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$Cu_2ZnGeSe_4$ single crystals: Growth, structure and temperature dependence of band gap

Ivan V. Bodnar [a], Vitaly V. Khoroshko [a], Veronika A. Yashchuk [a], Valery F. Gremenok [a,b], Mohsin Kazi [c], Mayeen U. Khandaker [d,e], Tatiana I. Zubar [b], Daria I. Tishkevich [b], Alex V. Trukhanov [b,f,g], Sergei V. Trukhanov [b,f,*]

[a] Belarussian State University of Informatics and Radioelectronics, 220013, Minsk, P. Brovka str., 6, Belarus
[b] Laboratory of Magnetic Films Physics, SSPA "Scientific and Practical Materials Research Centre of NAS of Belarus", 19, P. Brovki str., 220072 Minsk, Belarus
[c] Department of Pharmaceutics, College of Pharmacy, PO BOX-2457, King Saud University, Riyadh 11451, Saudi Arabia
[d] Centre for Applied Physics and Radiation Technologies, School of Engineering and Technology, Sunway University, Bandar Sunway 47500, Selangor, Malaysia
[e] Faculty of Graduate Studies, Daffodil International University, Daffodil Smart City, Birulia, Savar, Dhaka – 1216, Bangladesh
[f] Smart Sensors Laboratory, Department of Electronic Materials Technology, National University of Science and Technology MISiS, Moscow 119049, Russia
[g] L.N. Gumilyov Eurasian National University, Astana, 010000, Kazakhstan

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ABSTRACT

This work describes the production of single crystals of the semiconducting quaternary compound $Cu_2ZnGeSe_4$ using a gas chemical method in which iodine was used as a transporter. For all the synthesized samples, their phase state, crystal structure syngony and lattice constants were refined. The unit cell of the studied compound is characterized by tetragonal symmetry. The transmission spectrum was applied to calculate the band gap, which is depicted as temperature function in 20–300 K range. It was fixed that the band gap increases by 12% with decreasing temperature.

1. Introduction

Currently, the four-component compounds Cu_2ZnSnX_4 (X = S and Se) seems to be the most promising for solar energy conversion due to direct interband transitions, as well as high values of the absorption coefficient and band gap [1–3]. The substitution of sulfur by selenium leads to the optimization of the parameters of solar energy conversion [4–6]. However, devices already manufactured have reached their peak efficiency and further improvements have been blocked by technological difficulties [1–6].

The development of technologies for the production of solar cells, in turn, requires knowledge of the phase diagrams and physicochemical properties of promising compounds, which until now are either insufficiently studied or contradictory [7–9].

Nonlinear optical $Cu_2ZnGeSe_4$ single crystals were first obtained in the 1960 s [10]. Recently, their potential has been assessed for practical use as solar [11] and thermoelectric cells [12]. The absorption spectra of $Cu_2ZnGeSe_4$ show strong photon absorption throughout the visible range [13]. The photoreactive behavior indicates their potential application in solar energy conversion systems [11]. Features of the crystal structure, results of thermal analysis, studies of optical band gaps, IR transparency and second harmonic generation responses have been previously obtained [13]. Electronic structure calculations have also been carried out [14].

Therefore, therein the growing of single crystals of the semiconducting quaternary compound $Cu_2ZnGeSe_4$ using a gas chemical method in which iodine using as a transporter was described as well as their phase state, crystal structure syngony and lattice constants were established.

2. Materials and methods

The single-crystal alloys of $Cu_2ZnGeSe_4$ composition were obtained from preliminarily synthesized corresponding polycrystals. Source

* Corresponding author at: Laboratory of Magnetic Films Physics, SSPA "Scientific and Practical Materials Research Centre of NAS of Belarus", 19, P. Brovki str., 220072 Minsk, Belarus.
E-mail address: s.v.trukhanov@gmail.com (S.V. Trukhanov).

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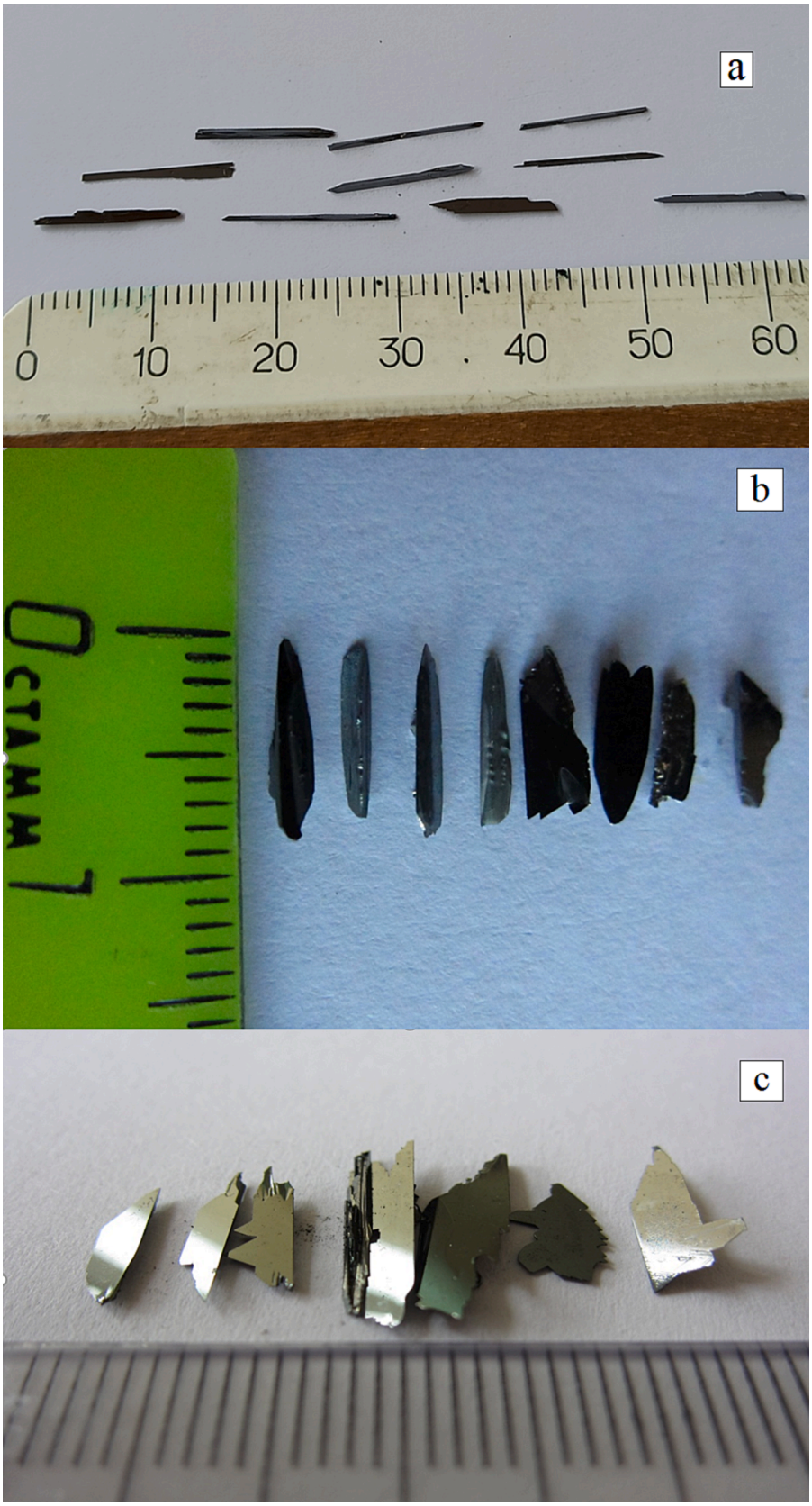

Fig. 1. $Cu_2ZnGeSe_4$ single crystals: a – needle-like; b – prismatic; c – plate-like.

Table 1
XRD parameters for $Cu_2ZnGeSe_4$ crystals.

hkl	$2\theta_{obs}$	$2\theta_{cal}$	d_{obs}	d_{cal}	*I*,%
112	27.71	26.68	3.2166	3.2198	100
220	45.74	45.74	1.9820	1.9820	15
204	46.14	46.11	1.9658	1.9666	60
312	54.30	54.30	1.6879	1.6879	25
303	55.02	55.07	1.6675	1.6662	14
400	66.66	66.68	1.4018	1.4015	7
008	67.91	67.88	1.3791	1.3795	4
332	73.62	73.65	1.2855	1.2850	5
413	74.26	74.30	1.2758	1.2754	23
424	84.88	84.88	1.1414	1.1414	11
228	85.70	85.69	1.1326	1.1327	6
512	91.17	91.18	1.0783	1.0782	5
336	91.72	91.72	1.0733	1.733	4.3
1.1.10	92.90	92.91	1.0627	1.0627	4.0

elements such as copper, zinc, germanium and selenium of high purity were used as 2:1:1:4 (~25 g each). The growth of single crystals was carried out in two sealed ampoules inserted into each other. The outer ampoule had a quartz holder attached to a vibrator. Stirring during heating contributed to the formation of a stoichiometric composition and prevented the rupture of the ampoules.

Initially, the temperature increased up to ~ 1000 K (50 K/h rate) with an isothermal hold of ~ 2 hs. After that, the temperature also increased up to ~ 1200 K, and the ampoule was again kept for 2 hs with vibromixing. After holding, the stirring was turned off and the directional crystallization of the melt took place at a temperature decrease down to ~ 1020 K (~ 100 K/h rate). Finally, homogenization annealing would be carried out for 300 hs.

The synthesized preforms were mixed into powder and ~ 5 g of which was then placed in an ampoule (d ~ 16–22 mm and l ~ 170 mm), which had two compartments. Powder was loaded into one compartment, while an evacuated and sealed capillary with iodine in an amount of 5 mg/cm^3 was placed in the other. The ampoules were pumped out to ~ 10^{-3} Pa pressure. The capillary with iodine was opened magnetically. The prepared ampoules were placed horizontally in a two-zone furnace.

During heating, the temperature of the reaction zone of the powder was maintained at ~ 100 K below the temperature of the crystallization zone. This was required to form metal iodides and prevent the formation of additional crystallization centers. Subsequently, the temperature in both zones was equalized at 970 K, with a gradual increase in the reaction zone up to 1050 K in 170 hs.

Acicular single crystals grown under the specified conditions were standard, whose photographs are shown in Fig. 1a. It should be noted that an increase in the inner diameter of the ampoule to 20–22 mm at a reduced temperature difference between the zones of 70–80 K and an iodine concentration of ~ 5 mg/cm3 led to the growth of prismatic and lamellar single crystals, whose photographs are shown in Fig. 1b, 1c.

The chemical composition of the grown single crystals was established by X-ray microanalysis. The electron beam of a "Stereoscan-360" scanning electron microscope was appied as the exciter of the bremsstrahlung of the sample. An "AVALON-8000" X-ray spectrometer was utilized. The relative error of the component contents was found as ± 5 %.

The phase content, crystal structure and unit cell parameters of the investigated samples were found by XRD analysis. The diffractograms were collected by the «DRON-3 M» diffractometer in CuK_α-radiation and nickel filter. The accuracy of fixing the angles was performed with steps of one hundredth of the Bragg angle.

The ransmission spectra were collected at the absorption edge in temperature range of 20–300 K by the "MDR-23" monochromator. For these measurements the samples were crushed and polished on one side, while the other one was mirror-smooth. The thickness of the samples was ~ 20 μm. Samples with a thickness of ~ 20 μm were also treated with Br_2:C_2H_5OH (1:3) to remove the mechanically damaged surface layer.

3. Results and discussion

The results of XRD microanalysis showed that the content of chemical elements in the obtained samples (Cu:Zn:Ge:Se = 26.21:11.30:13.66:48.83) corresponded to the initial filling.

Table 1 and Fig. 2 contain the main crystal structure parameters such as the diffraction patterns, the angles of reflection (2θ), the interplanar spacing (*d*), the relative reflective intensity (I/I_0), the Miller indices (*hkl*)

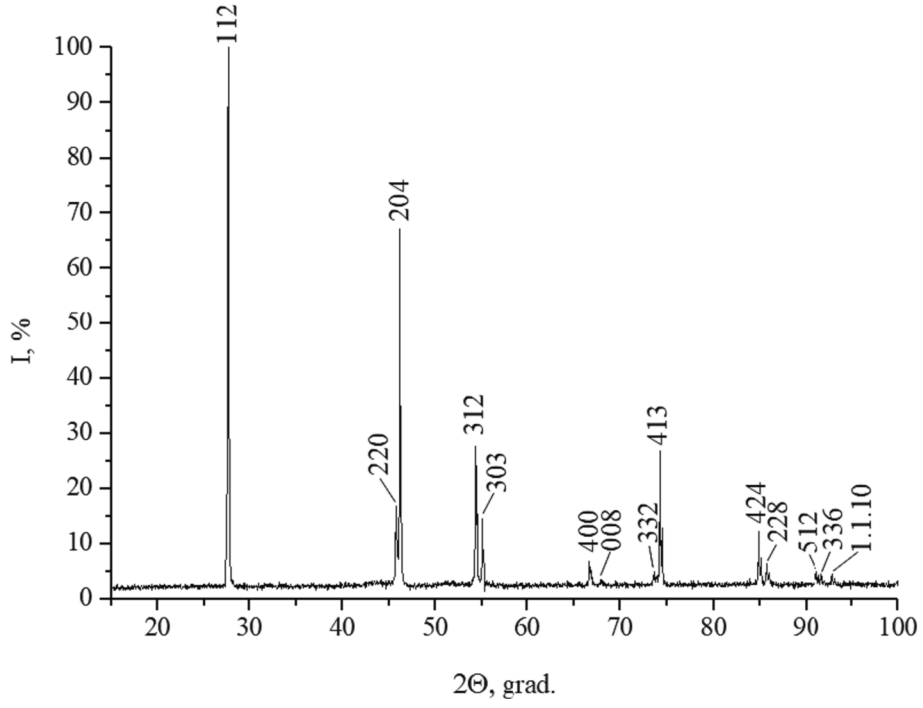

Fig. 2. XRD pattern of $Cu_2ZnGeSe_4$ single crystals.

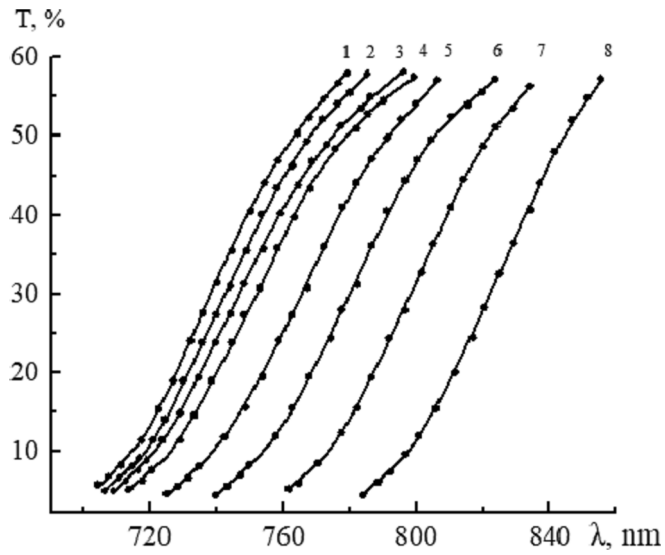

Fig. 3. The transmission spectra of $Cu_2ZnGeSe_4$ single crystals.

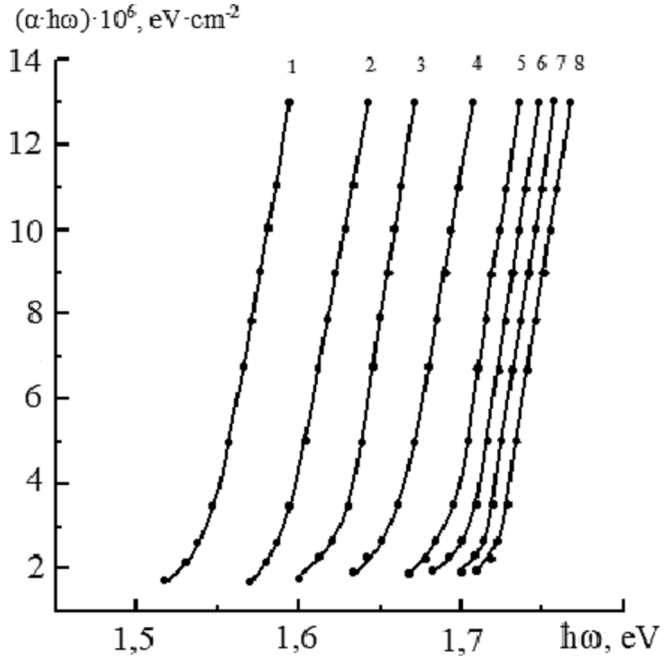

Fig. 4. The spectral dependences $(\alpha\cdot\hbar\omega)^2$ on the photon energy ($\hbar\omega$) for $Cu_2ZnGeSe_4$ single crystals.

for the obtained samples. It was found that the ratio of peaks in the diffraction patterns is described by tetragonal symmetry. The lattice constants of $Cu_2ZnGeSe_4$ were $a = 5.607 \pm 0.005$ Å, $c = 11.04 \pm 0.01$ Å which were extracted from high angles reflections ($2\theta > 60°$). These values correlate well with the data obtained in [10–16].

Fig. 3 shows the transmission spectra of the obtained alloys for the absorption edge in temperature 20–300 K range. It is clearly seen that as the temperature decreases, the spectra shift towards short waves.

The absorption coefficients (α) was extracted from the obtained transmission spectra with help of the formulas [17–19], taking into account multiply internal reflection in plane-parallel sample:

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

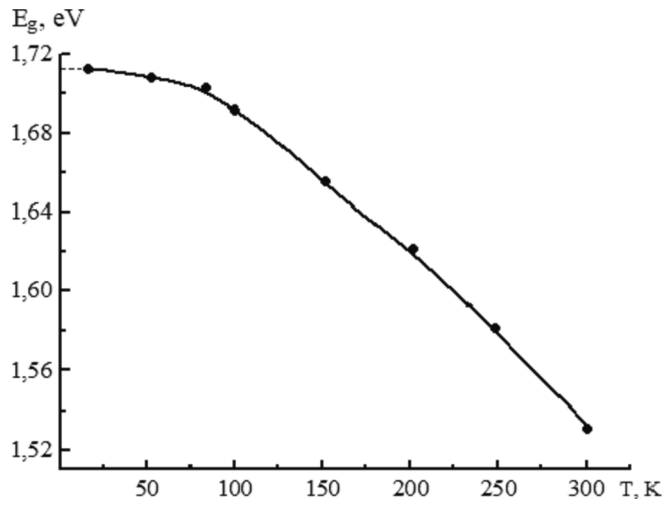

Fig. 5. The temperature dependence of the band gap $E_g(T)$ of $Cu_2ZnGeSe_4$ single crystals.

where d is the thickness of the sample; T is the transmission coefficient; R is the reflection coefficient.

The spectral relation of the absorption coefficient is written as follows taking into account that the $Cu_2ZnGeSe_4$ has direct interband electron transitions:

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

where A is the constant; E_g the band gap width.

Fig. 4 shows the dependences $(\alpha\cdot\hbar\omega)^2$ on the photon energy ($\hbar\omega$) for the obtained samples. As can be clearly seen, these curves have pronounced linear segments. This fact, together with the data of XRD analysis, confirms the equilibrium and homogeneity of the obtained single crystals. For them the band gap was obtained by extrapolating the linear sections of this dependence to their intersection with the abscissa axis. The band gap values obtained for the sample under study were 1.53 eV (300 K), 1.70 eV (80 K), and 1.71 eV (20 K).

The Fig. 5 demonstrates the temperature - reation of the band gap $E_g(T)$ for the obtained samples. It can be reliably verified that the band gap increases with decreasing temperature. This behavior of the extracted dependence is typical for most semiconductors.

The band gap vs. temperature corresponds to the ratio [20]:

$$E_g(T) = E_g(0) - \frac{\chi \bullet \Theta}{2}\left(\sqrt{41 + \frac{\pi^2}{6} \bullet \left(\frac{2T}{\Theta}\right)^2 + \left(\frac{2T}{\Theta}\right)^4} - 1\right), \quad (3)$$

where $E_g(0)$ is the band gap for T = 0 K; χ is a parameter defined as the temperature derivative of the band gap $E_g(T)$ ($\chi = -dE(T)/dT|_{T\to\infty}$); θ is a phonon effective temperature, associated with Debye temperature (θ_D) by the expression: $\theta = (3/4)\theta_D$.

Fig. 5 shows the temperature dependence of the band gap obtained according to (3). It is clearly seen that the obtained results of the study are in good agreement with the calculated values [21–25]. The parameter χ was found to satisfy the experimental data Eg(T). Promising electronic properties [26–28] of the resulting compounds will be obtained and discussed further [29–31]].

4. Conclusions

In this work, single crystals of the quaternary compound $Cu_2ZnGeSe_4$ were grown by chemical gas transfer. Their chemical composition, crystal structure and optical properties were investigated. It was found that the unit cell of the obtained sample is characterized by tetragonal

symmetry with parameters equal to a = 5.607 ± 0.005 Å, c = 11.04 ± 0.01 at room temperature. The band gap was extracted from the transmission spectra in the temperature 20–300 K range and its temperature relation was depicted. It was found that the band gap increases with decreasing temperature.

5. Institutional review board statement

Not applicable.

6. Informed consent statement

Not applicable.

7. Data availability statement

Not applicable.

CRediT authorship contribution statement

Ivan V. Bodnar: Conceptualization, Methodology, Data curation, Writing – review & editing, Supervision, Project administration. **Vitaly V. Khoroshko:** Conceptualization, Methodology, Software, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision. **Veronika A. Yashchuk:** Methodology, Software, Validation, Investigation, Data curation, Writing – original draft, Visualization. **Valery F. Gremenok:** Methodology, Software, Validation, Resources, Visualization, Project administration. **Mohsin Kazi:** Software, Validation, Formal analysis, Resources. **Mayeen U. Khandaker:** Software, Validation, Formal analysis, Resources, Funding acquisition. **Tatiana I. Zubar:** Software, Validation, Visualization. **Daria I. Tishkevich:** Software, Validation, Visualization. **Alex V. Trukhanov:** Conceptualization, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Sergei V. Trukhanov:** Conceptualization, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

[1] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y.u. Zhu, D. B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency, Adv. Energ. Mater. 4 (2014) 1301465, https://doi.org/10.1002/aenm.201301465.

[2] T.K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y.u. Zhu, D.B. Mitzi, Beyond 11% efficiency: characteristics of state-of-the-art $Cu_2ZnSn(S, Se_)4$ solar cells, Adv. Energ. Mater. 3 (2013) 34–38, https://doi.org/10.1002/aenm.201200348.

[3] I. Repins, C. Beall, N. Vora, C. DeHart, D. Kuciauskas, P. Dippo, B. To, J. Mann, W. C. Hsu, A. Goodrich, R. Noufi, Co-evaporated $Cu_2ZnSnSe_4$ films and devices, Sol. Energy Mater. Solar. Cells. 101 (2012) 154–159, https://doi.org/10.1016/j.solmat.2012.01.008.

[4] G.M. Ford, Q. Guo, R. Agrawal, H.W. Hillhouse, Earth abundant element $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ nanocrystals for tunable band gap solar cells: 6.8% efficient device fabrication, Chem. Mater. 23 (2011) 2626–2629, https://doi.org/10.1021/cm2002836.

[5] C.-I. Lee, C.-D. Kim, Optical properties of undoped and Co^{2+}-doped $Cu_2ZnGeSe_4$ crystals, J. Kor. Phys. Soc. 37 (2000) 364–367.

[6] C. Persson, Electronic and optical properties of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$, J. Appl. Phys. 107 (2010), 053710, https://doi.org/10.1063/1.3318468.

[7] H. Matsushita, T. Maeda, A. Katsui, T. Takizawa, Thermal analysis and synthesis from the melts of Cu-based quaternary compounds Cu–III–IV–VI4 and Cu2–II–IV–VI4 (II=Zn, Cd; III=Ga, In; IV=Ge, Sn; VI=Se), J. Cryst. Growth 208 (2000) 416–422, https://doi.org/10.1016/S0022-0248(99)00468-6.

[8] Q. Guo, G.M. Ford, W.-C. Yang, C.J. Hages, H.W. Hillhouse, R. Agrawal, Enhancing the performance of CZTSSe solar cells with Ge alloying, Sol. Energy Mat. Sol. Cells 105 (2012) 132–136, https://doi.org/10.1016/j.solmat.2012.05.039.

[9] Q. Shu, J.H. Yang, S. Chen, B. Huang, H. Xiang, X.G. Gong, S.H. Wei, Cu2Zn(Sn, Ge)Se4 and Cu2Zn(Sn, Si)Se4 alloys as photovoltaic materials: Structural and electronic properties, Phys. Rev. B 87 (2013), 115208, https://doi.org/10.1103/PhysRevB.87.115208.

[10] R. Nitsche, D.F. Sargent, P. Wild, Crystal growth of quaternary 1_2246_4 chacogenides, J. Cryst. Growth. 1 (1967) 52–53, https://doi.org/10.1016/0022-0248(67)90009-7.

[11] L. Shi, P. Yin, Phosphate-free synthesis, optical absorption and photoelectric properties of Cu_2ZnGeS_4 and $Cu_2ZnGeSe_4$ uniform nanocrystals, Dalton Trans. 42 (2013) 13607–13611, https://doi.org/10.1039/C3DT50993A.

[12] M. Ibáñez, R. Zamani, A. LaLonde, D. Cadavid, W. Li, A. Shavel, J. Arbiol, J. R. Morante, S. Gorsse, G.J. Synder, A. Cabot, $Cu_2ZnGeSe_4$ nanocrystals: synthesis and thermoelectric properties, J. Am. Chem. Soc. 134 (2012) 4060–4063, https://doi.org/10.1021/ja211952z.

[13] C.W. Sinagra, F.O. Saouma, C.O. Otieno, S.H. Lapidus, J.-H. Zhang, A.J. Craig, P. Grima-Gallardo, J.A. Brant, K.A. Rosmus, K.E. Rosello, J.I. Jang, J.A. Aitken, Synthesis, structure, linear and nonlinear optical properties of noncentrosymmetric quaternary diamond-like semiconductors, $Cu_2ZnGeSe_4$ (CZGSe) and the novel $Cu_4ZnGe_2Se_7$, J. Alloys Compd. 888 (2021), 161499, https://doi.org/10.1016/j.jallcom.2021.161499.

[14] D. Chen, N.M. Ravindra, Electronic and optical properties of Cu2ZnGeX4 (X=S, Se and Te) quaternary semiconductors, J. Alloys Compd. 579 (2013) 468–472, https://doi.org/10.1016/j.jallcom.2013.06.048.

[15] O.V. Parasyuk, L.D. Gulay, Ya.E. Romanyuk, L.V. Piskach, Phase diagram of the Cu_2GeSe_3 –ZnSe system and crystal structure of the $Cu_2ZnGeSe_4$ compound, J. Alloys Compd. 329 (2001) 202–207. 10.1016/S0925-8388(01)01606-1.

[16] H. Matsushita, A. Katsui, Materials design for Cu-based quaternary compounds derived from chalcopyrite-rule, J. Phys. Chem. Sol. 66 (2005) 1933–1936, https://doi.org/10.1016/j.jpcs.2005.09.028.

[17] Y.I. Ukhanov, Optical properties of semiconductors, Nauka, Moscow, 1977 [in Russian].

[18] S.I. Rembeza, Methods for measuring the main parameters of semiconductors, VSU, Voronezh, 1989 [in Russian].

[19] R. Willardson, Optical properties of semiconductors, Mir, Moscow, 1970 [in Russian].

[20] R. Passler, Basic model relations for temperature dependencies of fundamental energy gaps in semiconductors, Phys. Stat. Sol. B 200 (1997) 155–172, https://doi.org/10.1002/1521-3951(199703)200:1%3C155::AID-PSSB155%3E3.0.CO;2-3.

[21] A.Z. Tuleushev, F.E. Harrison, A.L. Kozlovskiy, M.V. Zdorovets, Evolution of the absorption edge of PET films irradiated with Kr ions after thermal annealing and ageing, Optical Mater. 119 (2021), 111348, https://doi.org/10.1016/j.optmat.2021.111348.

[22] M.V. Zdorovets, A.L. Kozlovskiy, D.B. Borgekov, D.I. Shlimas, Influence of irradiation with heavy Kr^{15+} ions on the structural, optical and strength properties of BeO ceramic, J. Mater. Sci.: Mater. Electron. 32 (2021) 15375–15385, https://doi.org/10.1007/s10854-021-06087-y.

[23] A.L. Kozlovskiy, A. Alina, M.V. Zdorovets, Study of the effect of ion irradiation on increasing the photocatalytic activity of WO_3 microparticles, J. Mater. Sci.: Mater. Electron. 32 (2021) 3863–3877, https://doi.org/10.1007/s10854-020-05130-8.

[24] A.L. Kozlovskiy, M.V. Zdorovets, Study of hydrogenation processes in radiation-resistant nitride ceramics, J. Mater. Sci.: Mater. Electron. 31 (2020) 11227–11237, https://doi.org/10.1007/s10854-020-03671-6.

[25] I.V. Korolkov, N. Zhumanazar, Y.G. Gorin, A.B. Yeszhanov, M.V. Zdorovets, Enhancement of electrochemical detection of Pb^{2+} by sensor based on track-etched membranes modified with interpolyelectrolyte complexes, J. Mater. Sci.: Mater. Electron. 31 (2020) 20368–20377, https://doi.org/10.1007/s10854-020-04556-4.

[26] D.I. Shlimas, A.L. Kozlovskiy, M.V. Zdorovets, Study of the formation effect of the cubic phase of $LiTiO_2$ on the structural, optical, and mechanical properties of $Li_{2\pm x}Ti_{1\pm x}O_3$ ceramics with different contents of the *X* component, J. Mater. Sci.: Mater. Electron. 32 (2021) 7410–7422, https://doi.org/10.1007/s10854-021-05454-z.

[27] A.L. Kozlovskiy, D.I. Shlimas, M.V. Zdorovets, Synthesis, structural properties and shielding efficiency of glasses based on TeO_2-(1-x)ZnO-xSm_2O_3, J. Mater. Sci.:

Mater. Electron. 32 (2021) 12111–12120, https://doi.org/10.1007/s10854-021-05839-0.
[28] A. Kozlovskiy, K. Egizbek, M.V. Zdorovets, M. Ibragimova, A. Shumskaya, A. A. Rogachev, Z.V. Ignatovich, K. Kadyrzhanov, Evaluation of the efficiency of detection and capture of manganese in aqueous solutions of $FeCeO_x$ nanocomposites doped with Nb_2O_5, Sensors 20 (2020) 4851, https://doi.org/10.3390/s20174851.
[29] M.V. Zdorovets, A.L. Kozlovskiy, D.I. Shlimas, D.B. Borgekov, Phase transformations in FeCo – Fe_2CoO_4/Co_3O_4-spinel nanostructures as a result of thermal annealing and their practical application, J. Mater. Sci.: Mater. Electron. 32 (2021) 16694–16705, https://doi.org/10.1007/s10854-021-06226-5.
[30] A.L. Kozlovskiy, M.V. Zdorovets, Synthesis, structural, strength and corrosion properties of thin films of the type CuX (X = Bi, Mg, Ni), J. Mater. Sci.: Mater. Electron. 30 (2019) 11819–11832, https://doi.org/10.1007/s10854-019-01556-x.
[31] I.Z. Zhumatayeva, I.E. Kenzhina, A.L. Kozlovskiy, M.V. Zdorovets, The study of the prospects for the use of $Li_{0.15}Sr_{0.85}TiO_3$ ceramics, J. Mater. Sci.: Mater. Electron. 31 (2020) 6764–6772, https://doi.org/10.1007/s10854-020-03234-9.