

<i>Cryst. Res. Technol.</i>	36	2001	4-5	457-464
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Crystal Data, Electrical Resistivity, and Hall Mobility of n-Type AgIn_5S_8 Single Crystals

The X-ray diffraction has revealed that AgIn_5S_8 is a single phase crystal of cubic spinel structure. The value of the unit cell parameter for this crystal is 1.08286 nm. The electrical resistivity and Hall effect of n-type AgIn_5S_8 crystals are measured in the temperature range of 50-400 K. A carrier effective mass of $0.20 m_0$, an acceptor to donor concentration ratio of 0.8 and an acoustic phonons deformation potential of 20 eV are identified from the Hall effect measurement. The Hall mobility data are analyzed assuming the carrier scattering by acoustic and polar optical phonons, and ionized impurities.

Keywords: AgIn_5S_8 crystal, resistivity, mobility, acoustic, polar, scattering mechanism

(Received February 9, 2001; Accepted April 24, 2001)

1. Introduction

Ternary semiconductor compounds like AgIn_5S_8 and CuIn_5S_8 have different application in device technology. The presence of the three different chemical components in these semiconductors, permits the altering of their physical properties. Thus, these compounds span many areas of fundamental and technological interests, such as magnetism, ferroelectricity and superconductivity (DEB, ZUNGER; RADAUTSAN, SCHWAB). The band gap of AgIn_5S_8 and CuIn_5S_8 is 1.7 and 1.5 eV, respectively, which is suitable for a terrestrial solar cell absorber layer. Hence these compounds are quite interesting as candidates in solid state photovoltaic and photochemical cell applications (NOMURA et al.).

Some of the optical, structural and electrical properties of AgIn_5S_8 and CuIn_5S_8 have been studied by many authors (ENDO et al., USUJIMA et al., PAORICI et al., ORLOVA et al., KITAMURA et al.). However, -up to our knowledge- there are a few reports about the electrical properties of AgIn_5S_8 crystals. In our previous investigations, we have reported the active optical modes in both crystals using Raman and infrared measurements (GASANLY et al. 1993) and have revealed the donor-acceptor pair recombination in AgIn_5S_8 single crystals by means of low-temperature photoluminescence measurements (GASANLY et al. 1999).

The main purpose of this paper is to report the structural properties and to describe the experimental results on the temperature dependence of the electrical resistivity and Hall coefficient of AgIn_5S_8 crystals. The impurity levels, the carrier effective mass, and the carrier scattering mechanisms, are also determined.

2. Experimental Procedure

Crystals of AgIn_5S_8 were prepared by the modified Bridgman method, the structure of which was defined by the X-ray powder diffraction spectra using a Philips PW1740 diffractometer

with a monochromatized Cu $K\alpha$ radiation ($\lambda = 0.154049$ nm) at scanning speed of $0.02^\circ 2\theta$ /sec. For reliable resistivity and Hall measurements, the electrical contacts were obtained by the thermal deposition of gold (99.999%) under pressure of $\sim 10^{-6}$ Torr using suitable masks. Current-voltage measurements showed that the obtained contacts are ohmic. The electrical measurements were carried out by the standard d. c. technique. The d. c. Hall effect measurements were carried out at a magnetic field of 1.0 T using EM7-HV electromagnet connected to a Lake-shore 450 Gaussmeter. The conductivity and Hall measurements of the crystals were carried out in a temperature region of 50-400 K. The measurements were handled using a Lake-shore automated Hall measuring system that consists of Keithley 7065 Hall effect card, Keithley 7152 low current switch card, Keithley 6512 electrometer, Keithley 220 current source, Keithley 4853 autoranging digital picoammeter, Keithley 2182 digital voltmeter, and Lake-shore closed cycle helium cryostat attached to a Lake-shore 340 Cryogenic temperature controller. The crystals dimensions were measured by using a travelling microscope and found to be $0.2 \times 0.2 \times 0.1$ cm³.

3. Results and Discussion

The measurements represented here, were carried out on several samples, and good reproducibility was observed. The X-ray diffraction patterns of the samples have revealed that AgIn_3S_8 is a single phase of cubic spinel structure. X-ray diffractograms of this compound were indexed by using a computer program "TREOR-90". The Miller indices (hkl), the observed and calculated interplanar spacings (d) and the relative intensities (I/I_0) of the diffraction lines are listed in Table 1. The calculated and observed interplanar spacings are found to be in good agreement with each other. The value of the unit cell parameter for this crystal (a) was found to be 1.08286(8) nm. This value is in good agreement with those reported by several authors (USUJIMA et al., ORLOVA et al.). An examination of results obtained shows that no forbidden reflections ($hk0$) with $h+k=4n+2$ were detected for this compound (see Table 1). The absence of 200, 420, and 600 reflections indicate that there was no "A" site ordering as was observed in the analogous chromate spinel (HIROTAKE, CHIRBA). Thus, the crystal should be assigned to the conventional space group $Fd\bar{3}m$.

Both the hot probe technique and the sign of Hall coefficient (R_H) indicates that the samples exhibits n -type conduction. The ratio of length to width of the sample is 1.2, thus no corrections were made for the shortening effect of the current electrodes. The crystals exhibit an electrical resistivity (ρ), Hall mobility (μ), and carrier concentration (n) of $3.8 \Omega \text{ cm}$, $77.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $2.1 \times 10^{16} \text{ cm}^{-3}$ at room temperature, respectively. The value of Hall mobility is high as compared to that reported by PAORICI et al. and it is in good agreement with that reported by USUJIMA et al.. The difference in the values of the electrical resistivity and carrier concentration reported here from that in literature (USUJIMA et al., PAORICI et al., ORLOVA et al.) can be attributed to the deficient sulfur amount used.

To establish the dominant scattering mechanism in the samples, the temperature dependence of electrical resistivity and Hall mobility was examined in the temperature range of 50-400 K. General view of the resistivity as a function of reciprocal temperature is shown in Fig. 1. The figure depicts that the resistivity of AgIn_3S_8 single crystals increases with decreasing temperature. The decrement in the resistivity is more pronounced at low temperatures. A logarithmic plot of r as a function of T^{-1} gives a slope of ~ 0.2 in the region of $200 \text{ K} < T < 400 \text{ K}$, ~ 0.7 in the region of $130 \text{ K} < T < 190 \text{ K}$ and ~ 1.6 below 130 K. The variation of these slopes with temperature is probably due to the domination of thermal lattice vibrations which in turn affect the scattering of the carriers when temperature increases as will be shown later through the Hall mobility analysis.

Table 1: X-ray powder diffraction data for AgIn_5S_8 crystal

hkl	$d_{\text{obs.}} (\text{\AA}^\circ)$	$d_{\text{cal.}} (\text{\AA}^\circ)$	I/I_0
111	6.1417	6.1475	13
220	3.7684	3.7677	16
311	3.2133	3.2073	100
222	3.0765	3.0771	10
400	2.6659	2.6657	40
331	2.4468	2.4467	6
422	2.1762	2.1767	15
511	2.0527	2.0567	56
440	1.8861	1.8861	88
531	1.8025	1.8028	7
620	1.6878	1.6879	6
533	1.6280	1.6280	19
622	1.6087	1.6091	8
444	1.5411	1.5414	13
711	1.4947	1.4950	7
642	1.4260	1.4263	8
731	1.3898	1.3899	30
800	1.3345	1.3348	15
660	1.2579	1.2582	6
751	1.2329	1.2331	17

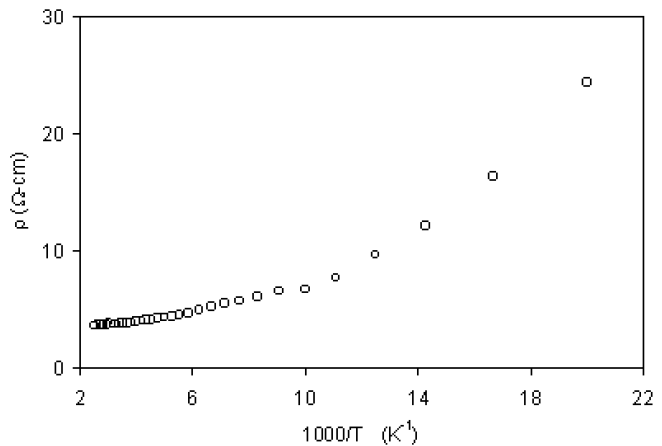


Fig. 1: Variation of electrical resistivity with reciprocal temperature.

The carrier concentration n , of AgIn_5S_8 crystals were calculated using the relation $n = 1 / eR_n$. As observed from the temperature variation of n shown in Fig. 2, the carrier concentration slightly decreases from $3.1 \times 10^{16} \text{ cm}^{-3}$ at 400 K to $1.4 \times 10^{16} \text{ cm}^{-3}$ at 210 K and then remains constant indicating that the carriers of these samples are degenerate in the remaining temperature region ($50 \text{ K} < T < 210 \text{ K}$) consisting with the results reported by other authors (USUJIMA et al., PAORICI et al.).

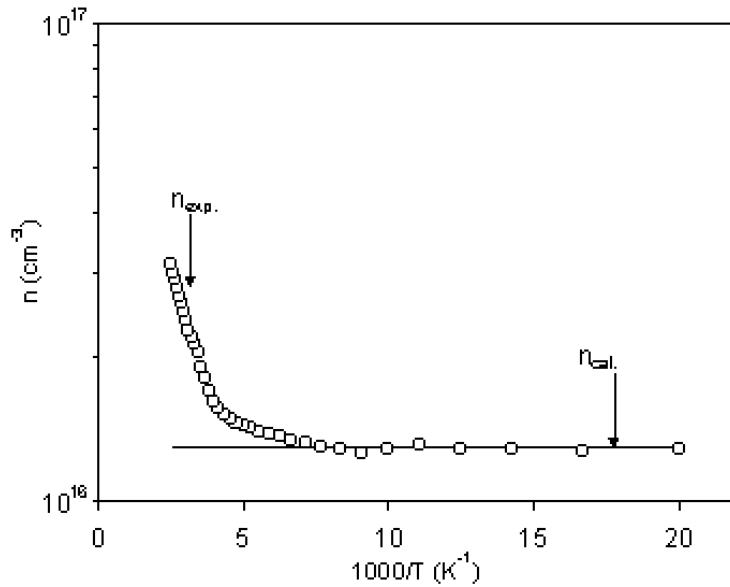


Fig. 2: Variation of carrier concentration with reciprocal temperature.

The Hall mobility calculated from the relation $m = s / ne$ was found to decrease with increasing temperature in the temperature region of 240 K < T < 400 K. In the region of 210 K < T < 240 K, the mobility increment with temperature is very slow. Below 210 K the mobility increases with temperature increasing (see Fig. 3). A logarithmic plot of mobility as a function of temperature is found to be linear with a slope of around (-3/2) in the temperature region of 240 K < T < 400 K which is the indication of lattice scattering mechanism. The logarithmic plot of μ versus T below 210 K has a slope of approximately (3/2) indicating that the mobility is limited by the scattering of ionized impurity.

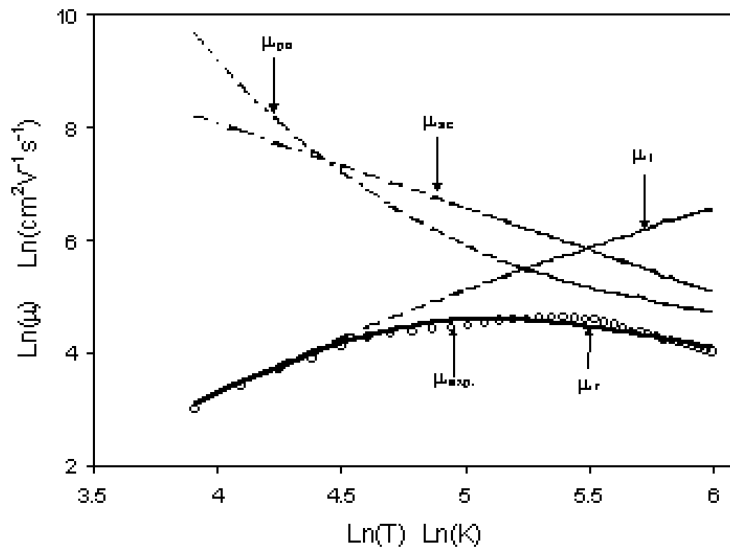


Fig. 3: Variation of Ln(μ) as a function of Ln(T) for AgIn₃S₈ crystals.

The temperature dependence of Hall mobility above 240 K could then be quantitatively interpreted using the acoustic phonon scattering mobility given as (WILEY p.127)

$$m_{ac} = 3.17 \times 10^{-5} \frac{du^2}{(m^*/m_0)^{5/2} E_1^2 T^{3/2}}, \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \quad (1)$$

where d is the density in g/cm^3 , E_1 is the deformation potential in eV for acoustic phonons, m^* is the effective mass of the carriers, m_0 is the free electron mass and u is the average sound velocity which could be estimated from the formula,

$$u = \frac{kq_D}{\hbar} \left(\frac{V}{6p^2} \right)^{1/3}. \text{ cm/s} \quad (2)$$

Here q_D is the Debye temperature estimated by Lindemann's melting rule and V , the average atomic volume, is $a^3/4$ where a is the lattice parameter.

In computing the acoustic phonons scattering mobility, the value of d was taken as 4.94 g/cm^3 (ORLOVA et al.), the atomic volume was calculated from the X-ray results, q_D was estimated using $T_{\text{melt}} = 1078 \pm 10 \text{ }^\circ\text{C}$ obtained by melting the crystal in a tantalum wire wounded quartz tube under a pressure of 10^{-4} Torr, and found to be 250 K. The value of melting temperature is in good agreement with that reported by PAORICI et al.. m^*/m_0 was defined from the single donor-single acceptor model which will be considered later in details through the analysis of ionized impurity scattering mobility (μ_i). Thus the only remaining fitting parameter was the acoustic phonons deformation potential E_1 . However, the scattering mechanism by acoustic phonons (μ_{ac}) could not account for the experimental values unless an extraordinary large deformation potential was assumed ($\sim 35 \text{ eV}$). Thus, the scattering by polar optical phonons was also taken into account. The mobility due to the scattering by polar optical phonons is given as, (WILEY p.134),

$$m_{po} = 25.4 \frac{T^{1/2}}{q} \left(\frac{1}{e_\infty} - \frac{1}{e_s} \right)^{-1} \left(\frac{m_0}{m^*} \right)^{3/2} (e^z - 1) G(z). \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \quad (3)$$

In this expression, e_∞ is the optical relative dielectric constant, $z = q/T$, where q is the characteristic temperature of optical phonons and $G(z)$ is a tabulated function. The values of $e_\infty = 4.5$ and $e_s = 10.3$ were determined using the infrared (IR) reflectivity measurements on the same crystals in our previous investigation (GASANLY et al. 1993). The value of the characteristic temperature $q = 298 \text{ K}$ was calculated from the relation $\hbar c n = kq$, where $n = 265 \text{ cm}^{-1}$ is the frequency of the most intensive longitudinal optical mode observed through IR measurements (GASANLY et al. 1993). The values of the theoretical polar phonon scattering mobility with that of acoustic phonons scattering mobility are plotted in Fig. 3.

The ionized impurity scattering mobility, the acoustic phonons scattering mobility and the polar phonons scattering mobility are related to give the combined mobility μ_T through the relation

$$\frac{1}{m_T} = \frac{1}{m_{po}} + \frac{1}{m_{ac}} + \frac{1}{m_i}. \quad (4)$$

The ionized impurity scattering mobility is given by the Brooks-Herring equation (PUTLEY). The temperature dependence of μ_i is calculated from

$$\mu_i = \frac{3.28 \times 10^{15} e_s^2 T^{3/2}}{(N_a + N_d) \left(\frac{m^*}{m_0} \right)^{1/2} \left[\ln(b+1) - \frac{b}{b+1} \right]} \quad (5)$$

where

$$b = \frac{1.29 \times 10^{14} \left(\frac{m^*}{m_0} \right) e_s T^2}{N^*} . \quad (6)$$

N^* is the effective screening density and given by,

$$N^* = n + \frac{(n + N_a)(N_d - N_a - n)}{N_d} . \quad (7)$$

Here N_a and N_d are the acceptor and donor impurity concentrations presented in the crystals.

To get information about the carriers effective mass m^* and the impurity concentrations present in the AgIn₅S₈ crystals, the temperature dependence of the carrier concentration was analyzed by using the single donor-single acceptor model (BLACKMORE) in which the dependence of carrier concentration (n) on temperature is given as,

$$\frac{n(n + N_a)}{N_d - N_a - n} = \mathbf{b} N_c \exp\left(-\frac{E_d}{kT}\right) \quad (8)$$

$$\text{with } N_c = 4.83 \times 10^{15} \left(\frac{m^*}{m_0} \right)^{3/2} T^{3/2} , \text{ cm}^{-3} \quad (9)$$

where \mathbf{b} is the degeneracy factor. Assuming both types of impurities to be present in the crystals and using the three dimensional expression for N_c , the temperature dependence of n in Eqn. (8) could be rewritten as,

$$n = \frac{2(N_d - N_a)}{1 + \frac{N_a}{\mathbf{b}N_c} \exp(E_d/kT) + \left[\left(1 + \frac{N_a}{\mathbf{b}N_c} \exp\left(\frac{E_d}{kT}\right) \right)^2 + \frac{4(N_d - N_a)}{\mathbf{b}N_c} \exp\left(\frac{E_d}{kT}\right) \right]^{1/2}} . \quad (10)$$

By substituting the degeneracy factor $\beta = 2$ and $E_d = 0.06$ eV, which is the value of donor ionization energy, obtained from the photoluminescence spectra measurements of AgIn₅S₈ crystals (GASANLY et al. 1999), a computer numerical analysis was handled using Eqn. (10). The best fitting curve to the experimental data, obtained from the temperature dependent Hall effect measurements, is represented by the solid line in Fig. 2. As a result of this fitting procedure, data regressions provide the determination of the acceptor and donor

concentrations in addition to the impurity effective mass ratio. The values of N_d , N_a , and $\left(m^*/m_0\right)$ were found to be 7.0×10^{16} , $5.7 \times 10^{16} \text{ cm}^{-3}$ and 0.20, respectively. The obtained value of $\left(m^*/m_0\right) = 0.20$ coincides with the reported for CuIn_5S_8 (KITAMURA et al.) where similar behavior of mobility was observed. It should be noted that these values are obtained in the temperature region of $50 \text{ K} < T < 210 \text{ K}$ where the ionized impurity scattering mobility is dominant. The strong deviation of the experimental data from the calculated ones, using Eqn. (10), above 210 K could possibly be attributed to the existence of some other assorted compensating acceptor levels originating from the variation in stoichiometry (i.e., sulfur vacancies) which accommodate acceptor trapped electrons in the crystals (BLACKMORE).

Using the values of N_d , N_a , m^*/m_0 and e_s , the ionized impurity scattering mobility was calculated. The calculated temperature dependence of μ_i is shown in Fig. 3. Then using Eqn. (4), the total mobility was evaluated and plotted in the same figure. The calculated theoretical μ_T agrees well with that obtained from the Hall effect experiments. The value of the fitting parameter $E_i = 20 \text{ eV}$ is reasonable when compared with that for other materials.

The above mentioned analysis revealed that the Hall mobility of AgIn_5S_8 is limited by the scattering of acoustic combined with optical polar phonons above 210 K and the scattering of ionized impurities below 210 K. Similar type of mobility behavior was reported for CuIn_5S_8 crystals (KITAMURA et al.).

Conclusions

The X-ray diffraction analysis revealed that AgIn_5S_8 is a single phase of cubic spinel structure related to the conventional space group $Fd\bar{3}m$. The value of the unit cell parameter for this crystal is found to be 1.08286 nm. The crystal reveals an n -type conductivity. The electrical resistivity and Hall coefficient were measured in the temperature range between 50 and 400 K. The carriers effective mass is determined as $0.20 m_0$ with an acceptor and donor carrier concentrations of 5.7×10^{16} and $7.0 \times 10^{16} \text{ cm}^{-3}$, respectively. The Hall mobility is limited by the scattering of acoustic and optical polar phonons at high temperatures combined with ionized impurity scattering as temperature decreases.

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