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TEMPERATURE DEPENDENCE OF THE BAND GAP OF $AgIn_7S_{11}$ SINGLE CRYSTALS

Abstract. $AgIn_7S_{11}$ single crystals are herein grown by the vertical Bridgman method. The composition of the obtained single crystals is determined by X-ray microprobe analysis as well as the crystal structure – by X-ray diffraction analysis. It is shown that the obtained single crystals are crystallized in the cubic spinel structure. Using transmission spectra in the temperature range 10–320 K we determined the band gap of these single crystals and plotted its temperature dependence. This dependence is similar to that of the majority of semiconductor materials, namely, E_g increases with decreasing the temperature. We showed the agreement of the calculated and experimental values.

Keywords: Bridgman method, single crystals, crystalline structure, transmission spectra, band gap

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ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ ШИРИНЫ ЗАПРЕЩЕННОЙ ЗОНЫ МОНОКРИСТАЛЛОВ $AgIn_7S_{11}$

Аннотация. Вертикальным методом Бриджмена выращены монокристаллы $AgIn_7S_{11}$. Методом рентгеноспектрального анализа определен их состав, рентгеновским методом – кристаллическая структура. Показано, что полученные монокристаллы кристаллизуются в кубической структуре шпинели. По спектрам пропускания в интервале температур 10–320 К определена ширина запрещенной зоны указанных монокристаллов и построена ее температурная зависимость. Данная зависимость имеет вид, характерный для большинства полупроводниковых материалов: с понижением температуры E_g возрастает. Показано, что расчетные и экспериментальные величины согласуются между собой.

Ключевые слова: метод Бриджмена, монокристаллы, кристаллическая структура, спектры пропускания, ширина запрещенной зоны

Для цитирования. Температурная зависимость ширины запрещенной зоны монокристаллов $AgIn_7S_{11}$ / И. В. Боднарь [и др.] // Вес. Нац. акад. навук Беларусі. Сер. фіз.-мат. навук. – 2023. – Т. 59, № 1. – С. 81–86. https://doi.org/10.29235/1561-2430-2023-59-1-81-86

Introduction. In_2S_3 and $AgIn_5S_8$ compounds belong to the group of defective semiconductors with vacancy concentrations in the cationic sublattice of 33 and 25 %, respectively. It is assumed that the vacancies orderly occupy the nodes of the lattice at a rate of four electrons per node.

In_2S_3 and $AgIn_5S_8$ compounds are of interest owing to the fact that they have *n*-type conductivity and high radiation resistance. Moreover, these compounds are not affected by alien atoms, which means that impurities are electrically inactive. Their optical absorption coefficient lies within the spectral range of solar radiation and reaches large values ($\alpha > 10^4$ cm^{-1}). According to this fact, these compounds provide a high absorption capacity of incident radiation in thin films [1, 2]. The presence of direct interband transitions in these materials with an energy of 2.25 eV for In_2S_3 and 1.82 eV for $AgIn_5S_8$ at room temperature makes these materials promising for the creation of highly efficient radiation-resistant solar energy converters, IR-detectors, and optical filters, light-emitting diodes, electro-optical modulators and other devices on their basis [3–10].

Experimental technique. $AgIn_7S_{11}$ single crystals were preliminarily synthesized from elementary components of semiconductor purity by the two-temperature method [11]. The single crystals under study were grown by the vertical Bridgman method according to the method described below. The resulting polycrystalline ingots were reloaded into double quartz ampoules, which had a slight taper in the melt region, in order to reduce crystallization centers, and ended with a cylindrical capillary to form a single-crystal seed. After the ampoules were evacuated, a quartz rod was used as a holder. It was welded to the outer ampule from below and fixed in the vibrator. While heating the ampoule in the furnace, vibrational mixing was used to help to remove the gas inclusions from the melt. This technique improves the quality of the resulting single crystals.

The furnace temperature was raised to ~1380 K at a rate of 250 K/h and kept for 2 h until solidification of the melt completed. To homogenize the resulting ingots, they were annealed at 1100 K for 400 h. The single crystals grown under such a condition had a diameter of ~16 mm and a length of ~40 mm and were homogeneous, which was established by X-ray spectroscopy and X-ray diffraction (XRD) analyses.

The elemental composition of these single crystals was determined using a Stereoscan-360 setup. An AVALON-8000 X-ray spectrometer was used as an X-ray spectrum analyzer.

X-ray studies were carried out on the samples which were obtained by grinding single crystals. Samples were annealed in a vacuum at a temperature of 700 K for 2 h, to remove the mechanical stresses arising during grinding.

The transmission spectra in the temperature range T = 10–320 K were measured using a setup consisting of a closed-cycle helium refrigerator, a monochromator, a silicon CCD ruler, a halogen lamp as a radiation source, and a personal computer. To carry out measurements, plane-parallel plates were cut from the grown single crystals perpendicular to their growth axis. These samples were mechanically ground and polished from both sides. Just before the spectra measurement, the samples were subjected to treatment in an etchant with the composition – Br_2:C_2H_5OH = 1:3 to remove the damaged layer formed during the mechanical treatment of single crystals. The thickness of the samples was ~20 μm.

Results and discussion. The results of X-ray microprobe analysis showed that the content of elements in the grown single crystals Ag : In : S = 5.83 : 36.13 : 58.04 satisfactorily agreed with the specified composition in the initial charge Ag : In : S = 5.27 : 36.84 : 57.89.

X-ray diffraction pattern, reflection angles (2θ), interplanar distances (d), relative reflection intensities (I/I_0 (transmitted light intensity/the intensity of the light incident on the sample)), Miller indices (h, k, l) for $AgIn_7S_{12}$ single crystals are presented in Fig. 1 and in the Table. It shows that the presented diffraction pattern contains a system of lines characteristic of the cubic structure of the spinel. The unit cell parameter calculated by the least squares method is a = (10.803 ± 0.005 Å).

Results of X-ray Analysis of $AgIn_7S_{11}$ Single Crystals

d, Å	2θ, grad	I/I_0, %	h, k, l
6.2751	14.21	10	1, 1, 1
3.8944	23.30	23	2, 2, 0
3.3472	27.40	100	3, 1, 1
3.2107	28.67	7	2, 2, 2
2.8139	33.19	32	4, 0, 0
2.3484	40.99	8	4, 2, 2
2.2349	43.57	42	3, 3, 3
2.0850	47.63	81	4, 4, 0
2.0120	49.96	3	5, 3, 1
1.9123	53.66	4	6, 2, 0
1.8631	55.77	9	5, 3, 3
1.8483	56.45	6	6, 2, 2
1.7937	59.18	9	4, 4, 4
1.7561	61.30	3	7, 1, 1
1.7067	64.50	10	6, 4, 2
1.6798	66.49	17	7, 3, 1
1.6438	69.57	8	8, 0, 0

End of table

d, Å	2θ, grad	I/I_0, %	*h*, *k*, *l*
1.5977	74.61	3	8, 2, 2
1.5848	76.41	10	7, 5, 1
1.5679	79.26	8	8, 4, 0
1.5447	85.72	7	9, 3, 1
1.5409	88.58	13	8, 4, 4

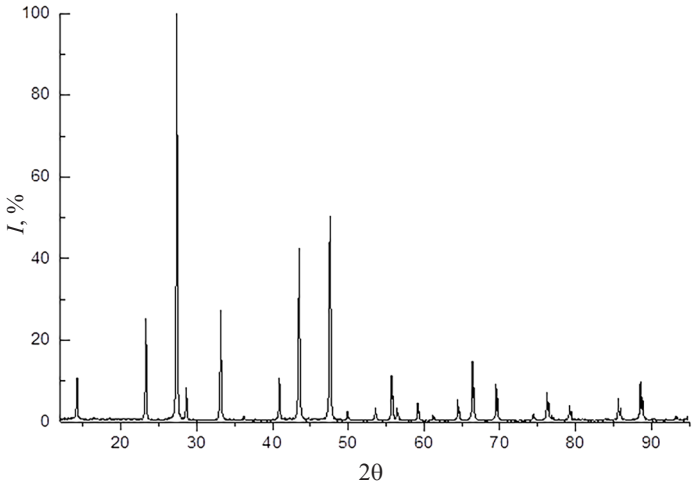

Fig. 1. X-ray diffraction pattern of $AgIn_7S_{11}$ single crystals

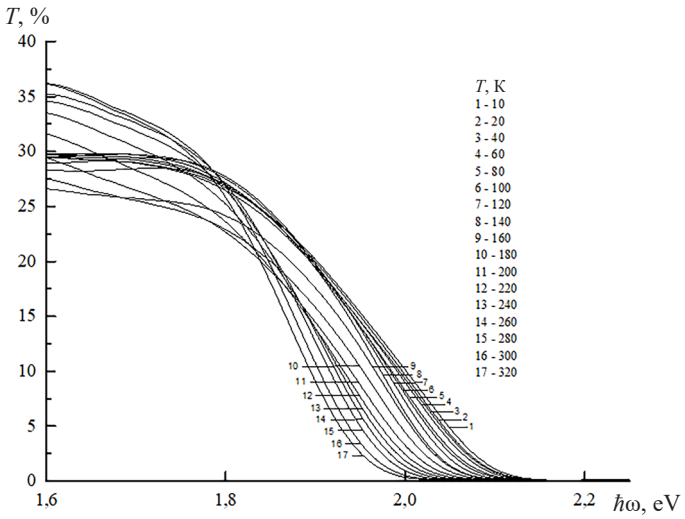

Fig. 2. Transmission spectra of $AgIn_7S_{11}$ single crystals

Figure 2 shows the transmission spectra of these single crystals in the region of the absorption edge in the temperature range $T = 10–320$ K. It can be seen that the spectra are shifted to the short-wavelength region with decreasing the temperature.

The absorption coefficient (α_{opt}) is calculated from the obtained transmission spectra (T_{opt}) using formula (1), which considers multiple internal reflection in a plane-parallel sample [12–14]:

$$\alpha = \frac{1}{d_o} \ln \left\{ \frac{(1-R)^2}{2T_{opt}} + \sqrt{\left[\frac{(1-R)^2}{2T_{opt}} \right]^2 + R^2} \right\}, \quad (1)$$

where d_o is the sample thickness, T_{opt} is the transmittance, R is the reflectance.

If we assume that $AgIn_7S_{11}$ single crystals, as well as In_2S_3 and $AgIn_5S_8$ compounds, are materials with direct interband electron transitions from the valence band to the conduction band, then the spectral dependence of the absorption coefficient can be written in the following form:

$$\alpha_{opt} = 1/d_o, \tag{2}$$

where d_o is the sample thickness.

Spectral dependences $(\alpha \cdot \hbar\omega)^2$ on the photon energy ($\hbar\omega$) for $AgIn_7S_{11}$ single crystals are shown in Fig. 3. It can be seen that these dependences have pronounced linear sections, which indicates (as well as the X-ray data) the equilibrium and homogeneity of the grown single crystals. The band gap is determined by extrapolation of straight sections of the dependence $(\alpha \cdot \hbar\omega)^2$ on ($\hbar\omega$) to the intersection with the abscissa axis. The obtained band gap values (E_g) of $AgIn_7S_{11}$ single crystals are 1.927, 2.028, and 2.039 eV at 300, 80, and 10 K, respectively.

Figure 4 shows the temperature dependence of the band gap $E_g(T)$ of $AgIn_7S_{11}$ single crystals obtained from the experimental data of transmittance measurements in the temperature range 10–320 K (points). It is shown that this dependence has a form typical for the majority of semiconductor materials, namely, E_g increases with decreasing the temperature [10–12].

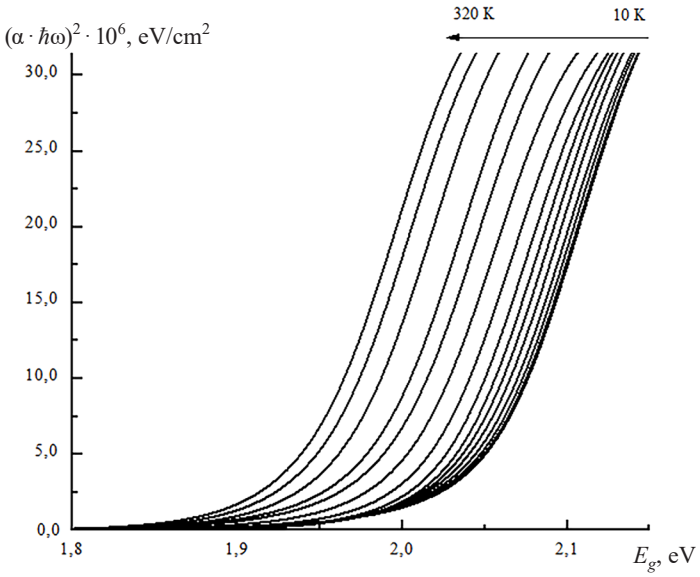

Fig. 3. Spectral dependences $(\alpha \cdot \hbar\omega)^2$ on the photon energy ($\hbar\omega$) of $AgIn_7S_{11}$ single crystals

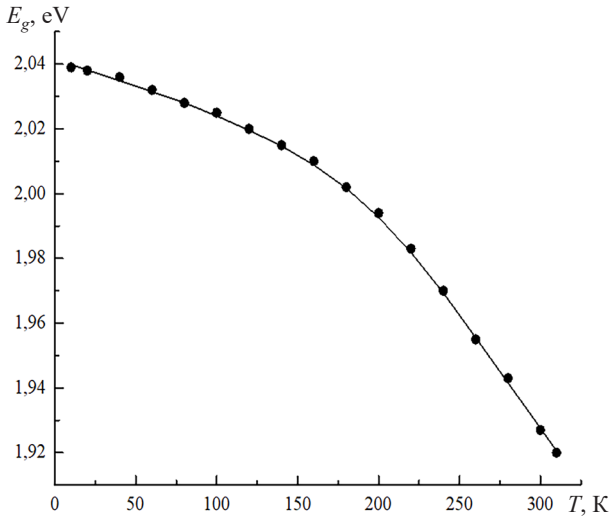

Fig. 4. Temperature dependence of the band gap $E_g(T)$ of $AgIn_7S_{11}$ single crystals

To describe the temperature dependence of the band gap, the following expression is used [13]:

$$E_g(T) = E_g(0) - \frac{\chi \cdot \Theta}{2}\left(\sqrt[4]{1 + \frac{\pi^2}{6}\cdot\left(\frac{2T}{\Theta}\right)^2 + \left(\frac{2T}{\Theta}\right)^4} - 1\right), \quad (3)$$

where $E_g(0)$ is the band gap at $T = 0$ K, χ is the parameter that determines the slope of the line tangent to the curve $E_g(T)$ ($\chi = -dE_g(T)/dT|_{T\to\infty}$), Θ is the effective phonon temperature related to the Debye temperature (Θ_D) by the expression $\Theta = (3/4)\Theta_D$.

The value of χ is determined by finding the dependence that satisfies the experimental data $E_g(T)$ in the temperature range 10–320 K. The calculated dependence $E_g(T)$ from expression (3) is shown as a solid line in Fig. 4. It can be seen that the experimental results are in good agreement with the calculated values.

Conclusion. Using the Bridgman method (vertical version), $AgIn_7S_{11}$ single crystals were grown from polycrystalline ingots preliminarily synthesized by the two-temperature method. The composition of the obtained single crystals and their structure are determined by X-ray microprobe analysis, and the XRD analysis, respectively. It is established that these single crystals are crystallized in the structure of a cubic spinel. The band gap of $AgIn_7S_{11}$ single crystals is determined using the transmission spectra in the region of the intrinsic absorption edge in the temperature range 10–320 K. Its temperature dependence $E_g(T)$ is plotted. We show that with decreasing the temperature the value E_g increases from 1.920 eV at 320 K to 2.039 eV at 10 K.

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