Growth, crystal structure and temperature dependence of the band gap of Cu_2ZnGeS_4 single crystals

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Cu_2ZnGeS_4 single crystals were grown by chemical vapor transport reaction method. Their composition and crystal structure were determined. It was shown that the obtained single crystals crystallize in a tetragonal structure. The band gap of the obtained single crystals was determined basing on transmission spectrum in the region of the absorption edge in temperature range of 10−320 K. It was found that band gap width increases with decreasing of temperature.

Keywords: Bridgman method, single crystals, crystal structure, transmission spectrum, band gap.

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1. Introduction

Recently, the issue of creating new efficient semiconductor materials, on the basis of which semiconductor devices with new functionality can be created, has become increasingly important. These materials include quaternary compounds with the general formula $Cu_2A^{II}B^{IV}X_4^{VI}$, where $A^{II} = Zn, Cd$; $B^{IV} = Si, Ge, Sn$ and $X^{VI} = S, Se, Te$, which form the large class of structurally related compounds. These materials have direct band gap, large optical absorption coefficient ($\sim 10^4\,cm^{-1}$) and band gap from 1.0 to 2.5 eV. This makes these materials candidates for creating high-efficiency solar cells on their basis [1–5].

Cu_2ZnGeS_4 compound also belongs to these materials. There is limited information in the literature about the growth of single crystals of this compound, and the available data on the physicochemical properties are contradictory, which is most likely due to different methods of growing and the nature of the melting of this compound [6–8].

This paper presents data on the growth of Cu_2ZnGeS_4 single crystals by chemical vapor transport reaction method, determination of their composition, crystal structure, transmission spectra, and changes in the band gap in the temperature range of 10−300 K.

2. Experimental procedure

Cu_2ZnGeS_4 single crystals were grown by chemical vapor transport reaction method using iodine as a carrier. To grow these single crystals, we used polycrystalline rods obtained by directional crystallization of the flux in vertical single-zone furnace. Initial materials were copper, zinc, germanium, and sulfur with purity of > 99.999%. Elemental components taken in the ratios $Cu_2ZnGeS_4 = 2 : 1 : 1 : 4$ in the amount of ∼ 15−20 g, were loaded into double quartz ampoules with a bottom elongated in the form of cone. Before loading the components, the ampoules underwent thermochemical treatment.

After the ampoule was evacuated to residual pressure of ∼ 10^{-3} Pa, it was placed into second quartz ampoule of larger diameter, which was also evacuated. Quartz rod was welded from below to the outer ampoule, which served as a holder, which was attached to the vibrator. In the process of heating the ampoules in the furnace, vibratory mixing was used, which greatly accelerates the formation of the compound and prevents the integrity of the ampoules from breaking.

In the initial period, the temperature in the furnace was raised at a rate of ∼ 50 K/h to ∼ 720 K. At the specified temperature, isothermal exposure was carried out for ∼ 2−3 h with the application of vibration. This is necessary so that such easily volatile substance as sulfur at this temperature, when its vapor pressure does not exceed 10^5 Pa, has time to partially or completely react with copper, zinc and germanium. Then, at the same rate, the temperature was raised to ∼ 1400 K (without turning off the vibrational mixing) and again held for 2 h. After that, the vibration was turned off and the directional crystallization of the melt was carried out, lowering the temperature of the furnace at a rate of ∼ 2 K/h to ∼ 1080 K; and at this temperature the resulting rods were annealed for 300 h.

The resulting polycrystalline rods were atomized into powder and used to grow single crystals. Processes of transfer for initial materials and the growth of single crystals were carried out in quartz ampoules with inner diameter of ∼ 20 mm and length of ∼ 180 mm. Initially, the ampoule consisted of two sections. The compound Cu_2ZnGeS_4 was loaded into one of them in the form of powder in the amount of 3−5 g, into the other — the capillary with iodine,

previously evacuated and soldered. The carrier concentration was $\sim 5\,mg/cm^3$. The ampoule was evacuated, and then, using „magnetic“ hammer, the capillary with iodine was opened, which was distilled into the section where the powder of the compound was located. The prepared ampoule was placed in the horizontal two-zone furnace. The heating was carried out in such a way that the temperature of the reaction zone, where the powder of the compound was located, was $\sim 100\,K$ lower than the temperature of the crystallization zone. This is necessary for the reaction behavior between crystals and iodine with formation of metal iodides and for cleaning the crystallization zone from possible uncontrolled crystallization centers. After a given time, the temperature in the zones was equalized and 970 K was set, and then the temperature in the reaction zone was increased until formation the temperature gradient between the zones of $\sim 80\,K$.

View of plate-like single crystals grown under such conditions is shown in Fig. 1. The composition of the grown single crystals was defined by means of a microprobe X-ray spectrum analysis using „Cameca-MBX 100“ system. The relative error in determining the components was $\pm 5\%$. The structure and parameters of the crystal lattice cell were found using X-ray methods. The angular positions of the diffraction spectrum lines were recorded using DRON 3M X-ray machine in CuK_α-radiation with graphite monochromator.

Transmission spectra in the temperature range of $T = 10-320\,K$ were recorded in the system consisting of the closed-cycle helium refrigerator, monochromator, silicon linear CCD array photodetector, halogen lamp as the radiation source, and personal computer. For measurements, the grown single crystals were ground and polished on one side (the other side was mirror-smooth). To remove the damaged layer formed during the mechanical processing of single crystals, immediately before measuring the spectra, the samples were subjected to treatment in a chemical etchant with the composition — $Br_2 : C_2H_5OH = 1:3$. The thickness of the samples was $\sim 20\,\mu m$.

Figure 1. Photograph of single crystals of the compound Cu_2ZnGeS_4.

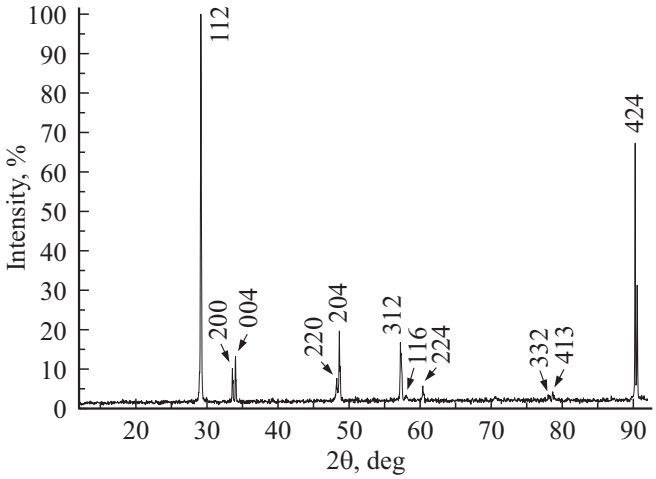

Figure 2. Diffraction pattern of crystals Cu_2ZnGeS_4.

3. Results and discussion

The data of X-ray microprobe measurements showed that the content of elements in the grown single crystals is Cu : Zn : Ge : S = 25.66 : 12.14 : 12.95 : 49.25, which satisfactorily agrees with the given composition in the initial charge Cu : Zn : Ge : S = 25.00 : 12.50 : 12.50 : 50.00.

Diffraction pattern, reflection angles (2θ), interplanar distances (d), relative reflection intensities (I/I_0), Miller indices (hkl) for single crystals Cu_2ZnGeS_4 are presented in Fig. 2 and in the table.

The results of X-ray studies have shown that all recorded diffraction patterns contain reflection maxima characteristic of a tetragonal structure (kesterite). From the measured values of the diffraction angles, the interplanar distances for different reflection planes were calculated, from which the lattice cell parameters were determined by the least squares method. For the investigated compound Cu_2ZnGeS_4 they are equal to: $a = 5.342 \pm 0.005$ Å, $c = 10.51 \pm 0.01$ Å.

Figure 3 shows the transmission spectra of such single crystal in the region of the absorption edge in the temperature range $T = 10-320\,K$. It can be seen that

Results of X-ray analysis of crystals Cu_2ZnGeS_4

Experiment		Calculation		hkl	I/I_0
2θ, deg	d, Å	2θ, deg	d, Å		
29.09	3.07	29.14	3.06	112	100
33.53	2.6703	33.57	2.6671	200	10
34.07	2.6293	34.02	2.6329	004	12
48.25	1.8844	48.26	1.8842	220	7
48.57	1.8727	48.59	1.8721	204	18
57.24	1.6080	57.26	1.6076	312	14
57.99	1.5890	58.00	1.5888	116	3.6
60.31	1.5333	60.34	1.5327	224	6
77.98	1.2242	77.98	1.2242	332	3.5
78.69	1.2149	78.68	1.2151	413	4.1
90.24	1.0870	90.25	1.0869	424	60

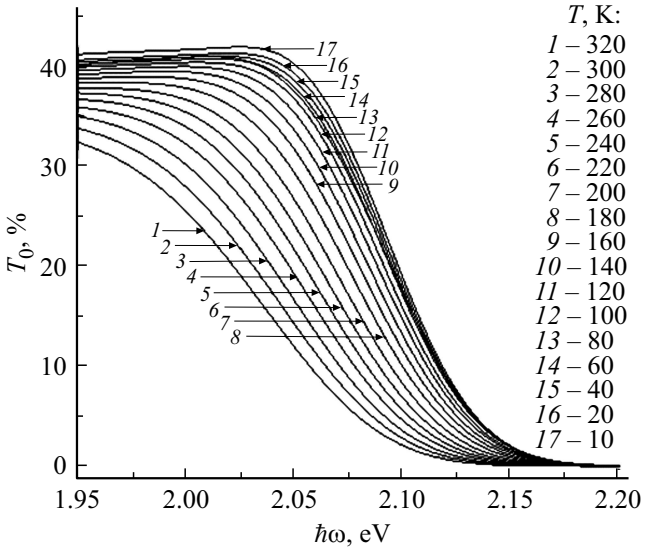

Figure 3. Transmission spectra of single crystals Cu_2ZnGeS_4.

with decreasing temperature the spectra shift to short-wave region.

From the measured transmission spectra T_{opt}, the absorption coefficient α was calculated using the formula (1), which takes into account multiple internal reflections in the plane-parallel sample [9–11]:

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

where d is sample thickness, T_{opt} is transmittance, R is reflection coefficient.

It is known that compounds $Cu_2A^{II}B^{IV}X_4^{VI}$, to which the compound Cu_2ZnGeS_4 also belongs, are materials with direct band gap, therefore the spectral dependence of the absorption coefficient can be written in the following form:

$$\alpha = A \frac{(\hbar\omega - E_g)^{1/2}}{\hbar\omega}, \qquad (2)$$

where A is constant, E_g is band gap.

Spectral dependences of $(\alpha\hbar\omega)^2$ on photon energy $(\hbar\omega)$ for single crystals Cu_2ZnGeS_4 are shown in Fig. 4. It can be seen that these dependences have pronounced linear sections, which confirms (as well as X-ray data) the equilibrium and homogeneity of the grown single crystals. The band gap was determined by extrapolation of straight segments of the dependence $(\alpha\hbar\omega)^2$ from $(\hbar\omega)$ to the intersection with the abscissa axis. The values of the band gap obtained by us for single crystals are equal to: 2.068, 2.112 and 2.113 eV at 300, 80 and 10 K, respectively.

Figure 5 shows the temperature dependence of the band gap $E_g(T)$ of single Cu_2ZnGeS_4 crystal, obtained on the basis of experimental data from measurements of the transmittance in temperature range of 10–320 K (points). It can be seen that this dependence has the form characteristic of most semiconductor materials, and with decrease in temperature E_g increases [10–13].

The following expression was used to describe the temperature dependence of the band gap [14]:

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

where $E_g(0)$ is band gap at $T = 0$ K; χ is parameter defining the slope ratio of the tangent to curve $E_g(T)$ $(\chi = -dE(T)/dT|_{T\to\infty})$; θ is effective phonon temperature related to the Debye temperature θ_D by $\theta = (3/4)\theta_D$.

The value of χ was determined by finding the dependence that in the best way satisfies the experimental data $E_g(T)$

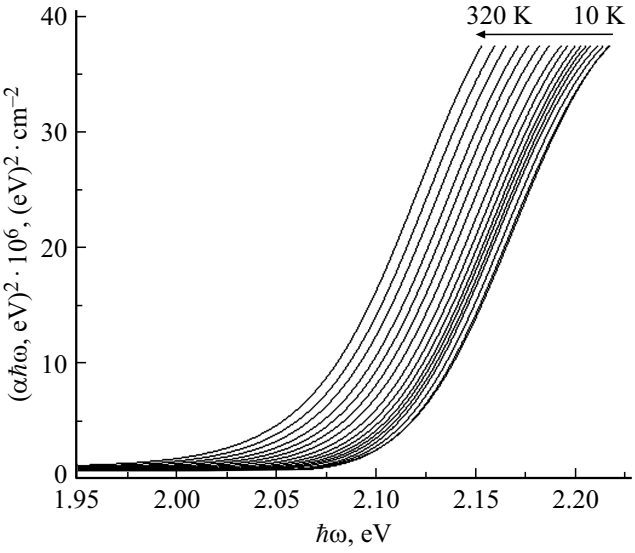

Figure 4. Spectral dependences of $(\alpha\hbar\omega)^2$ on the photon energy of single crystal Cu_2ZnGeS_4.

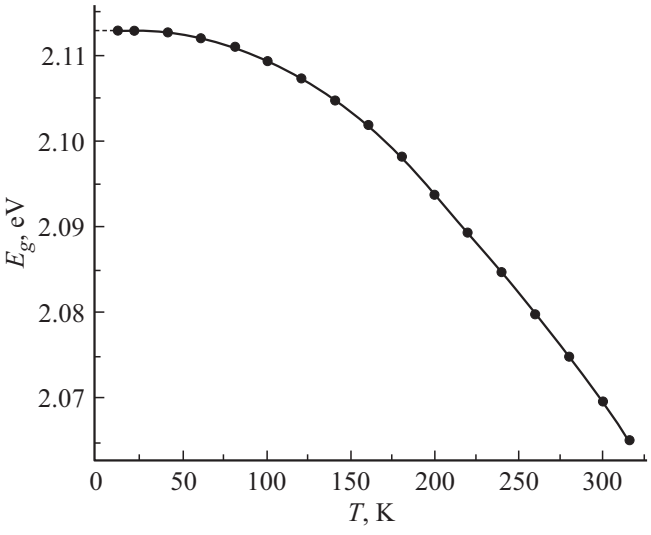

Figure 5. Temperature dependence of the band gap $E_g(T)$ of single crystal Cu_2ZnGeS_4.

in the temperature range of 10−320 K. The calculated dependence $E_g(T)$ according to relation (3) is shown in Fig. 5 as the solid line. It can be seen that the calculated values are in good agreement with the experimental results.

4. Conclusion

Single crystals of the compound Cu_2ZnGeS_4 have been grown by chemical vapor transport reaction method. The composition of the obtained single crystals and their structure were determined. It was shown that the compound Cu_2ZnGeS_4 crystallizes in the tetragonal structure with parameters $a = 5.342 \pm 0.005$ Å, $c = 10.51 \pm 0.01$ Å.

From the transmission spectra in the temperature range of 10−320 K, the band gap of single crystals was determined and its temperature dependence was plotted. It was found that the band gap increases with decreasing temperature from 2.064 eV at $T = 320$ K up to 2.113 eV at $T = 10$ K.

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Conflict of interest

The authors declare that they have no conflict of interest.

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