ISSN 1063-7826, Semiconductors, 2020, Vol. 54, No. 12, pp. 1611–1615. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Fizika i Tekhnika Poluprovodnikov, 2020, Vol. 54, No. 12, pp. 1350–1354.

MICROCRYSTALLINE, NANOCRYSTALLINE, POROUS, AND COMPOSITE SEMICONDUCTORS

Band Gap of $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ Single-Crystal Alloys

I. V. Bodnar[a,*], A. A. Feschenko[a], and V. V. Khoroshko[a]

[a] *Belarusian State University of Information and Radio Electronics, Minsk, 220013 Belarus*

**e-mail: chemzav@bsuir.by*

Received August 10, 2020; revised August 15, 2020; accepted August 15, 2020

Abstract—In_2S_3, $AgIn_5S_8$, and $(In_2S_3)_x(AgIn_5S_8)_{1-x}$-alloy single crystals are grown by the Bridgman method. The composition and structure of the crystals are determined. It is established that both the initial compounds and their alloys crystalize with the formation of the cubic spinel structure. The unit-cell parameters of the single crystals are calculated, and the dependences of these parameters on the alloy composition are constructed. It is shown that, in the system, Vegard's law is satisfied. The transmittance spectra of the crystals in the region of the fundamental absorption edge are studied at room temperature, and the band gap (E_g) is determined. It is shown that E_g varies with the composition parameter x, with some deviation from a linear dependence.

Keywords: single crystals, crystal structure, alloys, transmittance spectra, band gap

DOI: 10.1134/S1063782620120039

1. INTRODUCTION

The compounds In_2S_3 and $AgIn_5S_8$ belong to imperfect semiconductors with concentrations of vacancies in the cation sublattice of ~33 and 25%, respectively [1]. The optical absorption coefficient of the compounds in the spectral region of solar radiation reaches $\alpha > 10^4$ cm^{-1}, which provides a high absorptivity of incident radiation in thin films [2, 3]. The electrical properties of the compounds remain practically unchanged upon exposure to various radiations and only slightly depend on the content of foreign impurities, which makes the materials promising as a basis for the production of a number of optoelectronic devices. In_2S_3 and $AgIn_5S_8$ crystals are promising materials for the production of surface-barrier structures [4, 5], high-efficiency photoconverters of solar radiation, light-emitting diodes emitting linearly polarized radiation, and electrooptical modulators [6–8].

Comprehensive studies and the search for processes of the mutual solubility of In_2S_3 and $AgIn_5S_8$ compounds open up fresh opportunities for extension of the region and for improvement of the accuracy of reproduction of the desired values of the parameters of such materials. However, to date, the sought-for and observed solubility in such materials has remained practically unexplored, specifically, what is most important, with the aim of clarifying the detailed dependences of the fundamental properties of the new phases on their atomic composition.

In this paper, we for the first time report on the results of studies of the crystal structure and the band gap of single-crystal alloys based on In_2S_3 and $AgIn_5S_8$ compounds.

2. EXPERIMENTAL

The compounds In_2S_3 and $AgIn_5S_8$ and alloys $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ were produced by the two-temperature method. In this method, a cell with the substance to be synthesized is arranged in a two-zone furnace, in which the temperatures of the zones are varied independently of each other. Silver and indium, whose purity was ~99.998%, were loaded into a quartz boat arranged at one end of the quartz cell. At the opposite end of the cell, sulfur taken in some excess with respect to the stoichiometric proportion. The excess was required to attain a ~2.0 atm excess pressure of sulfur vapors above the melt. After evacuation to a residual pressure of ~10^{-3} Pa, the cell was unsoldered from the vacuum system and placed into a horizontal two-zone furnace, so that the boat with the metal components was in the hot zone of the furnace, whereas sulfur was in the cold zone. Before loading into cells, the initial components were subjected to chemical and heat treatments.

The temperature of the hot zone was set at 1360–1420 K. The temperature of the cold zone was elevated to ~650 K at a rate of ~50 K h^{-1} and then kept at this level for ~2 h (for the reaction to occur between the metal components and sulfur vapors). For the reaction to proceed more completely, the temperature of the cold zone was elevated to ~800 K at the same rate and then again kept at this level for 1 h. Thereafter the tem-

Table 1. Results of X-ray spectral microanalysis of the In_2S_3, $AgIn_5S_8$, and $(In_2S_3)_x(AgIn_5S_8)_{1-x}$-alloy single crystals

Composition parameter x	Ag		In		S	
	calculation	experiment	calculation	experiment	calculation	experiment
0.0	7.14	7.29	35.72	35.03	57.14	57.68
0.2	6.57	6.87	36.06	35.21	57.37	57.92
0.4	5.77	6.45	36.53	35.84	57.79	57.71
0.5	5.27	5.83	36.84	36.13	57.89	58.04
0.6	4.65	4.96	37.21	36.98	58.14	58.06
0.8	2.95	3.09	38.25	37.93	58.80	58.98
1.0	–	–	40.00	40.36	60.00	59.64

perature of the hot zone was lowered to 850 K at a rate of 50 K h^{-1}, and the furnace was turned off.

The ingots produced by the above-described procedure were ground and reloaded into doubled quartz cells that had a slight conicity in the region of the melt to reduce the number of crystallization centers and ended with a cylindrical capillary to provide the formation of a single-crystal seed.

After evacuation of the cells, a quartz bar to be used as a holder was welded to the bottom of the outer cell and mounted in a shaker. Upon heating of the cells in the furnace, the content was subjected to vibratory intermixing which promoted the removal of gaseous inclusions. This in turn improves the quality of the single crystals produced.

The furnace temperature was elevated to 1360–1420 K (depending on the composition parameter x) and then, for the melt to be homogenized, the furnace was kept at this temperature for 2 h. After 2-h exposure, we conducted planar crystallization of the melt by lowering the furnace temperature at a rate of 2–3 K h^{-1} until the melt completely solidified. To homogenize the ingots produced, we annealed them at ~1080 K for 400 h. The single crystals grown under such conditions were 12–16 mm in diameter and 35–40 mm in length. The crystals were uniform and homogeneous, as established by X-ray spectral microanalysis and X-ray diffraction (XRD) analysis.

The elemental composition of the single crystals was determined using a Stereoscan-360 setup. For the analyzer of the X-ray spectrum, we used an AVALON-8000 X-ray spectrometer.

The X-ray studies were carried out for samples fabricated by grinding the single crystals. To remove strains produced upon grinding, the crystals were annealed in vacuum at a temperature of 700 K for 2 h.

The transmittance spectra in the region of the fundamental absorption edge were recorded with an MC-121 Proscan Special spectrophotometer. To perform the measurements, we cut out plane-parallel wafers from single crystals perpendicularly to the ingot axis. Then both sides of the wafers were mechanically ground and polished to thicknesses of ~20 μm. To remove strains produced upon mechanical treatment, we treated the samples in $C_2H_5OH:Br_2$ = 3:1 etchant.

3. RESULTS AND DISCUSSION

The results of X-ray spectral microanalysis are given in Table 1. It can be seen that the calculated and experimental quantities are in satisfactory agreement.

The XRD studies show that the diffraction patterns of the In_2S_3 and $AgIn_5S_8$ compounds and their alloys exhibit reflection peaks with indices characteristic of the cubic spinel structure (Fig. 1). Based on the measured diffraction angles, we calculated interplanar spacings for different reflection planes. From the interplanar spacings, we determined the unit-cell parameters by the least-squares method. These parameters are $a = 10.773 \pm 0.005$ Å for In_2S_3 and $a = 10.827 \pm 0.005$ Å for $AgIn_5S_8$. It is established that these parameters vary linearly with the composition parameter x, i.e., in accordance with Vegard's law.

The transmittance spectra of the In_2S_3 and $AgIn_5S_8$ single crystals and their alloys in the region of the fundamental absorption edge are shown in Fig. 2. It can be seen that the transmittance of the single crystals is higher than 60%.

From the experimental transmittance spectra $T_{opt}(\lambda)$, we calculated the absorption coefficient $\alpha_{opt}(\lambda)$ by a formula that takes into account multiple internal reflection in a plane-parallel sample [9–11]:

$$\alpha_{opt} = \frac{1}{d}\ln\left\{\frac{(1-R)^2}{2T_{opt}} + \sqrt{\left[\frac{(1-R)^2}{2T_{opt}}\right]^2 + R^2}\right\}. \quad (1)$$

Here, α_{opt} is the absorption coefficient, d is the sample thickness, T_{opt} is the transmittance, and R is the reflectance.

The single crystals under study are direct-gap materials with allowed electronic transitions from the

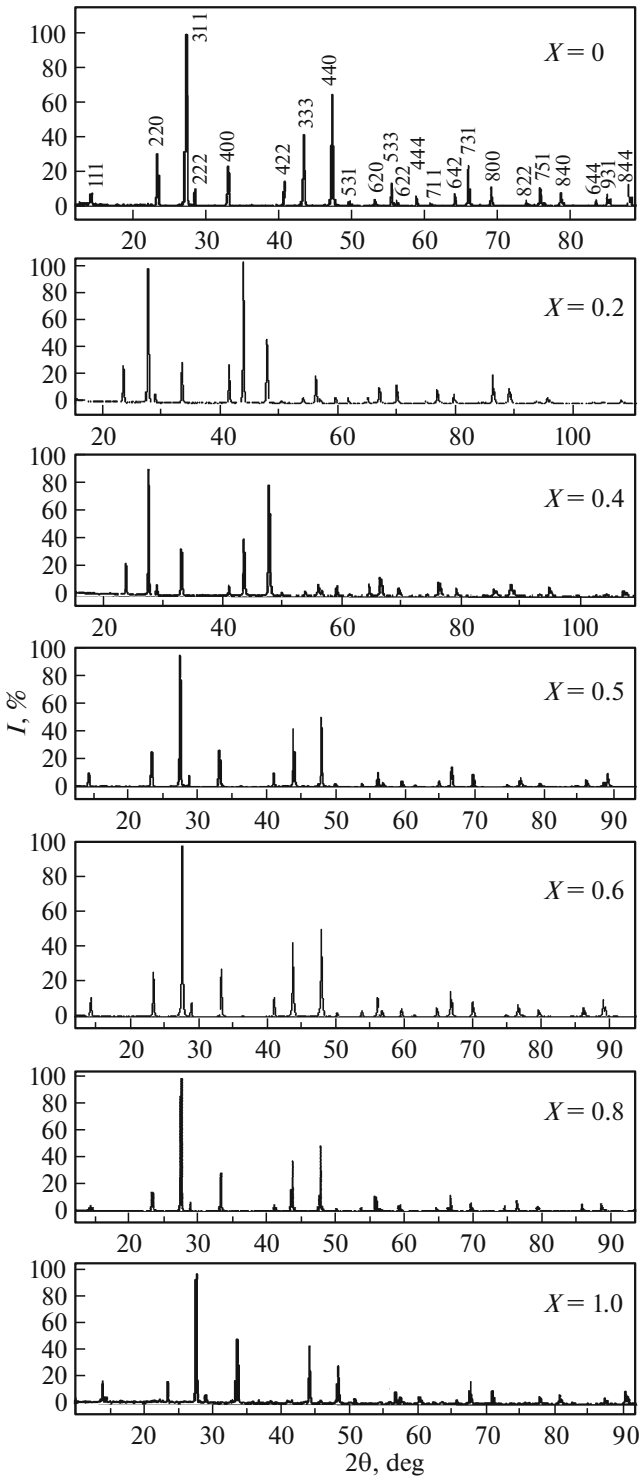

Fig. 1. Diffraction patterns of the In_2S_3, $AgIn_5S_8$ compounds and $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ alloys.

valence band to the conduction band. Therefore, the absorption spectrum is determined by the relation

$$\alpha_{opt} = A\frac{(h\nu - E_g)^{1/2}}{h\nu}, \quad (2)$$

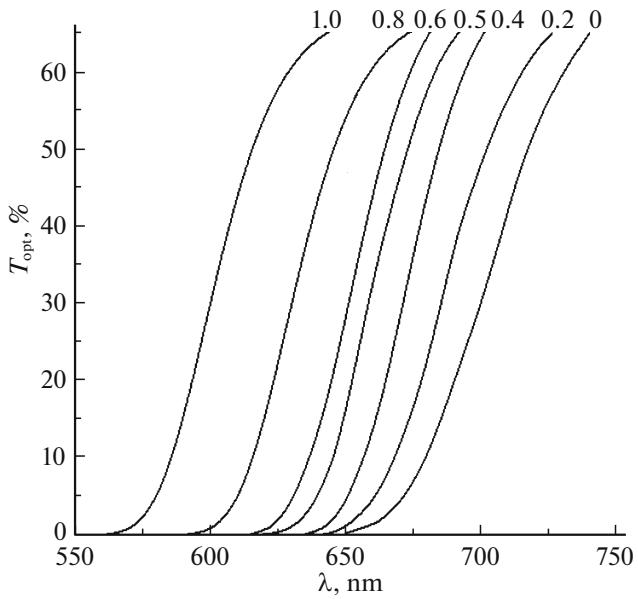

Fig. 2. Transmittance spectra of the In_2S_3 and $AgIn_5S_8$ single crystals and their alloys.

where A is a constant, ν is the radiation frequency, and E_g is the band gap.

The band gap of the single crystals was determined by extrapolating the straight portion of the dependence of the quantity $(\alpha\hbar\omega)^2$ on the photon energy $\hbar\omega$ until the dependence intersects the abscissa axis. Figure 3 shows the dependences of the quantity $(\alpha\hbar\omega)^2$ on the photon energy $(\hbar\omega)$ for the above-indicated compounds and some alloys on their basis. It is found that the band gaps of the In_2S_3 and $AgIn_5S_8$ compounds are 2.09 and 1.81 eV, respectively. These results for the initial compounds are in satisfactory agreement with the results reported in [12–15].

Using the experimentally determined values of E_g, we constructed the dependence of the band gap of $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ alloys on the composition parameter x (Fig. 4). It can be seen that the dependence is nonlinear, which is typical of alloys formed by complex semiconductor compounds.

To describe the behavior of the band gap of $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ alloys with x, $E_g(x)$, we used a quadratic dependence [16, 17]:

$$E_g(x) = E_A + (E_B - E_A - c)x + cx^2. \quad (3)$$

Here, E_A and E_B are the band gaps of the initial In_2S_3 and $AgIn_5S_8$ compounds and c is the nonlinearity parameter that characterizes the degree of deviation of E_g from the linear dependence for the medium composition ($x = 0.5$). The parameter c is determined from the expression

$$c = 4\Delta E(x = 0.5), \quad (4)$$

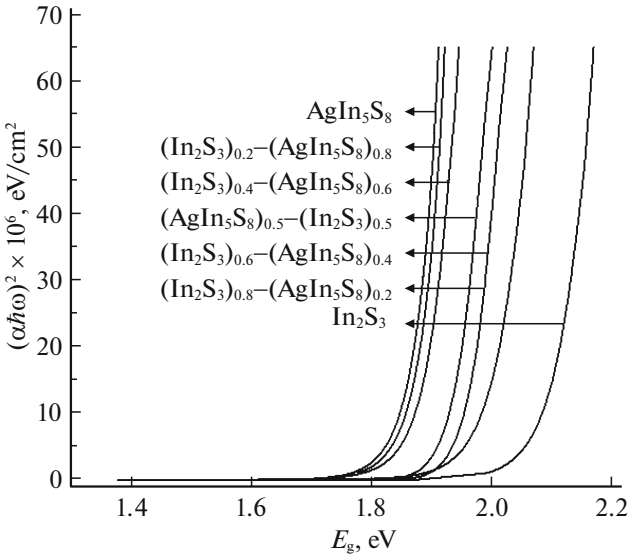

Fig. 3. Dependences of the quantity $(\alpha\hbar\omega)^2$ on the photon energy $\hbar\omega$ for $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ alloys.

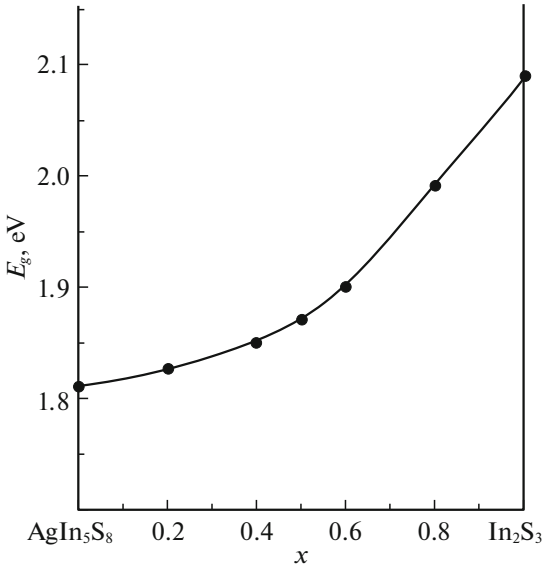

Fig. 4. Dependence of the band gap of $(In_2S_3)_x(AgIn_5S_8)_{1-x}$-alloy single crystals: (solid circles) the experimental data and (solid line) the result of calculation in accordance with formula (6).

where

$$\Delta E = (E_A + E_B)/2 - E_g(x = 0.5). \quad (5)$$

The dependence of E_g of $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ alloys on x is analytically described by the function

$$E_g^{295}(x) = 2.09 - 0.32x + 0.36x^2. \quad (6)$$

The dependence $E_g(x)$ calculated for the alloys is shown in Fig. 4 (solid line). It can be seen that the experimental data are adequately described by the dependence calculated by expression (3).

To interpret the deviation of $E_g(x)$ from the linear dependence, two approximations are used. These are Van Vechten–Bergstresser dielectric model [16] and Hill –Richardson pseudopotential model [17]. In the former model, it is believed that, in alloys, the decisive role in the deviation of $E_g(x)$ from the linear dependence is played by crystal-potential fluctuations caused by the random arrangement of substituents. In the latter model, it is thought that the deviation is a consequence of the nonlinear properties of the crystal field. Although the above-mentioned two models are based on different physical assumptions, both of the models satisfactorily describe experimental data for alloys based on both II–VI and III–V binary compounds and ternary compounds.

4. CONCLUSIONS

Single-crystal $(In_2S_3)_x(AgIn_5S_8)_{1-x}$ alloys are grown by planar crystallization of the melt (the vertical Bridgman method). The composition and structure of the alloys are determined. It is established that the alloys grown in the study crystallize with the formation of the cubic spinel structure. From the transmittance spectra in the region of the fundamental absorption edge, the band gap E_g of the materials is determined, and the dependence of E_g of the alloys on the composition parameter x is constructed. It is established that the variation in E_g with x is nonlinear. The dependence $E_g(x)$ is calculated in the context of the Van Vechten–Bergstresser model and Hill–Richardson model. Agreement between the experimental and calculated quantities is shown.

FUNDING

The study was supported by the Belorusian Republican Foundation of Fundamental Research, project no. F16-028.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. N. Kh. Abrikosov, V. F. Bankina, L. V. Poretskaya, E. V. Ckudnova, and S. N. Chizhevskaya, *Semiconducting Chalcogenides and Alloys Based on Them* (Nauka, Moscow, 1975) [in Russian].
2. K. Ramanatham, M. A. Contreras, C. L. Parkins, S. Asher, F. S. Hasoon, J. Keane, D Young, M. Romero, W. Metzger, R. Noufi, G. Ward, and A. Duda, Progr. Photovolt.: Res. Appl. **11**, 225 (2003).
3. F. Kessler, D. Gerrman, and M. Powalla, Thin Solid Films **480–481**, 491 (2005).

4. I. V. Bodnar', V. A. Polubok, V. Yu. Rud', and Yu. V. Rud', Semiconductors **37**, 1308 (2003).
5. I. V. Bodnar', E. A. Kudritskaya, I. K. Polushina, V. Yu. Rud', and Yu. V. Rud', Semiconductors **32**, 933 (1998).
6. B. Asenjo, A. M. Charro, M. T. Gutierrez, J. Gererro, and C. Maffiotte, Thin Solid Films **480–481**, 151 (2005).
7. T. Schulmeyer, A. Klein, R. Kniese, and M. Powalla, Appl. Phys. Lett. **85**, 961 (2005).
8. J. Sterner, J. Malstrom, and L. Stolt, Progr. Photovolt.: Res. Appl. **13**, 179 (2005).
9. Yu. I. Ukhanov, *Optical Properties of Semiconductors* (Nauka, Moscow, 1977) [in Russian].
10. S. I. Rembeza, *Methods for Measuring the Main Parameters of Semiconductors* (VGU, Voronezh, 1989) [in Russian].
11. R. K. Willardson and A. C. Beer, *Semiconductors and Semimetals*, Vol. 3: *Optical Properties of III–V Compounds* (Academic, New York, 1967).
12. V. A. Polubok, Dokl. BGUIR **6**, 58 (2008).
13. C. Paoricci, L. Zanotti, N. Romeo, G. Sberveglieri, and L. Tarricone, Mater. Res. Bull. **12**, 1207 (1977).
14. M. Isik and N. Gasanly, Phys. B (Amsterdam, Neth.) **478**, 127 (2015).
15. A. Usujima, S. Takeuchi, S. Endo, and T. Irie, Jpn. J. Apll. Phys. **20**, L505 (1981).
16. J. A. van Vechten, and T. K. Bergstresser, Phys. Rev. B **1**, 3351 (1970).
17. R. Hill, J. Phys. C: Sol. St. Phys. **7**, 521 (1974).

Translated by E. Smorgonskaya