PHOTOLUMINESCENCE PROPERTIES OF $ZnIn_2Se_4$

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The photoluminescence properties of ZnIn2Se4 were studied at 300K by use of confocal laser microspectrometry. For the first time, edge luminescence with a maximum at 674 nm was observed. Nonlinear intensity dependence of the photoluminescence on the excitation light is found.

Keywords: $ZnIn_2Se_4$, edge luminescence, antistructural defects.
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INTRODUCTION

Compounds $A^2B^3{}_2C^6{}_4$ (A – Zn, Cd; B – In, Ga; C – S, Se, Te) crystallizing in the space group S_4^2, attract the attention of researchers in connection with the possibility of their use in semiconductor instrument making. $ZnIn_2Se_4$ belongs to this defect chalcopyrite family. It also attracts attention of many researchers due to its potential application in various fields such as solar cells [1], memory devices [2], etc.

The photoelectric and optical properties of $ZnIn_2Se_4$ were studied in [3-8]. From optical measurements, the absorption edge was determined as 1.82 eV for direct transitions and 1.7 eV for indirect transitions [3]. In [5], the optical absorption of Co doped and undoped $ZnIn_2Se_4$ single crystals were studied. The bandgap values of undoped samples determined from the spectra were 1.774 eV for direct and 1.662 eV for indirect transitions at 300 K, and for doped samples, these values were determined as 1.413 eV and 1.277 eV, respectively. Photosensitive properties were studied in [4]. Photosensitive structures based on In / n-$ZnIn_2Se_4$ have been obtained. In this work, the bandgaps of n-$ZnIn_2Se_4$ for direct and indirect transitions were determined as E_{dir} = 2.1 eV and E_{ind} = 1.62 eV, respectively. The photoelectric memory effect was discovered in [2], where this effect is explained by the authors by the presence of double-charged acceptor levels and makes it possible for practical application as electro-optical memory devices. The authors assume that $ZnIn_2Se_4$ is a direct-gap semiconductor with a band gap of 1.9 eV. The optical properties of $ZnIn_2Se_4$ films were studied in [9]. The band gap for direct allowed optical transitions is determined as 2.065 eV and for indirect transitions as 1.69 eV. The calculated value of the band gap is 1.85 eV (DC) and 1.72 eV (DF) for $ZnIn_2Se_4$ [10], for the $ZnIn_2Se_4$ film from optical absorption spectra, the band gap is determined as 2.21 eV [11].

Very little is known at present about the luminescence of $ZnIn_2Se_4$. To our knowledge, the luminescence properties were studied only in [12, 13] in the temperature range 55-200 K. The authors attributed the broad luminescence band at 1.28 eV to the energy levels formed by complexes I and V_{Zn} or antisite defects of the A_B, B_A type.

We have previously investigated the radiative properties and energy levels in the band gap of $ZnIn_2Se_4$ in a wide temperature range of 10–300K [14]. The optical transmission of $ZnIn_2Se_4$ have been studied by us in [15]. The optical band gap at 293 K is defined as 1.72 eV. The transmission spectrum is also characterized by the presence of an absorption band at 850 nm.

In this work, in order to obtain additional information about the luminescence properties of $ZnIn_2Se_4$, we investigated photoluminescence at 300K using a confocal laser microspectrometer.

EXPERIMENTAL TECHNIQUES

$ZnIn_2Se_4$ crystals were synthesized by direct fusion of the initial highly pure components Zn, In, and Se in a stoichiometric quantities in graphitized quartz ampoules silica tubes in a vacuum of about 10^{-4} mm Hg. pillar. X-ray diffraction measurements were carried out on a Bruker D8 device. X-ray analysis of the powder showed that $ZnIn_2Se_4$ crystallizes in a tetragonal structure with the space group S_4^2 and with lattice parameters a = 5.709 Å, c = 11.449 Å, δ = 1-c / 2a≈-0.0027. As can be seen, in contrast to [16, 17], a slight tetragonal stretching of the lattice was found, which is rarely found in crystals of ternary compounds with tetrahedral coordination of atoms and structures such as chalcopyrite and thiogallate. Such a stretching of the $ZnIn_2Se_4$ lattice was also found in [4, 11, 18]. Figure 1 shows the X-ray diffraction pattern of $ZnIn_2Se_4$.

The photoluminescence spectra were recorded on a Nanofinder30 confocal laser microspectrometer (Tokyo Instr., Japan). Nd: YAG laser with the wavelength of λ_{ex}=532 nm and a maximum power of 10 mW was used as an excitation source. The radiation detector was CCD camera (1024 x 128 pixels), cooled by thermoelectric method to -100^{0}C, operating in the photon counting mode. The experiments were carried out at room temperature.

DISCUSSION OF THE RESULTS

Fig. 2 shows the spectrum of Raman scattering of light in $ZnIn_2Se_4$. The spectrum consists of eight lines at 68, 87, 100, 133, 168, 193, 204, 240 cm^{-1}. These values of the frequencies of vibrational modes

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coincide with the frequencies determined from the spectra of IR reflection and Raman scattering of light from [19-21]. For comparison, Table 1 presents the values of the frequencies of the vibrational modes.

Table 1.

Frequency values (in cm^{-1}) of vibrational modes of $ZnIn_2Se_4$

Mode symmetry	This work	[19]		[20]	[21]
	ω_R	ω_R	ω_{IR}	ω_{IR}	ω_R
E	68	-	67/68	68	67
E	87	86	85/85	87	86
B_2	100	100	101/104	102	99
A_1	133	135	-	-	132
E	168	165	164/165	-	167
E, B_2	193	-	196/203	-	193/199
E, B_2	204	204	-	202	
E, B_2	240	242	213/242	221	212/242

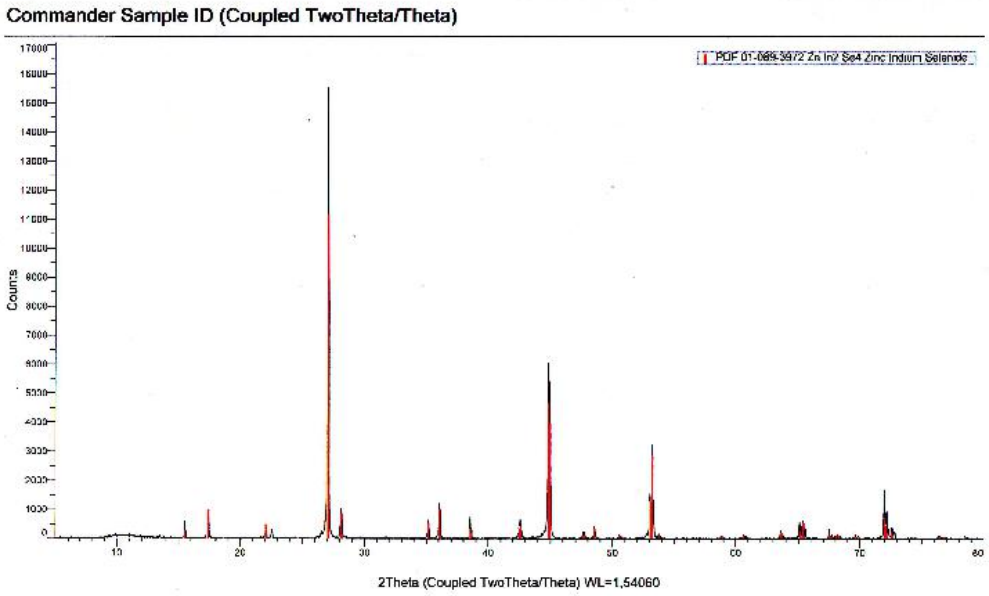

Fig. 1. X-ray diffraction pattern of $ZnIn_2Se_4$

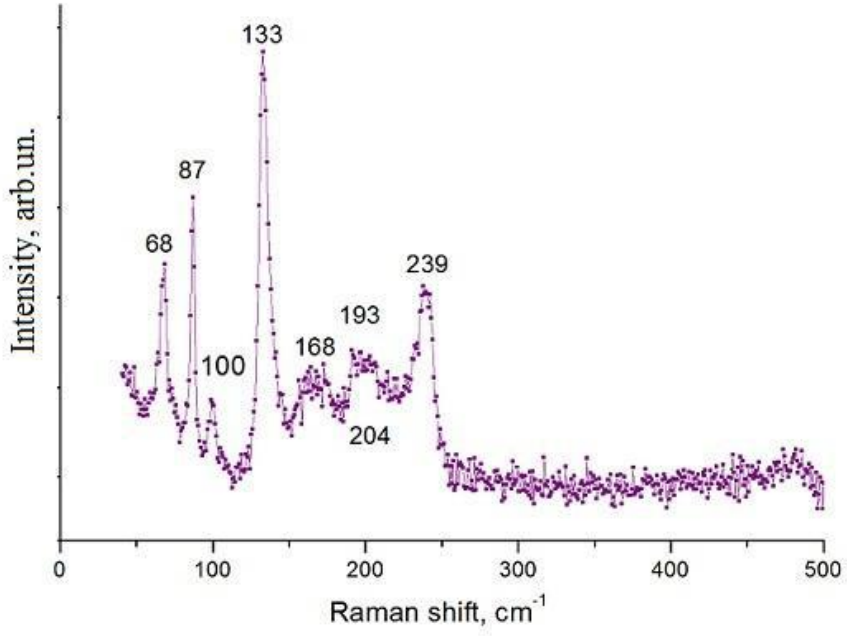

Fig. 2. Raman spectrum of $ZnIn_2Se_4$

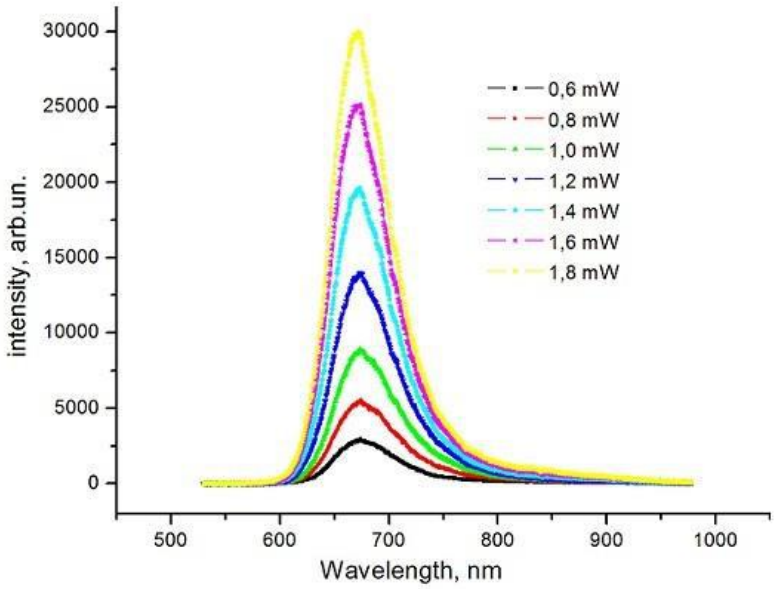

Fig. 3. Photoluminescence spectrum of $ZnIn_2Se_4$

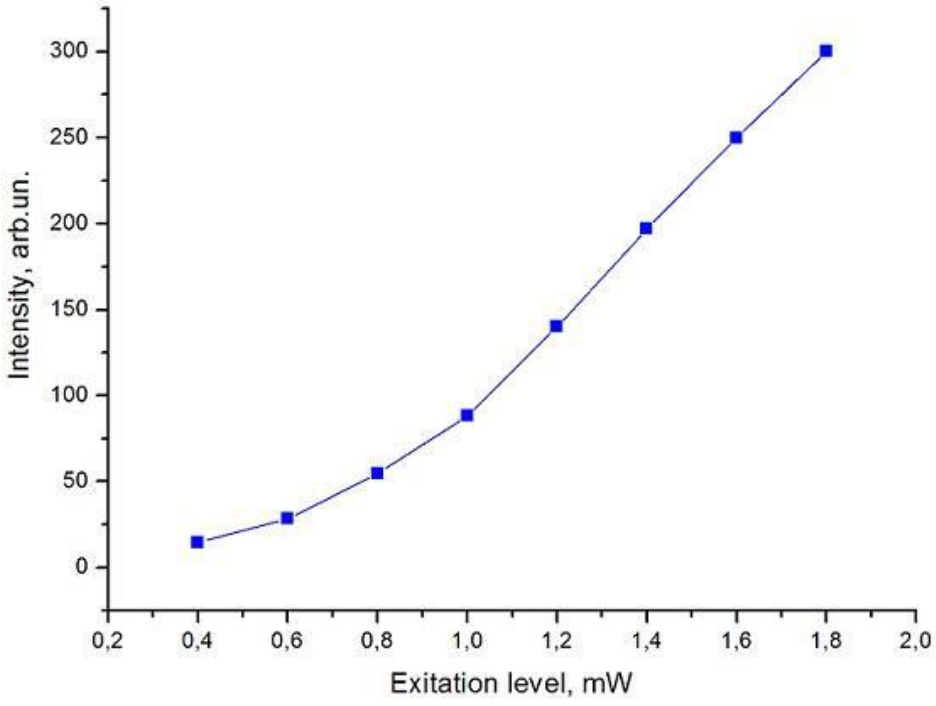

Fig. 4. Dependence of the photoluminescence intensity on the intensity of the exciting light in $ZnIn_2Se_4$

Figure 3 shows the photoluminescence spectra at different intensities of the exciting light. As can be seen from the figure, the spectrum consists of a band at 674 nm (~ 1.84 eV) with a half-width of ~ 60 nm, the half-width and position of which does not change with the intensity of the exciting light. A sharp rise of the band from the short-wavelength region and the position of the maximum suggest that this is edge luminescence. The stretched shape of the long-wavelength part of the spectrum indicates the presence of an impurity band in $ZnIn_2Se_4$ in the 850-900 nm region. The band at 850-900 nm is associated with impurity levels caused by antisite defects, which are characteristic for crystals of the $A^2B_2^3C_4^6$ class [22]. The temperature dependence of this impurity luminescence band was investigated by us in [14]. This emission band, in terms of the position of the maximum, slightly differs from the broad luminescence band observed in [12, 13] at 1.28 eV. In [12], the dependence of the intensity of this emission band on the excitation level was also investigated, and it was revealed that the dependence is characterized by superlinearity; $I_{PL} \sim I_{ex}^{1,4}$, at high temperatures (200K), and at low temperatures (90K), this dependence turned out to be linear ($I_{PL} \sim I_{ex}^{1,05}$).

Figure 4 shows the dependence of the photoluminescence intensity on the intensity of the exciting light. As can be seen from the figure, the

dependence has a nonlinear character $I_{PL} \sim I_{ex}^2$. It can be assumed that the emission band is associated with an interband radiative transition.

CONCLUSION

By using confocal laser microspectrometer, edge luminescence in $ZnIn_2Se_4$ with the maximum at 674 nm (1.84 eV) at 300 K has been detected for the first time. A quadratic character of the dependence of the luminescence intensity on the intensity of the exciting light has been established. This study of the emission properties shows that $ZnIn_2Se_4$ is promising material for use in optoelectronics.

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