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Crystal Growth and Characterization of $In_{1.9}As_{0.1}Se_3$

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Crystals of $In_{1.9}As_{0.1}Se_3$ were grown by chemical vapor transport with chlorine as the transport agent. The composition was determined by chemical, X-ray, and densitometric analyses. This phase is related to a high-temperature modification of In_2Se_3. $In_{1.9}As_{0.1}Se_3$ was found to be an *n*-type semiconductor with a band gap, determined from optical absorption data, of 1.4 eV. When used as an anode in liquid electrolyte photocells, this compound showed initial photo-currents in both acidic (HCl) and basic (NaOH) solutions. However, this compound was unstable as an operating photoelectrode.

Introduction

Mixed anion compounds containing both group Va and VIa elements have been the subject of numerous studies because of the wide variety of the structural types and physical properties they exhibit (*1, 2*). Recently, the new mixed anion compound $In_{2/3}PS$, which adopts a $CdCl_2$-related structure, was synthesized and studied (*3*). This phase is closely related to the large group of hypothiophosphate and hyposelenophosphate compounds of the type MPS_3 and $MPSe_3$ in which M = Mn, Fe, Co, Ni, Zn, Cd, Hg, or Sn (*4*). The characteristic structural feature of all these materials is the occurrence of P–P σ-bonded pairs. Although arsenic atoms often are bonded to one another (as in the skutterudite phase $CoAs_3$, for example (*5*), there are no reports of arsenic–sulfur or arsenic–selenium analogs of the MPS_3 or $MPSe_3$ compounds. Our attempts to synthesize a corresponding $MAsSe_3$ (M = In) phase were unsuccessful. However, crystals of a new compound $In_{1.9}As_{0.1}Se_3$, which is related to a high-temperature modification of In_2Se_3, were grown. The preparation, characterization, and potential use of this phase as an anode in a liquid electrolyte photocell is described. Recent work on the corresponding indium–arsenic–sulfur system which shows similar results has been reported (*6, 7*).

Preparation

Crystals of $In_{1.9}As_{0.1}Se_3$ were grown in sealed silica tubes (25 cm × 11 cm i.d.) by chemical vapor transport from the elements (*8*). Indium (J. Matthey and Co., 5–9's) was

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TABLE I

CRYSTAL GROWTH CONDITIONS

Nominal charge compositions	T (charge zone, °C)	T (growth zone, °C)	Results
$In_{0.67}AsSe_3$	650	600	Crystals of $In_{1.9}As_{0.1}Se_3$ and amorphous black phase
$In_{1.9}As_{0.1}Se_3$	650	600	Crystals of $In_{1.9}As_{0.1}Se_3$
$In_2As_{1.5}Se_3$	650	600	Crystals of $In_{1.9}As_{0.1}Se_3$

melt-refined under vacuum, arsenic (Leico, 5–9's) was purified by subliming the oxide under vacuum, and selenium (Leico, 5–9's) was used as obtained from the manufacturer. Different atomic ratios of In, Se, and As were used as charges and are shown in Table I. Large single crystals (5 × 5 × 0.1 mm) were grown when the charge zone of the furnace was maintained at 650°C and the growth zone cooled to 600°C over a period of 3 days and held for 7 days at that temperature. Chlorine (25 Torr) was used as the transport agent. The crystals grew as thin lustrous black plates perpendicular to the c_0 axis.

Characterization

The crystals were dissolved in boiling aqua regia, and the indium content determined by a complexometric titration using a standardized EDTA solution as the complexing agent and 1-(2-pyridylazo)-2-naphthol as the indicator (*9*). The EDTA was standardized with an indium solution of known molarity and indicator blanks were checked. An electron microprobe analysis for the arsenic and selenium content was performed, and the analytical results are presented in Table II. In addition, in order to confirm the stoichiometry, density measurements were performed by a hydrostatic technique with perfluoro (1-methyl-decalin) as the density fluid and with silicon crystals ($\rho = 2.328(2)$ g cm^{-3}) as a standard (*10*).

TABLE II

ANALYTICAL RESULTS

	Observed	Calculated (based on $In_{1.9}As_{0.1}Se_3$)
In (volumetric titration)	48.4(4)	47.2
As (electron microprobe CoAsSe standard)	1.5(6)	1.6
Se (electron microprobe CoAsSe standard)	53(2)	51.2

Both the chemical analysis and density measurements were repeated on crystals grown from the different charge compositions listed in Table I. Within experimental error, the crystals had the same stoichiometry.

A single crystal of $In_{1.9}As_{0.1}Se_3$ was examined by precession techniques (Mo$K\alpha$ radiation) and the crystallographic data are presented in Table III. The cell constants and symmetry of this phase resemble closely the high temperature modification of In_2Se_3 reported by Likforman *et al.* (*11*), and, except for a doubling of the value of c_0, the compound appears to be closely related to the arsenic-doped indium sesquisulfide phase reported by Diehl *et al.* (*6*). As indicated by a complete structural determination, the latter phase crystallizes with a double layer structure with indium atoms and a small fraction of vacancies occupying the octahedral sites. The arsenic atoms are statistically distributed in tetrahedral sites in the van der Waals gap. Although a complete structural determination of the indium–arsenic–selenium phase has not

TABLE III

CRYSTALLOGRAPHIC DATA[a]

System	$In_2Se_3(As)$ (hexagonal)	$In_2Se_3(H.T.)^{(10)}$ (hexagonal)	$In_2S_3(As)^{(6)}$ (trigonal)
a_0 (Å)	3.97	4.03	3.81
c_0	18.9	19.1	9.04
ρ_0 (gm/cm^3)	5.90(4)		
ρ_c (gm/cm^3)	5.95		

[a] Laue symmetry: $6/mmm$; systematic absences: $hh(2\bar{h})l$: $l = 2n + 1$; possible space groups: $P6_3mc$, $P\bar{6}2c$, $P6_3/mmc$.

been completed, it is probable that a similar arrangement exists with two double layers [i.e., Se–In–Se–In–Se · · · (As) · · · Se–In–Se–In–Se · · · (As)] establishing the translational periodicity in the c_0 direction.

Optical Properties

The optical absorption spectrum of a single crystal of $In_{1.9}As_{0.1}Se_3$ was recorded on a Cary 17 spectrophotometer operating in the absorption mode. As shown in Fig. 1, the optical absorption edge occurs at approximately 1.4 eV. This can be compared with the value of 1.2 eV found for In_2Se_3 (*12*).

Electrical Properties

$In_{1.9}As_{0.1}Se_3$ is an *n*-type semiconductor. The sign and number of majority carriers were determined from room temperature measurements of Seebeck and Hall coeffients, respectively. The number of carriers, *n*, was determined from the Hall coefficient, R_H, using the relation $n = 1/R_He$ where *e* is the magnitude of the electron charge. A single band model was used because the band gap of this compound is not small and because at room temperature this semiconductor is in its extrinsic region (see below). The results of these measurements are presented in Table IV.

Measurements of the electrical resistivity, ρ, were performed using the four-probe van der

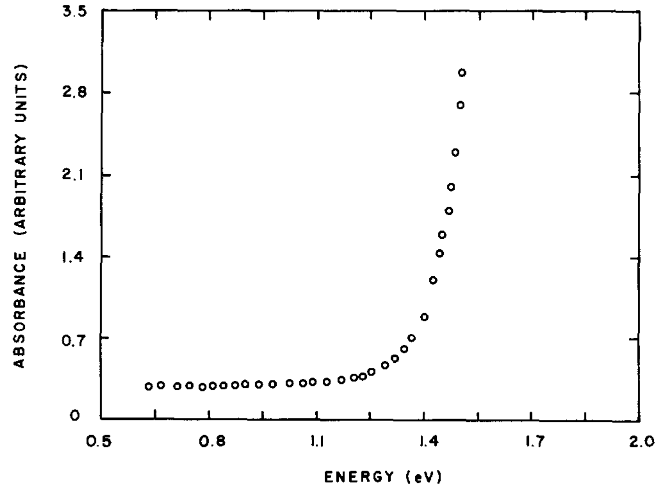

FIG. 1. Optical absorption spectrum of $In_{1.9}As_{0.1}Se_3$.

TABLE IV

OPTICAL AND ELECTRICAL PROPERTIES[a]

Electrical resistivity (Ω cm)	Seeback coefficient (μV/°K)	No. of carriers (1/cm^3)	Electrical activation energy (eV)	Optical absorption edge (eV)
0.4–31	−700(30)	2.1×10^{17}	0.12(1)	1.4

[a] The electrical activation energy was determined over the temperature range 150 to 300°K. All other values were measured at room temperature.

Pauw technique (*13*). All electrical contacts, including those for the photocurrent measurements described below, were made using an ultrasonic soldering device (12 Watt Generator, Sonobond Corp.) and indium alloy solders (Idalloy #2 and #4, Indium Corp. of America). The ohmicity of the contacts was checked prior to the resistivity measurements. A plot of ln ρ verses $10^3/T$ of a crystal of $In_{1.9}As_{0.1}Se_3$ is shown in Fig. 2. For this sample, a value of 0.13 eV was determined for the activation energy, E_a, of the impurity states ($\rho \propto \exp E_a/KT$). Although the value of ρ at room temperature did vary somewhat for different crystals E_a remained essentially constant (see Table IV). In addition, the activation energy was measured parallel and perpendicular to the c_0-axis of the crystal and was found to be the same (within experimental error) in both directions.

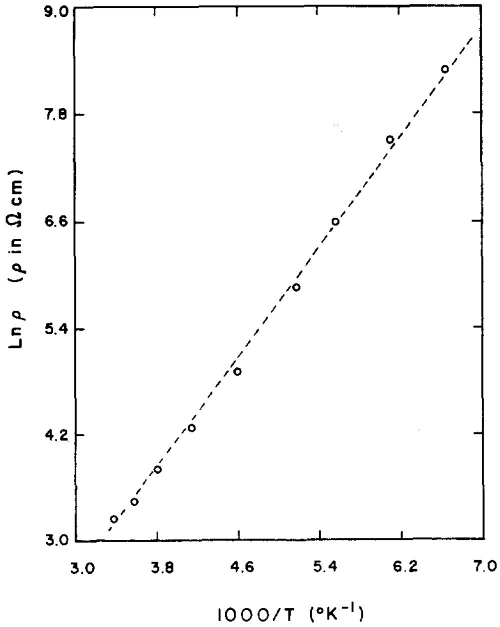

FIG. 2. Natural logarithm of the electrical resistivity vs $10^3/T$. The slope of the dashed line corresponds to an activation energy of 0.13 eV.

The properties of $In_{1.9}As_{0.1}Se_3$ as an anode in a photocell of the type $In_{1.9}As_{0.1}Se_3$/liquid electrolyte/Pt were investigated. Photoanodes were constructed from single crystals by attaching electrical leads as described above, and coating all but the crystal surface to be illuminated with an insulating varnish (Microstop, Michigan Chrome and Chemical Company). Light from a high-pressure 150-W xenon lamp was used to illuminate the anode.

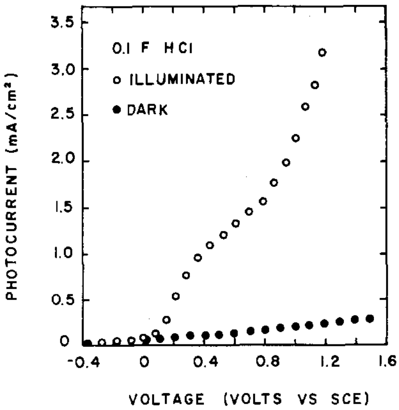

FIG. 3. Photocurrent vs anode voltage (measured relative to a standard calomel electrode). The anode voltage was varied by applying an external bias. The illuminated anode voltage at zero external bias was 0.44 V. Illumination: ~500 mW/cm^2. Electrolyte: 0.1 F HCl. Sample resistivity: 2.6 Ω cm.

The electrical circuit was completed by means of an external resistance R (1 KΩ). For those measurements requiring an external bias, a potentiostat was placed in series with R. The voltage drop across R was used to measure the current flowing in the photocell.

Measurable photocurrents were obtained using both acidic (0.1 F HCl) and basic (0.02 F NaOH) solutions as electrolytes. Figure 3 shows a plot of photocurrent vs voltage (between anode and a standard calomel electrode) for a typical crystal ($\rho = 2.6\ \Omega$ cm). The measurements were made in a 0.1 F HCl solution with increments of 0.1 V of the applied bias. During the time period ($\sim\frac{1}{2}$ h) in which these data were obtained, the photocurrent showed no appreciable decay. However, deterioration effects (a decay in the photocurrent, an increase in the dark current, and changes in color from black to red-brown on portions of the electrode surface) became quite noticeable after $\sim$10 h of operation. It may be possible to stabilize this electrode by the choice of an electrolyte containing an approximate redox couple (*14*).

Acknowledgments

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