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Effect of excitation intensity and temperature on photoluminescence of thin films of the $Cu_2ZnSnSe_4$ compound

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Received August 14, 2024
Revised August 24, 2024
Accepted August 25, 2024

The results of the study of the phase composition, structural characteristics and photoluminescence (PL) of thin films of the direct-gap compound $Cu_2ZnSnSe_4$ (CZTSe) with the kesterite structure are presented. X-ray spectral local microanalysis with energy dispersion showed that the ratio of elements in the CZTSe compound is: $[Cu]/[Zn + Sn] \sim 0.75$ and $[Zn]/[Sn] \sim 1.17$. Using X-ray diffraction analysis, the unit cell parameters of the CZTSe compound thin films were determined to be: $a \sim 5.692$ Å and $c \sim 11.33$ Å. Based on the measurement data of PL spectra and PL excitation spectra at temperatures in the range of $6-300$ K, the band gap width $E_g \sim 1.052$ eV of CZTSe thin films, the position of the energy levels of structure defects in the band gap were determined, and the mechanisms of radiative recombination of nonequilibrium charge carriers were established. The nature of growth defects in the structure of the CZTSe compound is discussed.

Keywords: $Cu_2ZnSnSe_4$, thin films, photoluminescence, band gap width, energy levels of defects.

DOI: 10.61011/PSS.2024.10.59621.215

1. Introduction

In recent years, considerable attention has been paid to the creation of solar energy phototransformers based on direct-band solid solutions with the structure of chalcopyrite $Cu(In,Ga)Se_2$ and $Cu(In,Ga)(S,Se)_2$ with an efficiency factor of $\sim 20.8-23.35\%$ [1–6]. However, the increase of the cost of the main elements In and Ga and the limited availability of their reserves in the Earth's crust indicate the need to use cheaper and more widespread Earth's crust elements such as Zn and Sn, which form the basis of direct-band compounds $Cu_2ZnSnSe_4$ (CZTSe), Cu_2ZnSnS_4 (CZTS) and solid solutions of $Cu_2ZnSn(S,Se)_4$ (CZTSSe) with kesterite structure. Therefore, the creation of solar cells based on CZTSe direct-band compounds and solid solutions of CZTSSe of *p*-type of conductivity in recent years has become one of the important scientific directions in the development of semiconductor photovoltaics [1,7–14]. The efficiency of solar cells based on thin films of CZTSSe solid solutions currently is $\sim 13.8-14.9\%$, which is considered promising and encouraging for these poorly studied direct-band semiconductors [1,7]. It is obvious that it is necessary to obtain new information about the phase composition, structural and optical characteristics of these semiconductor materials for further progress in the creation of solar cells based on CZTSe thin films and CZTSSe solid solutions, as well as for improving the efficiency of solar energy conversion. It should be noted that the width of the band gap E_g of thin films of the CZTSe compound presently varies in the range of $0.93-1.133$ eV depending on their deposition technology and temperature treatment [14–20]. Therefore, it is especially important to establish a reliable value of E_g of CZTSe compound and the mechanisms of radiative recombination of nonequilibrium charge carriers. New data are presented in this paper to determine the optical characteristics of CZTSe thin films in the temperature range of $6-300$ K. The results obtained reflect the real value E_g of CZTSe compound, the energy position of the levels of structural defects and their nature (acceptors and donors), which determine the

processes of radiative recombination in the spectral range of $\sim 0.8-1.1$ eV.

2. Method of samples obtaining and experimental procedure

Photoluminescence (PL) was studied on CZTSe films with a thickness of $\sim 2\,\mu$m formed on sodium-containing glass substrates with a pre-deposited molybdenum contact layer with a thickness of $0.5\,\mu$m (CZTSe/Mo/glass heterostructure). CZTSe thin films were formed by selenization of metal precursors deposited on substrates by magnetron sputtering of high-purity metals (Cu, Zn, Sn) at room temperature. The selenization of alternating nanoscale metal layers was carried out in the temperature range of $450-550^\circ$C [12]. Solar cells based on such CZTSe films with the structure of ZnO : Al/*i*-ZnO/CdS/CZTSe/Mo/glass had an efficiency of $\sim 3.2-8.1\%$ [11–13]. The microstructure of the surface, transverse cleavages and the elemental composition of CZTSe/Mo/glass thin films were analyzed by scanning electron microscopy with wave dispersion [12]. The phase composition and parameters of the lattice unit cell of the CZTSe compound were determined using Siemens D-5000 diffractometer in the Bragg–Brentano geometry with a source of monochromatic CuK_α radiation with a wavelength of $\lambda = 1.5405$ Å. The PL spectra of CZTSe thin films were recorded at temperatures of $6-300$ K in a closed-loop optical cryostat DE-202SE (Advanced Research Systems, USA) using a diffraction monochromator with a mirror lens focal length of $f \sim 100$ cm with a thermoelectrically cooled photomultiplier (HamamatsuH10330-75, Japan) installed at its output and operating in the infrared spectral range of $0.75-1.65\,\mu$m [11]. The PL spectra of CZTSe films were recorded using argon laser radiation at a wavelength of 514 nm with a power density in the range of $0.001 \sim 0.13$ W/cm^2. In the experiments, diffraction monochromators with $f \sim 60$ cm and $f \sim 30$ cm with detectors based on InGaAs $p-i-n$-photodiodes in the spectral range of $0.9-1.7\,\mu$m were used. PL spectra were also recorded using a solid-state laser with a wavelength of 532 nm in the range of radiation power density of $\sim 0.001-9$ W/cm^2. The spectral resolution for recording the PL spectra was ~ 0.5 meV. The luminescence excitation spectra (LES) were recorded on the basis of a diffraction monochromator with $f \sim 30$ cm illuminated by focused light from a tungsten incandescent lamp with a power of 170 W. The PL spectra were also recorded using laser pulsed radiation with a wavelength of 532 nm ($\tau_{imp} = 15$ ns, $f = 15$ Hz, $I_{exc} = 13-467$ kW/cm^2) and 337 nm ($\tau_{imp} = 8$ ns, $f = 525$ Hz, $I_{exc} = 150$ kW/cm^2).

3. Results and discussion

X-ray spectral local microanalysis with energy dispersion of CZTSe thin films in the CZTSe/Mo/glass structure performed using a scanning electron microscope demonstrated a copper deficiency relative to the total content of Zn and Sn at the level of $[Cu]/([Zn]+[Sn]) \sim 0.77$. The excess of zinc and the ratio of selenium to metals were: $[Zn]/[Sn] \sim 1.18$ and $[Se]/([Cu]+[Zn]+[Sn]) \sim 1.00$, respectively. The study of the microstructure of the surface and transverse cleavage of CZTSe thin films by scanning electron spectroscopy showed the presence of densely packed homogeneous nanoscale grains with dimensions of $\sim 50-500$ nm and film thickness of $\sim 2\,\mu$m, which corresponds to the results obtained earlier for similar solar cells [11,12]. The lattice cell parameters of CZTSe thin films in the CZTSe/Mo/glass structure, determined on the basis of X-ray diffraction measurements, were $a = 5.692$ Å, $c = 11.33$ Å.

Optical characteristics of thin films of CZTSe compound on Mo/glass substrates were determined at temperatures of $\sim 6-300$ K in a wide range of laser radiation power density of ~ 0.13 W/cm$^2-467$ kW/cm^2. The possibility of implementing various mechanisms of radiative recombination in the CZTSe compound by analyzing PL spectra at temperatures in the range of $\sim 4-300$ K with the participation of p-type and n-type structural defects was considered in Ref. [9,10,11–20]. The optical characteristics of CZTSe thin films on Mo/glass substrates were analyzed in this paper in accordance with the theory of interimpurity radiative recombination for highly compensated (nondegenerate) direct-band-gap semiconductors [21].

Figure 1 shows in a semi-logarithmic scale the PL spectra of CZTSe thin films in the CZTSe/Mo/glass structure measured in the temperature range of $6-240$ K when nonequilibrium charge carriers are excited by 514 nm laser with a power density of ~ 0.13 W/cm^2. As can be seen, the PL spectrum at $T = 6$ K contains a band of $TI_1 \sim 0.922$ eV with a half-width of ~ 85 meV and a tightened low-energy contour. The intensity of the band TI_1 decreases with an increase of temperature in the range of $T \sim 6-170$ K, the maximum shifts to the low energy region to ~ 0.856 eV, and the half-width increases from ~ 85 meV to ~ 180 meV. Additional bands appear in the PL spectra of the CZTSe compound in the high-energy region $\sim 0.93-1.00$ eV when the temperature rises from 105 to 240 K. It is assumed that the band TI_1 corresponds to the recombination of electrons from shallow quantum wells with holes trapped at localized levels of acceptors in the band gap. The band TI_2 is caused by the redistribution of radiative recombination channels on structural defects (acceptors and donors). The band BI corresponds to optical transitions (zone — localized acceptor states), and the band BB corresponds to interband transitions in accordance with the theory of interimpurity radiative recombination [21].

Figure 2 shows the PL and PLE spectra with their mathematical processing at $T = 6$ K, which is necessary to determine the width of band gap E_g of CZTSe compound thin films and establish the mechanisms of radiative recombination. PLE were recorded at the maximum intensity of the band of $TI_1 \sim 0.904$ eV.

The width of the band gap E_g was determined by mathematical processing of the PLE using the formulas (1), (2) and (3) [8,22–24]:

$$\alpha \propto \int_0^{\infty} (1/\sigma\sqrt{2\pi}) \exp(-1/2\left[(E_g - E_{g,mean})/\sigma\right]^2 \times (\sqrt{h\omega - E_g}/h\omega) dE_g, \quad (1)$$

where α —absorption coefficient, σ — parameter of gap fluctuations, $E_{g,mean}$ — average value of the band gap, $h\omega$ — photon energy [8].

$$I(E) \approx \alpha_0/\left[1 + \exp(E_g - E)/\Delta E\right], \quad (2)$$

where ΔE — the broadening parameter, α_0 — constant, E — the excitation energy at which the luminescence intensity is recorded [22].

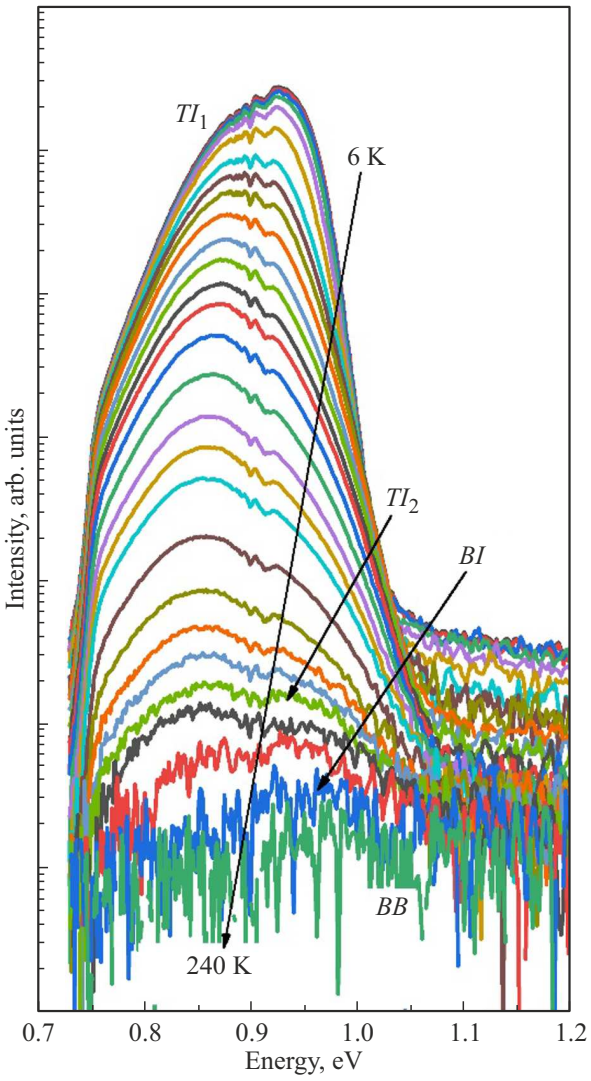

Figure 1. Photoluminescence spectra of a CZTSe thin film in the temperature range of 6–240 K at excitation power density of 0.13 W/cm^2.

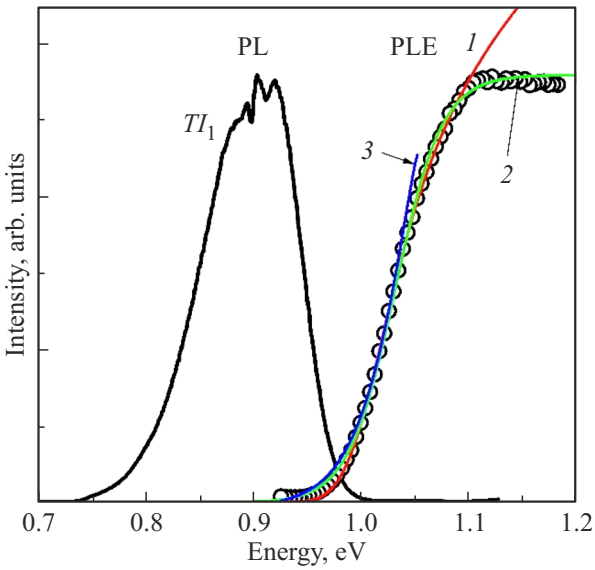

Figure 2. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the CZTSe thin film according to formulas (1), (2) and (3), respectively.

$$\alpha \exp\left(-2/5\sqrt{\pi}\left[2(E_g - h\upsilon)/\gamma_{opt}\right]^{5/4}\right), \quad (3)$$

where γ_{opt} — the amplitude of fluctuations in the electrostatic potential for optical transitions [8,23,24].

It was found based on the results of the PLE processing that E_g and the corresponding parameters are: $E_g = 1.010$ eV and $\sigma = 24$ meV (magnitude of zone fluctuations), $E_g = 1.031$ eV and $\Delta E = 22$ meV (broadening parameter), $E_g = 1.052$ eV and $\gamma_{opt} = 25$ meV (amplitude of potential fluctuations) according to the formulas (1)–(3), respectively. The highest value of $E_g = 1.052$ eV for CZTSe thin films is obtained by the formula (3) used for direct-band-gap semiconductors with a high concentration of chaotically distributed structural defects (charged donors and acceptors) in the crystal lattice, which determine the magnitude of potential fluctuations in CZTSe thin films [8,23–25]. The total amplitude of potential fluctuations and energy bands can be determined using the formula given in Ref. [17–25]:

$$\gamma^2 = \gamma_{opt}^2 + \sigma^2, \quad (4)$$

The total amplitude of potential fluctuations and band gap width in thin films at $T = 6$ K is $\gamma \sim 35$ meV based on this estimation. The presence of strong potential fluctuations in CZTSe thin films is also confirmed by experiments on high-energy shift of the band TI_1 at $T = 6$ K depending on the power density of laser radiation in a wide range of excitation levels from 0.001 to 4 W/cm^2. It was found that an increase of the excitation power density by one order of magnitude (j-shift) results in a shift of the maximum of the band TI_1 by 16 meV. The energy gap between $E_g = 1.052$ eV

and the band $TI_1 \sim 0.922$ eV at $T = 6$ K is 130 meV and ~ 196 meV for temperatures of 60–170 K. Such large values of the displacement of the PL band indicate the participation in the processes of radiative recombination of not only free and non-localized electrons in the shallow conduction bands „tails" with holes, but also electrons localized in deeper „tails", i.e. suggest the presence of deep energy levels of defects in the n-type structure in the band gap of CZTSe compound of *p*-type of conductivity. The bands previously detected in the PL spectra of the CZTSe compound in the energy range of < 0.96 eV were attributed to various channels of radiative recombination based on the theory of edge luminescence of direct-band-gap semiconductors [21]. In particular, the radiative recombination of free electrons with holes in deep localized acceptor states (BI) [9,12,13], electrons with holes in the „tails" valence band (BT) [11], DAP or $Q - DAP$ (donor-acceptor recombination) [10,14,16], recombinations (BT, BI and BB) [18], TI (tail–impurity) [17,19], as well as TI, BI and BB [20]. It should be noted that the attribution of optical transitions BB (zone–zone) to the energy range of < 0.96 eV in the study of CZTSe compound PL [17,18,20] and the determination of the value $E_g \sim 0.959$ eV based on the absorption spectra [17] does not agree with the known experimental data of $E_g \sim 1.01$–1.05 eV, defined in Ref. [9,12–14,26]. The measurements of the PL and LES spectra carried out in this work and the use of pulsed laser radiation made it possible to establish that E_g is in the region of > 1.01 eV and to clarify the mechanisms of radiative recombination. It is assumed that the processes of radiative recombination of nonequilibrium charge carriers (electrons, holes) in CZTSe thin films are determined by optical transitions TI_1, TI_2 and BI in the temperature range of ~ 6–205 K at energy levels of growth defects of the n-type and p-type structure and by interband transitions BB at $T \sim 240$ K, Figure 1. The bands TI_1 and TI_2 are caused by the recombination of electrons from shallow and deep quantum wells of the n-type with holes trapped at localized levels of acceptors in the band gap. At the same time, the energy levels of donors for the band TI_2 are localized in deep quantum wells below the electron flow level [21] (donor clusters of several defects), and holes are localized at energy levels of the p-type. The band BI is attributable to the radiative recombination of free electrons with localized holes on deep acceptors in the band gap.

Figure 3 shows the normalized PL spectra of CZTSe films recorded in the range of $T \sim 95$–148 K. In comparison with Figure1, the shift of the band TI_1 to the low-energy region is more clearly manifested on a linear scale without changing the shape of the low-energy contour. The contours of all PL bands overlap on the high-energy contour of the band TI_1 at $T > 95$ K in the energy range of 0.932–0.944 eV at the level of 15–55% of the normalized intensity of the bands with an increase of temperature from $T \sim 95$ to 148 K, Figure 3. This effect indicates the formation of a new band in the energy range of $TI_2 \sim 0.943$ eV and can only be explained by the monotonous redistribution of radiative recombination

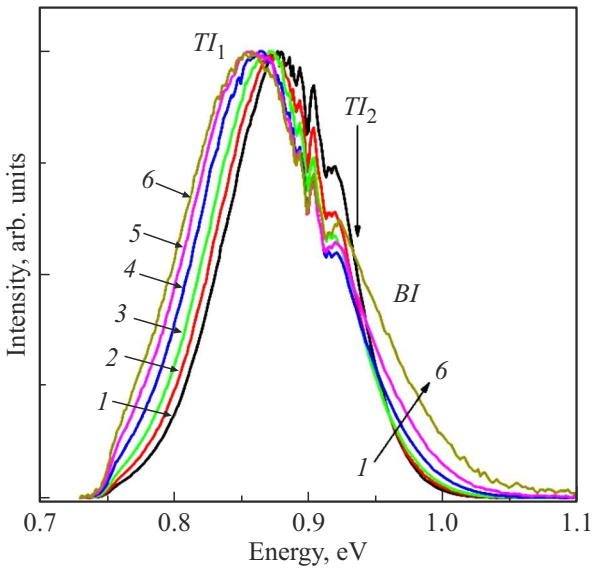

Figure 3. Normalized photoluminescence spectra of a CZTSe thin film at temperatures: *1* — 95, *2* — 105, *3* — 115, *4* — 129, *5* — 139, *6* — 148 K.

channels from TI_1 to TI_2, Figure 3 and Figure 1. In addition to this, the „tail" of the band contour significantly shifts in the energy range of ~ 0.946–1.050 eV and its intensity increases at the level of ~ 0.970 eV with the increase of the temperature which is attributable to the formation of a radiative recombination channel BI, Figure 3.

As an example, Figure 4 shows the PL spectra of the CZTSe film for temperatures ~ 6 K, 109 K, 139 K and 176 K with an approximation of the low-energy contour of the band TI_1 using the formula [21,18]:

$$I(\omega) \approx \exp\left[-(E_g^0 - \omega)^2/2\gamma^2\right], \qquad (5)$$

where E_g^0 — the band gap, γ — the magnitude of potential fluctuations.

The approximation of low-energy contours using the formula (5) showed a slight change of the magnitude of potential fluctuations depending on the temperature, which amounted the values: $\gamma \approx 53$, 47, 46 and 49 meV at $T \approx 6$, 109, 139 and 176 K, respectively, Figure 4. It should be noted that such an approximation was carried out for all the PL spectra shown in Figure 1. A significant shift of the band TI_1 to the low energy region and a change of its spectral contour, as well as the relative stability of the averaged (over 25 spectra) magnitude of potential fluctuations at the level of $\gamma \sim 49$ meV in the temperature range of ~ 6–176 K indicates a possible process of radiative recombination of nonequilibrium charge carriers. Since the CZTSe compound has a *p*-type of conductivity, the radiative recombination in the low-energy region at low temperatures and low excitation levels can be determined by optical transitions TI_1 and TI_2 involving electrons from shallow and deep (below the flow level) quantum wells, accordingly, with holes localized on acceptors in the band gap [21].

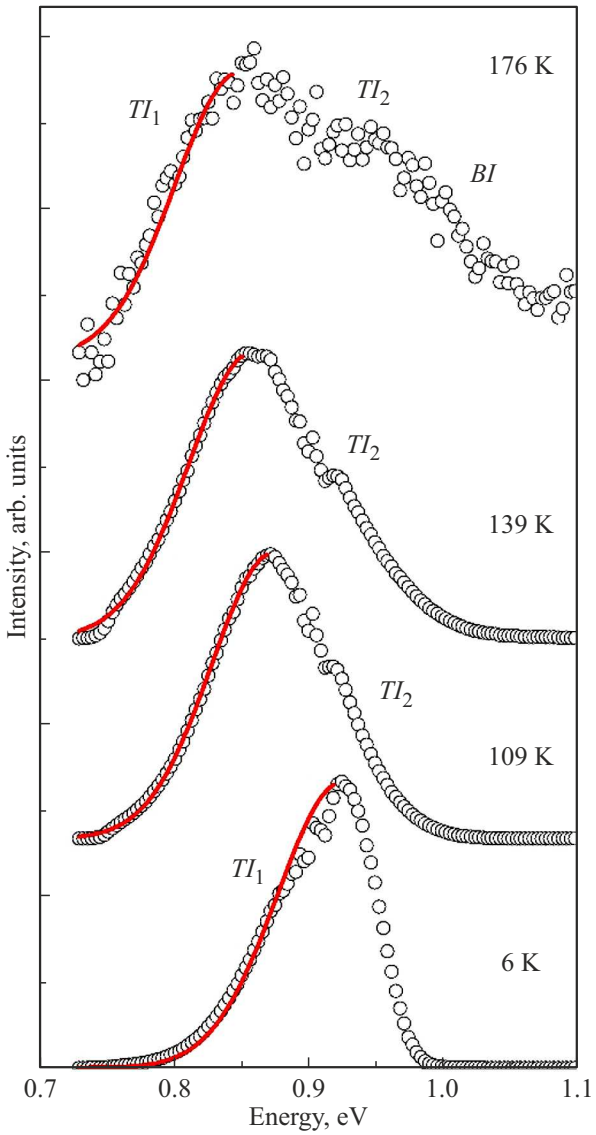

Figure 4. Photoluminescence spectra of the CZTSe film recorded at $T = 6-176$ K (circles) and approximation of the low-energy contour (solid line) of the band TI_1 using formula (5).

Figure 5 shows data on the dependence of the shift of the maximum of the bands TI_1, TI_2 and BI on temperature in the range of $T \sim 6-180$ K with different power densities of continuous-wave laser excitation of CZTSe films.

As can be seen from Figure 5, a low-energy shift of the band TI_1 by 66 meV from 0.922 eV up to 0.856 eV occurs at a power density of 0.5 W/cm^2 in the temperature range $T \sim 6-155$ K. The maximum of the band TI_1 is ~ 0.942 eV at $T = 6$ K with an increase of the power density of laser radiation to 9 W/cm^2 (dependence *2*, Figure 5) and it equals to ~ 0.933 eV at 80 K, i. e. it decreases by ~ 9 meV. A further increase of the temperature in the range of 80–175 K results in an increase of the energy of optical transitions TI_2 and BI, Figure 5. As can be seen, the minima of the energy position of the bands TI_1 and TI_2 are reached at different temperatures of 160 K and 80 K, and the ratio of the relative „deflections“ of 66 meV and 9 meV is ~ 7.3 times. These data indicate a significant impact of the temperature and power density of laser excitation on the redistribution of radiative recombination channels in the CZTSe compound.

Figure 6 shows the PL spectra of a CZTSe thin film in case of continuous-wave and pulsed laser excitation at $T = 10$ K.

It was found that the maximum of the band TI_1 has the following spectral positions at continuous-wave excitation power of 0.5, 2.5 and 9 W/cm^2: 0.922, 0.932 and 0.943 eV, respectively. The maximum of the band TI_2 has the following positions at pulsed laser excitation power of 13, 67 and 467 kW/cm^2: 0.949, 0.948 and 0.946 eV. Thus, an increase of excitation power results in a redistribution of radiative recombination channels, an increase of the intensity of the band TI_2 and the occurrence of two bands BI in the region of energies of above 0.95 eV in the energy region of $\sim 0.964-1.000$ eV and $BB \sim 1.043$ eV, respectively. It is assumed that the band BI is attributable to the radiative recombination of free electrons with holes on localized acceptors with a significant disordering of the crystal lattice due to a deviation of the composition of the CZTSe compound from stoichiometry, and the band BB is attributable to the band–band optical transitions [12,13]. Processing of the low-energy contour of the bands TI_1 and TI_2 using the formula (5) demonstrated that an increase of the power of continuous-wave radiation from 0.5 to 9 W/cm^2 does not change the magnitude of fluctuations of potential $\gamma = 53 \pm 1$ meV, (see contours *1–3*, in Figure 6). The pulsed excitation at a power densities of 13, 67 and 467 kW/cm^2 changes the coefficient $\gamma = 64$, 61 and 57 meV for contours *4, 5* and *6* respectively, Figure 6. Such a change of the magnitude of potential fluctuations from $\gamma = 64$ meV to $\gamma = 57$ meV with the

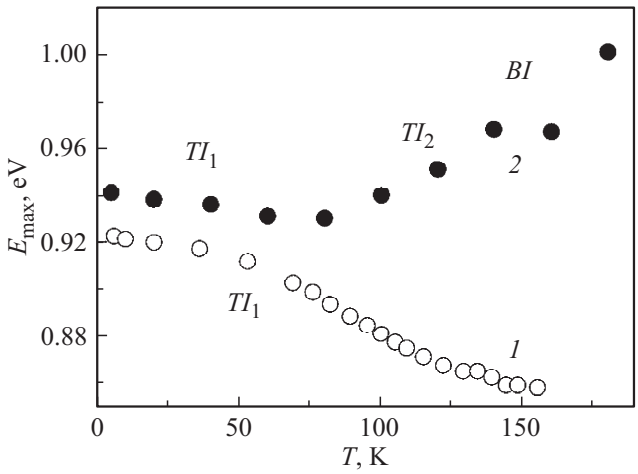

Figure 5. Dependence of the position of the maxima of the bands TI_1 (empty circles — *1*) and bands TI_1, TI_2 and BI (filled circles — *2*) on the temperature at the excitation power density: 0.5 W/cm^2 and 9 W/cm^2, respectively.

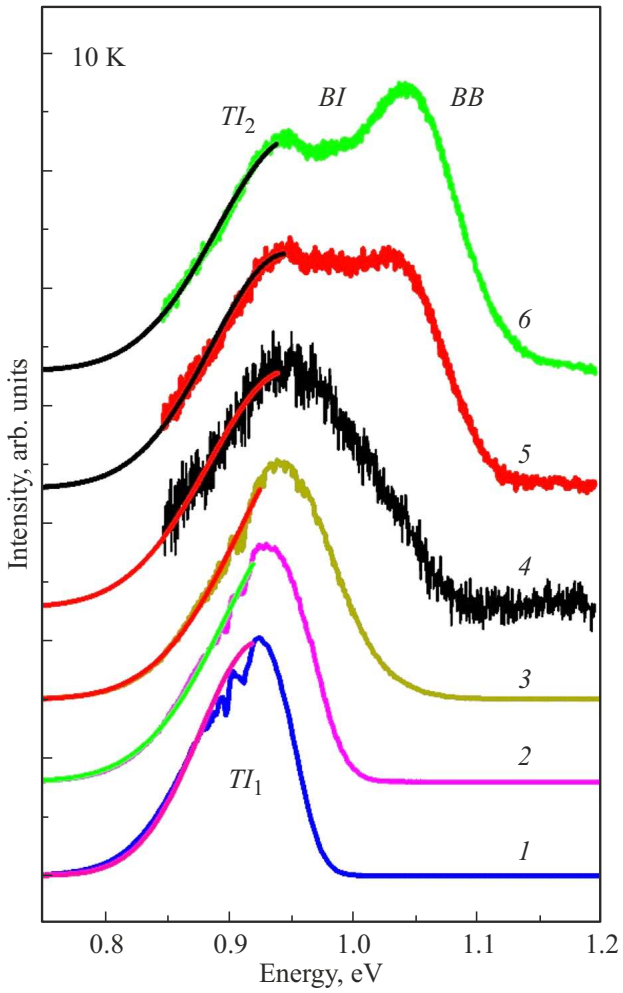

Figure 6. Photoluminescence spectra of CZTSe film at 10 K obtained with different power of continuous-wave laser radiation of /$\lambda = 532$ nm/ (I_{exc}, W/cm^2: *1* — 0.5, *2* — 2.5, *3* — 9) and pulse radiation of /$\lambda = 532$ nm, $\tau = 15$ ns/ (I_{exc}, kW/cm^2: *4* — 13, *5* — 67, *6* — 467). The solid colored lines on the contours of the bands of < 0.95 eV reflect the fitting using the formula (5).

increase of excitation power suggests a redistribution of radiative recombination channels TI_2 and BI, Figure 6. The conducted studies show the determining role of the laser radiation power density and experimental temperature on the redistribution of radiative recombination channels of nonequilibrium charge carriers in the CZTSe compound. It is important to note that the maximum difference of the energy position of the band TI_2 and TI_1 is ~ 93 meV in the low temperature range (10–155 K). In accordance with the theory of luminescence, the competitive process are: interimpurity recombination, with the participation of donors and acceptors [21]. Therefore, the mechanisms of radiative recombination in this energy range can have up to three maxima, two of them associated with the TI-channel, and one associated with the BI channel [21]. The shift of the band TI_2 by 3 meV to the low-energy region with an increase of power from 13 to 467 kW/cm^2 suggests a redistribution of recombination channels TI_2 and BI. It is assumed that the band TI_2 is attributable to the recombination of electrons trapped in localized states of the tails of the conduction band (donor clusters) with holes on one of the neighboring acceptors. In this case the localized states of the tail of the conduction band are below the percolation energy level [21]. Such a channel TI_2 of interimpurity recombination in highly compensated semiconductors corresponds to the transformation of donor-acceptor recombination [21]. Most importantly, the spectral position of the band TI_2 varies differently depending on temperature and excitation level, Figure 5 and Figure 6. The maximum of the band TI_2 shifts to the high energy region at low temperatures with the increase of the temperature regardless of the excitation level in accordance with the theory developed for interimpurity radiative recombination and is determined by the following dependence [21]:

$$\omega_m^{TI} = E_g^0 - \gamma_e - I_a + 2\sqrt{T\gamma_e}, \qquad (6)$$

where E_g^0 — the width of the band gap, γ_e — the magnitude of potential fluctuations, I_a — the depth of the acceptor level and T — temperature.

Using the formula (6) allows determining the position of the acceptor level (density of acceptor states in the band gap). The depth of the acceptor level is ~ 89 meV at $T = 10$ K based on certain numerical values $E_g = 1.052$ eV, $\gamma_e = 64$ meV. At the same time, the spectral position of the band $TI_2 \sim 0.949$ eV with respect to $E_g = 1.052$ eV indicates the presence of a deep donor level ~ 106 meV (maximum density of donor states), Figure 1 and Figure 6. Thus, the donor levels of ~ 106 meV are deeper than the acceptor levels of ~ 89 meV, with respect to the conduction band and the valence band, respectively. The detection of deep donor and acceptor levels in the band gap indicates the need to attribute the CZTSe compound to highly compensated direct-band-gap semiconductors.

The analysis of the temperature dependence of the PL spectra on temperature in case of pulsed laser excitation is an additional proof of the presence of a deep donor level. Figure 7 shows the emission spectra of the CZTSe film at various temperatures in the range of 10–300 K at a constant intensity of pulsed laser excitation of $I_{exc} = 150$ kW/cm^2.

It was found that an increase of temperature does not change the spectral position of the band TI_2, but results in a strong attenuation of its intensity in the range of $T \sim 10$–100 K, Figure 7. This confirms the attribution of the band TI_2 to the radiative recombination of electrons localized in the tails of the conduction band (donor clusters containing several defects) with holes at the energy levels of nearby acceptors in the CZTSe compound. The band BB is clearly manifested in the high-energy region because of the interband radiative recombination of free electrons from the conduction band with holes in the valence band (optical transitions zone–zone). Experiments demonstrated the following spectral position of the band BB: 1.036, 1.038, 1.041, 1.044 and 1.037 eV at temperatures of 10,

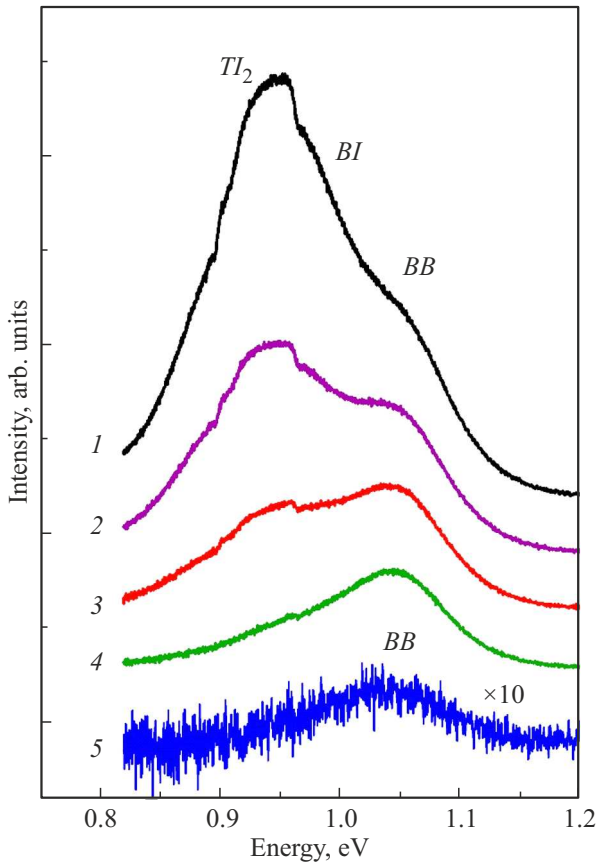

Figure 7. Photoluminescence spectra of CZTSe film at the power density of $I_{exc} = 150\,\text{kW/cm}^2$ of excitation by pulsed nitrogen laser ($\lambda_{exc} = 337\,\text{nm}$) and different temperatures T, K: *1* — 10, *2* — 60, *3* — 80, *4* — 100, *5* — 300.

60, 80, 100 and 300 K, respectively. The energy of optical transitions BB decreases by 7 meV in the temperature range of 100−300 K due to the manifestation of electron-phonon interaction in the direct-band-gap compound CZTSe.

It should be noted that the data on determining the optical characteristics of the CZTSe compound are limited and contradictory, due to its multicomponence and a significant deviation of the composition from the stoichiometry. As is known, the interpretation is based on the theory of classification of structural defects in the crystal lattice of the CZTSe compound [27]. For example, the PL broad bands are attributed to radiative recombination channels TI and TT on defective clusters $(2Cu_{Zn}^{-} + Sn_{Zn}^{2+})$ at the maximum reached value of $E_g = 0.959\,\text{eV}$ based on the measurement of the PL and processing of the fundamental absorption edge of CZTSe thin films obtained by molecular beam epitaxy [17]. A broad band with a maximum of $TI \sim 0.892\,\text{eV}$ is also attributed to radiative recombination on structural defects $(2Cu_{Zn}^{-} + Sn_{Zn}^{2+}$ at a value of $E_g = 1.133\,\text{eV}$ in the PL spectra of CZTSe thin films obtained by magnetron sputtering [19]. Broad bands belonging to different radiative recombination channels TI_1, TI_2, BI and interband transitions BB have been recently found in the PL spectra of CZTSe microcrystals in the region of energies of $< 0.94\,\text{eV}$ depending on the degree of disordering of the crystalline structure of the powders [20]. In accordance with the theory described in Ref. [27], the authors of Ref. [20] suggested that defective clusters $(2Cu_{Zn}^{-} + Sn_{Zn}^{2+})$ in CZTSe microcrystals can create deep cells for electrons $\sim 100\,\text{meV}$ below the conduction band in case of the presence of interband transitions BB less than 0.94 eV.

It is also assumed in accordance with the complex spectroscopic studies conducted in this paper (Figures 1−7) and the theory of classification of defects in the CZTSe compound with the kesterite structure [27] that self-compensating defect clusters $(2Cu_{Zn}^{-} + Sn_{Zn}^{2+})$ are determined by the radiative recombination channels TI_1 and TI_2 in the spectra of the PL of the CZTSe compound in the region of energies of up to 0.95 eV. The appearance of the band BI in the region of energies of more than 0.95 eV is attributable to the radiative recombination of free electrons with holes on the p-type defects Cu_{Zn}^{-} [27] with energy levels of $\sim 89\,\text{meV}$, Figure 6. Thus, the formation of a deep donor level of $\sim 106\,\text{meV}$ (maximum density of donor states) in the energy region $\sim 0.949\,\text{eV}$, determining the radiative recombination channel TI_2 and an acceptor level of $\sim 89\,\text{meV}$ (maximum density of acceptor states) determining the channel BI with the value $E_g = 1.052\,\text{eV}$ at $T \sim 10\,\text{K}$. The discovered effect of the redistribution of the intensity of the bands TI_2 and BI in the PL spectra of the CZTSe compound in the energy region of $\sim 0.936-0.964\,\text{eV}$ suggests the presence of competitive radiative recombination channels involving donors and acceptors. It is obvious that it is necessary to reduce the concentration of deep donors (defects Sn_{Zn}^{2+}) and increase the concentration of p-type defects, in particular, with smaller acceptor levels, which is important for practical applications for increasing the efficiency of photoconversion in solar cells created on the basis of a CZTSe compound with a deficiency of Cu in relation to the total content of Zn and Sn and an excess of zinc. It should be noted that the solar cells created on the basis of CZTSe thin films studied in this paper with the ratio of $Cu/(Zn + Sn) \sim 0.77$ and $Zn/Sn \sim 1.18$ had the efficiency of 6.4−7.4% [16].

The values of $E_g = 1.052\,\text{eV}$ defined in this paper and the interband transitions energies of $BB \sim 1.044\,\text{eV}$, are consistent with the previously defined values of $E_g = 1.051\,\text{eV}$ at $T = 4.2\,\text{K}$ and $E_g = 1.01\,\text{eV}$ at $T = 300\,\text{K}$, determined based on the spectral position of the fundamental absorption edge [26] and detected narrow line of $EX \sim 1.033\,\text{eV}$ of free excitons in the PL spectra in high-quality CZTSe thin films [14].

4. Conclusion

Mechanisms of radiative recombination in thin films of the CZTSe compound were determined based on the data of the spectral band positions and the redistribution

of radiation energies in photoluminescence spectra with temperature variations in the range of 10−300 K and the level of continuous-wave and pulsed excitation in the range of 0.01 W/cm^2−467 kW/cm^2. It was shown that thin films of the CZTSe compound belong to highly compensated (non-degenerate) direct-band-gap semiconductors with deep acceptor and donor levels. A broad photoluminescence band in the energy range of ~ 0.949 eV is attributable to the capture of electrons at the localized deep ~ 103 meV donor levels of defects in the conduction band tails and their recombination with localized holes on acceptors. The appearance of PL bands in the spectral region of > 0.95 eV is attributable to the radiative recombination of free electrons with holes localized on deep acceptors of ~ 89 meV and band-to-band optical transitions. The presence of competitive radiative recombination channels with the involvement of donors and acceptors in a strongly compensated direct-band-gap CZTSe compound with a kesterite structure was experimentally proven. At the same time, the processes of radiative recombination occur under conditions of stronger local fluctuations in the electrostatic potential of $\sim 64-53$ meV, due to the presence of donor and acceptor structural defects with deep energy levels, compared with fluctuations in the band gap of $\sim 24-22$ meV in a direct-band-gap compound CZTSe with a value of $E_g \sim 1.05-1.02$ eV in the temperature range of 10−300 K, respectively.

Funding

The study was performed within the State Research Program „Materials Science, New Materials and Technologies“, subprogram „Condensed State Physics and Development of New Functional Materials and Production Technologies“, assignment 1.4.4 and the project of the Ministry of Science and Higher Education of the Russian Federation („Spin“ No. 122021000036-3).

Conflict of interests

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov