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New photoluminophore nanocomposite based on organic compound with Eu^{3+} ions and copolymer styrene-butylmethacrilate

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ABSTRACT

New nanocomposite (NC) material on the base of thenoyltrifluoroacetone (TTA) coordinated with trivalent europium ions and structured with phenantroline ($Eu(TTA)_3Phen$) and copolymer from styrene and butylmethacrylate (1:1) (SBMA) was prepared. The visible photoluminescence spectra of composites excited with N_2-laser ($\lambda = 0.337$ μm) at room and $T = 78$ K temperatures were studied. For the $Eu(TTA)_3$-Phen/SBMA nanocomposite material emission bands located at 578, 590, 612, 675 and 705 nm can be attributed to the spin forbidden f–f transitions $^5D_0 \rightarrow {}^7F_i$ ($i = 0,1,2,3$ and 4), respectively. The more intensive luminescence band situated at 612 nm with the half width of 3 nm is connected to the Eu^{3+} ion electronic transition $^5D_0 \rightarrow {}^7F_2$. It was shown that the maximum intensity of photoluminescence occurs at the concentration of 15% of the $Eu(TTA)_3Phen$ in the SBMA polymer matrix.

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1. Introduction

At present the luminescent composites based on lanthanide complexes attract considerable attention due to scientific interests connected to their application in photonics and optoelectronics as waveguide optical amplifiers, solar cells, light emitting diodes, gas selective sensors, etc. [1,2]. More attractive are polymers doped with rare earths elements especially for optical waveguide amplifiers operating at 1.5 μm (so-called 'third telecommunication window'). The optical waveguide amplifiers of inorganic materials (silica or chalcogenide glasses) have limitations of doping with rare-earth elements because of the concentration quenching effect (e.g. for silica glasses the maximum doping level is limited up to 0.1 mole percent [3]). The clustering that leads to increasing of optical losses and quenching of the luminescence takes place at higher doping levels of rare earth-ions. This problem can be solved using organic systems. The polymers can be doped with concentrations much higher than silica glasses using different lanthanide complexes. Polymers composites doped with Eu^{3+} have been fabricated by different methods and have been investigated their optical and luminescence properties in [4–9]. The fluorescence in the visible region of the polymer of polymethylmethacrylate doped with Eu^{3+} ions was studied in [7,9]. In our previous papers we have reported some results on new composite materials from polymers and chalcogenide glasses doped with rare-earth ions [10,11]. We elaborated the technology of new fluorescence composite materials on organic compounds base excluding the presence of chalcogenide glass. In the present paper we continue investigations of the mentioned materials.

2. Experimental

2.1. Sample synthesis

The compounds tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanediono) aquaeuropium(III) ($Eu(TTA)_3 \cdot H_2O$) and tris(2-thenoyltrifluoroacetonate)(monophenanthroline) europium(III) ($Eu(TTA)_3$-Phen) were prepared using the method described in [12,13] by interaction of europium nitrate with thenoyltrifluoroacetonate in presence of sodium hydroxide. The purification was carried out by dissolution in benzene with the sequential precipitation in hexane.

The copolymer on styrene and butylmetacrylate (1:1) (SBMA) base synthesized at the Moldova State University was used. For obtaining of copolymer dissolution, the needed amount of copolymer was dissolved in benzene; the solution was kept for 1 h, and was mixed during another hour. After that the Europium complex was introduced in the mixture, also preliminary dissolved in benzene, and the solution was mixed during 30 min. The obtained mixture consisting from polymer, solvent, and complex of Eu^{3+} was deposited on the clean optical glass substrates. After the evap-

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oration of the solvent from substrates, the transparent achromatic films were obtained [14]. The thicknesses of the composite films were approximately 10 μm.

2.2. Optical and spectroscopic measurements

For optical transmittance and photoluminescence investigations UV–vis (300–800 nm) Specord CARL ZEISS Jena production and DFS-24 monochromators connected to the PC have been used. The photoluminescence (PL) spectra were measured at room and 78 K temperatures and by exciting of N_2-laser ($\lambda = 0.337$ μm).

3. Results and discussion

The microscopic investigations of the morphology of the NC surfaces show that the dimensions of $Eu(TTA)_3Phen$/SBMA particles, incorporated in the polymer matrix are undetectable, and hence their dimension is less than 100 nm.

The spectroscopy researches on each step of technology have shown that the compound of Eu^{3+} and their structure are not changed after incorporation into the copolymer. The transmission spectra of the $Eu(TTA)_3{\cdot}H_2O$ powder are presented on Fig. 1(a) and the thin films of $Eu(TTA)_3{\cdot}H_2O$/SBMA nanocomposites (NC) are presented on Fig. 1(b). The investigated composites are transparent ($T > 90\%$) at the wavelength $\lambda \geqslant 450$ nm. Wide absorption bands are observed in the wavelengths range of 500–600 nm. The strong absorption of NC at high-energy region of spectrum (350–400 nm) with characteristic bands of the presence of organic complex with ions of Eu^{3+} in nanocomposite has been detected. According to [10], this absorption bands is attributed to the electron transitions from the ground and first states $^7F_0$ and $^7F_1$ to the Stark components of the Eu^{3+} ion: $^7F_0 \rightarrow 5D4$, $^7F_0 \rightarrow {}^5G_4$, $^7F_0 \rightarrow {}^5G_2$, $^7F_1 \rightarrow {}^5L_7$, $^7F_1 \rightarrow {}^5L_6$.

Transmittance spectra of $Eu(TTA)_3Phen$/SBMA composites for different concentrations of $Eu(TTA)_3Phen$ complex are shown on Fig. 1(b). The increasing of the concentration of the Eu $(TTA)_3Phen$ complex in NC conducts to increasing of the absorption of composite and its shift in the red region of the spectrum. This is more evident for concentrations 15–20% of complex.

The photoluminescence spectra of powder $Eu(TTA)_3{\cdot}H_2O$ at 293 K and 78 K temperatures are presented on Fig. 2(a) and (b), respectively. Photoluminescence bands at room temperature are situated in the wavelengths range 550–730 nm and correspond to radiative transitions from the excited state $^5D_0$ to the levels ^7Fi

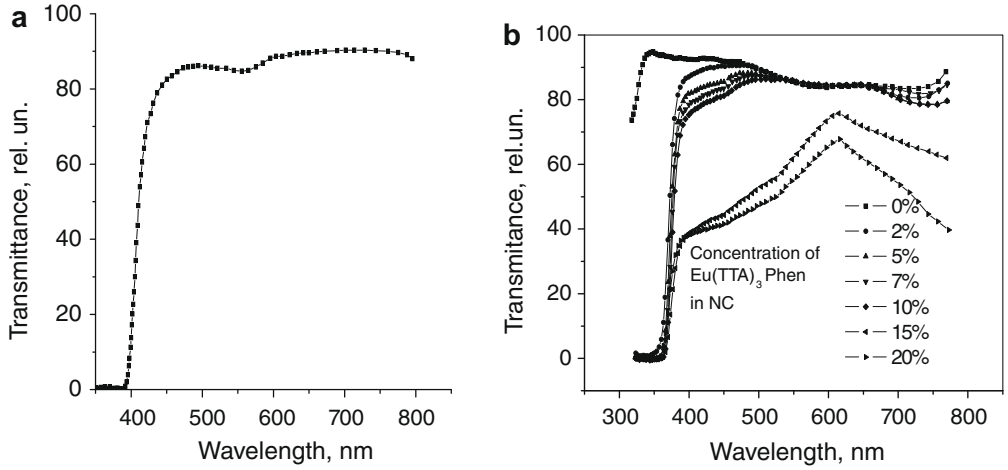


Fig. 1. Transmittance spectra of the thin films of nanocomposites: (a) the $Eu(TTA)_3{\cdot}H_2O$/SBMA at concentration 15% of Eu complex in NC, (b) the $Eu(TTA)_3Phen$/SBMA for different concentrations of the Eu^{3+}complexes in nanocomposites. $T = 298$ K.

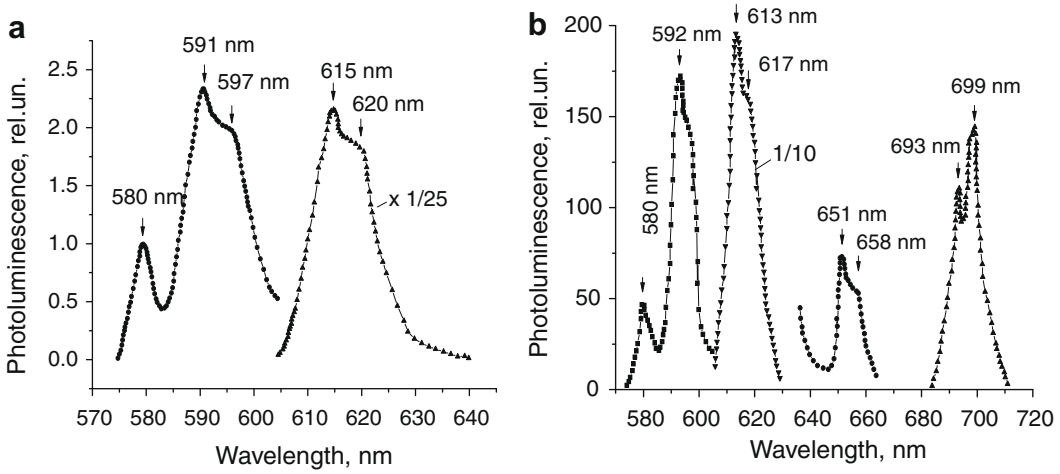


Fig. 2. Photoluminescence spectra: (a) of the $Eu(TTA)_3{\cdot}H_2O$ compound (powder) at 293 K temperature and (b) of the thin films of the $Eu(TTA)_3{\cdot}H_2O$/SBMA nanocomposites at 15% concentration of the Eu^{3+} complex in NC at 78 K.

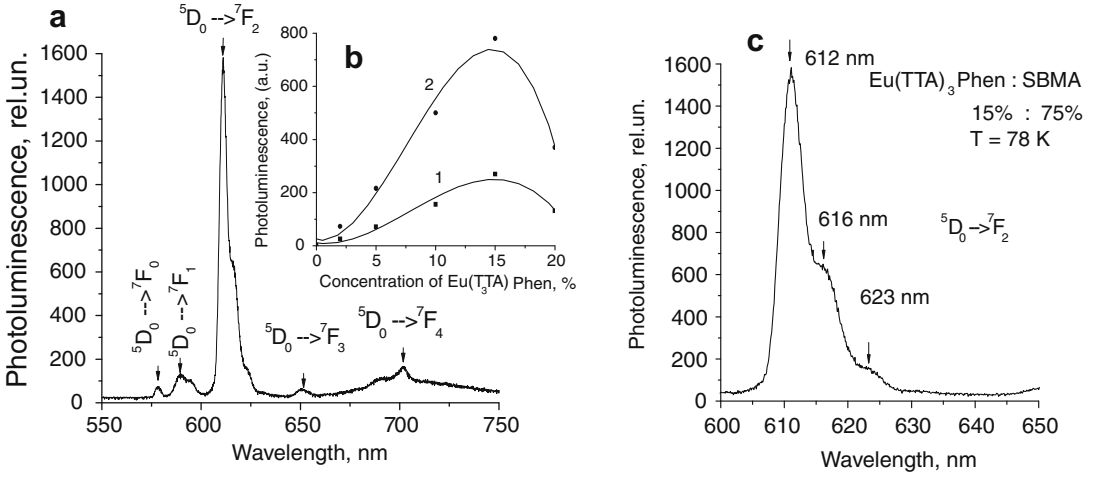


Fig. 3. (a) Photoluminescence spectra of the $Eu(TTA)_3Phen$/SBMA nanocomposite ($Eu(TTA)_3Phen$: SBMA 15: 75) (value of the wavelengths maxims of PL are indicated in text) (T = 78 K), (b) the maximum of the photoluminescence intensity of the Eu(TTA)3Phen/SBMA nanocomposites versus of Eu(TTA)3Phen concentrations in NC at 612 nm wavelength and at temperatures 293 K (curve 1) and 78 K (curve 2), (c) detailed display of photoluminescence of the $5D_0 \rightarrow 7F_2$ transition.

of the Eu^{3+} ion: $^5D_0 \rightarrow {}^7F_0$ (580 nm), $^5D_0 \rightarrow {}^7F_1$ (592 nm), and $^5D_0 \rightarrow {}^7F_2$ (613 nm). The increasing of the temperature conducts to the infrared shift of all photoluminescence bands. In both cases of $Eu(TTA)_3 \cdot H_2O$ powder and NC on its base these shifts are approximately 2–5 nm.

The photoluminescence spectra at liquid nitrogen temperature of the $Eu(TTA)_3Phen$/SBMA for 15 wt.% concentration of $Eu(TTA)_3$-Phen complex in the SBMA polymer matrix are presented on Fig. 3(a). The strong luminescence bands have been observed in the 570–720 nm range of wavelengths and are situated at 578, 590, 609, 612, 675 and 705 nm. If we will compare the photoluminescence spectra of $Eu(TTA)_3 \cdot H_2O$ powder and $Eu(TTA)_3Phen$/SBMA composites we can observe some non essential UV shift of the emission bands of the last. The maximums of emission bands in $Eu(TTA)_3Phen$/SBMA NC located at 578 nm ($^5D_0 \rightarrow {}^7F_0$), 590 nm ($^5D_0 \rightarrow {}^7F_1$), 612 nm ($^5D_0 \rightarrow {}^7F_2$) coincide with those which are found by other authors in the photoluminescence measurements of the $Eu(TTA)_3Phen$ compound [14]. According to Karasyov et al. [14], lowering of the temperature in the powder increase the intensity of the luminescence bands with the activation energy E_a = 15 meV that is less than in the respective crystal due to more weak relaxation processes as a result of the electron–phonon interaction. The maximum intensity of photoluminescence is reached at the 15% concentration of the $Eu(TTA)_3Phen$ in the SBMA polymer matrix of NC (Fig. 3).

The released energy of the excited state of the rare-earth ion may be radiative and non-radiative and depends on the spacing of the 4f levels. The strong photoluminescence in Eu^{3+} complexes with respect to others lanthanides (Sm^{3+}, Tb^{3+}, Dy^{3+} and Yb^{3+}) is connected to the fact that the prime emitting level ($^5D_0$) is far isolated of the lower-lying levels. In the future the mechanisms of energy transfer to rare-earth ions also will be taken into account.

4. Summary

Transmittance and photoluminescence spectra of the nanocomposites of $Eu(TTA)_3 \cdot H_2O$/SBMA and $Eu(TTA)_3Phen$/SBMA were fabricated and were investigated at room and liquid nitrogen temperatures. The observed photoluminescence bands are associated with the radiative transitions from the excited state $5D_0$ to the $^7F_4$–$^7F_0$ levels of the Eu^{3+} ion. The increasing of the intensity of the photoluminescence bands at the lowering of the temperature in the $Eu(TTA)_3 \cdot H_2O$/SBMA and $Eu(TTA)_3Phen$/SBMA nanocomposites is connected to weak relaxation processes as a result of the lowering the electron–phonon interactions.

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