

New luminescent compounds based on chalcogenides and organic materials

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Data concerning fabrication and luminescent properties of new composite materials on the base of organic coordination compounds of Eu(III) ($\text{Eu}(\text{TTA})_3\text{H}_2\text{O}$, $\text{Eu}(\text{TTA})_3\text{Phen}$ or $\text{Eu}(\text{DBM})_3\text{Phen}$) dispersed in SBMA copolymer are presented. From chemical solutions thick films of 10–50 μm thickness was prepared and investigated. The transmission spectra at room temperature before and after UV treatment were measured. The photoluminescence spectra was investigated at room temperature and at the temperature of liquid nitrogen for all prepared liquid solutions and films of composites at the following concentrations of the luminescent $\text{Eu}(\text{III})(\text{DBM})_3\text{Phen}$, %: 2,0; 5,0; 8,0; 10,0; 11,0; 12,0. The nature of the observed emission bands and the possible mechanisms of the radiative electron transitions in the investigated composite materials are discussed.

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1. Introduction

The development of new organic/inorganic nanostructured composite materials is very attractive for future implementation of new photonic and optoelectronic devices. Some general principles of nanotechnology and nanostructured materials, its properties and possible applications are presented in the review article [1].

Actually the definition of nanocomposite materials has broadened significantly and includes a large variety of systems and structures such as one-dimensional, two-dimensional (metal oxides, metal phosphates, chalcogenides), three-dimensional and amorphous materials. Now the main efforts of scientists are focused on the ability to obtain control of the nanoscale structures with the requested physical and optical characteristics through innovative synthesizing approaches. It was shown that the properties of nanocomposite materials depend not only of the properties of their individual host components but also on their morphology and different active additives, such as luminescent rare earth ions.

In the recent years the luminescent composites based on lanthanide complexes have attracted much attention due to scientific interests as well as for its wide variety of application in photonics and optoelectronics: planar optical amplifiers, solar cells, light emitting diodes, gas selective sensors, photonic devices, etc. [2,3]. It should be mentioned that for the rare-earth doped optical waveguide amplifiers of inorganic materials (silica and chalcogenide glasses) there are some limitations of doping due to the concentration quenching effects: for silica glasses the doping level is limited up to 0.1 mole percent [4]. This

problem is easy solving by using for this purpose organic systems. The polymer matrices can be doped too much higher concentrations than silica glasses, using different lanthanide complexes. For this goal a new composite on the base of thenoyltrifluoroacetone (TTA) and the aromatic β -diketonate dibenzoylmethane (DBM) of Europium(III) and organic copolymer from styrene and butylmethacrylate (SBMA) was used. In this paper the optical absorption without and under the UV treatment and photoluminescent properties of new composite materials on the base of $\text{Eu}(\text{TTA})_3\text{H}_2\text{O}$, $\text{Eu}(\text{TTA})_3\text{Phen}$ or $\text{Eu}(\text{III})(\text{DBM})_3\text{Phen}$ and copolymer (SBMA) were investigated.

2. Experimental

The method of preparation of compounds tris(2-thenoyltrifluoroacetato)aqueeuropium(III) ($(\text{Eu}(\text{TTA})_3\text{H}_2\text{O})$) and tris(2-thenoyltrifluoro-acetonato) (monophenanthroline)europium(III) ($\text{Eu}(\text{TTA})_3\text{Phen}$) was used as it was described by authors [5-7]. The method of the interaction of Europium nitrate with thenoyltrifluoroacetone in the presence of sodium hydroxide was utilized. The purification was carried out by dissolution in benzene, with the sequential precipitation of hexane. As a polymer the copolymer based on styrene and butylmethacrylate (1:1) (SBMA) there was used, which was synthesized in the Moldova State University.

According to [8] for preparation of complex copolymer, the needed amount of copolymer was dissolved in benzene. The solution was kept for 1 hour,

and was mixed another hour. After that the Europium complexes were introduced in the mixture, also preliminary dissolved in benzene, and the solution was mixed during 30 min. The obtained mixture consisted from polymer, solvent, and organic compound of Eu(III) was deposited on the clean optical glass. After the evaporation of the solvent, the transparent achromatic films were obtained. The thickness of the composite films was about $L \sim 10 \div 50 \mu\text{m}$. The luminescent composite $\text{Eu}(\text{DBM})_3\text{Phen}/\text{SBMA}$ was prepared by chemical method as described in [8] from solutions in benzene of the initial components $\text{Eu}(\text{DBM})_3\text{Phen}$ and SBMA. The transmission spectra at room temperature before and after UV treatment were measured. The photoluminescence spectra was investigated at room temperature and at the temperature of liquid nitrogen for liquid solutions and thick films at the following concentrations of the luminescent $\text{Eu}(\text{DBM})_3\text{Phen}$ in composites, %: 2,0; 5,0; 8,0; 10,0; 11,0; 12,0. The optical transmission spectra have been measured using the spectrophotometers SPECORD UV VIS (in the spectrum range $0.3 \div 0.8 \mu\text{m}$) and SPECORD 61 NIR (in the spectrum range $0.8 \div 3.2 \mu\text{m}$). The luminescence spectra were measured at room and nitrogen temperatures when excited with N_2 -laser ($\lambda = 0.334 \mu\text{m}$) using spectrophotometers DFS-24 and MDR-23.

3. Results and discussion

The transmission spectra for the $\text{Eu}(\text{TTA})_3\text{H}_2\text{O}/\text{SBMA}$ composites thick films are characterized with high transparent ($T \sim 90\%$) at the wavelength $\lambda \geq 450 \text{ nm}$ and with wide absorption band in the region of 500-600 nm of the spectrum. Some absorption bands in the region 350-400 nm described in [9] was assigned to the presence of Eu^{3+} , and are attributed to the electron transitions from the ground state ${}^7\text{F}_0$ and from the energy level ${}^7\text{F}_1$ to the Stark components of the Eu^{3+} ion: ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_1 \rightarrow {}^5\text{L}_7$, ${}^7\text{F}_1 \rightarrow {}^5\text{L}_6$.

Fig.1 shows the transmission spectra of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{SBMA}$ composite for different concentrations of $\text{Eu}(\text{TTA})_3\text{Phen}$. Increasing of the $\text{Eu}(\text{TTA})_3\text{Phen}$ concentration leads to increase of the absorption of composite and shifts of the absorption edge in red region of the spectrum. This is more evident for the higher concentrations of complex (15-20%), especially in the UV-region.

The strong absorption of the composites $\text{Eu}(\text{DBM})_3\text{Phen}/\text{SBMA}$ at $\lambda \leq 345 \text{ nm}$ according to [10] is assigned to the $\Pi \rightarrow \Pi^*$ transitions of the conjugated double bonds in the aromatic β -diketonate dibenzoylmethane (DBM) ligands. The absorption onset of a SBMA polymer film lies at $\sim 410 \text{ nm}$ and indicates that the host is transparent in the range of visible light. After the UV treatment of the composites the transparency in the visible region increases.

The photoluminescence spectra of composites $\text{Eu}(\text{TTA})_3\text{H}_2\text{O}$ powder at room ($T = 293 \text{ K}$) and at nitrogen ($T = 78 \text{ K}$) temperatures are characterized with the presence

of sharp emission bands situated in the region $550 \div 630 \text{ nm}$, and correspond to radiative transitions from the excited state ${}^5\text{D}_0$ to the ${}^7\text{F}_0$, ${}^7\text{F}_1$ and ${}^7\text{F}_2$ levels of the Eu^{3+} ion: ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ (580 nm), ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (590 nm), and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (620 nm). For the $\text{Eu}(\text{TTA})_3\text{H}_2\text{O}/\text{SBMA}$ composites thick films lowering of the temperature from 293 K up to 78 K lead to increasing of the photoluminescence intensity of the bands situated at 650 and 700 nm. The photoluminescence bands situated at 650 and 760 nm correspond to radiative transition from the excited state ${}^5\text{D}_0$ to the ${}^7\text{F}_3$ and ${}^7\text{F}_4$ levels of the Eu^{3+} ion, respectively.

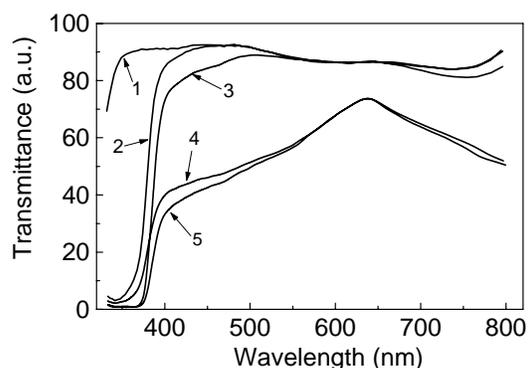


Fig. 1. The transmission spectra of the $\text{Eu}(\text{TTA})_3\text{Phen}/\text{SBMA}$ composites thin films for different concentrations of $\text{Eu}(\text{TTA})_3\text{Phen}$ in SBMA: 1 – 0%; 2 – 2%; 3 – 10%; 4 – 15%; 5 – 20%.

Fig.2 shows the photoluminescence spectra of the $\text{Eu}(\text{TTA})_3\text{Phen}/\text{SBMA}$ for 15 wt.% concentration of complex $\text{Eu}(\text{TTA})_3\text{Phen}$ in the SBMA polymer matrix at the nitrogen temperature.

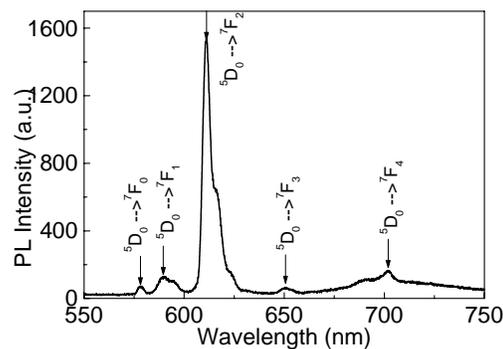


Fig. 2. The PL spectra of the $\text{Eu}(\text{TTA})_3\text{Phen}/\text{SBMA}$ composite for with 15 wt.% of concentration of complex $\text{Eu}(\text{TTA})_3\text{Phen}$ in the SBMA polymer matrix at $T = 78 \text{ K}$.

The strong luminescence bands were observed in the 570-720 nm situated at 578, 590, 611, 616, 650 and 702 nm. If we compare the photoluminescence spectra of

$\text{Eu}(\text{TТА})_3\cdot\text{H}_2\text{O}/\text{SBMA}$ powder and $\text{Eu}(\text{TТА})_3\text{Phen}/\text{SBMA}$ composites thick, we established that non essential shift of the emission bands take place. The emission bands in $\text{Eu}(\text{TТА})_3\text{Phen}/\text{SBMA}$ nanocomposite located at 578 (${}^5\text{D}_0\rightarrow{}^7\text{F}_0$), 590 (${}^5\text{D}_0\rightarrow{}^7\text{F}_1$), 611 (${}^5\text{D}_0\rightarrow{}^7\text{F}_2$) nm coincide with those observed by other authors [5]. No emission of ligands or polymer matrix is observed, indicated that the energy transfer from the polymer matrix to the Eu^{3+} ion is quite efficient. In [11] was mentioned that the effective interaction between the lanthanide ions and the host hybrid structure accounts for the increase of the emission overall quantum yield (36 %) and for the ${}^5\text{D}_0$ quantum efficiency (57 %) with respect to those of the complex alone (29 % and 27 %, respectively).

According to [5], lowering of the temperature increase the intensity of the luminescence bands with the activation energy $E_a=15$ MeV, less than in the respective crystal due to more weak relaxation processes as a result of the electron-phonon interaction. It was shown that the maximum intensity of photoluminescence occurs at the concentration of 15 % of the $\text{Eu}(\text{TТА})_3\text{Phen}$ in the polymer matrix of SBMA (Fig.3). The energy of the excited state rare-earth ion may be radiatively and non-radiatively and depends on the spacing of the 4f-levels. The strong photoluminescence in Eu^{3+} -doped complexes with respect to other lanthanides (Sm^{3+} , Tb^{3+} , Dy^{3+} , Yb^{3+}) is due to the fact that the prime emitting level (${}^5\text{D}_0$) is fairly isolated, with no close lower-lying levels. In the future the mechanisms of energy transfer to rare-earth ions also must be taken into account.

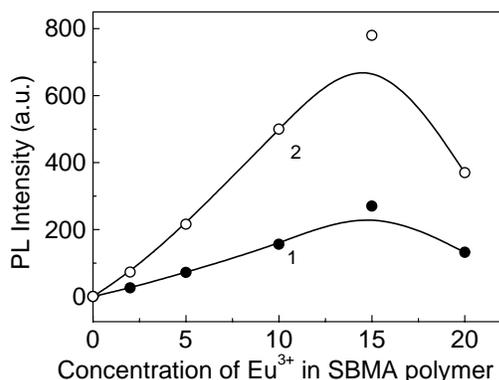


Fig. 3. The dependences of the photoluminescence intensity of the $\text{Eu}(\text{TТА})_3\text{Phen}/\text{SBMA}$ composite versus concentration of complex $\text{Eu}(\text{TТА})_3\text{Phen}$ in the SBMA polymer matrix at 293 K (curve 1) and 78 K (curve 2).

The emission spectrum of the $\text{Eu}(\text{DBM})_3\text{Phen}$ dispersed in SBMA polymer film exhibit well resolved peaks, characteristic of the europium ion and assigned to the transitions ${}^5\text{D}_0\rightarrow{}^7\text{F}_0$ (579 nm), ${}^5\text{D}_0\rightarrow{}^7\text{F}_1$ (592 nm), ${}^5\text{D}_0\rightarrow{}^7\text{F}_2$ (612 nm), ${}^5\text{D}_0\rightarrow{}^7\text{F}_3$ (654 nm), and ${}^5\text{D}_0\rightarrow{}^7\text{F}_4$ (702 nm) with the ${}^5\text{D}_0\rightarrow{}^7\text{F}_2$ transition at 612 nm being the dominant emission peak. ${}^5\text{D}_0\rightarrow{}^7\text{F}_2$ transition at 612 nm is a hypersensitive transition, i.e. the intensity of this

transition has a strong dependence of the chemical environment of the Eu^{3+} ion. The band situated at ~ 730 nm may be assigned with the fluorescence from the polymer complexes, implying efficient energy transfer from the triplet states of the β -diketonate ligands to the central lanthanide ions. Fig.4 represents the spectrum of the 8% $\text{Eu}(\text{DBM})_3\text{Phen}$ dispersed in SBMA polymer. The maximum photoluminescence intensity take place for the 10% $\text{Eu}(\text{DBM})_3\text{Phen}$ dispersed in SBMA polymer (Fig.5).

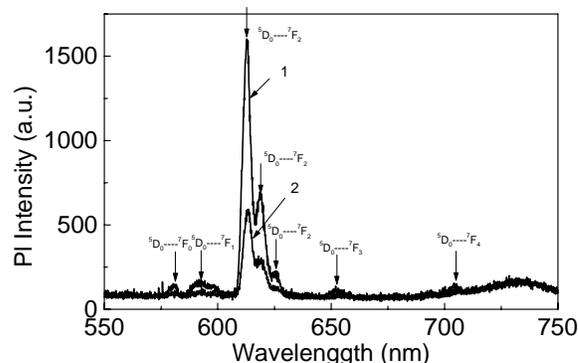


Fig. 4. Emission spectra of ~ 50 μm thick film lanthanide complex SBMA polymer with 5% $\text{Eu}(\text{DBM})_3\text{Phen}$ in SBMA at nitrogen (1) and at room (2) temperatures, $\lambda_{\text{exc}}=334$ nm

The time dependent photoluminescence decay for the Eu^{3+} doped composite polymer $\text{Eu}(\text{TТА})_3\text{Phen}/\text{SBMA}$ excited at different wavelengths and temperatures also was investigated. The lifetime was measured for the radiative transitions of the Eu^{3+} ion: 579 nm (${}^5\text{D}_0\rightarrow{}^7\text{F}_0$), 590 nm (${}^5\text{D}_0\rightarrow{}^7\text{F}_1$), 612 nm (${}^5\text{D}_0\rightarrow{}^7\text{F}_2$), and 705 nm (${}^5\text{D}_0\rightarrow{}^7\text{F}_4$) at room ($T=293$ K) and at nitrogen ($T=78$ K) temperatures.

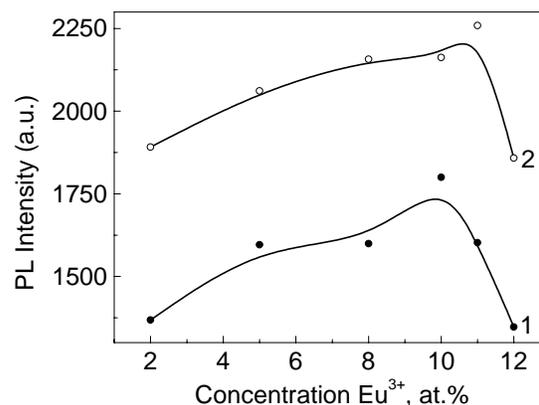


Fig. 5. PL intensity dependence at $\lambda=612$ nm of the $\text{Eu}(\text{DBM})_3\text{Phen}/\text{SBMA}$ composite vs. $\text{Eu}(\text{DBM})_3\text{Phen}$ concentration in SBMA copolymer for the solution (1) and thick film (2).

The lifetime τ measured at room temperature at two different wavelengths $\lambda=579$ and $\lambda=612$ nm give two different values of $\tau=12.5$ ms and $\tau=320$ ms, respectively.

The kinetics decay of the photoluminescence measured at $\lambda=590$ nm practically give the same lifetime of about $\tau=444$ ms for the room (293 K) and nitrogen (T=78 K) temperatures. These values are comparable to values measured for similar complexes as dopants in other polymer hosts [10].

4. Final remarks

On the base of study of photoluminescent properties of new polymeric composite materials based on organic coordination compounds of Eu^{3+} the emission bands have been established under the excitation with N_2 -laser ($\lambda=0.337 \mu\text{m}$). Luminescent spectra contain some sharp emission bands, which were identified with certain optical transitions corresponding energetically spectra of Eu^{3+} . The visible emission spectra of the composites on the base of thenoyltrifluoroacetone coordinated with trivalent europium ions and structured with phenantroline $\text{Eu}(\text{TTA})_3\text{Phen}$ and copolymer from styrene and butylmethacrylate (1:1) under the excitation with N_2 -laser ($\lambda=337$ nm) contain sharp emission bands located at 354, 415, 580, 587, 590, 596, 611.4, 616.5, 621, 652, 690, 700, 713 nm have been investigated. The maxima luminescence was attained at the concentration 15 wt.% of $\text{Eu}(\text{TTA})_3\text{Phen}$ in polymer matrices. It is more than 10 times in comparison with known doping concentrations. The kinetics decay of the photoluminescence measured at $\lambda=590$ nm practically give the same lifetime of about $\tau=444$ ms for the room (293 K) and nitrogen (T=78 K) temperatures.

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