JOURNAL OF SOLID STATE CHEMISTRY 26, 111–114 (1978)

Preparation and Properties of Two Indium Antimony Selenides

MICHEL SPIESSER

Laboratoire de Chimie Minerale A, U.E.R. de Chimie de Nantes, Nantes, France

AND ROBERT P. GRUSKA, S. N. SUBBARAO, CARLOS A. CASTRO, AND AARON WOLD*

Department of Chemistry, Brown University, Providence, Rhode Island 02912

Received January 13, 1978; in revised form March 17, 1978

Crystals of antimony-doped In_2Se_3 were grown by the Bridgeman method. This compound, whose composition is $In_{1.8}Sb_{0.2}Se_3$, appears to be isostructural with $In_{1.9}As_{0.1}Se_3$. The refined unit cell parameters are $a = 3.97(1)$, $c = 18.87(1)$ Å. Orthorhombic crystals of $InSbSe_3$ were grown from an isothermal melt. The refined unit cell parameters are $a = 9.43(1)$, $b = 14.02(5)$, and $c = 3.96(1)$ Å. These parameters agree with those determined for α-$InSbSe_3$ by other studies. The observed densities measured by a hydrostatic technique are 5.98(3) g/cm³ for $In_{1.8}Sb_{0.2}Se_3$ and 6.07(2) g/cm³ for $InSbSe_3$. The room temperature dc resistivity for $In_{1.8}Sb_{0.2}Se_3$ has been found to be 4.4×10^4 Ω-cm, whereas that of $InSbSe_3$ has been found to be 15.2(1) Ω-cm. A resistivity versus temperature study has beenn carried out for $InSbSe_3$ between 230 and 400°K. Optical studies indicate that $In_{1.8}Sb_{0.2}Se_3$ is an n-type semiconductor with a band gap of 1.1 eV and $InSbSe_3$ is a p-type semiconductor with a band gap of 0.92 eV.

Introduction

A high temperature phase of indium(III) sulfide has been stabilized at room temperature by doping with arsenic or antimony (*1*, *2*). The resulting n-type semiconductors have the stoichiometry $In_{1.9}As_{0.1}S_3$ and $In_{1.8}Sb_{0.2}S_3$. Crystals of an analogous arsenic-doped indium(III) selenide, $In_{1.9}As_{0.1}Se_3$, have recently been grown in this laboratory (*3*). This compound is structurally related to the doped indium sulfide; however, there is a doubling of the c-axis in the selenide. The compound $In_{1.9}As_{0.1}Se_3$ is hexagonal and the sulfides $In_{1.9}As_{0.1}S_3$ and $In_{1.8}Sb_{0.2}S_3$ are trigonal.

This work reports the synthesis and characterization of an antimony-doped indium selenide, $In_{1.8}Sb_{0.2}Se_3$. An impurity encountered in the initial synthesis of this phase was identified as $InSbSe_3$. The preparation and characterization of $InSbSe_3$ is also reported here.

Experimental

Single-phase crystals of $In_{1.8}Sb_{0.2}Se_3$ were grown by the Bridgeman method. Indium (J. Matthey and Co., 99.999%) was purified by zone melting under vacuum prior to use. Antimony (Gallard–Schlesinger, 99.999%) and selenium (Leico, 99.999%) were used without further purification. A sealed, evacuated silica tube containing the elements in the correct stoichiometric amounts was placed in an isothermal furnace at 860°C for 2 days to ensure a homogeneous melt. The sample was slow-cooled and then crushed and placed in a tube designed (*5*) to facilitate the growth of a single crystal during the

---

* Author to whom all correspondence should be addressed.

0022–4596/78/0262–0111$02.00/0

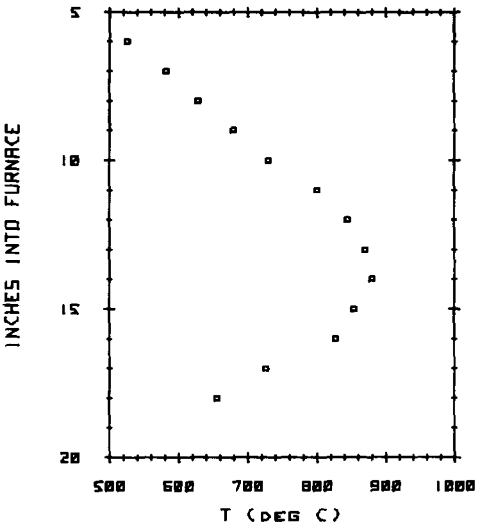

FIG. 1. Profile of the Bridgeman furnace.

Bridgeman process. The sample was suspended within the growth furnace (Hevi-Duty MK-2012) by means of silica hooks and kept at a temperature of 880°C for 1 day. It was then lowered at a rate of 7.2 cm/day (see Fig. 1 for the furnace profile) for another 3 days, after which the furnace was shut off and allowed to cool to room temperature. This process resulted in either a single crystal or several large grains which could be visually separated into single crystals.

Single crystals of $InSbSe_3$ were grown from the melt in an isothermal furnace. A sealed, evacuated 9-mm-i.d. silica tube containing the elements in stoichiometric amounts totaling 3 g was placed within an alundum core which had both ends closed with refractory wool. The core and tube were then heated to 825°C for 5 days and allowed to slow-cool. The product contained a number of grains which could be visually separated into single crystals.

X-ray Analysis

The samples prepared by the above procedures have been analyzed by X-ray diffraction of ground single crystals. A Norelco diffractometer with monochromatic radiation and a high-density copper source was used [$\lambda(\mathrm{Cu}K\alpha_1) = 1.5405$ Å]. Fast scans were obtained at a speed of 60°/hr in 2θ, whereas slow scans were made at a speed of 15°/hr. Precision lattice parameters were calculated from a least-squares refinement of observed versus calculated values of $\sin^2\theta$ using silicon as the internal standard ($a_0 = 5.430(1)$).

Density measurements of single crystals were made by a hydrostatic technique (*6*) using perfluoro-(1-methyldecalin) as the liquid. In both cases, the liquid was first calibrated using a high purity silicon crystal with its density taken as 2.328 g/cm^3. All measurements were carried out at 25 ± 2°C.

Electrical Measurements

The dc resistivities of single crystals of both compounds were obtained by the van der Pauw technique (*7*) utilizing a Hewlett–Packard 3450A voltmeter and a PAR TC-100.2AR constant-current supply. Indium alloy (Indalloy Solder no. 2) electrical contacts were applied to the crystal with an ultrasonic soldering device (Sonobond Corp. 12-W generator).

Optical Measurements

Optical absorption measurements were performed on thin crystals of both compounds at room temperature using a Cary 17 spectrophotometer operating in the absorbance mode.

Results and Discussion

The compound $In_{1.8}Sb_{0.2}Se_3$ is isostructural with $In_{1.9}As_{0.1}Se_3$ (*3*). The system is hexagonal; the possible space groups are $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$. The refined unit cell parameters for $In_{1.8}Sb_{0.2}Se_3$ are $a = 3.97(1)$, $c = 18.87(1)$ Å. Both these compounds appear to be closely related to the α-hexagonal phase of In_2Se_3 described by Popovic *et al.* (*8*). They reported two forms of α-In_2Se_3, one hexagonal and the other rhombohedral. The first was

TABLE I

DENSITIES AND ANTIMONY PERCENTAGES BY WEIGHT

Compound	Observed density (g/cm^3)	Calculated density (g/cm^3)	Observed percentage by weight antimony	Theoretical percentage by weight antimony
$In_{1.8}Sb_{0.2}Se_3$	5.98(3)	6.02	5.0(1)	5.5
$InSbSe_3$	6.07(2)	6.11	22.8(1)	23.7

obtained by slow-cooling in an isothermal furnace; the second was obtained by slow-cooling in a furnace with a temperature gradient. Doping with antimony apparently allows only the hexagonal form to crystallize, regardless of the cooling technique used. X-ray diffraction patterns of both $In_{1.8}Sb_{0.2}Se_3$ and the hexagonal form of α-In_2Se_3 give the same diffuseness of peaks (except for the 00*l* reflections).

The preparation of single crystals of $In_{1.8}Sb_{0.2}Se_3$ was initially attempted by chemical vapor transport from the elements using chlorine as the transport agent. Pure single-phase crystals could not be grown by this technique, however. X-ray diffraction patterns of the ground products showed the presence of two impurity phases, one of which could be eliminated by quenching the samples in water. The impurity phase remaining corresponded to the compound identified as $InSbSe_3$ by Guliev *et al.* (*4*).

All peaks on the X-ray diffraction patterns of $InSbSe_3$ samples prepared from the melt could be indexed using the refined unit cell parameters $a = 9.43(1)$, $b = 14.02(5)$, $c = 3.96(1)$ Å. These parameters agree with the orthorhombic unit cell reported for $InSbSe_3$ by Guliev *et al.* (*4*). This is a distorted hexagonal cell, with the translational periodicity in the a_0 direction being half the translational periodicity of $In_{1.8}Sb_{0.2}Se_3$ in the c_0 direction.

Crystals of $In_{1.8}Sb_{0.2}Se_3$ and $InSbSe_3$ were analyzed for antimony content (atomic absorption) by Jarrell–Ash Co. (Waltham, Mass.). The results are shown in Table I. Included in the table are the observed and calculated densities for both compounds.

The room temperature resistivity of $In_{1.8}Sb_{0.2}Se_3$ was found to be 4.4×10^4 Ω-cm. Because of its high resistivity, a temperature

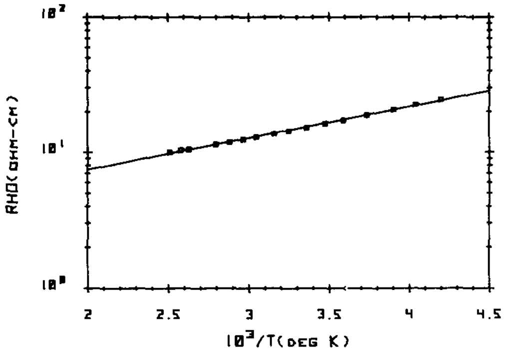

FIG. 2. Resistivity vs $10^3/T$ for $InSbSe_3$.

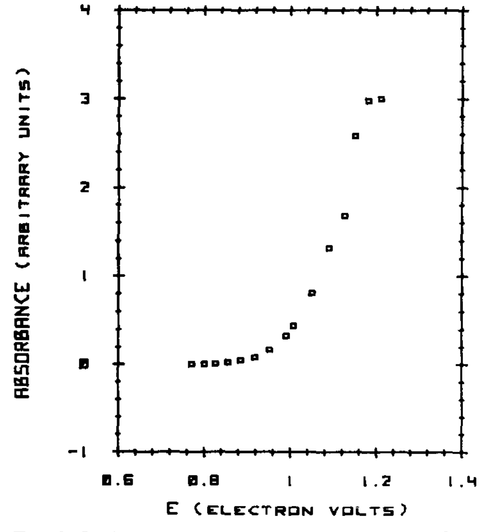

FIG. 3. Optical absorption spectrum of $In_{1.8}Sb_{0.2}Se_3$.

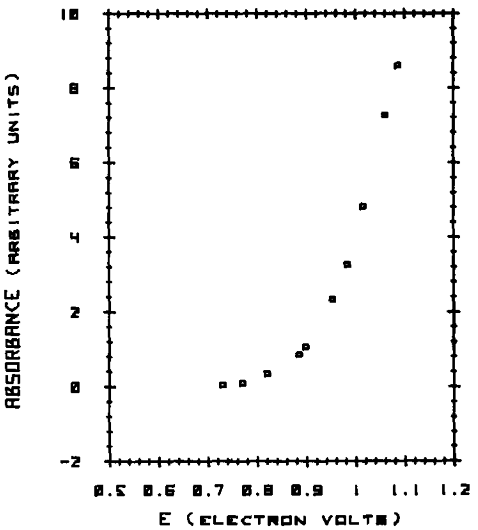

FIG. 4. Optical absorption spectrum of $InSbSe_3$.

dependence study was not undertaken. The sign of the Seebeck coefficient showed it to be an n-type semiconductor, as were $In_{1.9}As_{0.1}Se_3$ (*3*), $In_{1.9}As_{0.1}S_3$, and $In_{1.8}Sb_{0.2}S_3$ (*1*).

Figure 2 is a plot of ρ versus $1000/T$ over the temperature range 230 to 400°K for $InSbSe_3$. The line shown on the plot was fitted to the experimental data by the method of least squares and yields a standard error of 0.5%. The activation energy calculated from its slope was found to be 0.047 eV. This low value suggests that the resistivity measurements were made in the extrinsic region of this compound. The sign of the Seebeck coefficient showed $InSbSe_3$ to be a p-type semiconductor.

The optical absorption spectra for $In_{1.8}Sb_{0.2}Se_3$ and $InSbSe_3$ are shown in Figs. 3 and 4, respectively. The optical absorption edge occurs at approximately 1.1 eV for $In_{1.8}Sb_{0.2}Se_3$, as compared with 1.4 eV for $In_{1.9}As_{0.1}Se_3$ (*3*). The optical absorption edge for $InSbSe_3$ occurs at 0.92 eV.

Acknowledgments

This work was supported by the U.S. Army Research Office, Triangle Park, N.C., the National Science Foundation, Washington, D.C. (Grants GH 37104 and GF 39737), and the Materials Research Laboratory Program at Brown University.

References

1. R. DIEHL AND R. NITSCHE, *J. Cryst. Growth* **20**, 38 (1973).

2. R. DIEHL, C. CARPENTIER, AND R. NITSCHE, *Acta Crystallogr.* **B32**, 1257 (1976).

3. A. KATTY, C. A. CASTRO, J. P. ODILE, S. SOLED, AND A. WOLD, *J. Solid State Chem.*, in press.

4. T. N. GULIEV, E. V. MAGERRAMOV, AND P. G. RUSTAMOV, *Izv. Akad. Nauk. S.S.S.R., Neorg. Mater.* **13**(4), 627 (1977).

5. A. LYONS, D. SCHLEICH, AND A. WOLD, *Mat. Res. Bull.* **11**, 1155 (1976).

6. L. J. CABRI, *Amer. Mineralog.* **54**, 539 (1969).

7. L. J. VAN DER PAUW, *Phillips Res. Repts.* **16**, 187 (1961).

8. S. POPOVIC, B. CELUSTKA, AND D. BIDJIN, *Phys. Stat. Sol.* (*a*) **6**, 301 (1971).