

PHYSICAL CHEMISTRY
OF SOLUTIONS

Synthesis and Luminescence of Lead(II)-Activated Cadmium Sulfide in Poly(methyl methacrylate)

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Received January 22, 2016

Abstract—Optically transparent polymeric materials PMMA : Cd(Pb)S have been synthesized by polymerization of methyl methacrylate, which concurrently acts as a reaction medium for synthesis of metal sulfides, dispersion medium for the resulting colloidal solution forming during synthesis, and the base of compositions. Dependences of cadmium sulfide luminescence on the concentrations, concentration ratios of the initial compounds, reaction medium composition, and temperature have been established. The observed changes in the spectra are related to the introduction of lead(II) into compositions, complex formation on the surface of colloidal particles, and the effect of polar acetonitrile.

DOI: 10.1134/S0036023617010223

Synthesis and study of quantum dots (QDs) of inorganic semiconductors, in particular, cadmium chalcogenides, are of great current interest [1–6]. The luminescence properties of QDs are determined by quantum size effects. They are associated with charge recombination on the levels of extrinsic defects in nanosized semiconductor crystals. In the first case, luminescence appears on recombination of bound electron–hole pairs (excitons). In the second case, radiative transitions occur between the conduction band and valence band edge levels and the impurity energy levels in the gap of a semiconductor [4, 7, 8]. The luminescence bands related to the defects of the CdS crystal structure are observed in the wavelength range 400–500 nm. Broad luminescence bands caused by surface defects are observed at wavelengths >500 nm [7, 9–12].

Activation of semiconductors with metal ions (Cu²⁺, Mn²⁺, Pb²⁺, Zn²⁺, Ag⁺, etc.) changes the intensity and position of spectral bands, luminescence quantum yield, stability of luminescence characteristics, and stability of the forming particles [1, 13–16]. In addition, oxygen and sulfur atoms, which create defects on the QD surface [17], and a medium in which they are located [4, 7, 10, 11, 18] have an effect on the luminescence characteristics. In solution, they depend on solvation and complex formation on the particle surface [19, 20].

Semiconductor quantum dots are synthesized by molecular and electron beam epitaxy; by the Langmuir–Blodgett method; via hydrothermal, thermal, and colloidal approaches; through a sol–gel route [1,

7, 9, 10, 21–23]. The particle size and the type of crystal structure depend on the nature, reagent concentrations and concentration ratios, synthesis temperature, sulfide ion source, stabilization method, and stabilizer nature [24–27]. For example, the size of cadmium sulfide nanoparticles, as rule, does not exceed 10 nm. They are spherical. The crystal structure of CdS nanocrystals is polytypic: it is formed by wurtzite and sphalerite layers. With an increase in particle size, the wurtzite structure becomes predominant. Particles become rectangular [23, 28]. In solutions and polymeric matrices, particles are aggregated. The aggregate size is as large as tens of nanometers [8, 14].

With the use of several chalcogenides, core–shell structures or more complex compositions are produced. In these compositions, narrow-gap semiconductors are covered with wide-gap semiconductors, placed between two wide-gap semiconductors [29], or vice versa [30, 31]. Such structures have more stable luminescence characteristics. For example, in the CdS/ZnS system, this is caused by an increase in the content of luminescence sites “inside” the CdS crystals and a decrease of such site on the crystal surface, which ensures localization of exciton, blocks its direct annihilation, and maintains recombination luminescence [32].

Composite materials with new optical, magnetic, and mechanical characteristics, other than those of traditional composites, are created by forming nanostructures and controlling their size and shape [33–35]. Among the developed methods of synthesis, considerable attention focuses on the methods of synthe-

sion of compositions based on organic polymeric matrices and nanoparticles of different compounds [1–3, 13, 36]. One of the attractive routes to such compositions is colloidal synthesis. It affords semiconductor nanoparticles directly in a medium of monomers, so that liquid compositions can be converted into glass by block polymerization [8, 14, 37]. The sources of sulfide ions are usually H_2S and Na_2S [8, 37, 38], as well as organic sulfur-containing compounds [14, 22, 39]. Thioacetamide (TAA) as a sulfide source [14, 39] in colloidal synthesis makes it possible to use the method of nascent reagents [40]: hydrogen sulfide gradually forms immediately in the reaction mixture upon hydrolysis of thioacetamide.

This synthesis has the least effect on the resulting structure of the polymeric composition. It retains the extremely high light transparency of the composition: at wavelengths >400 nm, the transparency amounts to 90–92% at the absorbing layer thickness up to 5 mm. Colloidal particles in which the cores are nanosized semiconductor crystals are additionally stabilized by macromolecules that form a protective layer on the particle surface [8, 41]. In a polymer medium, colloidal particles are located inside the globules formed by macromolecules in the course of growth or in the voids that appear upon formation of a supramolecular polymer structure. In the latter case, the properties of the particle surface can be modified by introducing polar organic solvents into polymerized compositions; such solvents destroy complexes and form a protective solvation layer on the particle surface [42].

The processes that occur in multicomponent systems have an effect on the luminescence properties of semiconductor crystals and compositions as a whole, as well as on their stability. Consideration of the effect of numerous factors is a rather challenging task, and experimental studies of their complex influence are few in number.

In this context, the aim of this work was to establish dependences of the luminescence of cadmium sulfide activated in situ with lead(II) ions in the course of synthesis of PMMA:Cd(Pb)S compositions (PMMA is poly(methyl methacrylate)) on the reagent concentrations and concentration ratios, reaction mixture composition, and temperature.

EXPERIMENTAL

To prepare colloidal solutions of cadmium sulfide, a weighed portion of cadmium trifluoroacetate corresponding to the concentration 0.010 mol/L was dissolved in methyl methacrylate (Merck). Into this solution, a weighed portion of thioacetamide or an aliquot of its solution in methyl methacrylate (MMA) was introduced to obtain a solution with the Cd(II) : TAA ratio 1 : 1 or 1 : 2. The selected concentration of the reagents was appropriate to prepare colloidal solutions stable enough to be converted into glass. The choice of

cadmium trifluoroacetate is explained by the good solubility of trifluoroacetates in low-polarity organic solvents, including MMA [42]. Thioacetamide is also readily soluble in acrylate monomers. In solution, TAA is hydrolyzed. The evolved hydrogen sulfide reacts with metal salts to give sulfides. TAA is more producible than gaseous hydrogen sulfide; the use of the latter makes the synthesis more complicated and impedes the control of the sulfide ion concentration [8].

Cadmium trifluoroacetate was synthesized by the reaction of cadmium oxide (pure for analysis grade) with trifluoroacetic acid (pure for analysis grade) in water; then, the solvent was evaporated, and the salt was dried to obtain crystals. TAA was preliminarily recrystallized. Cadmium trifluoroacetate and TAA were identified by IR spectroscopy with the use of data [43, 44].

Solutions containing cadmium trifluoroacetate and TAA were heated to 70–90°C for 10–20 min to the development of a persistent yellow-green color of cadmium sulfide. To obtain polymeric materials, benzoyl peroxide was introduced into solutions in amounts corresponding to 0.10% of the monomer weight. Solutions were further heated at 60–70°C to the viscous state. Viscous solutions were placed into demountable glass cells and heated until their conversion into glass. The color of polymeric samples corresponded to the color of colloidal solutions. Samples of cadmium sulfide activated with lead(II) ions were synthesized analogously. In addition to cadmium trifluoroacetate, a weighed portion of lead trifluoroacetate corresponding to the required Cd : Pb molar ratio was introduced into a solution. Lead trifluoroacetate was synthesized from lead oxide (pure for analysis) and trifluoroacetic acid, analogously to the synthesis of cadmium trifluoroacetate, and identified by IR spectroscopy. Subsequent operations were carried out as described above. The Cd : Pb molar ratios in solutions changed from 1 : 0.0025 to 1 : 1.5. With increasing lead(II) content, the color of colloidal solutions and polymeric samples changed from yellow-green to yellow-orange at maximal Cd : Pb molar ratios.

The electronic absorption spectra of solutions and polymeric samples were recorded on Specord UV/Vis spectrophotometer in the range 200–800 nm with respect to MMA or a sample of unmodified PMMA of comparable thickness.

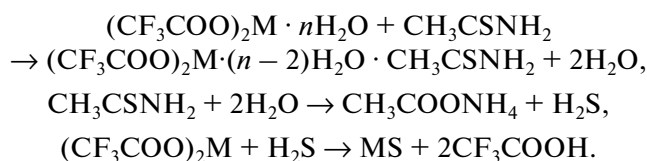
The luminescence excitation spectra and luminescence spectra were recorded on a Solar SM 2203 spectrofluorimeter (Belarus). Excitation light from a radiation source (a DKsSh 150-1M high-pressure xenon arc lamp) was incident perpendicular to the sample surface. Stationary luminescence was recorded at an angle of 45°.

TEM images were taken on a Philips CM12 transmission electron microscope. For taking TEM images, colloidal solutions were prepared on the basis of ethyl acetate (EA) (chemically pure grade). This

made it possible to rule out the effect of MMA polymerization during solution preparation. Solutions were applied to copper grids with an amorphous carbon coating, dried, and studied at different magnifications. To take TEM images of polymeric compositions, the corresponding sample was dissolved in dichloroethane (chemically pure), poured on the microscope support, and dried; a TEM image was taken from the resulting film.

RESULTS AND DISCUSSION

On heating solutions containing cadmium (lead) trifluoroacetate and thioacetamide, the following chemical reactions occurred:



An indication of the formation of cadmium sulfide is the gradual development of a yellow-green color characteristic of cadmium sulfide. In mixtures containing cadmium and lead salts at all Cd : Pb ratios used, the black color typical of lead sulfide was not observed. The change in color of cadmium sulfide solutions from yellow-green to yellow-orange after adding lead(II) ions indicated the introduction of Pb^{2+} into the structure of cadmium sulfide crystals. This assumption complies with the close, but still somewhat better solubility of lead sulfide as compared to that of cadmium sulfide [45], which determines the formation of metal sulfide particles in solution.

The TEM images show the structures that formed on heating the $\text{Cd}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$ (Fig. 1a) and $\text{Cd}(\text{CF}_3\text{COO})_2\text{-Pb}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$ solutions at Cd : Pb molar ratios 1 : 0.1 (Fig. 1b) and 1 : 1 (Fig. 1c). Colloidal particles 3–6 nm in size form spherical structures >20 nm in size. They are covered by complex compounds forming spatial assemblies. The surfaces of particles formed by CdS and Cd(Pb)S are different. The difference becomes more pronounced with an increase of the mole fraction of lead(II) in compositions (Fig. 1c). This is confirmed by the increase in Pb(II) ions on the particle surface and agrees with the above discussion about the influence of different solubility of lead and cadmium sulfides on the formation of particles. The particles in the polymeric composition are distributed more uniformly (Fig. 1d). Such a distribution is achieved upon long-term heating of samples in glass cells. Thermal polymerization is accompanied by degradation of aggregated structures and complex compounds. This is confirmed by “clarification” of the compositions accompanied by the enhancement of their light transmission and homogeneity.

The electronic spectra of polymeric samples show a spectral band in the range 280–500 nm correspond-

ing to the absorption of cadmium sulfide and lead(II)-activated cadmium sulfide (Fig. 2). The spectra do not display the narrow band at 270 nm observed in the spectra of solutions and assigned to the absorption of the C=S group of thioacetamide [19]. This is due to the fact that metal trifluoroacetates continue to react with thioacetamide on heating in the course of MMA polymerization.

The band gap width of cadmium sulfide was determined from the intercept of the tangent to the descending slope of the CdS absorption band with the abscissa, and the particle size was calculated as in [13] by the equation:

$$R = h(8\mu\Delta E_g)^{-1/2},$$

where h is the Planck constant; $\mu = [(m_e^*)^{-1} + (m_h^*)^{-1}]^{-1}$, $m_e^* = 0.21m_e$, and $m_h^* = 0.80m_e$ are the effective masses of electrons and holes in CdS; m_e is the electron rest mass; ΔE_g is the difference between E_g of a CdS nanoparticle and bulk crystal (2.4 eV).

In compositions containing cadmium sulfide, the particle size is ~3.1 nm (Fig. 2, spectrum 2, 470 nm). In compositions containing lead(II)-activated cadmium sulfide, an increase in the Cd(II) : Pb(II) molar ratio leads to an increase in the particle size from 4.5 to 6.0 nm [19]. The results are consistent with the data reported in [7, 9, 28, 37, 46]. The increase in the particle size is caused by the introduction of larger Pb^{2+} ions into their composition.

The luminescence spectrum of the PMMA:CdS composition excited at 370 nm (λ_{ex}) shows a composite band (Fig. 3, curve I^*). The luminescence excitation spectrum ($\lambda_1 = 680$ nm) shows a band in the wavelength range 280–470 nm with a half width of ~160 nm (Fig. 3, curve I). It consists of at least two components with maxima at about 350 and 410 nm. Recording the excitation spectra for non-maximum luminescence values (620 nm \rightarrow 680 nm \leftarrow 696 nm) made it possible to compare the spectra of the samples (Fig. 3, curves I , 2 and I^* , 2*).

From the position of the band in the spectrum (>500 nm) it follows that luminescence is caused by surface defects of cadmium sulfide particles. The resulting cadmium(II) vacancy complexes form energy levels acting as electron traps in the gap of CdS [8, 47]. Long-wavelength radiative transitions occur from these levels. In addition, defects of the CdS particle surface are created by sulfur and oxygen ions. They also give rise to energy levels in the gap of CdS. The bands corresponding to transitions from these levels are observed in the same spectral range [17, 48]. A considerable width and a complex contour of luminescence and luminescence excitation bands are associated with the particle surface inhomogeneity and particle dispersion.

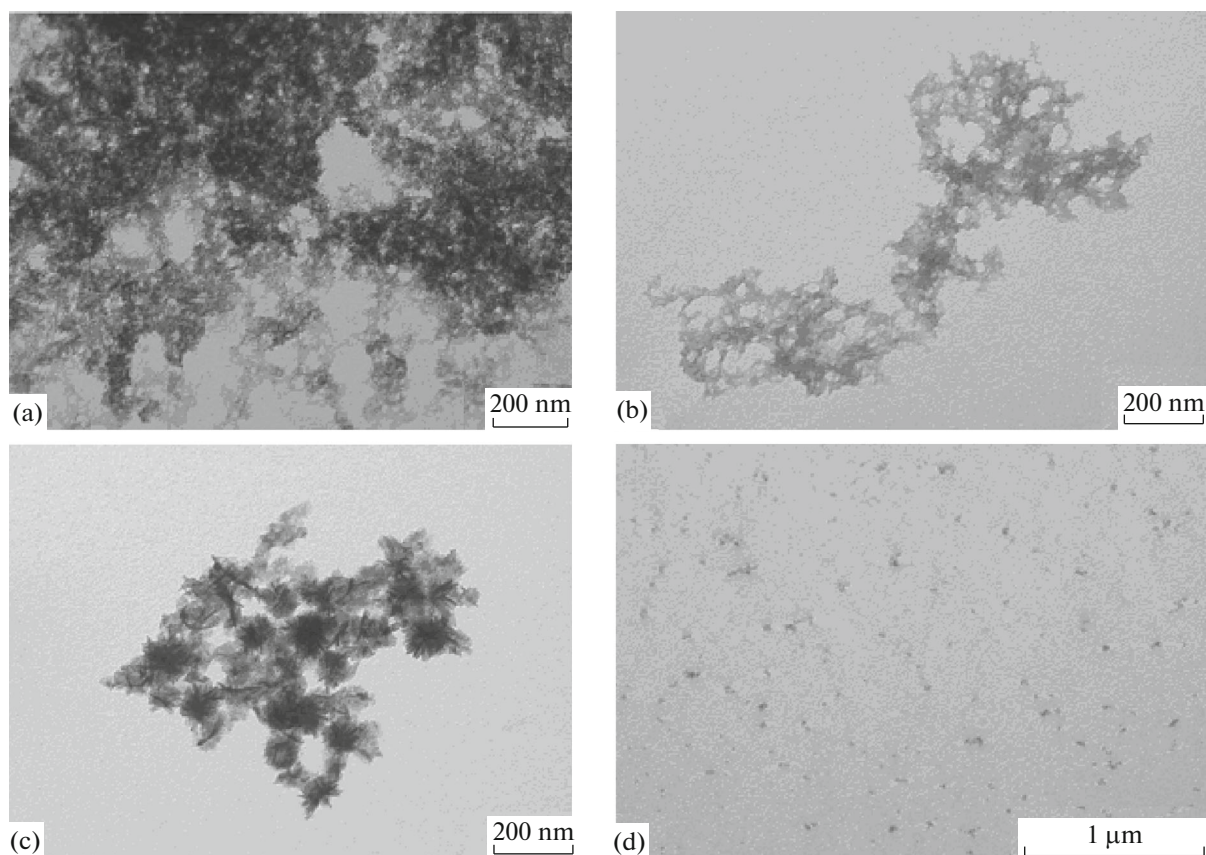


Fig. 1. TEM images of (a) the reaction products in a $\text{Cd}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$ solution; (b) reaction products in a $\text{Cd}(\text{CF}_3\text{COO})_2\text{-Pb}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$ solution, $\text{Cd} : \text{Pb} = 1 : 0.1$; (c) reaction products in a $\text{Cd}(\text{CF}_3\text{COO})_2\text{-Pb}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$, $\text{Cd} : \text{Pb} = 1 : 1$; (d) polymeric film $\text{PMMA}:\text{Cd}(\text{Pb})\text{S}$, $\text{Cd} : \text{Pb} = 1 : 1$.

The luminescence band shifts toward longer wavelengths with a decrease in polymerization duration from 24 to 8 h, its contour becomes smoother, and the peak intensity decreases by $\sim 30\%$. The band maximum is at 696 nm (Fig. 3, curve 2*). The band in the

luminescence excitation spectrum, as in the luminescence spectrum, becomes smoother for the shorter polymerization time. Its descending slope shifts slightly toward longer wavelengths (Fig. 3, curve 2). The position of the band in the luminescence spectrum and its response to the decrease in heat treatment time related to the reduction of the polymerization

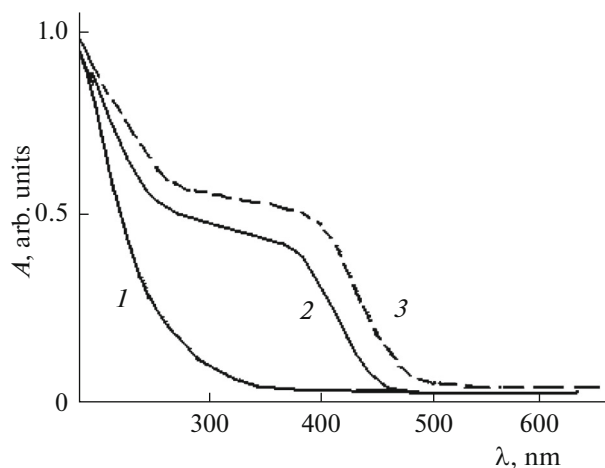


Fig. 2. Electronic absorption spectra of (1) PMMA, (2) $\text{PMMA}:\text{CdS}$, (3) $\text{PMMA}:\text{Cd}(\text{Pb})\text{S}$; $\text{Cd} : \text{Pb} = 1 : 1.5$.

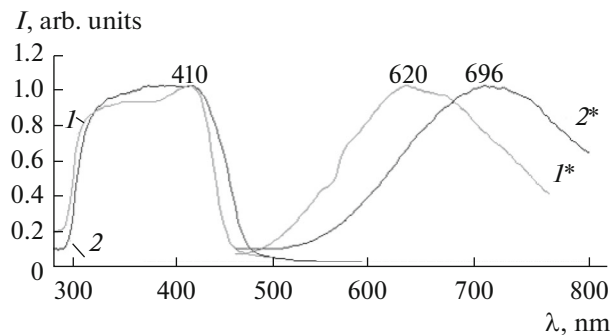


Fig. 3. Normalized (1, 2) luminescence excitation spectra ($\lambda_{\text{em}} = 680$ nm) and (1*, 2*) luminescence spectra ($\lambda_{\text{ex}} = 370$ nm) of the $\text{PMMA}:\text{CdS}$ composition: polymerization for (1, 1*) 24 h and (2, 2*) 8 h.

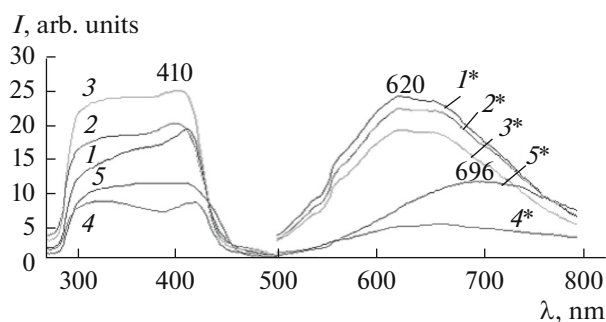


Fig. 4. (1–5) Luminescence excitation spectra (1–4, $\lambda_1 = 620$ nm; 5, $\lambda_1 = 680$ nm) and (1*–5*) luminescence spectra ($1^*–4^*$, $\lambda_{\text{ex}} = 410$ nm; 5^* , $\lambda_{\text{ex}} = 370$ nm) of PMMA:Cd(Pb)S compositions at Cd : Pb (1, 1^*) 1 : 0.0025, (2, 2^*) 1 : 0.005, (3, 3^*) 1 : 0.01, (4, 4^*) 1 : 1.5, (5, 5^*) 1 : 0 (polymerization time for 5 and 5^* was 8 h, in the other cases, 24 h).

duration, as well as the change in the band position in the excitation spectrum, highlight the effect of complex formation and aggregation on the formation of the surface of CdS particles and on their size. This effect is confirmed by TEM data (Fig. 1). The ligands in complex formation are trifluoroacetate ions and TAA as well as oligomers surrounding CdS particles in the polymeric matrix.

The introduction of lead(II) ions into compositions in small amounts with respect to cadmium(II) ions increases the luminescence intensity (Fig. 4). This effect is related to the increase of the number of defects of the cadmium sulfide surface induced by Pb^{2+} . However, a further increase in the concentration of Pb(II) ions reduces the luminescence intensity. This is explained by the formation of the Pb(Cd)S shell (formed by lead sulfide) on the cadmium sulfide surface and by complex formation involving lead sulfide, which leads to “blocking” of luminescent sites. This assumption is based on the different solubilities of cadmium and lead sulfides [45]. During the formation of the solid phase, this difference can be responsible for a gradual increase in the lead(II) content from the center to the periphery of particles. Similar effects of “healing” of defects on the nanoparticle surface have been discussed [8, 30–32].

The position of the band maximum (620 nm) in the luminescence spectra of compositions containing cadmium(II) and lead(II) in low molar ratios was not changed upon luminescence excitation by radiation with $\lambda < 450$ nm. Upon excitation at $\lambda = 474$ nm, the luminescence band almost disappeared, while a weak band at 550 nm persisted. Upon excitation at $\lambda > 450$ nm, an insignificant absorption was observed, which was absent in the other spectral curves. This absorption can be related to the luminescence band at 550 nm. The spectra showed one more weak band at 430 nm. It was observed only in the spectra of compositions containing CdS and Cd(Pb)S at small lead(II) concentra-

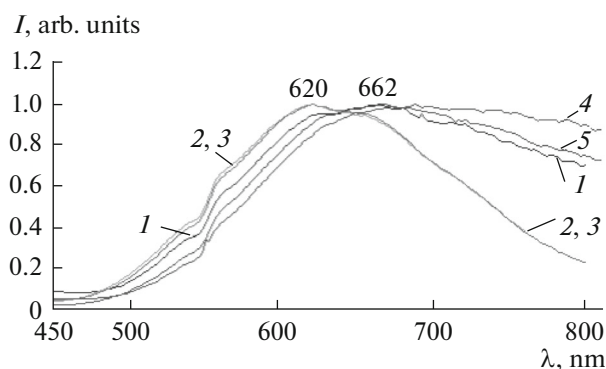


Fig. 5. Luminescence spectra of the PMMA:Cd(Pb)S composition at different Cd : Pb molar ratios ($\lambda_{1,\text{max}}$, nm): (1) 1 : 1.5 (662), (2) 1 : 0.01 (620), (3) 1 : 0.005 (620), (4) 1 : 1.5 + 8 vol % AN (662–690), and (5) 1 : 1.5 + TAA (Cd : TAA = 1 : 2) (665–668).

tions. These bands can be related to structural defects in the bulk of CdS and Cd(Pb)S crystals.

At large Cd : Pb molar ratios, the luminescence maximum shifts toward longer wavelengths. For the compositions with Cd : Pb = 1 : 1.5, the following trend in the shift of luminescence maximum as a function of the excitation wavelength, $\lambda_{\text{ex}} - \lambda_1$ (nm): 420–656, 410–662, and 370–664. The shift of the luminescence band and its maximum increased when polar acetonitrile (AN) (chemically pure) was introduced into compositions and with an increase in the content of TAA taken for synthesis (Fig. 5). The largest displacement was observed with a decrease in polymerization duration for the compositions containing lead(II) ions. For example, the decrease in the polymerization time from 24 to 8 h led to the shift of the luminescence maximum to 750 nm (Cd : Pb = 1 : 1.5) [49].

The introduction of 8 vol % of acetonitrile into compositions containing cadmium(II) and lead(II) in large ratios led to a twofold increase in luminescence intensity. In the spectra of compositions containing the same amount of AN at Cd : Pb < 1 : 0.01, the luminescence band with a maximum at >620 nm nearly completely vanished. A weak luminescence band with a maximum at 550 nm did not change (Fig. 6). The luminescence intensity at 620 nm also increased with the TAA concentration.

The changes observed in the spectra are caused by the effect of complex formation and solvation on the particle surface. The introduction of AN leads to the degradation of the complexes. The luminescent sites on the surface of particles coated with the Pb(Cd)S shell are “unblocked.” As a result, the luminescence intensity for the compositions increases. At any Cd : Pb ratios, acetonitrile has no effect on the luminescence sites in the bulk of Cd(Pb)S particles. At low Cd : Pb molar ratios, the Pb(Cd)S shell covering CdS is not formed, AN solvates the surface of Cd(Pb)S particles; the resulting solvates are likely responsible for

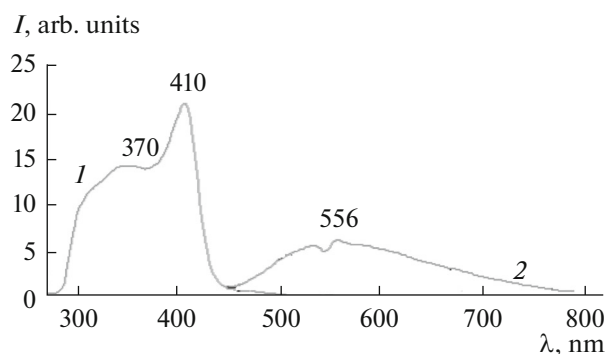


Fig. 6. (1) Luminescence excitation spectrum ($\lambda_l = 680$ nm) (2) luminescence spectrum ($\lambda_{ex} = 370$ nm) of the PMMA: Cd(Pb)S: AN composition; Cd : Pb = 1 : 0.005, 8 vol % AN.

the disappearance of luminescence arising from surface defects of cadmium sulfide.

The increase in luminescence intensity with an increase in concentration of TAA taken for synthesis is explained by the increase in the yield of metal sulfides at all stages of synthesis.

Thus, we have shown that the luminescence of cadmium sulfide depends on the Cd : Pb ratio, heat treatment duration of the reaction mixture, the amount of TAA, and the introduction of polar acetonitrile into compositions. These factors have an effect on the particle size, form defects in the crystal bulk and on their surface, thus “blocking” or removing complexes from luminescent sites.

ACKNOWLEDGMENTS

We are grateful to A.A. Biryukova (Kuznetsov Siberian Institute of Technical Physics, Tomsk) for studying the compositions by TEM.

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Translated by G. Kirakosyan