocrystals In_6Se_7 have been investigated over the temperature range 148-528 K. The crystal was grown by a modified Bridgman technique. The investigation showed that our samples are P-type conducting. The forbidden energy gap was calculated and found to be 0.52 eV, whereas the ionization energy of the impurity level was 0.077 eV. The values of the electrical conductivity, Hall coefficient and carrier concentration at room temperature, were 9.56×10^{-4} Ω^{-1} cm^{-1}, 10.04×10^6 cm^3 C^{-1} and 9.964×108 cm^{-3} respectively. The Hall mobility at room temperature (μ_H), was found to be 13.1×103 cm^2 V^{-1} S^{-1}. Also the dependence of the Hall mobility on temperature was presented graphically.

Keywords: Chalcogenides, Crystal Growth, Semiconductor.

Introduction

The indium selenides belong to the A^{III} B^{VI} compounds, interesting for their semi conducting and optical properties [1]. Research on the In-Se Phase diagram has been reported by many authors [2-7] but still remains incompletely studied [8-9]. Through studies on A^{III} B^{VI} semiconductor compounds, especially $A_6^{III}B_7^{VI}$, In_6Se_7 was not thoroughly investigated. The most stable phases existing in In-Se system are InSe,In_2Se_3,In_4Se_3 and ln_6Se_7 as reported by [1,7,10-13]. From these, In_6Se_7 has been hardly investigated. The In_6Se_7 phase was found to be hexagonal [14]. With a = 0.8919 nm and c = 1 .4273 nm. Crystals of In_6Se_7 are layer defected semiconductors [15], the physical properties of which have not yet been investigated sufficiently thoroughly. The available independent data do not give the possibility to draw general conclusions. In our opinion, the reason is the difficulty to obtain well defined and reproducible samples. For these reasons, it would be desirable to investigate in great detail the temperature dependence of the electrical properties to throw light on the actual behavior of this semiconductor compound. In the present work an attempt was made to get more insight in the main physical properties of In_6Se_7 by measuring and analyzing the electrical conductivity, and Hall coefficient of In_6Se_7 single crystal prepared by a modified Bridgman technique.

Experimental Technique

The prepared crystal samples were obtained by direct fusion of the constituents in stoichiometric proportion. 8.0ll g indium with purity 99.9999% representing 55.485% and 6.909g selenium with the same purity representing 44.515%, were used as starting materials in the growth experiment. Crystals were grown in a local laboratory and details of the experimental equipment for crystal growth by a special design based on Bridgman technique described elsewhere [16]. The mixture was enclosed in quartz ampoules internally coated with a thin layer of carbon to prevent contamination of the charge. The charged ampoule was sealed off at a pressure of approximately 10^{-5} torr. The composition was firstly kept at temperature higher than the melting point for several hours, in order to obtain uniform material throughout. After the direct fusion, the ampoule was shaken in order to complete the reaction of the whole content, and then it was allowed to enter the other zones of the furnace. The ampoule was moved in the furnace zones between the temperature 980 and 380 K for about 15 days. The recorded velocity of the molten zone was almost 1.6 mm/h. The melting point of In_6Se_7 has been precisely determined in the middle zone of the furnace as 903 K according to the published phase diagram [12]. Afterwards the ampoule was then cooled down from 903 K to 380 K. The prepared material showed that it is strongly crystalline as identified with diffraction chart, and the diffraction data did not show the presence of any secondary phase. Crystals of In_6Se_7 appear in the form of thin needles elongated a long the b-axis. Well defined single crystals suitable samples with mean dimensions 8.5 $\times$ 3.l $\times$ l.3 mm^3 and mirror polished surfaces were prepared for electrical measurements. These were performed in a vacuum glass cryostat in the temperature interval 148 K to 533 K using a specimen container evacuated to 10^{-2} Torr. Electrical conductivity and Hall coefficient were measured by a DC compensation method.

Electrical measurements were made with the aid of silver contact. These contacts were Ohmic in the range of the applied electrical voltage. The Ohmic nature of the contacts was checked by recording the current-voltage characteristics. A study of the Hall effect was carried out in magnetic field employing a direct current. A magnetic field of 0.5 tesla was employed for Hall coefficient measurements. In order to avoid thermogalvanomagnetic effects, several measurements were carried out for temperature values, by reversing the direction of both the current and the magnetic field.

Results and Discussion

Figure 1 represents the temperature dependence of the electrical conductivity of In_6Se_7 single crystal. As illustrated in the figure a much less rapid increase in conductivity is observed in the low temperature range with a linear relation up to 222 K. After this region the electrical conductivity exponentially increase with a relatively speed rate in the temperature range extending from 222 up to 310 K. Linearity increase of the conductivity is observed in the high temperature range above 310 K. The room temperature conductivity was evaluated according to the equation $\sigma_{imp} = \sigma_{0imp}\, e^{-\Delta E_{a,d}/2KT}$ where σ_{0imp} is a factor that depends weakly on temperature, ΔE_a is the impurity ionization energy in p-type semiconductor, ΔE_a is the impurity ionization energy in n-type semiconductor, and was found to reach a value of $\sigma = 9.56 \times 10^{-4}$ $Ohm^{-1}cm^{-1}$. From the impurity region of electrical conductivity, the depth of impurity centers was found to be 0.077 eV. The width of the forbidden gap ΔE_g was evaluated using $\sigma_i = \sigma_{0i}\, e^{-\Delta Eg/2KT}$ where σ_{0i} denotes the pre-exponential expression, and σ_i is the intrinsic conductivity, and from the high-temperature slope of the conductivity curve, the width was found to be 0.52 eV. This value indicates that our crystals are of a narrow energy gap. The calculated energy gap width in the present work is larger than that reported in the literature [17,18]. On the other hand, this value is smaller than that obtained by other authors [15,19]. Not only this result contradicted those obtained by other authors, but also the published values for ΔEg disagreed with each other. We may attribute the discrepancy between the values of ΔEg partially to the presence of the large number of intrinsic defects that affects strongly the motion of scattering of current carriers and phonons. On the other hand it is thought that the technology used to grow these crystals may influence its physical properties. In this paper, we tried to elucidate this confusion, but more experimental data were necessary to explain this contradiction. The temperature dependence of the Hall coefficient for In_6Se_7 specimen is shown in Fig. 2. It is obvious that the sign of the Hall coefficient is positive in the entire temperature range of investigation. This indicates that the compound In_6Se_7 monocrystal is a brilliant p-type semiconductor which is in reasonable agreement with the published results [15,17]. The Hall coefficient at room temperature was evaluated as 10.8×10^6 cm^3/C. Determination of the energy gap and ionization energy from Hall data is possible by using the equation $R_HT_{3/2}$ = const. exp(Eg/2KT) and plotting the relation between $\log R_H T^{3/2}$ and 1000/T as shown in Fig. 3. In the temperature region in which the conductivity is predominantly intrinsic, the forbidden band width was estimated to be 0.53eV.The depth of the acceptor level was determined from the region in which the conductivity is predominantly due to impurity atoms and was found to be 0.067 eV. These values are in good agreement with the values obtained from the temperature dependence of electrical conductivity. The most sticking feature of the Hall mobility is its temperature dependence as illustrated in Fig. 4.

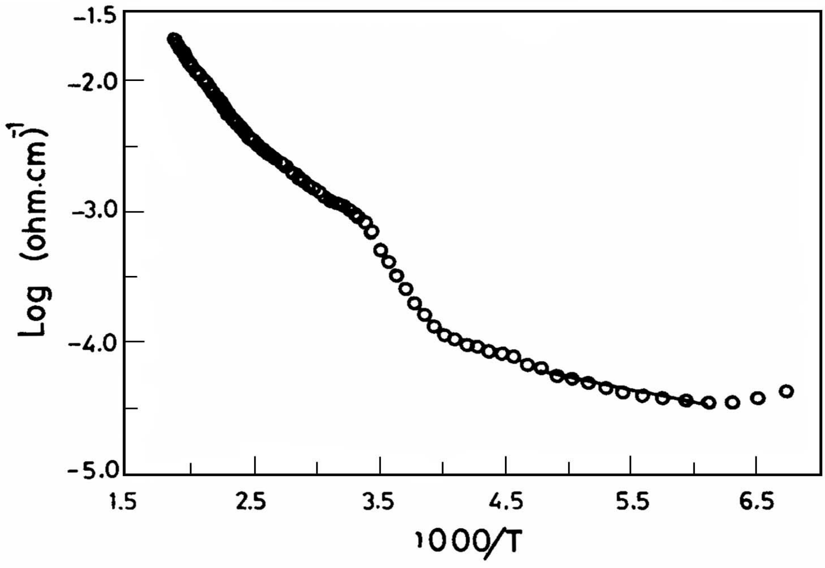

Fig. 1. Temperature dependence of electrical conductivity.

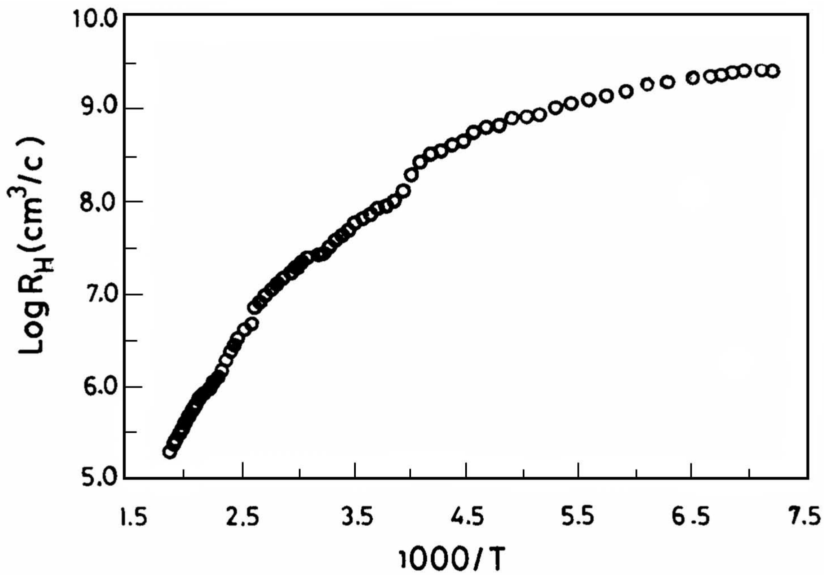

Fig. 2. Temperature dependence of Hall effect.

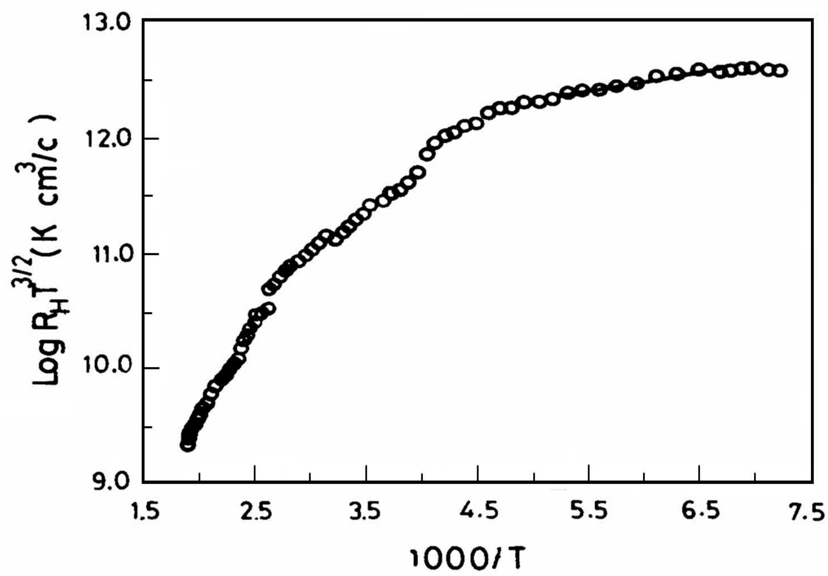

Fig. 3. Relation between R_H $T^{3/2}$ and 1000/T.

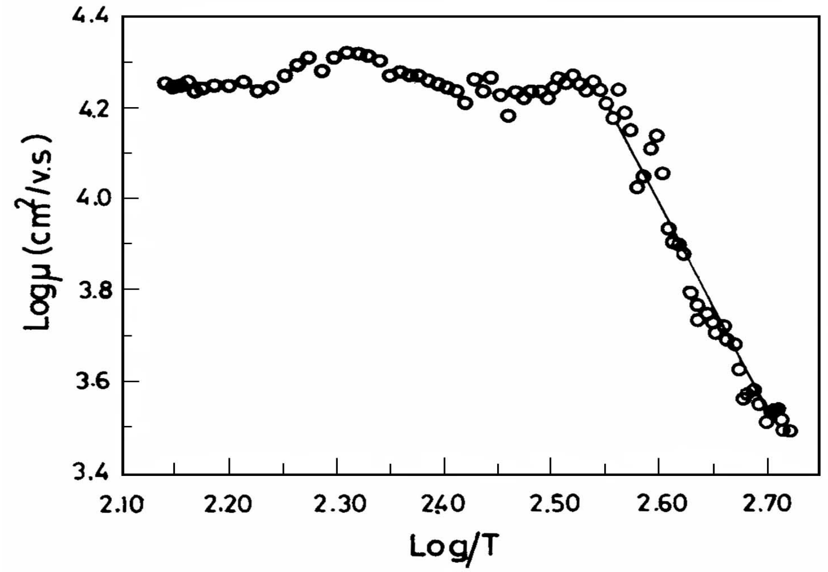

Fig. 4. Behavior of Hall mobility as a function of temperature.

The logarithm of $R_H\sigma$ against logT is plotted in Fig. 4. This plot results in a straight line, the slope of which allows the determination of the exponent n in the relation μ_p α T^n. In the temperature range 340- 525 K, it was found that the exponent n is –4.661. This value for n is unusually large compared with that obtained for lattice scattering in other semiconductors. This dependence indicates that the phonon scattering mechanism is responsible for the mobility in the high temperature range. In this region of temperature the mobility is always seen to decrease with increasing temperature and appears to be unaffected by impurity scattering effect in the low temperature range as seen from the figure. At room temperature the hole mobility of 13.1×10^3 cm^2/Vs was obtained in these measurements for the In_6Se_7 sample. Calculation of the diffusion coefficient for holes gave a value of 327.5 cm^2/s. Assuming that the effective mass for holes is equal to the rest mass and using the value for the hole mobility at room temperature, the mean free time could be determined and its value was equal to 4.078×10^{-13} sec. Also the diffusion length of holes in the In_6Se_7 specimen was evaluated as 3.65×10^{-5} cm. In order to examine the behavior of the carrier concentration in this sample with temperature, one can illustrate in Fig. 5 the temperature dependence of charge carrier concentration. The carrier concentration, calculated under the usual approximation that makes the Hall mobility equal to the drift mobility. It can be stated that at room temperature the concentration reaches a value of 9.964×10^8 cm^{-3}. The variation of the carrier density with temperature appears to be nearly linear except in the temperature range 220-300 K which represents the region of transition to intrinsic conduction.

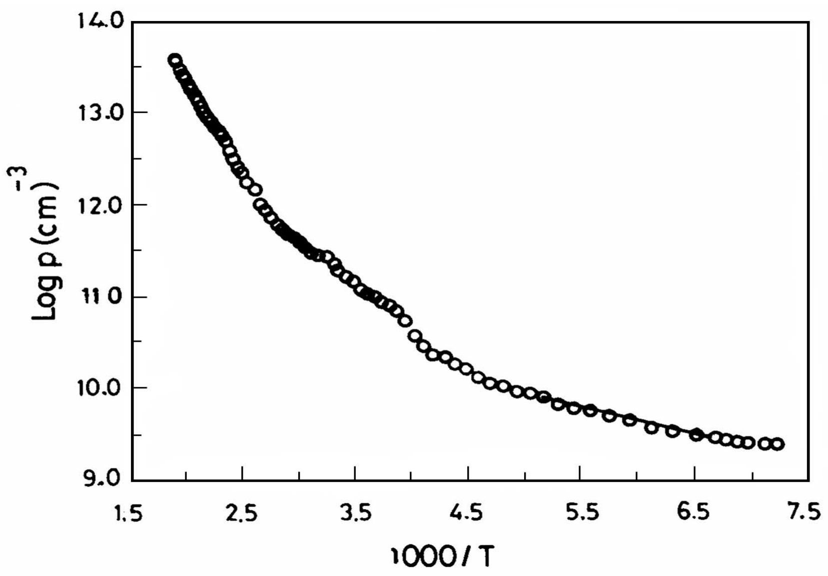

Fig. 5. Variation of carrier concentration with temperature.

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الخصائص الكهربائية لسداسي الإنديوم وسباعي السيلينيوم

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المستـخلص. تمت دراسـة الموصلية الكـهربائيـة ومعـامل هـول لبلورة أحادية من سـداسي الإنديوم ، وسبـاعي السلينيـوم في المدى من درجات الحرارة من ١٤٨–٥٢٨ كلفن. تمَّ تحضير وتجهيز البلورات المستخدمة معمليًا باستخدام تقنية بريد جمان. أمكن عن طريق قياس معامل هول تحديد نوعية التوصيل الحادث وأمكن التعرف على أن هذه البلورة من نوع P-type. ومن دراسة الموصلية الكهربائية تم حساب طاقة الفجوة ، ووجد إنها 0.52eV كما تم حساب مستوى طاقة الشوائب الآخذة وكانت قيمته 0.077eV. وحسبت قيم الموصلية الكهربائية ومعامل هول وتركيز ناقلات الشحنة عند درجة حرارة الغرفة وكانت $9.65x10^{-4}Ohm^{-1}cm^{-1}$ و $10.8x10^{6}cm^{3}/C$ و $9.964x10^{8}cm^{3}$ على التوالي، أما الحركية μ_H ، فكانت $13.1x10^{3}cm^{2}/VS$. كما تم توضيح اعتماد حركية هول على درجة الحرارة.