

Research of Photoluminescence Spectra of $ZnS_xSe_{1-x}:Mn$ Nanocrystals Obtained by Method of Self-propagating High-temperature Synthesis

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We investigated photoluminescence spectra of nanocrystals of $ZnS_xSe_{1-x}:Mn$ solid solutions obtained by the method of self-propagating high-temperature synthesis. At room temperature, these nanocrystals luminesced in the visible area of spectrum for all values of the parameter x . Six individual bands were discovered in photoluminescence spectra of $ZnS_xSe_{1-x}:Mn$ nanocrystals by the method of fourth-sixth derivative spectroscopy. For compounds with $x = 1$, these bands are characterized by maxima of emission: $\lambda_{max} = 639$ nm (1), 616 nm (2), 600 nm (3), 580.5 nm (4), 555 nm (5), 530.5 nm (6), respectively. Probably, bands 1-5 are related to Mn^{2+} ions in different local environment. The maxima position of emission of 4-5 individual bands does not almost depend on x parameter value, maxima of 2-3 bands are monotonously displaced in a short-wave area with the increase of x parameter. Maximum of band emission 1 changes the hopping position in the range of x values: $x = 0.2 \div 0.4$, which is related to hopping change of local environment of Mn^{2+} ions in MnS phase. To all appearance, 6 band's emission is not elementary, therefore its position of maximum of emission depending on the parameter value of x has hopping character.

Keywords: ZnS_xSe_{1-x} nanocrystals, Self-propagating high-temperature synthesis, PL spectra, Method of derivative spectroscopy, Individual emission bands, Structural defect, Crystal lattice.

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1. INTRODUCTION

ZnS_xSe_{1-x} solid solutions are perspective materials for creation of light-emitting diodes, lasers, luminescent matrices, sources of white light, photoelectric receptors of short-wave radiation, solar panels [1-3]. The alloying of ZnS_xSe_{1-x} solid solutions allows to get such materials with n - and p -type conductivity and also emitting structures in the whole visible range of wavelengths that extends their practical application domain substantially. Additional interest in these solutions is conditioned by their use in optoelectronic structures in the form of nanocrystals (NC) [4-5]. Therefore, the development of perspective technologies of NC synthesis is a vital task. In order to obtain $ZnS_xSe_{1-x}:Mn$ NC we used the method of self-propagating high-temperature synthesis (SHS). This method is characterized by a number of advantages: small time of technological process, possibility of obtaining final product in large volumes, low cost and energy consumption per unit of product, simplicity of used equipment and its environmental safety [6, 7].

$ZnS:Mn$ NC [8, 9], $ZnSe$ NC [10] and $ZnS_xSe_{1-x}:Mn$ NC [11] were obtained by this method before. Besides, individual bands of emission in photoluminescence (PL) spectra of $ZnS_xSe_{1-x}:Mn$ NC were investigated only for parameter value $x = 1$ [12]. In this work, we stated the study problem of PL individual bands behavior in emission spectra of $ZnS_xSe_{1-x}:Mn$ in the whole range of x values.

2. METHODOLOGY OF EXPERIMENT AND CHARACTERISTICS OF OBTAINED NC

Synthesis of NC of $ZnS_xSe_{1-x}:Mn$ solid solutions was performed according to methodology described in the

work [11]. $MnCl_2$ salt in an amount of 10^{-2} wt. % was added to the initial charge for alloying of ZnS_xSe_{1-x} NC by Mn^{2+} ions. As a result, NC with the mixed crystal structure were obtained. Their sizes were within the limits of 55 ± 5 nm according to the data of X-ray diffraction (XRD) analysis. The fraction of the hexagonal phase in the ZnS NC was $\sim (65 \pm 5)\%$, the cubic phase $\sim (35 \pm 5)\%$. When the parameter x decreased, the fraction of cubic phase in the $ZnS_xSe_{1-x}:Mn$ NC increased and hexagonal phase decreased. The fraction of hexagonal phase was $(30 \pm 5)\%$ and cubic one $(70 \pm 5)\%$ in the $ZnSe$ NC [11].

The parameters of the NC crystal lattice of ZnS_xSe_{1-x} solid solutions in the cubic phase were in the range from $a = 5.386$ Å (for $x = 1$) to $a = 5.633$ Å (for $x = 0$). These values turned out to be smaller than the parameters of the crystal lattice of single crystals of ZnS_xSe_{1-x} solid solutions, that are within $a = 5.4093$ Å (for $x = 1$) to $a = 5.6687$ Å (for $x = 0$) [13]. This, in turn, testifies the strain stresses specific to NC. Degrees of microdeformations ($\Delta a/a$) of the ZnS_xSe_{1-x} NC crystal lattice lie in the range from $5 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$. The minimum degree of microdeformations is specific to compounds with $x = 1$ and $x = 0.9$, and the maximum degree – to compounds with $x = 0.2$. The dislocation densities ranged from $5 \cdot 10^{10}$ to $1 \cdot 10^{12}$. The minimum dislocation density was specific to compounds with $x = 1$ and $x = 0$, and maximum – for compounds with $x = 0.1$ and $x = 0.2$. The obtained data allow to presume that there is a substantial transformation of crystal lattice of the ZnS_xSe_{1-x} NC in composition with $x = 0.2$ [11].

PL of NC was excited by emission of the diode ($\lambda_{ex} = 408$ nm). The PL spectra were registered according to standard methodology at room temperature; photoelectric multiplier – 136 was used as a radiation detector.

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3. RESULTS OF EXPERIMENT AND THEIR DISCUSSION

PL spectra of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC in the whole range of x values at room temperature were registered in the red-orange spectrum region. PL of the $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC in comparison to the spectra of bulk crystals were characterized with a greater half-width 10-15 nm ($E = 0.004-0.005$ eV) and were displaced in the short-wave region of spectrum 10-15 nm ($E = 0.005$ eV). The spectral maximum of emission was displacing monotonously in a short-wave area with the increase of x parameter (Fig. 1). Half-width of experimental PL spectra of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC is within the limits of values 92-114 nm (0.34-0.41 eV), besides PL spectra are characterized with asymmetric form (Fig. 2). It indicates that the experimental PL spectra are not elementary. The half-width of PL spectra

depending on the x parameter was characterized by complex dependence. In the range of values $x = 0-0.4$, the half-width of PL spectra decreases monotonously from a maximal value at $x = 0$, then it increases reaching the extremum at $x = 0.6-0.8$. In the range of $x = 0.8-1$, half-width of PL spectra diminishes. The obtained experimental facts (Fig. 1) indicate about possible appearance of new individual bands and also about the intensity redistribution of individual bands which compose the experimental PL spectra of the $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC. Besides, it should be noted that the considerable changes of half-width of PL experimental spectra take place in the range of values $x = 0-0.4$. As it was mentioned above, according to data of XRD analysis, there is a substantial crystal lattice rearrangement of the $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC in this range of x values.

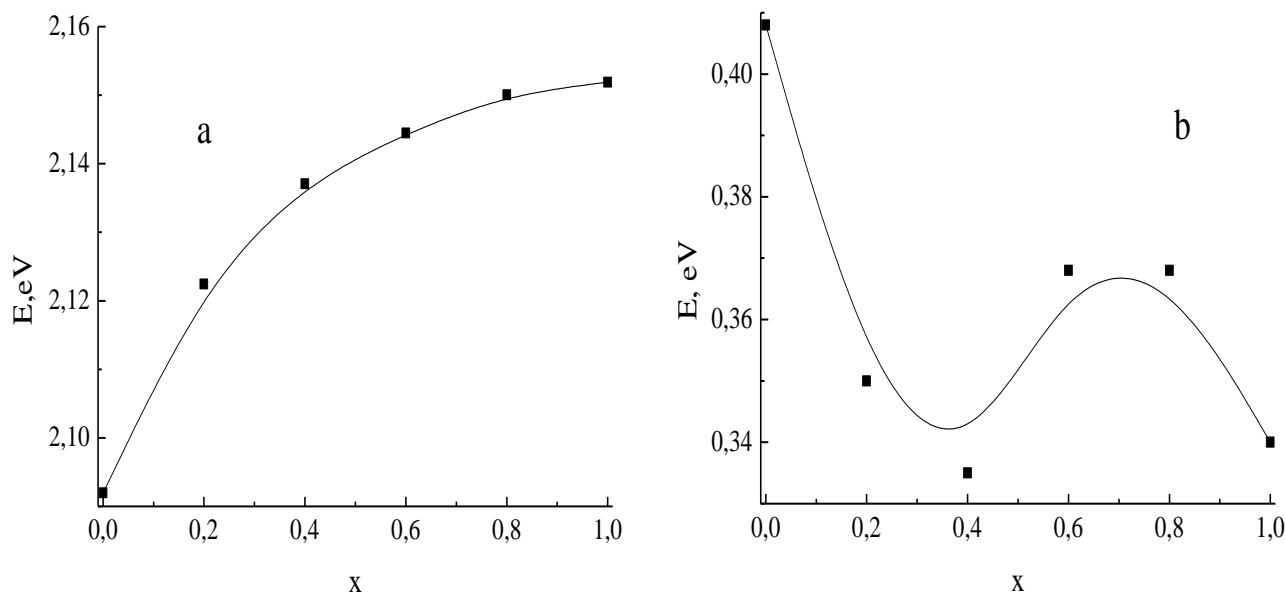


Fig. 1 – Smoothed dependences of maximum position (a) and half-width (b) of PL spectra in the $\text{ZnS}_x\text{Se}_{1-x}$ NC on the parameter x

The noise reaches 4-8 % in the experimental PL spectra of the $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC in a maximum of amplitude. The maximum amplitude of noise was observed for $\text{ZnS}_{0.2}\text{Se}_{0.8}\text{Mn}$ NC and the minimum one was observed for ZnS:Mn NC. The smoothing of spectra was conducted by Tikhonov method. The constants of smoothing were obtained based on methodology presented in the work [14]. The decomposition on individual bands was conducted by the method of derivative spectroscopy using the fourth, fifth and sixth derivatives. As the obtained values of parameters of individual bands, which are the constituents of the experimental PL spectrum, contain errors because of measuring's noise and calculation errors, we clarified the obtained results with least-squares method [14]. The obtained results of decomposition of PL spectra of the $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC on individual bands for some compositions are presented in Fig. 2.

In ZnS:Mn NC we detected six individual bands with $\lambda_{\max} = 639$ nm ($E = 1.939$ eV) – 1, $\lambda_{\max} = 616$ nm ($E = 2.012$ eV) – 2, $\lambda_{\max} = 600$ nm ($E = 2.066$ eV) – 3, $\lambda_{\max} = 580.5$ nm ($E = 2.135$ eV) – 4, $\lambda_{\max} = 555$ nm ($E = 2.233$ eV) – 5, $\lambda_{\max} = 530.5$ nm ($E = 2.337$ eV). The obtained result agrees well with the data of determina-

tion of position of individual bands in ZnS:Mn monocrystals and in ZnS:Mn NC [12, 15] by Alentsev-Fock method. The detected PL bands are in all compounds of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC. Wherein the position of a maximum of individual bands depending on the value of x parameter displaces within the limits of 30 nm (0.08 eV) and spectrum half-width changes within the limits of 8 nm (0.02 eV). So, in ZnSe:Mn NC, these bands of emission are characterized by the following parameters: $\lambda_{\max} = 675.5$ nm ($E = 1.835$ eV) – 1*, $\lambda_{\max} = 642.5$ nm ($E = 1.929$ eV) – 2, $\lambda_{\max} = 613$ nm ($E = 2.022$ eV) – 3, $\lambda_{\max} = 583.5$ nm ($E = 2.124$ eV) – 4, $\lambda_{\max} = 550$ nm ($E = 2.255$ eV) – 5, $\lambda_{\max} = 528.5$ nm ($E = 2.345$ eV) – 6. The results of the detection of individual PL bands in ZnSe:Mn NC were compared with the results of the work [16], where the individual PL bands were detected in ZnSe:Mn monocrystals by Alentsev-Fock method (Fig. 3). Six elementary bands were also detected in these crystals: $\lambda_{\max} = 679$ nm ($E = 1.825$ eV) – 1', $\lambda_{\max} = 644$ nm ($E = 1.925$ eV) – 2', $\lambda_{\max} = 615$ nm ($E = 2.015$ eV) – 3', $\lambda_{\max} = 587.5$ nm ($E = 2.11$ eV) – 4', $\lambda_{\max} = 551$ nm ($E = 2.25$ eV) – 5', $\lambda_{\max} = 533$ nm ($E = 2.325$ eV) – 6'.

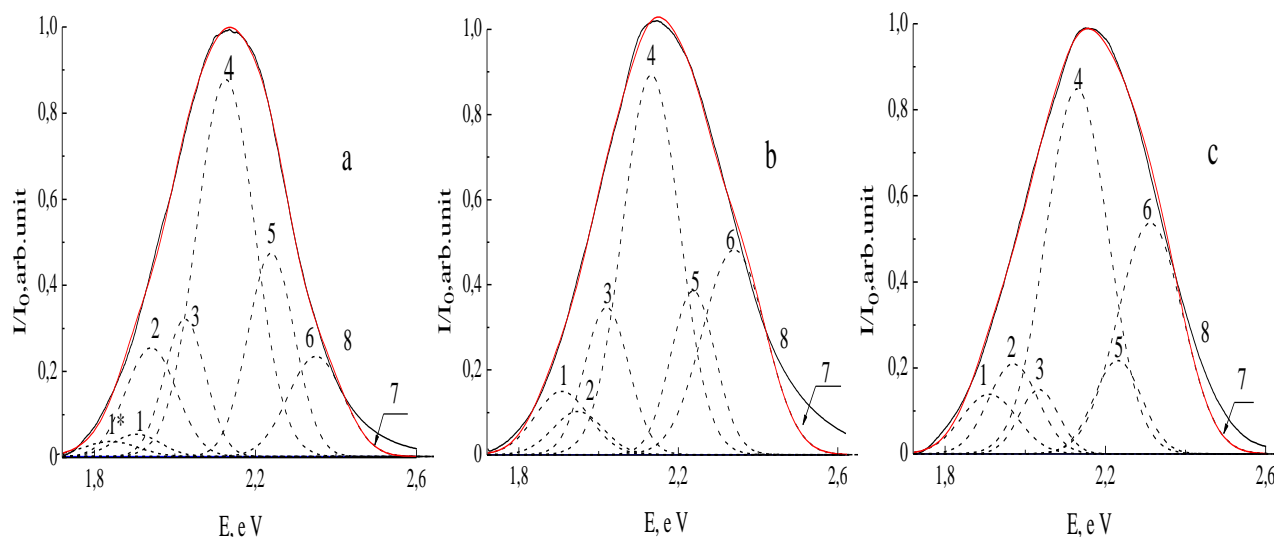


Fig. 2 – PL spectra of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC for the values of parameter $x = 0.4$ (a), 0.6 (b), 0.8 (c): individual bands of PL with $\lambda_{\text{max}} = 650.5$ nm ($E = 1.905$ eV) – 1, $\lambda_{\text{max}} = 638.5$ nm ($E = 1.941$ eV) – 2, $\lambda_{\text{max}} = 612$ nm ($E = 2.025$ eV) – 3, $\lambda_{\text{max}} = 583$ nm ($E = 2.126$ eV) – 4, $\lambda_{\text{max}} = 553.5$ nm ($E = 2.239$ eV) – 5, $\lambda_{\text{max}} = 525$ nm ($E = 2.36$ eV) – 6 for compounds with $x = 1$; 7 – an integral PL spectrum (sum of individual bands), 8 – an experimental PL spectrum, 1* – individual PL band $\lambda_{\text{max}} = 673$ nm ($E = 1.841$ eV) observed in compounds with $x = 0.4$, $T = 300$ K

As seen from comparison of maxima position of individual bands 1'-6' and 1*-6', they correlate well, differing from each other by position of maxima of individual bands displaced to the short-wave area no more than 5 nm (0.02 eV). It should be noted that the half-widths of spectra in NC exceed the half-widths of corresponding bands in monocrystals on average of 10-20 nm (0.04-0.06 eV). Such distinction can be conditioned by the microdeformations of crystal lattice of ZnSe:Mn NC.

The sum of all detected individual bands, that is the integral PL spectrum, is presented by the curve 7 in Fig. 2 and Fig. 3. Almost the complete coincidence of integral PL spectrum with the experimental PL spectrum of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC (curve 8) testifies the correct decomposition of experimental spectrum on individual bands. We observed certain deviation between curves 7 and 8 on the edges of PL spectra, where the ratio noise/signal increases sharply.

In works [8, 12], the emission of individual bands 1-5 in monocrystals and ZnS:Mn NC was related to Mn^{2+} ions, which were in different local environment. The position of maxima of individual bands of emission 4-5 in $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC almost does not depend on the value of x parameter, maxima of bands 2-3 are monotonously displacing to the short-wave region with the increase of x parameter (Fig. 4). It should be noted that individual band 1 is traced in compounds with the value of $x = 0.4 \div 1$. A maximum of emission changes unevenly from $\lambda_{\text{max}} = 650.5$ nm ($E = 1.905$ eV) to $\lambda_{\text{max}} = 673$ nm ($E = 1.841$ eV) at less values of x . A band with $\lambda_{\text{max}} = 675.5$ nm ($E = 1.835$ eV) is stabilized in compounds with the value of $x = 0 \div 0.2$. We marked individual band 1 as band 1* after hopping changing the position of the emission maximum in compound with value $x = 0 \div 0.4$.

As it was mentioned above [12], this band of emission can be related to Mn^{2+} ions in phase $\alpha\text{-MnS}$. Besides, according to research data of EPR spectra of Mn^{2+} ions in $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC [11] it was shown that Mn^{2+} ions

are not in the mixed environment in NC with the parameter $x = 0.2 \div 0.9$. They are in environment of sulphur ions, although XRD analysis data testify the presence of triple connections in this range of x values. Crystal structure of $\text{ZnS}_x\text{Se}_{1-x}$ NC is characterized by the maximum degree of microdeformations and dislocation density in compounds with $x < 0.2$. According to EPR data, local environment of Mn^{2+} ions changes unevenly exactly in these compounds – now they are surrounded by selenium ions. The constant of ultrafine splitting in EPR spectra of Mn^{2+} ions diminishes unevenly from $A = 6.88 \div 6.91$ mT to $A = 6.55$ mT. A similar result was observed in $\text{ZnS}_x\text{Se}_{1-x}$ bulk crystals. It is this circumstance that can explain the hopping change of maximum position of individual band 1 and its transformation into the individual band of emission 1* (Fig. 4), and also hopping change of half-width of experimental PL spectra in $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC compounds with the parameter $x \sim 0.2$ (Fig. 1).

The behavior of the individual band of emission 6 depending on the value of x parameter also deserves attention. By the appearance, this band is not elementary either. This individual band of emission can be associated with the isolated vacancies of sulphur or uncontrolled copper admixtures [17]. Besides, it should be noted that obtaining of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC by SHS method is accompanied by the formation of anionic vacancies (S, Se) in connection with high volatility of anionic components. Maybe therefore the maximum position of emission band depending on x parameter does not have a monotonous character, but is a hopping one.

4. CONCLUSIONS

$\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC spectra obtained by SHS method were investigated. PL spectra of these NC in the whole range of x values were concentrated in the visible spectral region at room temperature. The half-width of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ PL spectra was maximal for compound

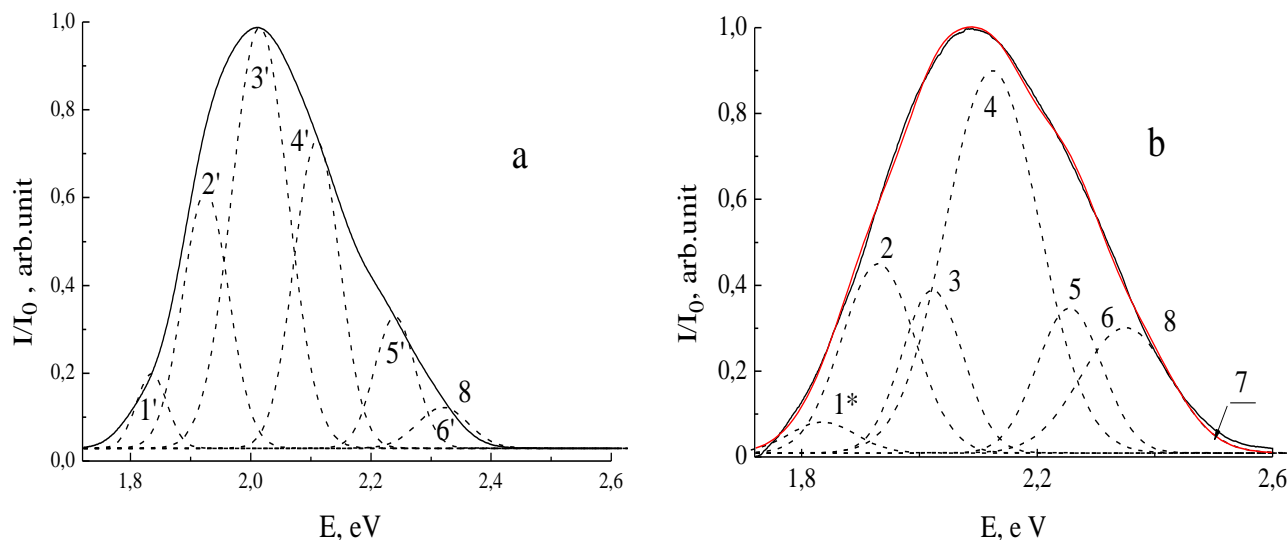


Fig. 3 – PL spectrum of ZnSe:Mn monocrystals (a) and detected individual bands in it by Alentsev-Fock method: $\lambda_{\max} = 679$ nm ($E = 1.825$ eV) – 1', $\lambda_{\max} = 644$ nm ($E = 1.925$ eV) – 2', $\lambda_{\max} = 613$ nm ($E = 2.015$ eV) – 3', $\lambda_{\max} = 587.5$ nm ($E = 2.11$ eV) – 4', $\lambda_{\max} = 551$ nm ($E = 2.25$ eV) – 5', $\lambda_{\max} = 533$ nm ($E = 2.325$ eV) – 6' according to data of the work [16]; PL spectrum of ZnSe:Mn NC (b) and detected PL individual bands in it by derivative spectroscopy method with $\lambda_{\max} = 675.5$ nm ($E = 1.835$ eV) – 1*, $\lambda_{\max} = 642.5$ nm ($E = 1.929$ eV) – 2, $\lambda_{\max} = 613$ nm ($E = 2.022$ eV) – 3, $\lambda_{\max} = 583.5$ nm ($E = 2.124$ eV) – 4, $\lambda_{\max} = 550$ nm ($E = 2.255$ eV) – 5, $\lambda_{\max} = 528.5$ nm ($E = 2.345$ eV) – 6; 7 – an integral PL spectrum (sum of individual bands), 8 – an experimental PL spectrum, $T = 300$ K

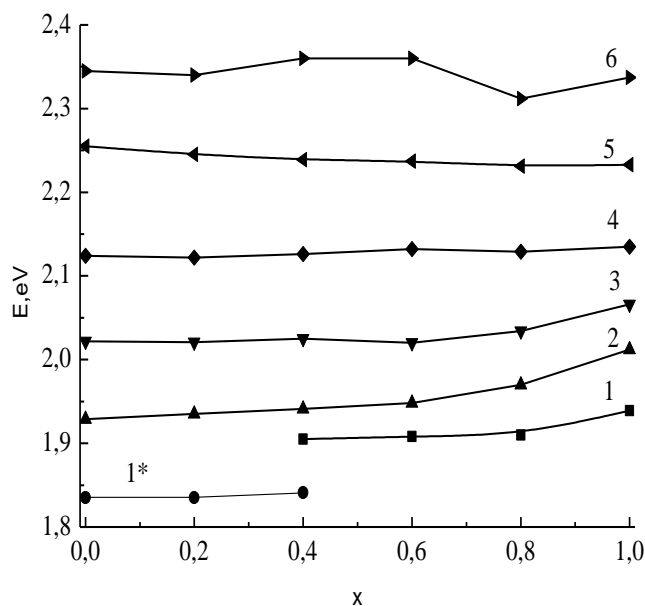


Fig. 4 – Dependence of maxima position of elementary PL bands in $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC depending on x parameter: $\lambda_{\max} = 675.5$ nm ($E = 1.835$ eV) – 1*, $\lambda_{\max} = 642.5$ nm ($E = 1.929$ eV) – 2, $\lambda_{\max} = 613$ nm ($E = 2.022$ eV) – 3, $\lambda_{\max} = 583.5$ nm ($E = 2.124$ eV) – 4, $\lambda_{\max} = 550$ nm ($E = 2.255$ eV) – 5, $\lambda_{\max} = 528.5$ nm ($E = 2.345$ eV) – 6 for composition with $x = 0$, $\lambda_{\max} = 639$ nm ($E = 1.939$ eV) – 1 for compound with $x = 0.4$, $T = 300$ K

with $x = 0$ and minimal for compound with $x = 0.4$ and $x = 1$. Six individual bands were detected by the fourth to sixth order derivative spectroscopy method in the PL spectra of $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC. For compound with $x = 1$, these bands are characterized by such maxima of emission: $\lambda_{\max} = 639$ nm (1), 616 nm (2), 600 nm (3), 580.5 nm (4), 555 nm (5), 530.5 nm (6), respectively. The position change of maxima of individual emission bands in $\text{ZnS}_x\text{Se}_{1-x}\text{Mn}$ NC was analyzed depending on the value of x parameter. The features of the behavior of individual

emission bands 1 and 6 are established. Band 1 changes its position unevenly in the range of values $x = 0.2 \div 0.4$, which is related to hopping change of local environments of Mn^{2+} ions in MnS phase. Probably, band 6 represents a superposition of a few elementary bands. Possibly, this band of emission is connected with sulphur vacancies or uncontrolled copper admixtures. Therefore, the maximum position of emission of band 6 depending on x parameter does not have a monotonous character, but is a hopping one.

REFERENCES

1. P.F. Smet, I. Moreels, Z. Hens, D. Poelman, *Materials* **3**, 4 (2010).
2. T.P. Tang, W.L. Wang, S.F. Wang, *J. Alloy. Compd.* **488**, 1 (2009).
3. C.V. Gopi, M. Venkata-Haritha, S.K. Kim, H.J. Kim, *Nano-scale* **7**, 29 (2015).
4. H. Yang, S. Santra, P.H. Holloway, *J. Nanosci. Nanotech.* **5**, 9 (2005).
5. H.K. Sadekar, A.V. Ghule, R. Sharma *J. Alloy. Compd.* **509**, 18 (2011).
6. E.A. Levashov, A.S. Mukasyan, A.S. Rogachev, D.V. Shtansky, *Int. Mater. Rev.* **62**, 4 (2017).
7. A.A. Borisov, L.T. De Luca, A.G. Merzhanov, *Self-propagating high-temperature synthesis of materials*. (Vol. 5. CRC Press: 2002).
8. Y.Y. Bacherikov, A.V. Gilchuk, A.G. Zhuk, R.V. Kurichka, O.B. Okhrimenko, S.E. Zelensky, S.A. Kravchenko, *J. Lumin.* **194**, 8 (2018).
9. C.W. Won, H.H. Nersisyan, H.I. Won, D.Y. Jeon, J.Y. Han, *J. Lumin.* **130**, 6 (2010).
10. G. Liu, X. Yuan, J. Li, K. Chen, Y. Li, L. Li, *Mater. Design* **97**, 33 (2016).
11. A.V. Kovalenko, Ye.G. Plakhtii, O.V. Khmelenko, *Functional Mater.* **25**, 4 (2018).
12. Y. Bacherikov, A.G. Zhuk, O.B. Okhrimenko, D.L. Kardashov, S.V. Kozitskiy, *Semiconductor Physics Quantum Electronics & Optoelectronics* **18**, 2 (2015).
13. T. Taguchi, Yo. Kawakami, Yo. Yamada, *Physica B: Condensed Matter* **191**, 23 (1993).
14. S.M. Vovk, *Radio Electronics, Computer Science, Control* **3**, 44 (2017).
15. A.V. Kovalenko, E.G. Plakhtiy, S.M. Vovk, *Ukr. J. Phys. Opt.* **19**, 133 (2018).
16. A.A. Andreev, N.D. Borisenko, A.V. Kovalenko, *Inorg. Mater.* **19**, 3 (1983).
17. S.S. Kumar, M.A. Khadar, K.G.M. Nair, *J. Lumin.* **131**, 786 (2011).

Дослідження спектрів фотолюмінесценції нанокристалів $ZnS_xSe_{1-x}Mn$, отриманих методом самопоширюваного високотемпературного синтезу

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Досліджено спектри фотолюмінесценції нанокристалів твердих розчинів $ZnS_xSe_{1-x}Mn$, отриманих методом самопоширюваного високотемпературного синтезу. При кімнатній температурі ці нанокристали при всіх значеннях параметра x люмінесціювали у видимій області спектра. Методом похідної спектроскопії четвертого-шостого порядків у спектрах фотолюмінесценції нанокристалів $ZnS_xSe_{1-x}Mn$ виявлено шість індивідуальних смуг. Для складу з $x = 1$ ці смуги характеризуються такими максимумами випромінювання: $\lambda_{max} = 639$ нм (1), 616 нм (2), 600 нм (3), 580.5 нм (4), 555 нм (5), 530.5 нм (6) відповідно. Смуги 1-5, ймовірно, пов'язані з іонами Mn^{2+} в різному локальному оточенні. Положення максимумів випромінювання індивідуальних смуг 4-5 практично не залежить від значення параметра x , максимуми смуг 2-3 монотонно зміщуються в короткохвильову область зі збільшенням параметра x . Максимум випромінювання смуги 1 стрибкоподібно змінює своє положення в діапазоні значень $x = 0.2 \div 0.4$, що пов'язано зі стрибкоподібною зміною локального оточення іонів Mn^{2+} у фазі MnS . Смуга випромінювання 6, напевно, не є елементарною, тому положення її максимуму випромінювання в залежності від значення параметра x носить стрибкоподібний характер.

Ключові слова: Нанокристали ZnS_xSe_{1-x} , Самопоширюваний високотемпературний синтез, Спектри фотолюмінесценції, Метод похідної спектроскопії, Індивідуальні смуги випромінювання, Дефекти структури, Кристалічна ґратка.