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THE INFLUENCE OF THE STABILIZER AND THE BUILDER ON THE OPTICAL AND LUMINESCENCE PROPERTIES OF COLLOIDAL BINARY SOLID SOLUTION $(Zn_xCd_{(1-x)})$S-manganese

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Abstract.
The possibility of synthesis of colloidal phosphors based on binary solid solutions $Zn_xCd_{(1-x)}S$, containing manganese, in the presence of a stabilizer – PVA, modifying agent - PEG-400 and sodium chloride. We investigated the optical and luminescent properties, phase composition of the colloidal solid solution. There was a high brightness of the photoluminescence, and getting orange luminescence of colloidal solid solutions.

Key words: phosphors colloidal stabilizer, builders, orange luminescence.

The present level of electronic equipment requires the development of new high-luminescent materials. Zinc sulfide phosphors, as highly efficient and highly stable material retains a leading position in the present. In this case, it is of interest the development of new non-traditional methods of production of phosphors, including research and development of colloidal phosphor-based colloidal solid solutions.

Previously, we showed promising application of colloidal solid solutions based on zinc sulfide with added cadmium, and the ability to improve the optical and luminescent properties of these solutions in the presence of polyvinyl alcohol (PVA) [1]. Despite the wide range of studies on the properties of PVA, many issues remain unresolved, is incomplete information on the processes of complex systems based on PVA with the addition of sodium chloride and 4% (by weight) of manganese. Remains poorly understood system PVA - zinc sulfide doped with 4% (by weight) of manganese with the addition of cadmium in the presence of sodium chloride and builder.

In this paper we present the results of a study of optical and luminescent properties of colloidal binary solid solution $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese.

To obtain these systems used colloidal method. This method of deposition of the equipment is simple, economical, flexible technology and availability of the phosphors of controlled composition and properties, as well as the ability to adjust the particle size phosphors [2].

Reactants crystalline: zinc acetate $(CH_3COO)_2Zn{\cdot}2H_2O$, cadmium nitrate $Cd(NO_3)_2{\cdot}\ 4H_2O$, zinc manganese acetate $(CH_3COO)_2Mn{\cdot}4H_2O$ manganese acetate, sodium sulfide $Na_2S\ \cdot\ 9H_2O$ (precipitator), sodium chloride and redistilled water. These inorganic salts have the qualification of "chemically pure". Of these inorganic salts, an aqueous solution of zinc acetate, cadmium nitrate and sodium sulfide at a concentration of 1 mol/l. Stabilizer - polyvinyl alcohol – $[CH_2\text{-}CH\ (OH)]_n$ –, highest grade, grade 16/1. The stabilizer used to prevent aggregation of the colloidal particles of the solid semiconductor binary solution $Zn_xCd_{(1-x)}S$

during the deposition. PEG-400, $HO(CH_2CH_2O)_nH$ was used as a modifying agent.

Dispersed colloidal binary solid solution based on zinc sulfide with the addition of cadmium containing 4% (by weight) of manganese was obtained as the corresponding sulfide deposition of an aqueous solution of sodium sulfide while draining reagents with constant stirring under normal conditions. Soon as you add sodium sulfide visually observed the formation of sparingly soluble sulfides. Sulfide deposition was carried out in normal conditions. Sulfide precipitate was separated, dispersed particles precipitate was dried in a vacuum oven at 100 ° C.

PL spectra of colloidal binary solid solution $Zn_xCd_{(1-x)}S$: 4%Mn obtained on spectrofluorimeters AvaSpec-3648. The excitation was performed fluorescent energy-saving low-pressure mercury lamp brand MD BLB -30 W E 27, with a wavelength of $\lambda = 365$ nm.

PL brightness measured on the device type IL 1700 «Research Radiometer» in ft-L and multiplication by a constant equal to 3.425 transferred brightness characteristics, in cd/m^2. This paper shows the values of the relative brightness of the studied colloidal samples, measured relative to the undoped colloidal binary solid solution $Zn_xCd_{(1-x)}S$.

Electronic spectra of diffuse reflection (ESDO) of the samples of colloidal binary solid solution $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese, received a spectrophotometer Specord M-200 (Analytik Jena, Germany) in the wavelength range 200-900 nm . The optical analog of the standard used Spectrolon magnesium oxide. By diffuse reflectance spectra measured optical band gap (SHZZ).

PL spectra and ESDO recorded at room temperature. Information of the absorption spectra of the samples obtained from the diffuse reflectance spectra. To do this, diffuse reflectance spectra of the samples treated specially by the equation Gurevich – Kubelka – Munk [3, 4]

$$F = (1-R)^2/2R \qquad (1)$$

where, F– function Gurevich – Kubelka – Munk, R-reflectivity, %.

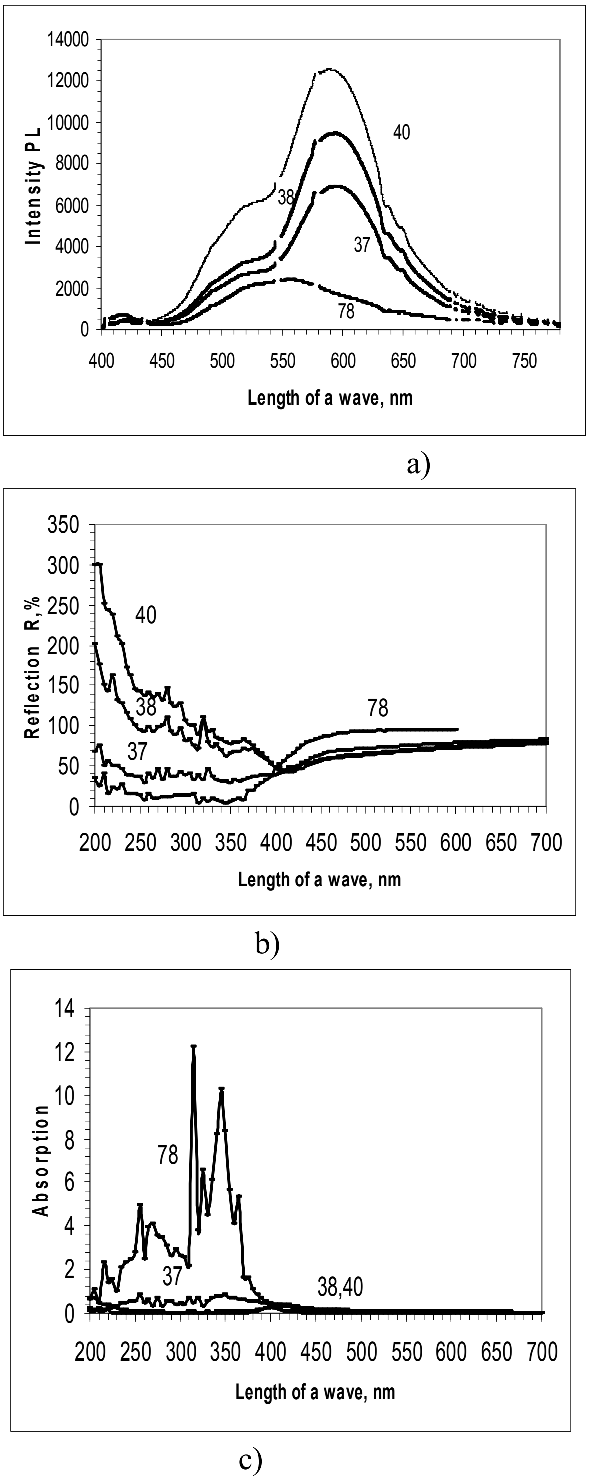
$$\alpha/s = (1-R)^2/2R \qquad (2)$$

where, α – constant absorption, s – constant light scattering

Without taking into account the scattering of light:

$$F = \alpha \qquad (3)$$

Figure 1 a-c show the PL spectra, diffuse reflection, absorption of colloidal binary solid solution $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese in the presence of sodium chloride, PVA and PEG-400.



a)

b)

c)

Fig.1. - Photoluminescence (a) and diffuse reflection b) and absorption c) of colloidal

binary solid solution $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese in the presence of sodium chloride: no PVA and PEG-400 (sample number 37) with PVA (sample number 38), with the PVA and PEG-400 (sample number 40), and without additives and without 4% (by weight) of manganese (sample number 78).

In Fig. 1a shows that the PL spectra of the studied colloidal binary solid solutions $Zn_xCd_{(1-x)}S$ are located throughout the visible spectrum. PL spectra of the studied colloidal binary solid solutions $Zn_xCd_{(1-x)}S$ differ in the luminescence intensity. PL spectrum of colloidal binary solid solution $Zn_xCd_{(1-x)}S$ (sample number 78) has a wide maximum bandwidth of the wavelength λ = 538 nm (photon energy of 2.3 eV) to λ = 570 nm (2.18 eV photon energy) (Fig. 1a). Broad luminescence band of colloidal solid solution (sample number 78) contains a defect luminescence. Defect luminescence band, but has the shape of the shoulder on the left branch of the PL spectrum, is shown in all the spectra of colloidal binary solid solutions $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese, regardless of the presence of the stabilizer (sample number 37 without PVA) (sample number 38 with PVA) and PEG-400 (sample number 40). At a wavelength of about 538 nm defect luminescence of colloidal binary solid solutions $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese, regardless of the presence of the stabilizer (sample number 37 without PVA) (sample number 38 with PVA) and PEG -400 (sample number 40) goes to the orange luminescence.

The maximum intensity of colloidal binary solid solution $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese in the presence of sodium chloride, is the wavelength λ = 590-594 nm (photon energy ≈ 2,1 eV). Manganese in excess of 4% (by weight) in the presence of sodium chloride in 1.4 times increase in the maximum PL intensity of colloidal binary solid solution $Zn_xCd_{(1-x)}S$ based on zinc sulfide with the addition of cadmium (sample number 37). Adding a stabilizer in the synthesis of colloidal solid solution $Zn_xCd_{(1-x)}S$ allows a 1.8-fold increase in the PL intensity at the maximum (sample number 38), and the addition in the synthesis of more and PEG-400 PL intensity increases by 2.6 times maximum (sample number 40).

Diffuse reflectance spectra (Fig. 1b) and the absorption spectra (Fig. 1c) of colloidal binary solid solutions $Zn_xCd_{(1-x)}S$ differ in the degree of reflection and absorption of light. Colloidal binary solid solution $Zn_xCd_{(1-x)}S$ without additives and without 4% (by weight) of manganese (sample number 78) has the highest UV absorption (Fig. 1b, c). Manganese in excess of 4% (by weight) increased UV absorption (sample number 37, Fig. 1 b, c). Polymeric organic additives to prevent aggregation of dispersed particles of colloidal binary solid solution, in the form of PVA (sample number 38) and PEG-400 (sample number 40) reduces the absorption of UV (Fig. 1 b, c). The absorption spectrum of colloidal binary solid solution $Zn_xCd_{(1-x)}S$ without additives and without 4% (by weight) of manganese (sample number 78, Figure 1) in the UV region has pronounced seven UV absorption maxima. Fundamental absorption edge of the UV colloidal binary solid solution $Zn_xCd_{(1-x)}S$ (sample number 78, Fig. 1) has a well-defined vertical portion terminating washed gently falling part of the wavelength axis. If we extrapolate the end of the vertical section of the fundamental absorption edge (sample number 78 in Figure 1) on the x-axis, then its intersection with the x-axis is at a wavelength of 370 nm (photon energy of 3.35 eV). Blurring the tip, slowly approaching the x-axis at a wavelength of about 450-480 nm (photon energy 2.76 eV - 2.58 eV).

Direct link between the PL spectra (Fig. 1a) and reflection spectra (Fig. 1b), the absorption spectrum (Fig. 1c) of colloidal binary solid solution without additives and without 4% (by weight) of manganese (sample number 78) were found. Namely, the highest UV absorption of colloidal solid solution both supplements and without 4% (by weight) of manganese (sample number 78, Fig. 1b, c) corresponds to the lowest PL intensity (Fig. 1a). However, 4% (by weight) of manganese without additives (sample number 37) increases the absorption of UV and, consequently, improves the PL intensity is about 3-fold (Fig. 1a, sample number №

37). But the presence of PVA (sample number 38, Fig. 1b, c) and PVA and PEG-400 (sample number 40, Fig. 1b, c) to prevent aggregation, screening the colloidal particles from the exciting UV, allowed to increase the intensity of the PL 1.5 times (PVA, sample number № 38, Fig. 1a) and 2.2 times (PVA and PEG-400, sample number № 39, Fig. 1). The positive effect of PVA without sodium chloride and other alloying additions to the PL intensity has been previously described.

The relative brightness of the photoluminescence study of colloidal binary solid solutions $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese in the presence of NaCl, is: no additives 1.4 (sample number 37), PVA - 3.6 (sample № 38), with the PVA and PEG-400 -5.3 (sample number 40). The relative brightness of the photoluminescence study of colloidal solid solutions of the relative colloidal binary solid solution without 4% (by weight) of manganese and no additives in the presence of sodium chloride (sample number 78). The absolute value of the PL intensity of the colloidal solid solution (sample number 78) of 9.1 cd/m^2.

Quantitative elemental analysis of colloidal binary solid solution $Zn_xCd_{(1-x)}S$ based on zinc sulfide with the addition of cadmium was carried out by atomic absorption spectrometry instrument QUANT-2AT. Atomic-absorber spectrometry allowed to determine the elemental composition of the colloidal solid solution and the value of «x» in the chemical formula of a solid solution of colloidal $Zn_xCd_{(1-x)}S$. The value of «x» is equal to 0.88 and the chemical formula of colloidal-based solid solution of zinc sulfide with the addition of cadmium ($Zn_{0,88}Cd_{0,12}$)S.

X-ray diffraction (XRD) colloidal precipitation of solid solutions was confirmed by the chemical composition of the solid solution of colloidal $Zn_xCd_{(1-x)}S$.

Shooting X-ray diffraction was carried out on the device "Diffracted" in the wavelength λ (Cu Kα-radiation) = 1,54178 Å with a curved coordinate detector in the range of Bragg diffraction angles 2θ 17,4-60,6 °. As an internal standard, we used aluminum oxide [5].

In Fig. 2 - shows diffraction patterns of the studied colloidal binary solid solutions $Zn_xCd_{(1-x)}S$.

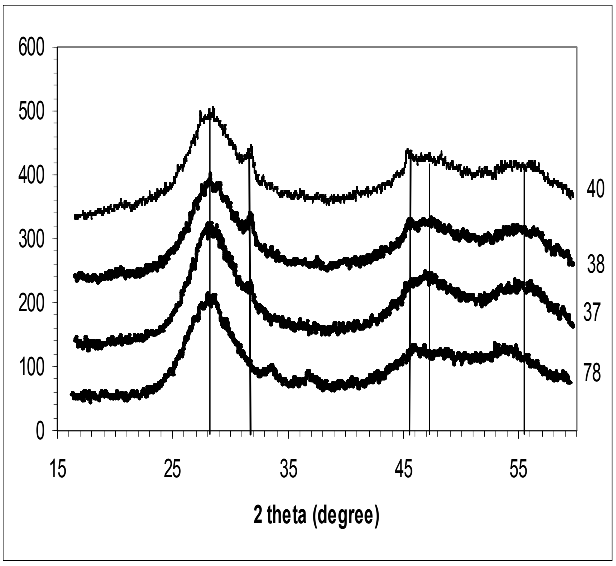


Fig. 2 - X-ray diffraction of colloidal binary solid solution $Zn_xCd_{(1-x)}S$, containing 4% (by weight) of manganese in the presence of sodium chloride: no PVA and PEG-400 (sample number 37), PVA (sample number 38), with PVA and PEG-400 (sample number 40), and without additives and without 4% (by weight) of manganese (sample number 78).

Each diffraction peak in the diffraction pattern (Fig. 2), noting the development of the x-axis vertical lines with a characteristic only of the diffraction peak set Bragg angles 2θ.
Indexing of X-rays were performed using the tabular data of the International catalogs ASTM (JC PDS). Phase is considered to be established at the coincidence of the two or three most intense peaks in the diffraction pattern with the data file cabinets JC PDS. All study colloidal binary solid solutions $Zn_xCd_{(1-x)}S$ based on zinc sulfide with the addition of cadmium containing 4% (by weight) of manganese in the presence of sodium chloride, stabilizers, modifiers as indicated by the two-phase (Table).

As the table shows, the difference in lattice parameters of the colloidal solid solution (sample number 38) and the solid solution (JCPDS № 24-1137) is 0.35%.
The average value of the lattice parameter of the solid solution $Zn_{0,88}Cd_{0,12}S$ (sample number 38) and the solid solution $Zn_{0,9}Cd_{0,1}S$ (JCPDS № 24-1137) is 5,467 Å and 5,431 Å, respectively.
The difference in the lattice parameters of

Table - Composition of the solid phase of the colloidal solid solution $Zn_xCd_{(1-x)}S$: 4% Mn, NaCl

Experimental data		Data ICPDS	
$Zn_xCd_{1-x}S$: 4%Mn, PVA, NaCl (Samp. № 38)		$Zn_{0,9}Cd_{0,1}S$ № 24-1137, S.G.: F $\bar{4}$3m	
2θ	a_{hkl}, Å	2θ	a_{hkl}, Å
28,3	a_{111}5,461	28,48	a_{111}=5,426
47,2	a_{220}=5,447	47,316	a_{220}=5,433
55,52	a_{311}=5,492	56,146	a_{311}=5,433
	a_{cp} =5,467		a_{cp}=5,431
		NaCl № 05-0628, S.G.: F m3m	
31,71	a_{200}=5, 644	31,718	a_{200}=5,642
45,55	a_{220}=5,634	45,488	a_{220}=5,612
	a_{cp} 5,639		a_{cp} 5,627

sodium chloride (sample number 38) and sodium chloride (JCPDS № 05-0628) is 0.2%. The average value of the lattice parameter of sodium chloride (sample number 38) and sodium chloride (JCPDS № 05-0628) is 5, 639 Å and 5,627 Å, respectively.

Conclusions

1. By atomic absorption spectrometry and X-ray analysis established formula colloidal binary solid solution based on zinc sulfide with the addition of cadmium $Zn_{0,88}Cd_{0,12}S$.
2. It is shown that colloidal solid solution $Zn_{0,88}Cd_{0,12}S$: 4% Mn, gives luminescence orange color with a pronounced maximum at a wavelength of λ = 590-594 nm in the presence of sodium chloride.
3. Polyvinyl alcohol can increase the intensity and relative brightness PL colloidal binary solid solution $Zn_{0,88}Cd_{0,12}S$: 4%Mn in the presence of sodium chloride in 1.8 and 2.75 times, respectively.
4. Polyvinyl alcohol and modifying agent can increase the intensity and the relative brightness of the photoluminescence of colloidal binary solid solution $Zn_{0,88}Cd_{0,12}S$: 4%Mn in the presence of sodium chloride in 2.6 and 5.3 times, respectively.

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