Synthesis and Luminescence Spectra of Poly(methyl methacrylate)/CdS:Ln(III) Composites

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Abstract—Cadmium sulfide was prepared by colloidal synthesis in methyl methacrylate (MMA). Europium and terbium salts were added to the colloidal solutions. Using MMA radical polymerization, we synthesized PMMA/CdS:Eu(III), PMMA/CdS:Tb(III), and PMMA/CdS:Eu(III):Tb(III) luminescent composites. Their luminescence is due to defects in the CdS crystals and the $^5D_0 \rightarrow {}^7F_j$ and $^5D_4 \rightarrow {}^7F_j$ electronic transitions of the Eu^{3+} and Tb^{3+} ions, respectively. It depends on the composition of the materials, complexation on the surface of the colloidal particles, heat treatment time during synthesis, excitation wavelength, and other factors.

Keywords: colloidal synthesis, composites, poly(methyl methacrylate), nanoparticles, cadmium sulfide, europium(III), terbium(III), luminescence

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INTRODUCTION

Increased research interest in quantum dots (QDs) is aroused by the possibility of resolving important problems in instrument engineering, biology, ecology, and medicine [1]. It is caused by the quantum size effect: the dependence of the physical and chemical properties of nanoparticles on their size [2–4]. In connection with this, considerable research effort has been concentrated on methods for the synthesis of nanostructures and composites with controlled properties of particles and investigation of their properties [5–11].

Cadmium and zinc chalcogenide QDs have been studied best. They range in average particle size from 3 to 7 nm [3, 10, 12–14]. At minimum dimensions, their structure is just in the early stages of formation. It comprises a number of polytypes. Spherical shapes prevail. As their size increases, the particles become rectangular. In the case of cadmium sulfide, this is due to the formation of the wurtzite structure [3, 15]. The visible and near-IR luminescence of CdS nanoparticles is commonly attributed to radiative recombination at structural defects and impurities in the bulk and on the surface of crystals [12, 16–20].

Combining the unique properties of inorganic semiconductor nanoparticles and favorable processing properties of optical polymers, their composites have attracted considerable attention [21, 22]. Luminescence spectra of composites depend on their composition, the synthesis technique used, and other factors.

Luminescence is also significantly influenced by the activation of semiconductors with the Cu^{2+}, Ag^+, Mn^{2+}, and Pb^{2+} ions and surface formation conditions [1, 14, 23, 24]. It has been pointed out that more stable luminescence characteristics are offered by core/shell structures or more complex composites prepared by combining different semiconductors [25–27].

A combination of the particle size and synthesis method allows heterogeneous composites to retain optical transparency. One such method is colloidal synthesis. In this method, QDs are produced in situ in a monomer (or in a mixture of monomers), which is a key component of composites and serves as a reaction and dispersion medium [12, 28, 29]. Composites can be converted to a glassy state by monomer block polymerization [7, 30–32]. This approach ensures internal integrity, without destroying the structure formed in the monomer in the composite "assembly" process.

Metal sulfides can be synthesized using H_2S [7, 28], Na_2S [12, 33], sulfur, and organosulfur compounds [8, 14, 26, 33]. The size of nonaggregated colloidal chalcogenide particles in polymer matrices typically does not exceed 10 nm [12, 14, 34]. Judging from their properties, they can be thought of as QDs [35] placed in a specific optical polymer medium. The size of aggregated particles reaches tens of nanometers [25, 34]. In a polymer matrix, they reside inside of globules formed by macromolecules and in spaces resulting from the formation of the supramolecular structure of

the polymer. Colloidal particles and aggregates are coated with a layer of complexes. Its thickness depends on the nature of precursors and heat treatment conditions [14, 34].

No less interesting are the optical properties of lanthanides, which continue to attract intense attention [36−43]. Lanthanides can be embedded into polymer matrices using (meth)acrylates, β-diketonates, nitrates, trifluoroacetates, and other compounds [31, 44−46]. Approaches for the synthesis of metal-containing polymers were classified by Pomogailo and Savost'yanov [47]. The highest optical transmission was achieved by modifying polymers with metal trihaloacetates [30, 31].

In our studies, we used CdS and poly(methyl methacrylate) (PMMA), because their properties are well studied, as well as Eu^{3+} and Tb^{3+}, because these lanthanides offer bright luminescence, which is relatively easy to sensitize and not very easy to quench. Combining the properties of three distinct components—inorganic semiconductor, metal ions, and polymer—in one composite is aimed at synthesizing novel optical materials combining the spectral properties of metal-containing modifiers with the favorable processing properties and low cost of polymers [48].

The purpose of this study was to synthesize cadmium sulfide and its complexes with lanthanides(III) by an emerging reagent method in an acrylate monomer medium, assess the mutual effects of the substances on their luminescence properties, and understand how these properties depend on physicochemical factors in optically transparent PMMA-based polymer composites.

EXPERIMENTAL

Cadmium sulfide was synthesized in situ by reacting cadmium trifluoroacetate with thioacetamide (TAA) (C_2H_5NS, foreign-made) during heating in methyl methacrylate (MMA) (Merck), in the course of the synthesis of PMMA/CdS and PMMA/CdS:Ln(III) composites, like in previous work [14, 32]. The cadmium trifluoroacetate and TAA concentrations in solutions were 0.010 mol/L. The cadmium trifluoroacetate solutions were prepared by dissolving an appropriate weighed amount of the salt in MMA. To the salt solutions was added an aliquot of the TAA solution in MMA. The resultant solutions were heated at a temperature from 70 to 90°C for 10−20 min. The formation of CdS was evidenced by the development of a yellow-green color, characteristic of this sulfide. The observed opalescence of the solutions confirmed their colloidal nature. Europium or terbium trifluoroacetate or their mixture was added independently of the cadmium-containing modifier after the formation of CdS in the solutions. The europium trifluoroacetate concentration in the solutions was varied from 0.0050 to 0.20 mol/L. The concentration of terbium trifluo-

roacetate or a mixture of europium and terbium trifluoroacetates was 0.10 mol/L. Raising the lanthanide trifluoroacetate concentration to 0.20 mol/L led to an increase in the viscosity and, hence, stability of the colloidal solutions.

PMMA/CdS and PMMA/CdS:Ln(III) (Ln(III) = Eu(III), Tb(III)) composites or their mixture in a glassy state was synthesized by radical block polymerization of MMA as described elsewhere [30]. To this end, benzoyl peroxide (0.1 wt % with respect to the MMA) was added to the solutions, which were then heated at a temperature of 60−70°C until a viscous state was obtained. The viscous solutions were loaded into dismountable glass cuvettes and heated further until the composites converted into a glassy state. The polymerization time was 8 or 24 h, depending on the nature of the material. The composites thus obtained had the form of yellow-green transparent "glasses." They were identical in color to the solutions. The color was due to the presence of CdS in the composites. The addition of europium and terbium trifluoroacetates to the composites had no effect on their color. The transmission of the matrix of the composites at wavelengths above 480 nm and a sample thickness of ≤0.50 cm was 90−92%.

The choice of the starting reagents was prompted by the good solubility of the metal trifluoroacetates [49] and TAA in MMA, a well as by the favorable processing properties of TAA, as distinct from gaseous hydrogen sulfide, and its ability to form sulfides through reaction with metal salts.

The metal trifluoroacetates were synthesized by reacting appropriate oxides with trifluoroacetic acid in an aqueous media [49] and were identified by IR spectroscopy using previous data [50]. The thioacetamide was further purified by recrystallization.

IR spectra were measured in the range from 4000 to 400 cm^{-1} on an Infralum FT 801 Fourier transform IR spectrometer (samples pressed with KBr). The absorption spectra of the composites were measured on a Specord UV VIS spectrophotometer in the spectral range 250−800 nm relative to air and unmodified PMMA plates of comparable thickness. Luminescence excitation and luminescence spectra were measured on a Solar CM 2203 spectrofluorometer (Belarus). The excitation beam from a light source (DKsSh 150-1M high-pressure xenon arc lamp) was incident along the normal to the sample surface. Steady state luminescence was detected at 45°. The excitation spectra were obtained near the peak emission wavelength in the luminescence spectrum. To assess the influence of modifier composition and concentration on the luminescence intensity, all of the luminescence spectra were taken at the same sample thickness: 0.40 ± 0.01 cm.
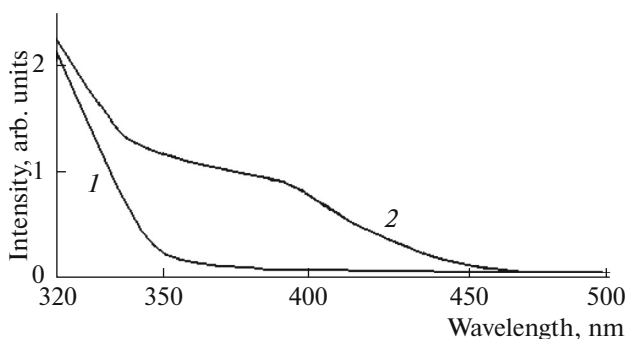
Fig. 1. Absorption spectra of (*1*) PMMA and (*2*) a PMMA/CdS composite.

Fig. 2. Luminescence spectra of PMMA/CdS composites at different excitation wavelengths and polymerization times: (*1*) 322 nm (24 h), (*2*) 396 nm (24 h), (*3*) 396 nm (8 h); $C_{Cd(II)} = C_{TAA} = 0.010$ mol/L polymerizable mixture.

RESULTS AND DISCUSSION

Unmodified PMMA is transparent to electromagnetic radiation with $\lambda > 350$ nm (Fig. 1, spectrum *1*). The absorption spectrum of a PMMA/CdS composite shows a broad band in the range 350–450 nm, corresponding to interband electronic transitions in CdS (Fig. 1, spectrum *2*). The peak position of the absorption band is near 390 nm. Its descending side extends to the range $\lambda > 450$ nm. From the abscissa intercept of a tangent (470 nm), we evaluated the band gap of CdS and estimated its particle size as described by Piven et al. [23]:

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

where h is Planck's constant; $\mu = [(m_e^*)^{-1} + (m_h^*)^{-1}]^{-1}$, $m_e^* = 0.21m_e$, $m_h^* = 0.80m_e$ are the effective electron and hole masses in CdS, respectively; m_e is the electron rest mass; and ΔE_g is the difference in E_g between a CdS nanoparticle and a bulk CdS crystal (2.4 eV). In this way, the particle size was estimated at ~3.1 nm. This result correlates with calculation and transmission electron microscopy (TEM) data [12, 14, 34].

In the red through near-IR spectral region, the PMMA/CdS materials have a broad, composite luminescence band (Fig. 2, spectra *1*, *2*), which is centered at 620 nm and has a full width at half maximum (FWHM) of ~180 nm. It is due to the CdS nanoparticles and arises from radiative recombination involving defect levels produced by sulfur and oxygen ions [51, 52], as well as by cadmium ions, which form complexes with components of the matrix on the surface of the particles [34]. From the viewpoint of electronic transitions, the long-wavelength CdS luminescence is commonly attributed to the return of $(n - 1)d^{10}$ electrons of the cadmium ions from antibonding Cd–S and Cd–O orbitals to bonding ones [53]. A change in the excitation wavelength from 322 to 395 nm has essentially no effect on the characteristics of the band. At the same time, in the short-wavelength region an additional, weak luminescence band emerges, peaking
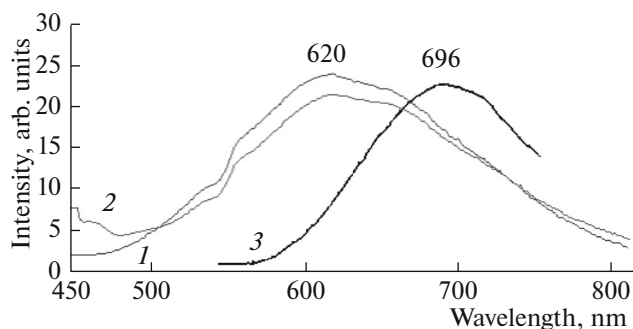
at <430 nm. Its position agrees with previous data [12, 14] and it arises from excitonic transitions due to defects in the bulk of CdS crystals.

Reducing the polymerization time (and accordingly the heat treatment time of the composites) from 24 to 8 h causes the luminescence band to shift to longer wavelengths. Its peak position shifts to the 700 nm range (Fig. 2, spectrum *3*). The shift is attributable to the more important role of interimpurity donor–acceptor transitions related to defects on the surface of the CdS crystals under complexation conditions. The defects produce energy levels ("traps") in the band gap of the semiconductor, and transitions from these levels account for the long-wavelength position of the luminescence band. The ligands in the complexes are trifluoroacetate ions, TAA molecules, and oligomers, which form a dispersion medium for the colloidal particles. The formation of a layer of complexes on the surface of particles was demonstrated previously by TEM results [12, 14, 34].

The spectra of the PMMA/CdS:Ln(III) composites contain, in addition to the broad luminescence band of CdS, narrow luminescence lines of the lanthanides. In the case of the europium-containing composites, the lines arise from the $^5D_0 \rightarrow {}^7F_{0, 1, 2, 3, 4}$ electronic transitions of the europium(III) ion (Figs. 3–5). The peak emission wavelengths are 585, 598, 620, 658, and 702 nm. The strongest line is that peaking at 620 nm. It arises from the $^5D_0 \rightarrow {}^7F_2$ electric dipole electronic transition, which is very sensitive to changes in the symmetry of the environment of the europium(III) ion, and is responsible for the red emission of the composites under excitation in the near-UV spectral region. Because of its low intensity, the band due to the $^5D_0 \rightarrow {}^7F_0$ electronic transition was only detected for the sample with the highest europium(III) concentration (Fig. 3, spectrum *5*) or under luminescence excitation in the intrinsic absorption band of the europium(III) ion (Fig. 5, spectrum *1*). The luminescence spectra of the PMMA/CdS:Eu(III) composite (Fig. 3), as well as those of a PMMA/Ln(III) composite [49],
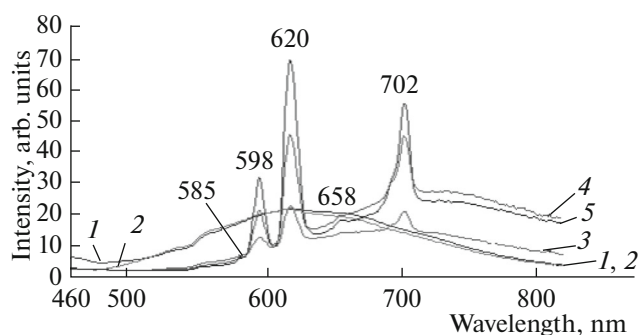
Fig. 3. Luminescence spectra of the PMMA/CdS (*1*) and PMMA/CdS:Eu(III) composites at various europium concentrations, mol/L polymerizable composite (Cd : Eu molar ratio): (*2*) 0.0050 (1 : 0.5), (*3*) 0.050 (1 : 5), (*4*) 0.10 (1 : 10), (*5*) 0.20 (1 : 20) (λ_{ex} = 396 nm).
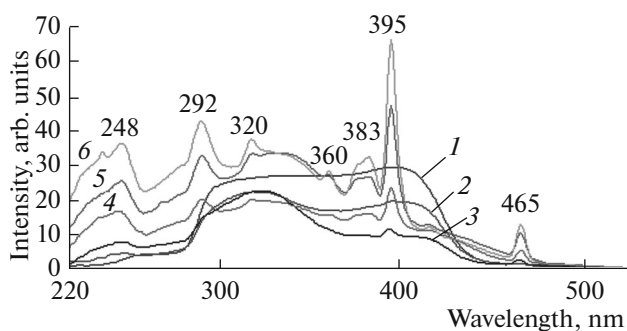

Fig. 4. Luminescence excitation spectra of the PMMA/CdS (*1*) and PMMA/CdS:Eu(III) composites at various europium(III) concentrations, mol/L polymerizable composite (Cd : Eu molar ratio): (*2*) 0.0050 (1 : 0.5); (*3*) 0.010 (1 : 1), (*4*) 0.050 (1 : 5), (*5*) 0.10 (1 : 10), (*6*) 0.20 (1 : 20) (λ_{em} = 620 nm).

differ from luminescence spectra of crystalline europium trifluoroacetate [49] in that they have broader, structureless bands, with a redistribution of the intensity of individual components of the bands. In the spectra of the PMMA/CdS:Ln(III) composites, the peak positions of the bands corresponding to the $^5D_0 \rightarrow {}^7F_{1, 2, 4}$ electronic transitions are shifted by a few nanometers. For example, the bathochromic shift of the strongest band, $^5D_0 \rightarrow {}^7F_2$, is 4 nm (616 → 620 nm). In the PMMA/CdS:Eu(III)−PMMA/Eu(III)−(CF$_3$COO)$_3$Eu · 3H$_2$O series, the peak position of the band due to the $^5D_0 \rightarrow {}^7F_4$ electronic transition is shifted by 702, 703, and 705 nm, respectively. The differences in peak position are associated with the inhomogeneous broadening of the band because the europium(III) ions have inequivalent coordinations and, accordingly, different fields are produced by their environments. They are attributable to the effect of the amorphous matrix (PMMA) and the inhomogeneity of the europium(III) complexes on the surface of the CdS particles and the complexes in the bulk of the polymer matrix, unrelated to the CdS particles. The small magnitude of the observed effects can be accounted for by the fact that the 4*f* valence electrons of the europium(III) ion are shielded by the $5s^25p^6$ outer electrons. The peak intensity of the europium(III) luminescence bands increases linearly with increasing europium(III) concentration in the composites ($I = 6.26 + 327C_{Eu(III)}$ with $r = 0.989$ for the $^5D_0 \rightarrow {}^7F_2$ band, centered at 620 nm). The linear increase in the intensity of the bands indicates that, over the entire concentration range studied, the concentration quenching of luminescence has a negligible effect. It also provides indirect evidence that it is appropriate to compare the luminescence intensities in different samples under the identical luminescence measurement conditions chosen.

Increasing the europium(III) content of the composites (Cd : Eu molar ratio) causes the broad luminescence band of CdS to shift to longer wavelengths (620 → 700 → 730 nm). This behavior also confirms

that europium(III) participates in complexation on the surface of the colloidal CdS particles and demonstrates that it is related to the position of the "trap" levels produced in the band gap of the semiconductor by surface defects formed with the participation of europium(III) ions. The shift is similar to that observed with decreasing polymerization time. This coincidence is quite justified: in both cases, the shift is due to the more important role of complexation on the surface of the colloidal particles. The relative increase in the intensity of the band corresponding to the $^5D_0 \rightarrow {}^7F_4$ electronic transition of europium(III) (702 nm) in the spectrum of the PMMA/CdS:Eu(III) composite (Fig. 3, spectra *3−5*) can be accounted for by an additive contribution that increases as the luminescence band of CdS shifts to longer wavelengths. The absence of narrow bands in the spectrum (Fig. 3, spectrum *2*) is due to the low europium concentration in this composite, given that their molar absorption coefficient does not exceed 10 cm^{-1} mol^{-1} L.

The luminescence excitation spectra of the composites show bands related to active absorption by the CdS and europium(III) ions (Fig. 4). The cadmium
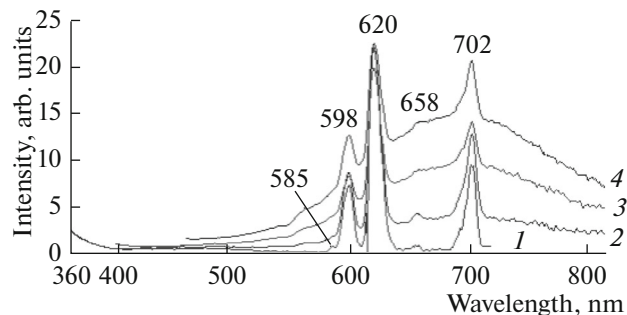

Fig. 5. Luminescence spectra of the PMMA/CdS:Eu(III) composite with $C_{Cd(II)} = 0.010$ mol/L polymerizable composite and $C_{Eu(III)} = 0.050$ mol/L polymerizable composite (Cd : Eu molar ratio = 1 : 5) at various excitation wavelengths: (*1*) 248, (*2*) 292, (*3*) 322, and (*4*) 396 nm.
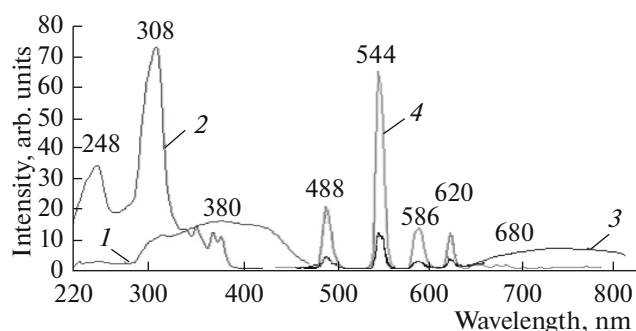
Fig. 6. (*1, 2*) Excitation and (*3, 4*) luminescence spectra of the PMMA/CdS:Tb(III) composite: λ_{em} = (*1*) 680 and (*2*) 544 nm, λ_{ex} = (*3*) 380 and (*4*) 308 nm.
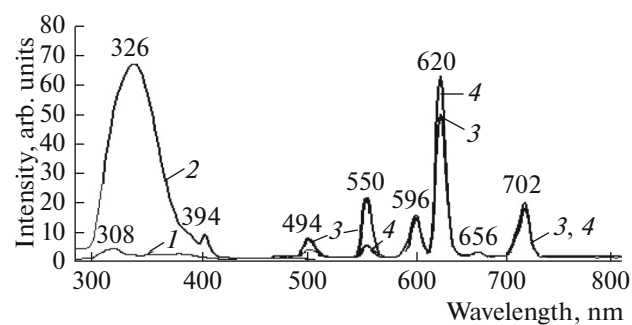

Fig. 7. (*1, 2*) Excitation and (*3, 4*) luminescence spectra of the PMMA/CdS:Eu(III):Tb(III) composite: λ_{em} = (*1*) 550 and (*2*) 620 nm, λ_{ex} = (*3*) 308 and (*4*) 326 nm.

sulfide is responsible for the broad, composite band in the wavelength range 280–450 nm, which includes at least two inhomogeneously broadened components peaking at 330 and 400 nm (Fig. 4, spectrum *1*). Its width and complex shape can be accounted for by the formation of several types of luminescence centers. They are related to defects in the bulk of the CdS crystals and different defect species on their surface (sulfur ions, oxygen, and cadmium vacancy complexes). Inhomogeneous surface defects produce acceptor "trap levels" of various energies in the band gap of CdS, as evidenced by the complex, inhomogeneously broadened luminescence band of CdS (Fig. 3). The incorporation of europium(III) into the composites reduces the intensity of the excitation band of CdS (Fig. 4, spectra *2, 3*). The reduction in the intensity of the longer wavelength component of the band is due to the rearrangement of the luminescence centers as a result of the complexation on the surface of the CdS particles. This shows up as a shift of the luminescence band of CdS and its peak to longer wavelengths (620 → >700 nm) with increasing europium(III) concentration (Fig. 3). In addition, a number of composite bands differing in intensity and width emerge in the spectrum in the wavelength range from 220 to 470 nm (Fig. 4, spectra *2–6*). The narrow bands peaking at wavelengths of 465, 395, and 292 nm are due to an active intrinsic absorption by the europium(III) ions. The strongest of them is the band peaking at 395 nm. It is commonly attributed to the $^7F_0 \rightarrow {}^5L_6$ electronic transition [46]. Like that of the luminescence bands, the intensity of the 395 nm band increases linearly with increasing europium(III) concentration in the composites. The broad bands centered in the range 250–400 nm, except the band of CdS, are due to organic chromophores in the composition of the ligands. They are responsible for the sensitization component of the europium(III) luminescence. The band peaking around 240 nm is commonly attributed to an active intrinsic absorption by the europium(III) ions in the crystal lattices of inorganic hosts [54, 55]. This leads us to assume that some of the europium(III) ions are incorporated into the crystal lattice of CdS.

At a given composition, changing the excitation wavelength from 248 to 396 nm increases the relative CdS luminescence intensity (Fig. 5) and slightly reduces the europium(III) luminescence intensity. This behavior is related to the excitation of different luminescence centers as the excitation wavelength is varied. Excitation in the absorption range of CdS leads to its luminescence, whereas excitation in the intrinsic absorption region of europium(III) ions results in europium(III) luminescence. Moreover, we observe a sensitization effect: the organic ligands absorb and europium(III) luminesces.

Similar effects show up in the spectra of the PMMA/CdS:Tb(III) composites (Fig. 6). The broadband absorption and luminescence are due to interband electron transitions with the participation of impurity levels located in the band gap of CdS. The narrow absorption bands are due to electron transitions from the ^7F_J electronic ground state of terbium(III) to its excited states. The luminescence bands correspond to the reverse transitions of the 4*f* electrons from the $^5D_4$ metastable state to the ^7F_J electronic ground state of the terbium(III) ion. In the polymer matrix, the bands are also inhomogeneously broadened. Their position differs little from that of the bands in the spectra of the PMMA/Tb(III) composite and crystalline terbium trifluoroacetate [49]. It agrees with previous data [40, 55]. The strongest band is that corresponding to the $^5D_4 \rightarrow {}^7F_5$ electronic transition of the terbium(III) ion (544 nm). This transition is responsible for the green emission of the composites under excitation in the near-IR spectral region. A brighter luminescence is observed under excitation at wavelengths λ = 300–320 nm (Fig. 6). This range contains intrinsic absorption bands of terbium(III) and bands of its complexes with organic ligands. We observe a sensitization effect.

Upon the incorporation of europium(III) and terbium(III) into CdS-containing composites, their excitation and luminescence spectra show bands of all the luminescent substances (Figs. 7, 8). Whether the relative intensity of the bands in the luminescence spectrum of the composite increases or decreases
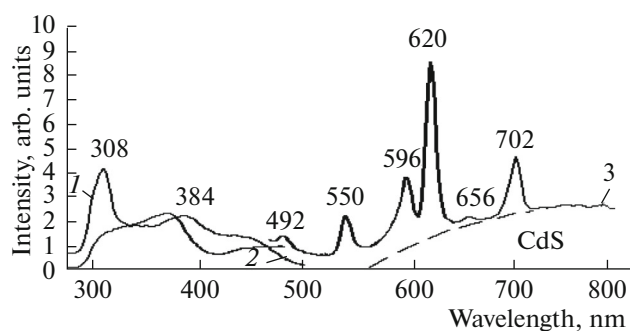
Fig. 8. (*1, 2*) Excitation and (*3*) luminescence spectra of the PMMA/CdS:Eu(III):Tb(III) composite: λ_{em} = (*1*) 550 and (*2*) 680 nm, λ_{ex} = (*3*) 384 nm.
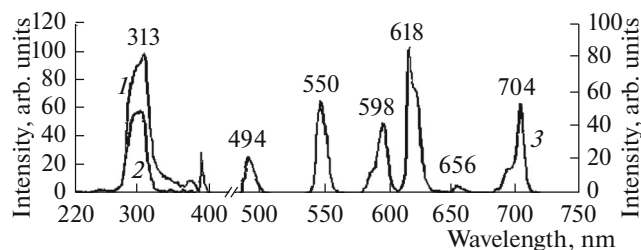

Fig. 9. (*1, 2*) Excitation and (*3*) luminescence spectra of the PMMA/Eu(III):Tb(III) composite: λ_{em} = (*1*) 617 and (*2*) 550 nm, λ_{ex} = (*3*) 313 nm.

depends on the excitation wavelength. This is due to different luminescence centers and the possibility of a sensitization effect for centers of a given composition. For example, under excitation in the absorption region of CdS, the spectrum shows its corresponding luminescence band (Fig. 8, spectrum *3*). Excitation in the intrinsic absorption region of the terbium(III) ion and its complexes gives rise to a terbium(III) luminescence (Fig. 7, spectrum *3*). Excitation in the intrinsic absorption region of the europium(III) ion and its complexes increases the intensity of the europium(III) luminescence bands (Fig. 7, spectrum *4*). Under polychromatic excitation, all the components of the composite luminesce.

The mutual effect of the substances shows up as a shift of individual luminescence bands: for example, 488 → 494 and 544 → 550 nm, respectively, for the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ electronic transitions of the terbium(III) ion. The peak positions of the bands are also shifted relative to those in the spectrum of the PMMA/Eu(III),Tb(III) composite: 598 → 596, 618 → 620, and 704 → 702 nm (Fig. 9). The observed changes are related to the redistribution of the fraction of the individual components of the Stark structure of the bands. They cannot be explained merely by summation of the intensities of closely spaced bands. It seems likely that they are related to symmetry changes in the environment of the luminescing ions upon interaction between the substances, which makes *f–f*

electron transitions allowed or increases their degree of forbiddenness. The relative terbium(III) luminescence intensity in the composites is observed to decrease, which may be due to partial excitation energy transfer from terbium(III) to europium(III) ions [46]. The mutual positions of the energy levels of their complexes favor this process. Another important condition for sensitization—direct physicochemical interaction between an energy donor and acceptor—is probably satisfied as a result of the complexation on the surface of the colloidal cadmium sulfide particles.

CONCLUSIONS

We have synthesized optically transparent polymer composites containing CdS, europium trifluoroacetate, and/or terbium trifluoroacetate. The luminescence excitation and luminescence spectra of the composites are combinations of the spectra of the constituent luminescent substances. The mutual effect of the substances shows up as a shift of the peak positions of the bands and changes in their relative intensities. The luminescence intensity of each of the luminescent substances or their mixture depends on excitation conditions. We assume that the lanthanide ions in the composites are always included in complexes on the surface of the CdS particles or are present as impurities in the CdS lattice or in the bulk of the polymer matrix, where they do not interact with the cadmium-containing modifier.

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