

POLYMERIC SYSTEMS
AND TECHNOLOGIES

Synthesis and Absorption and Luminescence Spectra of Poly(methyl methacrylate):Cd(Mn,Pb)S Composites

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Abstract—The reaction of cadmium, manganese, and lead trifluoroacetates with thioacetamide in methyl methacrylate yielded colloidal solutions of metal sulfides with different Cd(II) : Mn(II) : Pb(II) molar ratios. The colloidal particles were separated from solutions and examined by electron microscopy. Glassy polymer composites poly(methyl methacrylate):Cd(Mn)S and poly(methyl methacrylate):Cd(Mn,Pb)S were prepared by thermal polymerization of methyl methacrylate in the bulk. The transmittance of the composites at wavelengths larger than 480 nm is 92% at the sample thickness of 0.40 cm. The luminescence of the composites in the visible range is associated with cadmium sulfide. The corresponding absorption bands were recorded in the luminescence excitation spectra in the wavelength interval 300–450 nm. The effect of the matrix, Mn(II) and Pb(II) ions, and synthesis conditions on the absorption and luminescence properties of the composites was determined.

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Metal-containing optical polymers selectively absorb or transmit electromagnetic radiation, exhibit luminescence, and conduct electric current [1–5]. The metal atoms in the polymers are incorporated in organic or inorganic compounds. In a polymer matrix, they form intermolecular bonds with macromolecules or are directly bonded with them by chemical bonds. There is much interest in composites containing inorganic semiconductors, in particular, metal chalcogenides [6–8]. In optically transparent polymer matrices, semiconductors form quantum dots (QDs). One of the methods for their preparation is colloid synthesis. It is performed directly in the medium of the monomers. Then, the composites are converted to the glassy state by bulk polymerization of the monomers [9]. As a result, the composites preserve internal integrity, uniformity, and high transparency. Soluble metal salts, in particular, haloacetates [10], are used in the synthesis as metal-containing precursors, and hydrogen sulfide [8, 9] is used as a sulfur-containing agent. We believe that the use of sulfur-containing organic compounds is preferable. They are soluble in the monomers, and operations with gaseous hydrogen sulfide

are eliminated. Significant influence on the spectroscopic properties is exerted by activation of semiconductors with lead, zinc, copper, and silver cations [6, 7]. The composites with quantum dots having the core–shell structure have particular properties. They can be used as light-converting materials in optics, light engineering, and electronics. However, data on the luminescence of composites of complex cationic composition in optical polymer matrices are limited.

In this study, we examined the spectroscopic and luminescence properties of cadmium sulfide synthesized in situ by the reaction of cadmium trifluoroacetate with thioacetamide in the course of preparation of poly(methyl methacrylate):Cd(Mn,Pb)S composites.

EXPERIMENTAL

Cadmium and manganese sulfides and cadmium sulfide activated with Mn(II) and Pb(II) ions were synthesized by the reaction of the metal trifluoroacetates or their mixtures with thioacetamide (TAA, C₂H₅NS,

imported) with heating in methyl methacrylate (Merck) and ethyl acetate (EA, chemically pure grade). Ethyl acetate was used in some experiments with solutions to eliminate the effect of the solvent polymerization taking place with methyl methacrylate. The cadmium trifluoroacetate concentration in the solutions was 0.010 M. The molar ratio of thioacetamide and cadmium trifluoroacetate was 1 : 1. The Cd(II) : Mn(II) molar ratio was 1 : 0, 1 : 0.01, 1 : 0.05, 1 : 1, and 0 : 1, and the Cd(II) : Mn(II) : Pb(II) molar ratio was 1 : 0.1 : 0.1. Solutions of cadmium and manganese trifluoroacetates were prepared by dissolving the required amounts of the salts in methyl methacrylate or ethyl acetate. When preparing multicomponent solutions, the weighed portion of cadmium trifluoroacetate was dissolved first, after which the calculated amount of manganese trifluoroacetate or of a mixture of manganese and lead trifluoroacetates was added to the solution. Then, an aliquot of a solution of thioacetamide in the same solvent was added. The resulting solution containing the metal salts and thioacetamide was heated at 70–80°C for 10–20 min. The formation of metal sulfides was judged from the change in the solution color.

The choice of the starting compounds was governed by good solubility of metal trifluoroacetates and thioacetamide in low-polarity organic solvents, by technological convenience of using thioacetamide in contrast to gaseous hydrogen sulfide, and by the capability of thioacetamide to form sulfides in reactions with metal salts.

Metal trifluoroacetates were synthesized by the reaction of the corresponding oxides with trifluoroacetic acid in aqueous solution [11]. In the crystalline form, the salts were isolated by slow evaporation of the acidified solutions on a water bath, followed by drying in air. The salts were identified by IR spectroscopy using data of [12]. Thioacetamide was additionally purified by recrystallization.

The polymer composites PMMA : Cd(Mn,Pb)S in the glassy state were synthesized by bulk radical polymerization of methyl methacrylate as reaction and dispersion medium simultaneously. The synthesis was performed similarly to [13]. To this end, benzoyl peroxide in an amount of 0.1 wt % relative to methyl methacrylate was introduced into methyl methacrylate solutions after the formation of metal sulfides in them, and the mixtures were heated to 60–70°C until they became viscous. The viscous solutions were loaded into dismountable glass cells, and the heating was continued until the composites

became glassy. Plates of size 2 × 2 cm were cut for the studies. The plate thickness was 0.41 ± 0.01 cm.

The excitation and luminescence spectra of the samples recorded with an SM 2203 spectrofluorimeter (Solar, Belarus) under the conditions of normal incidence of the excitation light from a DKsSh 150-1M high-pressure xenon arc lamp on the sample surface. Stationary luminescence was recorded at an angle of 45°. The excitation spectra were recorded in the region of photoluminescence maximum. The electron micrographs (TEM) were taken with a CM12 transmission electron microscope (Philips, Netherlands). Colloidal solutions were applied onto copper gauzes with amorphous carbon coating, dried, and examined at different magnifications. The colloids isolated from the solutions were dissolved in 1-butanol prior to applying onto the microscope support.

RESULTS AND DISCUSSION

On heating, the reaction mixtures containing the cadmium salt or mixtures of cadmium and manganese salts or of cadmium, manganese, and lead salts at molar ratios Cd : Mn < 1 : 1 acquired a canary color characteristic of cadmium sulfide. The reaction mixtures containing the manganese salt or a mixture of cadmium and manganese salts at the molar ratio Cd : Mn = 1 : 1 remained colorless. All the solutions were transparent. The concentrated solutions showed opalescence under illumination. The opalescence confirmed the colloidal nature of the solutions. The solutions remained stable for several hours, and the most stable solutions, even for several days. Upon breakdown of colloidal solutions, precipitates formed on the bottom of the reaction vessel. The color of the precipitates corresponded to the color of the solutions. The solutions over the precipitates became colorless. The time within which the solutions were stable was sufficient for their curing to the glassy state by polymerization of methyl methacrylate.

Figure 1 shows the TEM micrographs of the colloidal solutions. Structures forming with time in the course of substance aggregation are seen. Colloidal particles of metal sulfides of size 4–5 nm (TEM) form spherical aggregates of size up to 40 nm. In addition, complex compounds are formed in the solutions, coating the colloidal particles with a shell. Trifluoroacetate ions and thioacetamide can serve as ligands in the complexes.

The colloidal solutions were broken down by additional heating. The products of the reaction of metal

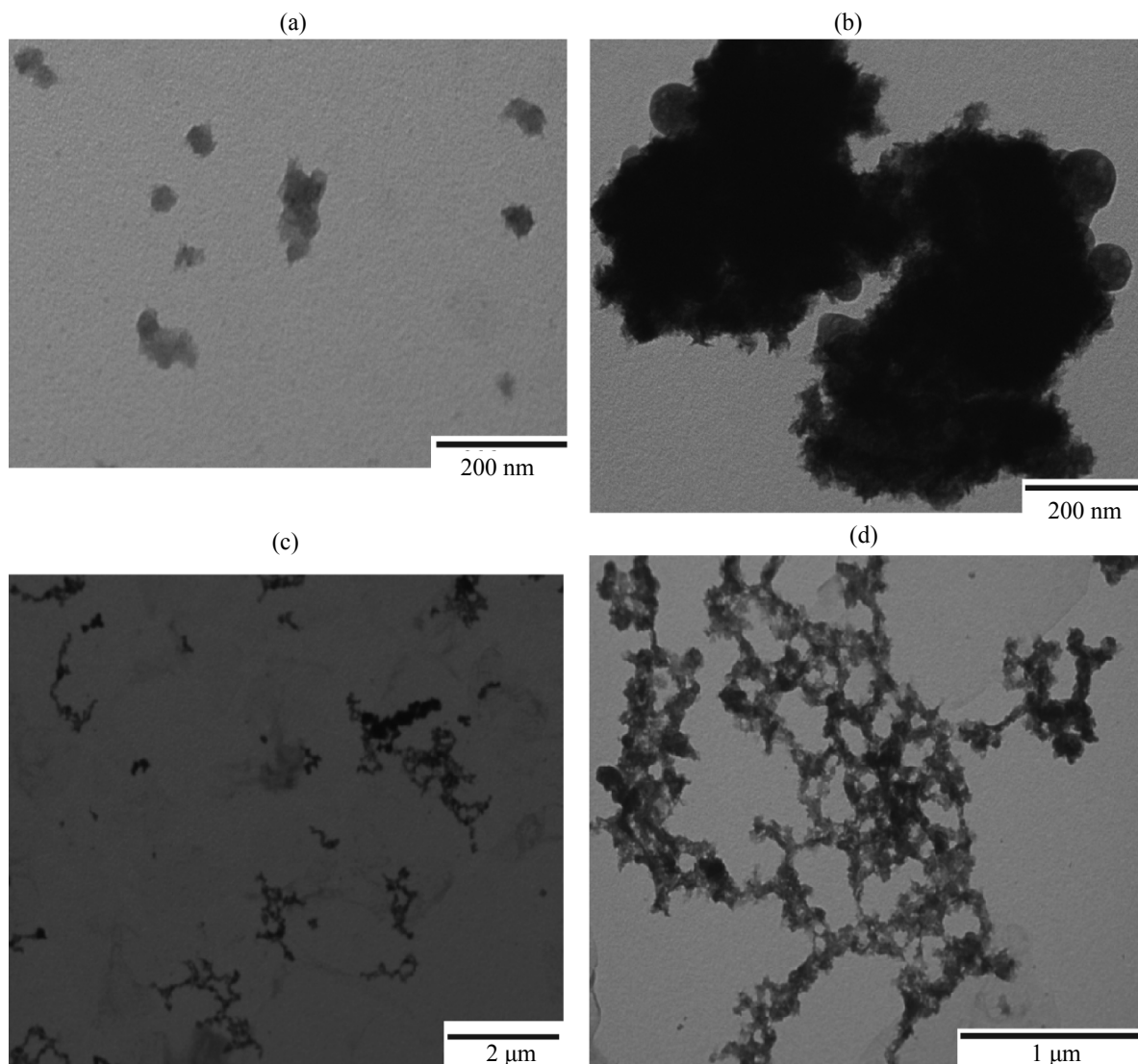


Fig. 1. TEM images of products formed in the reaction of cadmium and manganese trifluoroacetates with thioacetamide. (a) Nucleating aggregates, (b) aggregate fragment, and (c, d) aggregates formed with time.

trifluoroacetates with thioacetamide precipitated and were separated and dried in air to the pasty state. The color of the substances obtained corresponded to the color of the initial colloidal solutions. The absence of elemental sulfur in the precipitates was confirmed by the negative test of the products for solubility in toluene and benzene [14]. The TEM micrographs of the colloids are shown in Fig. 2. Differences in the images of the systems containing Mn(II) ions are associated with considerable difference in the solubility between manganese sulfide, on the one hand, and cadmium and lead sulfide, close to each other in solubility, on the other hand [15]. In the first case, we can assume the formation of a solid solution of cadmium and lead sulfide with the concentration of lead ions increasing

to the periphery, and in the second case, the formation of core-shell particles. The shell is formed by manganese sulfide. In all the cases, the particles are coated to a greater or lesser extent with the shell of the complexes.

A weak band is observed in the luminescence spectra of the colloidal solutions (Fig. 3a). In accordance with the position in the spectrum, this band is associated with the surface defects of cadmium sulfide particles (“surface” luminescence”). Significant long-wave shift of this band confirms the occurrence of the complexation on the surface of the colloidal particles [7]. The luminescence band of the separated colloids (Fig. 3b) is better defined, and its intensity is slightly higher. This is associated, first, with the transition from the solution to the solid phase and,

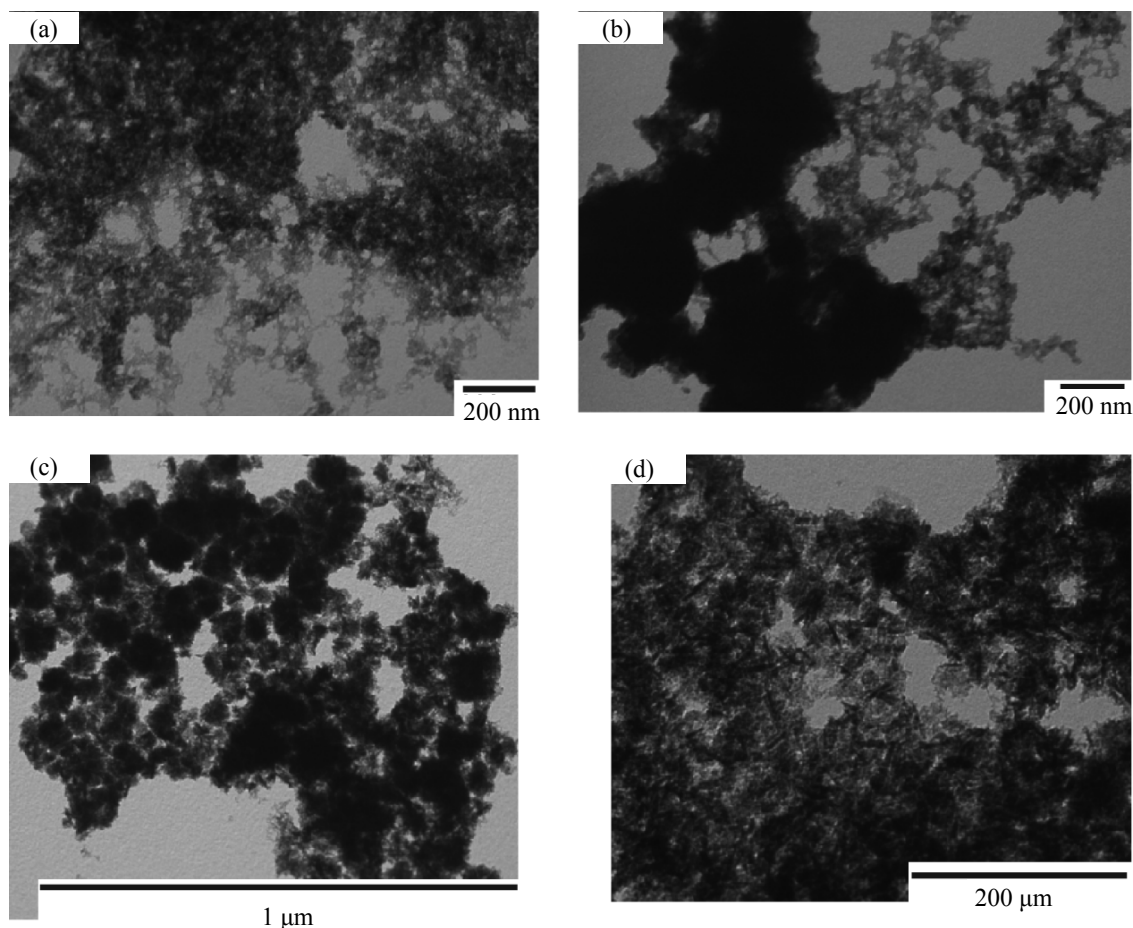


Fig. 2. TEM images of colloids isolated from the solutions. (a) $\text{Cd}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$, (b) $\text{Cd}(\text{CF}_3\text{COO})_2\text{-Pb}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$, and (c, d) $\text{Cd}(\text{CF}_3\text{COO})_2\text{-Mn}(\text{CF}_3\text{COO})_2\text{-TAA-EA}$. Molar ratio $\text{Cd} : \text{Pb} = \text{Cd} : \text{Mn} = 1 : 0.1$. The colloids were applied onto the microscope support after dissolution in 1-butanol.

second, with increased yield of cadmium sulfide under the conditions of more intense heating of the solutions in the course of colloid separation. The position and intensity of this band are independent of the excitation radiation wavelength.

The colloidal solutions were converted to the glassy state by methyl methacrylate polymerization in the bulk on heating. The $\text{Cd}(\text{II})$ concentration in all the initial solutions subjected to polymerization was 0.010 M. The $\text{Mn}(\text{II})$ concentration in the solution with the molar ratio $\text{Cd} : \text{Mn} : \text{Pb} = 0 : 1 : 0$ was 0.040 M. The polymerization lasted for 24 h. As a result, $\text{PMMA}:\text{Cd}(\text{Mn},\text{Pb})\text{S}$ composites were obtained. The $\text{Cd} : \text{Mn} : \text{Pb}$ molar ratios in the composites were 1 : 0 : 0, 1 : 0.01 : 0, 1 : 0.05 : 0, 1 : 0.1 : 0, 1 : 1 : 0, 1 : 0.1 : 0.1, and 0 : 1 : 0. After the polymerization, the majority of the polymer samples preserved the yellow-green color of the initial solutions. Its intensity decreased, especially at higher manganese

content. The $\text{PMMA}:\text{Cd}(\text{Mn})\text{S}$ ($\text{Cd} : \text{Mn} = 1 : 1$) and $\text{PMMA}:\text{MnS}$ composites in the course of polymerization acquired the red color characteristic of manganese sulfide. The samples underwent “clarification.” This may be due to the decomposition of the complex compounds on heating in the course of the polymerization. The spectrum of one of the samples is shown in Fig. 4. The light transmittance of the composites at $\lambda > 480$ nm was 92% (0.40 cm).

In the luminescence spectra of the composites (Fig. 5), there is a composite band consisting of at least four components with the maxima at 426, 556, 620, and 665 nm. On introducing $\text{Mn}(\text{II})$ into the formulation, the luminescence intensity increased relative to the $\text{PMMA}:\text{CdS}$ composites. Introduction of $\text{Pb}(\text{II})$ led to a decrease in the luminescence intensity. This fact confirms the above assumption that the character of formation of the semiconductor particles is different in different

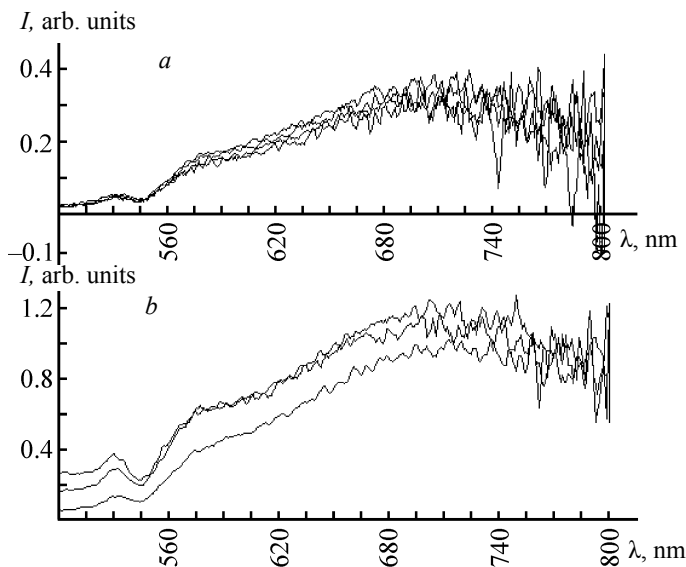


Fig. 3. Luminescence spectra of the (a) $(\text{CF}_3\text{COO})_2\text{Cd}$ -TAA-EA system after heating and (b) colloid isolated from the $(\text{CF}_3\text{COO})_2\text{Cd}$ -TAA-EA system. Excitation radiation wavelength 330, 365, and 400 nm. (*I*) Luminescence intensity and (λ) wavelength; the same for Fig. 5.

systems. The change in the intensity is associated with changes in the defectiveness of the surface of CdS particles on incorporation of Mn(II) and Pb(II).

With decreasing time of heat treatment in the course of polymerization, the long-wave component of the luminescence band increases in intensity and undergoes red shift toward wavelengths larger than 700 nm, whereas the band with the maximum at 426 nm disappears.

An increase in the intensity of the short-wave components of the luminescence band is associated with the breakdown of the “shell” of the complexes under the

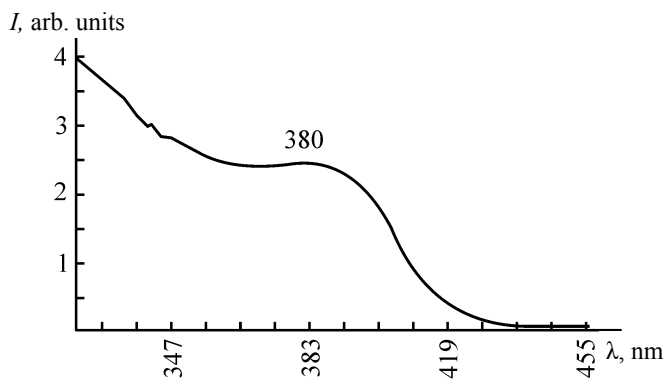


Fig. 4. Absorption spectrum of the PMMA:Cd(Mn)S composite. Molar ratio Cd : Mn = 1 : 0.1, spectrum recorded relative to air, sample thickness 0.40 cm. (*I*) Absorption intensity and (λ) wavelength; the same for Fig. 6.

action of elevated temperature and by the continuing reaction of cadmium sulfide formation in the course of polymerization of the composites. The action of these factors led to alteration of the surface of the colloidal particles and to further formation of the crystal structure of their cores. This is confirmed by the appearance of the luminescence band with a maximum at 426 nm.

The luminescence bands with maxima at 620 and 665 nm, like those in the spectra of the solutions, are associated with defects on the particle surface. The band with a maximum at 556 nm was insensitive to variation of the colloid composition and synthesis conditions. Therefore, it can be attributed to the defectiveness of the crystal of cadmium sulfide activated with Mn(II) and Pb(II) ions. The strongest luminescence was observed upon excitation by the radiation with $\lambda = 330$ and 334 nm. The maximum of the luminescence band of the PMMA : Cd(Mn)S composites at such excitation is in the interval 610–620 nm. Upon introduction of lead(II) into the composites, the band maximum shifted toward longer wavelengths. A slight red shift of the luminescence band maximum of the PMMA : Cd(Mn)S composites from 602 to 620 nm with an increase in the excitation radiation wavelength from 262 to 410 nm was observed. The band with a maximum at 426 nm is associated with the “volume” luminescence. It is due to defects in the volume of the CdS crystal lattice. As the manganese content of the composites was increased to the Cd : Mn molar ratio of 1 : 1, the intensity of this band decreased, and on introducing Pb(II) it disappeared.

The absorption bands corresponding to the luminescence were recorded in the excitation spectra (Fig. 6). These bands are composite. There are at least two compo-

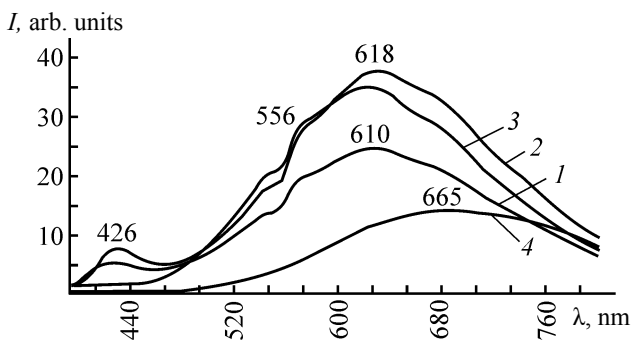


Fig. 5. Luminescence spectra of the PMMA:Cd(Mn,Pb)S composites. $\lambda_{\text{ex}} = 330$ nm. Cd : Mn : Pb molar ratio: (*I*) 1 : 0 : 0, (2) 1 : 0.1 : 0, (3) 1 : 1 : 0, and (4) 1 : 0.1 : 0.1.

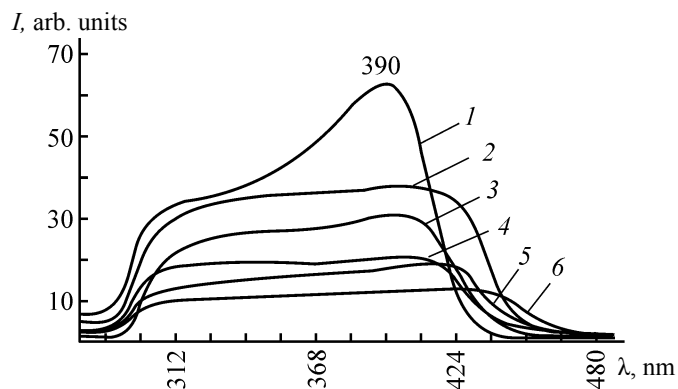


Fig. 6. Luminescence excitation spectra of the PMMA: Cd(Mn,Pb) S composites, $\lambda_{lum} = 620$ nm. Cd : Mn : Pb molar ratio: (1) 1 : 1 : 0, (2) 1 : 0.1 : 0, (3) 1 : 0 : 0, (4) 1 : 0.05 : 0, (5) 1 : 0.01 : 0, and (6) 1 : 0.1 : 0.1.

nents with the maxima at approximately 330 and 400 nm. This is associated with nonuniformity of the luminescent sites. Introduction of a large amount of Mn(II) considerably enhances the long-wave component of the absorption band, and in other features the spectra are typical.

CONCLUSION

Colloidal solutions were prepared, and optically transparent polymer composites poly(methyl methacrylate): Cd(Mn,Pb)S with different concentrations of Mn(II) and Pb(II) were synthesized. The position of the spectrum bands and the luminescence intensity of the composites are associated with the defectiveness of the surface of cadmium sulfide particles. These characteristics strongly depend on the complexation on the particle surface. In addition, a luminescence band originating from defects in the volume of the crystal structure of cadmium sulfide and of cadmium sulfide activated with Mn(II) ions is observed.

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