

Luminescent properties of $\text{ZnS}_x\text{Se}_{(1-x)}$ mixed crystals obtained by solid-phase synthesis and melt-growing

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Received September 20, 2017

The luminescence characteristics of $\text{ZnS}_x\text{Se}_{(1-x)}$ mixed crystals (MC) obtained by solid-phase synthesis and melt-growing were studied. In X-ray luminescence spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ powdered MC synthesized from ZnS and ZnSe powders, where $x = 0.90$ to 0.99 , a non-elementary band with $\lambda_{max} \sim 520$ nm (I_1) was observed, but for $\text{ZnS}_x\text{Se}_{(1-x)}$ with low concentrations of ZnS ($x = 0.05$) the luminescence band with $\lambda_{max} = 600\text{--}630$ nm (I_2) was a dominate. In X-ray luminescence spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC ($x = 0.05$ to 0.3) obtained by the melt growth only I_2 luminescence band with shifted maximum from 610 nm to 590 nm at sulfur concentration increasing was observed. It is shown that for the composition of $\text{ZnS}_{0.15}\text{Se}_{0.85}$ MC annealed in zinc vapor the light yield of X-ray luminescence is 1.6 times higher than in the commercial ZnSe(Te) crystals. In consideration of this fact it might be supposed, that this MC can find application in scintillation detectors of X-ray and low-energy gamma radiation.

Keywords: $\text{ZnS}_x\text{Se}_{(1-x)}$ mixed crystals, solid-phase synthesis, luminescence, scintillator, radiation detector.

Исследованы люминесцентные характеристики смешанных кристаллов (СК) $\text{ZnS}_x\text{Se}_{(1-x)}$, полученных твердофазным синтезом и выращиванием из расплава. В спектре рентгенолюминесценции порошкообразных СК $\text{ZnS}_x\text{Se}_{(1-x)}$, полученных твердофазным синтезом из порошков ZnS и ZnSe при $x = 0,90\text{--}0,99$, наблюдалась неэлементарная полоса с $\lambda_{max} \sim 520$ нм (I_1), однако, при малых концентрациях ZnS ($x = 0,05$) доминирует полоса люминесценции с $\lambda_{max} = 600\text{--}630$ нм (I_2). Для кристаллических СК $\text{ZnS}_x\text{Se}_{(1-x)}$, полученных выращиванием из расплава, для интервала значений $x = 0,05\text{--}0,3$ наблюдалась исключительно полоса I_2 с максимумом, сдвигающимся с 610 нм до 590 нм по мере увеличения концентрации серы в СК. Показано, что в смешанных кристаллах состава $\text{ZnS}_{0,15}\text{Se}_{0,85}$, отожженных в парах цинка, световой выход рентгенолюминесценции в 1,6 раза выше, чем у коммерческих кристаллов ZnSe(Te). Учитывая этот факт, можно предположить, что данный СК может найти применение в сцинтилляционных детекторах рентгеновского и мягкого гамма-излучения.

Люмінесцентні властивості змішаних кристалів $ZnS_xSe_{(1-x)}$, отриманих твердофазним синтезом і вирощуванням з розплаву. С.М.Галкін, О.Г.Трубаєва, О.І.Лалаянц, І.А.Рибалка, О.А.Шевченко, К.Ю.Брильова, Л.О.Голінка-Безшійко.

Досліджено люмінесцентні характеристики змішаних кристалів (ЗК) $ZnS_xSe_{(1-x)}$, що отримані твердофазним синтезом і вирощуванням з розплаву. У спектрі рентгенолюмінесценції порошкоподібних ЗК $ZnS_xSe_{(1-x)}$, що отримані твердофазним синтезом з порошків ZnS і $ZnSe$ при $x = 0,90...0,99$, спостерігалася неелементарна смуга з $\lambda_{max} \sim 520$ нм (I_1), однак при малих концентраціях ZnS ($x = 0,05$) домінує смуга люмінесценції з $\lambda_{max} = 600-630$ нм (I_2). Для кристалічних ЗК $ZnS_xSe_{(1-x)}$, що отримані вирощуванням з розплаву, для інтервалу значень $x = 0,05...0,3$ у спектрі рентгенолюмінесценції спостерігалася виключно смуга I_2 з максимумом, що зсувається з 610 нм до 590 нм в залежності від збільшення концентрації сірки у кристалі. Показано, що в змішаних кристалах складу $ZnS_{0,15}Se_{0,85}$, відпалених у парах цинку, світловий вихід рентгенолюмінесценції у 1,6 рази вищий, ніж у комерційних кристалів $ZnSe(Te)$. З огляду на це можна припустити, що даний ЗК може знайти застосування у сцинтиляційних детекторах рентгенівського і м'якого гамма-випромінювання.

1. Introduction

Today in material science much attention is given for investigation of the properties of phosphors based on mixed crystals (MC) of $ZnS_xSe_{(1-x)}$. The possible reasons of such behavior is: presence of a continuous series of solid solutions throughout the composition range [1]; a variety of production methods (solid phase synthesis, gas phase growth and melt growth); possibility of varying optical and electrical characteristics due to change in the band gap from 2.7 eV ($ZnSe$) to 3.7 eV (ZnS) [2].

The basic components of $ZnS_xSe_{(1-x)}$ — $ZnSe$ and ZnS compounds — have stable cubic structure of the sphalerite at standard conditions and metastable hexagonal wurtzite structure at temperature above 1300 K or at room temperature in the case of doping by elements that distort lattice [3, 4]. The lattice parameters for $ZnSe$ and ZnS sphalerite structures are 0.56687 nm and 0.54093 nm, respectively. Therefore the formation of solid solutions over whole range of compositions is happened [5]. It makes possible to obtain the mixed crystals with a band gap in the interval from 2.7 to 3.7 eV at $T = 300$ K.

The optical, electrical, and structural characteristics of $ZnS_xSe_{(1-x)}$ MC depending from the compositions and the conditions of production were investigated in [1, 2, 6–10]. The results of studies of photo-, radio-, and cathode-luminescence are presented in [11–13]. The main results of above noted studies was investigations of conditions for defect formation the effect of oxygen, copper and other impurities on the luminescence of $ZnS_xSe_{(1-x)}$ crystals. Energy levels of possible defects and mechanisms of radiative processes are given. Unfortunately, these papers do not pay attention to the

conditions for obtaining and optimizing of the parameters of $ZnS_xSe_{(1-x)}$ MC suitable for use in the scintillation X-ray detectors.

It is known [14–16] that crystals of $ZnSe$ doped with tellurium $ZnSe(Te)$ or aluminum $ZnSe(Al,O)$ have found application in the detectors of ionizing radiation. Their application as high-efficiency scintillators began after a detailed analysis of the physicochemical regularities of luminescent defect complexes formation and the development of technological conditions of crystal production with the specified scintillation properties.

The purpose of this work was to study of properties of $ZnS_xSe_{(1-x)}$ MC with wide range x value, obtained by solid-phase synthesis and melt growth, to determine the conditions for obtaining of $ZnS_xSe_{(1-x)}$ with characteristics close to or superior the parameters of $ZnSe(Te)$ and $ZnSe(Al,O)$ scintillators.

2. Experimental

Solid-phase synthesis of $ZnS_xSe_{(1-x)}$ samples was carried out by sintering a mixture of ZnS and $ZnSe$ powders with a particle size in the range from 5 to 50 μm . The sintering of the powders was carried out in a horizontal furnace in a quartz reactor under an atmosphere of hydrogen. The sintering conditions ($T = 1200$ K, $t = 7$ h) were chosen subject to the granule size and the calculated rate of solid-phase reaction.

$ZnS_xSe_{(1-x)}$ crystals were grown from pre-sintered charge with the values of $x = 0.05$; 0.1; 0.15; 0.2 and 0.3. Before growing, the raw material was annealed in a quartz crucible at 1170 K during 5 h in hydrogen atmosphere for removing of oxygen impurities. The crystal growth was carried out by the Bridgman-Stockbarger method in the graphite crucibles with a diameter of

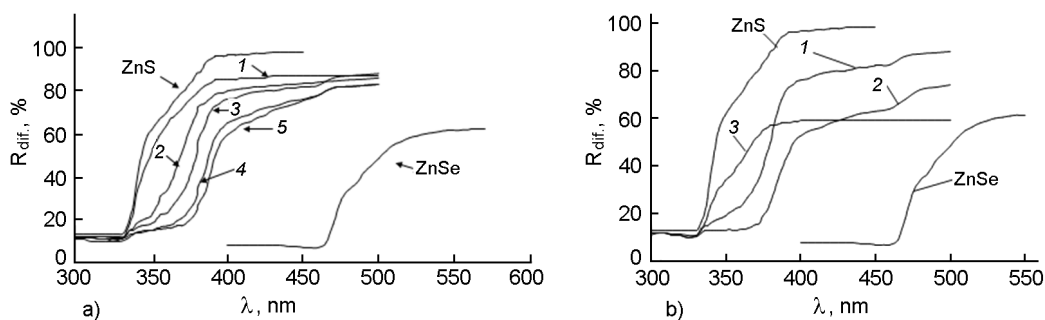


Fig. 1(a). The diffuse reflection spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ powders annealed in hydrogen atmosphere with different values of x in the samples: 1 — $\text{ZnS}_{0.99}\text{Se}_{0.01}$, 2 — $\text{ZnS}_{0.97}\text{Se}_{0.03}$, 3 — $\text{ZnS}_{0.95}\text{Se}_{0.05}$, 4 — $\text{ZnS}_{0.94}\text{Se}_{0.06}$, 5 — $\text{ZnS}_{0.9}\text{Se}_{0.1}$.

Fig. 1(b). The diffuse reflection spectra before and after additional thermal annealing of $\text{ZnS}_{0.94}\text{Se}_{0.06}$ sample: 1 — before annealing; 2 — annealing in Ar (18 h); 3 — annealing in Ar (18 h), and then in Zn (72 h).

20 mm under inert gas of Ar at a pressure $P = 10^7\text{--}10^9$ Pa; the crystallization rate was 7 mm/h; the heater temperature was from 1870 to 2000 K depending from the composition of the initial raw materials.

The annealing of the test samples was carried out in hydrogen atmosphere during 3 h at $T = 1170$ K, in argon atmosphere during 18 h at $T = 1170$ K and zinc vapor during 48 h at $T = 1230$ K, $P = 5 \cdot 10^7$ Pa. The composition of the main components of the samples was measured using the inductively coupled plasma optical emission spectrometry (ICP-OES). The sensitivity of the method to S and Se is about 1 ppm (1 mg/L).

The phase composition of the powder samples was analyzed by measuring the diffuse reflectance spectra (SF-4 spectrophotometer with PDO-1 attachment).

X-ray luminescence spectra were measured using the KSVU-23 spectrophotometric complex. The X-ray source was the X-ray apparatus REIS-I (Cu, $U = 10\text{--}45$ kV). Zinc selenide crystals doped with aluminum and tellurium were as comparison samples.

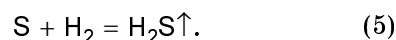
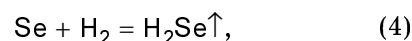
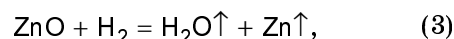
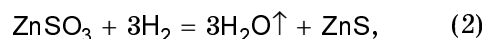
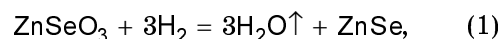
Optical transmission in the visible spectral range was measured with Shimadzu UV mini-1240 single-beam spectrophotometer.

Relative light yield measurements were carried out on Smiths Heimann AMS-1 apparatus with X-ray emitter voltage of 140 kV (W-anode) and Si-photodetector. After mathematical processing of the photodetector signal, the data of the signal amplitude and afterglow at the predetermined time intervals were received.

3. Results and discussion

ZnS and ZnSe powders with the particle size of 5–50 μm and purity class of 5N were

used for solid-phase synthesis of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC. At the sintering of ZnS and ZnSe in a reducing hydrogen atmosphere powders were obtained homogeneous in color. The hydrogen in the sintering ampoule was used due to the need of reduction of oxidized surface layers of the chalcogenides. Zinc sulphide and selenide in a fine-dispersed state are oxidized fast in atmospheric oxygen. As a result of ZnS and ZnSe oxidation on the powder surface there are ZnSO_3 , ZnSeO_3 , ZnO and also sulfur and selenium, which can be reduced at high temperatures according to the reactions:



Completeness of the solid-phase sintering reaction of ZnS and ZnSe powders after annealing was controlled by measurement data of diffuse reflectance spectra of the samples. This method was used due to the fact that for solid solutions based on A^2B^6 (including $\text{ZnS}_x\text{Se}_{(1-x)}$) it was characteristic the variation of band gap width (E_g) from the composition. The value of band gap width can be estimated from the diffuse reflection spectra by approximation the fundamental absorption band edge on the energy axis. The reaction completeness was determined according to the shape of the diffuse reflec-

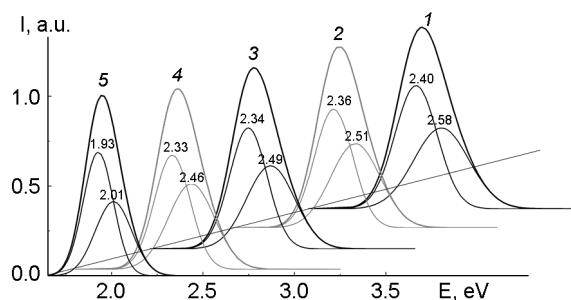


Fig. 2. Normalized X-ray luminescence spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ powders with decomposition into Gaussians. The numbers of the curves correspond to the compositions: 1 — $\text{ZnS}_{<0.99}\text{Se}_{0.01}$, 2 — $\text{ZnS}_{0.97}\text{Se}_{0.03}$, 3 — $\text{ZnS}_{0.95}\text{Se}_{0.05}$, 4 — $\text{ZnS}_{0.9}\text{Se}_{0.1}$, 5 — $\text{ZnS}_{0.05}\text{Se}_{0.95}$.

tion curve, i.e. the presence of bends due to the summation of absorption bands of several compounds in the mixture, which more pronounced in the short-wave region of diffuse reflectance spectra.

Analysis of the diffuse reflection spectrum of $\text{ZnS}_{0.95}\text{Se}_{0.05}$ sample annealed in hydrogen atmosphere (Fig. 1a, curve 3) show presence of two bends specific for ZnSe (470 nm) and $\text{ZnS}_{0.95}\text{Se}_{0.05}$, which indicates the incomplete of the solid-phase reaction and presence of two phases in the test sample. The additional annealing of $\text{ZnS}_{0.94}\text{Se}_{0.06}$ MC was carried out in argon atmosphere at the temperature of 1170 K and then in zinc vapor at $T = 1230$ K for determination of the possibility of complete solid-phase synthesis. Fig. 1b shows the diffuse reflection spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ samples 1 — before annealing; 2 — annealing in Ar (18 h); 3 — annealing in Ar (18 h), and then in Zn (72 h). According to diffuse refractions spectra (Fig. 1b) we can conclude that annealing of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC in Ar atmosphere does not lead to formation of the homogeneous composition (ZnSe phase was present), as evidenced by the bend at 470 nm (Fig. 1b, curve 2). Further annealing in zinc vapor leads to the formation of the monophasic composition. It is confirmed by the spectrum (Fig. 1b, curve 3) in which there are no bends at the edge of the diffuse reflection spectrum in 330–380 nm region but there is increase of absorption in 380–470 nm region, which indicates the formation of optically active point defects.

It is known that ZnS compound is characterized by luminescence bands with maxima at 460 nm (2.70 eV) and 520 nm (2.38 eV), which are associated with the presence of the isoelectronic impurity of

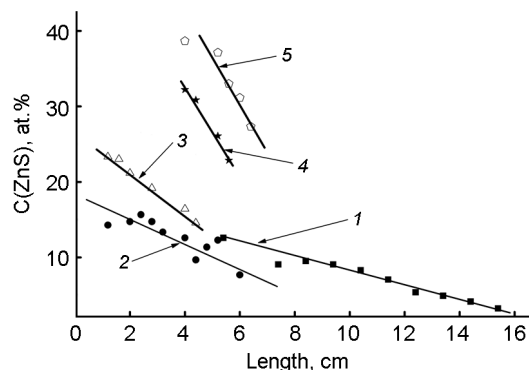


Fig. 3. Dependences of sulfur concentration on the boule length of $\text{ZnS}_x\text{Se}_{(1-x)}$ crystals: 1 — $\text{ZnS}_{0.05}\text{Se}_{0.95}$, 2 — $\text{ZnS}_{0.1}\text{Se}_{0.9}$, 3 — $\text{ZnS}_{0.15}\text{Se}_{0.85}$, 4 — $\text{ZnS}_{0.25}\text{Se}_{0.75}$, 5 — $\text{ZnS}_{0.3}\text{Se}_{0.7}$.

oxygen and traces of copper in the crystals [17, 18]. Figure 2 shows the normalized X-ray luminescence spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ powders, where $x = 0.05 \div 0.99$, with decomposition into Gaussians with maxima responsible for ZnS luminescence. The ratios of the Gaussian amplitudes of $\text{ZnS}_x\text{Se}_{(1-x)}$ powdered MC were practically unchanged for different compositions of MC (Fig. 2: $x = 0.99$ (curve 1), $x = 0.97$ (curve 2), $x = 0.95$ (curve 3), $x = 0.90$ (curve 4) and $x = 0.05$ (curve 5)), but the energy positions of the maxima of luminescence bands have shifted to higher energies with increasing sulfur content. Such behavior can be attributed to an increase in the band gap width due to increase of sulfur concentration. Note that the luminescence spectrum of $\text{ZnS}_{0.05}\text{Se}_{0.95}$ sample was decomposed into Gaussians bands with maxima at 616 nm (2.01 eV) and 642 nm (1.93 eV) (Fig. 2, curve 5) which correspond to the donor-acceptor luminescence bands of ZnSe crystals [5]. In X-ray luminescence spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ powdered obtained by solid-phase synthesis of ZnS and ZnSe, where $x = 0.90 \dots 0.99$, an intense non-elementary band with $\lambda_{max} \sim 520$ nm (I_1) is observed, but at the low ZnS concentrations ($x = 0.05$) the luminescence band dominates with $\lambda_{max} = 600\text{--}630$ nm (I_2).

In according to noted data we can conclude that the applied technique of solid-phase synthesis of $\text{ZnS}_x\text{Se}_{(1-x)}$ powdered MC does not make it possible to obtain homogeneous samples in the phase composition, as evidenced by the data of diffuse reflection and X-ray luminescence spectra. In the future, we plan to continue the experiments of $\text{ZnS}_x\text{Se}_{(1-x)}$ powdered MC obtaining by

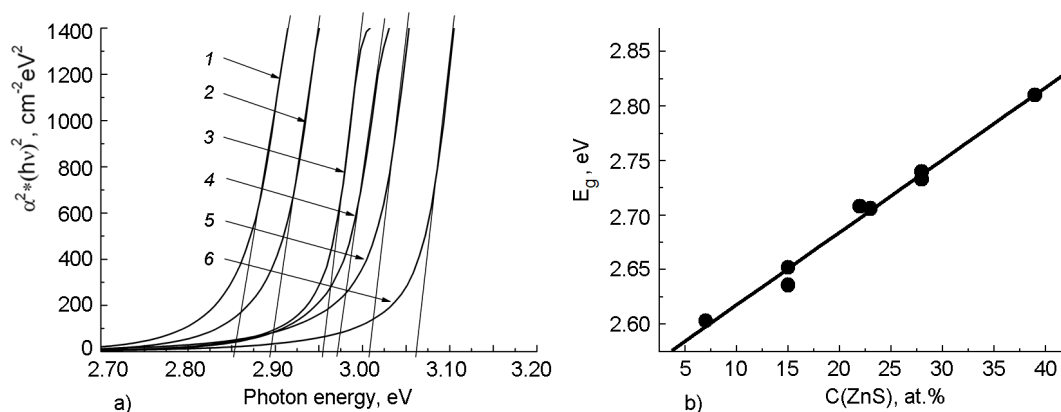


Fig. 4(a). Extrapolation of functions of the dependence of $\alpha^2 (hv)^2$ on $h\nu$ for different compositions of $ZnS_xSe_{(1-x)}$ crystals to the value $\alpha = 0$. The numbers of the curves correspond to the initial compositions of the raw materials for crystal growth: 1 — $ZnS_{0.05}Se_{0.95}$, 2 — $ZnS_{0.1}Se_{0.9}$, 3 — $ZnS_{0.15}Se_{0.85}$, 4 — $ZnS_{0.2}Se_{0.8}$, 5 — $ZnS_{0.25}Se_{0.75}$, 6 — $ZnS_{0.3}Se_{0.7}$.

Fig. 4(b). The change of E_g in $ZnS_xSe_{(1-x)}$ MC calculated for the test compositions from the data in Fig. 4(a).

solid-phase synthesis with use of a fluxing agent for acceleration of the chemical reaction.

We have studied the possibility of obtaining of $ZnS_xSe_{(1-x)}$ mixed crystals with homogeneous phase composition by another method. Therefore, $ZnS_xSe_{(1-x)}$ MC were grown from the melt by the Bridgman-Stockbarger method. The mixed crystal growth with a high concentration of sulfur from the melt is difficult due to the high melting point of MC (about 2050 K) and, in addition, sulfur has a high chemical activity relative to carbon (crucible material). Therefore, the x range was chosen with predominance of selenium content, i.e. $x = 0.05$ to 0.3. Six $ZnS_xSe_{(1-x)}$ crystals were grown from the raw materials which were previously prepared as mixtures of ZnS and ZnSe powders with the next compositions: 1 — $ZnS_{0.05}Se_{0.95}$, 2 — $ZnS_{0.1}Se_{0.9}$, 3 — $ZnS_{0.15}Se_{0.85}$, 4 — $ZnS_{0.2}Se_{0.8}$, 5 — $ZnS_{0.25}Se_{0.75}$, 6 — $ZnS_{0.3}Se_{0.7}$. The obtained crystals were cut into washers for the composition analysis and measurement of optical properties.

Fig. 3 shows the dependence of sulfur concentration from $ZnS_xSe_{(1-x)}$ crystal length. As we can see from Fig. 3, the concentration of zinc sulphide decreases from the nose to the tail part of crystalline boules. This is due to the segregation process and the chemical interaction of sulfur with the graphite of the growth crucible and the entrainment of sulfur from the melt in the form of gaseous carbon disulfide [17, 19].

Optical band gap width in $ZnS_xSe_{(1-x)}$ MC was determined according to the Tautz method [20] using the optical transmission spectra (Fig. 4a). For direct-gap semiconductors, particularly $ZnS_xSe_{(1-x)}$, value of E_g was calculated according to the next expression:

$$\alpha h\nu = A_0 \cdot (h\nu - E_g)^{1/2}, \quad (6)$$

where $h\nu$ — the photon energy, α — the absorption coefficient of $ZnS_xSe_{(1-x)}$ MC for a given photon energy, and A_0 — a coefficient dependent on the dielectric parameters and the effective mass of the current carriers in the MC. The degree of 1/2 in Formula 6 is taken considering of direct-gap $ZnS_xSe_{(1-x)}$. Figure 4b shows the linear character of change of the band gap width with change of the raw materials composition.

X-ray luminescence spectra of the crystal samples for all compositions ($x = 0.05$ to 0.3) (Fig. 5) have the wide band with a maximum at 590–610 nm, so it can be concluded that the nature of radiative transitions is identical. X-ray luminescence spectrum of ZnSe(Al) has a practically identical with $ZnS_xSe_{(1-x)}$ in the shape and maximum $\lambda_{max} = 595$ nm (I_2) conditional of luminescence of the defective luminescence center $\{V_{Zn}-O_{Se(S)}-Zn\}$ [3].

In [7] authors have shown that in $ZnS_xSe_{(1-x)}$ MC obtained by deposition from the gas phase at $x = 0.2$ the photoluminescence bands with maxima at 460 nm (I_1)

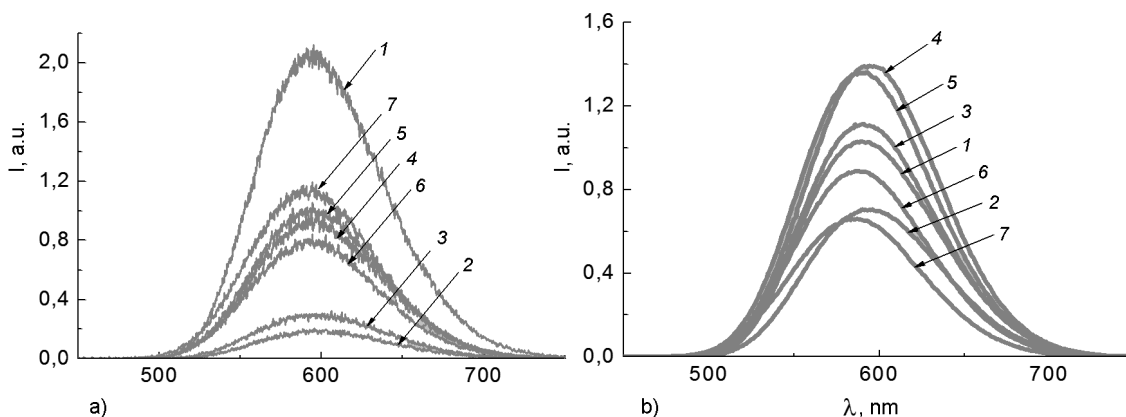


Fig. 5. X-ray luminescence spectra of unannealed (a) and annealed in zinc vapor (b) $\text{ZnS}_x\text{Se}_{(1-x)}$ crystals with $x = 0.05$ to 0.3 in comparison with $\text{ZnSe}(\text{Al},\text{O})$ crystal, where: 1 — $\text{ZnSe}(\text{Al},\text{O})$, 2 — $\text{ZnS}_{0.05}\text{Se}_{0.95}$, 3 — $\text{ZnS}_{0.1}\text{Se}_{0.9}$, 4 — $\text{ZnS}_{0.15}\text{Se}_{0.85}$, 5 — $\text{ZnS}_{0.2}\text{Se}_{0.8}$, 6 — $\text{ZnS}_{0.25}\text{Se}_{0.75}$, 7 — $\text{ZnS}_{0.3}\text{Se}_{0.7}$.

Table. The relative light yield and the afterglow of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC in comparison with $\text{ZnSe}(\text{Te})$ and $\text{ZnSe}(\text{Al},\text{O})$ crystals

No. Sample	Relative light yield, %	Afterglow, % after		
		5 ms	15 ms	25 ms
ZnSe(Te)	100	0,30	0,17	<0,02
ZnSe(Al)	95	0,40	<0,02	<0,02
ZnS	75	58,04	39,74	31,77
ZnS 5 % – ZnSe 95 %	98	0.24	<0.02	<0.02
ZnS 10 % – ZnSe 90 %	84	0.15	<0.02	<0.02
ZnS 15 % – ZnSe 85 %	159	0.40	<0.02	<0.02
ZnS 20 % – ZnSe 80 %	122	0.54	<0.02	<0.02
ZnS 25 % – ZnSe 75 %	103	0.37	<0.02	<0.02

and 590 nm (I_2) were observed. It was indicated that the band (I_2) is associated with complexes of point defects (zinc vacancy V_{Zn} and a shallow donor as impurities of Al, In, Cl). Authors [7] have shown the shift of the band maximum (I_2) to the short-wave region with increasing sulfur concentration which was confirmed by our research results. We explain this fact through increasing the band gap width of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC and rise of the concentration of the luminescent defect centers which have in its composition oxygen impurity substituting chalcogen.

In our experiments at the growing of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC from the melt the growth chamber also contains oxygen desorbed from the graphite parts of the growth furnace. Melt growing conditions are not equilibrium due to high temperature gradients and thermal evaporation of volatile zinc leads to the formation of predominantly zinc vacancies

[11]. Zinc vacancies (V_{Zn}) with oxygen in the anion sublattice ($\text{O}_{\text{Se}(\text{S})}$) and interstitial zinc (Zn_i) form the associates $\{V_{\text{Zn}}^{2-}\text{O}_{\text{Se}(\text{S})}\cdot\text{Zn}_i^+\}$. When the crystals are annealed in zinc vapor the centers of radiative recombination $\{V_{\text{Zn}}^{2-}\text{Zn}_i^+\cdot\text{O}_{\text{Se}(\text{S})}\cdot\text{Zn}_i^+\}$ are formed due to the vacancy transfer of zinc from the $V_{\text{Zn}}^{2-}\text{O}_{\text{Se}(\text{S})}$ defective complexes. The similar defective complex with luminescence maximum of 600 nm is characteristic for zinc selenide crystals [3]. High intensity of radiative recombination (including the participation of these defects) is associated with a low formation energy of electron-hole pairs in zinc chalcogenides [21]. Figure 5(b) shows X-ray luminescence spectra of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC after annealing in zinc vapor. It can be seen that luminescence intensity of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC has increased significantly in comparison with $\text{ZnSe}(\text{Al},\text{O})$ crystal. Figure 5 also shows that the maximum intensity of X-ray luminescence is ob-

served for $\text{ZnS}_x\text{Se}_{(1-x)}$ unannealed samples at $x = 0.3$, and for annealed in zinc vapor crystals at $x = 0.15$.

In the Table it is shown the measurements data of the relative light yield and the afterglow level of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC in comparison with $\text{ZnSe}(\text{Te})$ and $\text{ZnSe}(\text{Al},\text{O})$ crystals. As can be seen from the Table, the maximal relative light yield of $\text{ZnS}_x\text{Se}_{(1-x)}$ MC is observed at $x = 0.15$ and exceeds X-ray luminescence efficiency of commercial $\text{ZnSe}(\text{Te})$ and $\text{ZnSe}(\text{Al},\text{O})$ crystals by 1,6 times. At the same time, the afterglow of this $\text{ZnS}_{0.15}\text{Se}_{0.85}$ MC is not worse than that of $\text{ZnSe}(\text{Al},\text{O})$. In consideration of the high light yield and the low level of afterglow, it can be assumed that $\text{ZnS}_x\text{Se}_{(1-x)}$ MC is promising for use in X-ray and low-energy gamma radiation scintillation detectors.

4. Conclusions

The possibility of obtaining of $\text{ZnS}_x\text{Se}_{(1-x)}$ luminescent material in powdered and monocrystalline forms is shown. Luminescent properties of $\text{ZnS}_x\text{Se}_{(1-x)}$ samples MC with the wide range of x values obtained by solid-phase synthesis and melt-growing are studied.

Disperse phosphors on the basis of $\text{ZnS}_x\text{Se}_{(1-x)}$ solid solutions are obtained by solid-phase synthesis method. It is shown that for the compositions (where $x = 0.90\div 0.99$) the emission spectrum of the samples lies in the range of 500–520 nm, which can be related to the radiative transitions characteristic of zinc sulphide. For the sample of $\text{ZnS}_{0.05}\text{Se}_{0.95}$ the luminescence maximum is at 620 nm, which indicates the presence of the ternary complex $\{\text{V}_{\text{Zn}}-\text{O}_{\text{Se}(\text{S})}-\text{Zn}\}$ similarly to $\text{ZnSe}(\text{Al},\text{O})$ crystals.

For the first time it is shown that in $\text{ZnS}_x\text{Se}_{(1-x)}$ MC grown from the melt by the Bridgman-Stockbarger method in the range of x values from 0.05 to 0.3 the maximum intensity of X-ray luminescence is observed at $x = 0.3$ for unannealed samples, and at $x = 0.15$ for annealed in zinc vapor crystals. Probably, this is due to the peculiarities of the formation of defect complexes during annealing in zinc vapor.

$\text{ZnS}_{0.15}\text{Se}_{0.85}$ crystals have the value of light yield in 1,6 higher than $\text{ZnSe}(\text{Al},\text{O})$ and the afterglow below 0.02 % after 15 ms after excitation. It gives grounds to

consider $\text{ZnS}_x\text{Se}_{(1-x)}$ MC to be promising for use in X-ray and low-energy gamma radiation scintillation detectors.

Acknowledgement. Publication is based on the research provided by the grant support of the State Fund for Fundamental Research of Ukraine (Project No. F79/125-2017). Research was conducted in the scope of the IDEATE International Associated Laboratory (LIA).

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