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Luminescence properties of Eu^{3+}/thenoyltrifluoroacetonate composites

M. S. IOVU*, A. M. ANDRIESH, S. A. BUZURNIUC, V. I. VERLAN, M. I. CARAMAN[a], V. E. ZUBAREV[b]
Centre of Optoelectronics of the Institute of Applied Physics, Academy of Sciences of Moldova, Str. Academiei 5, MD-2028 Chisinau, Republic of Moldova
[a]*Moldova State University*
[b]*Institute of Chemistry of the Academy of Sciences of Moldova*

New composite material on the base of thienyltrifluoroacetonate (TTA) coordinated with trivalent europium ions without and with polymer from styrene and butylmethacrilate (1:1) (SBMA) was prepared. The visible emission spectra of the composites at room temperature and at T=78 K when excited with Ar-laser (λ=0.33 µm). For the Eu^{3+}/TTA composite material some sharp emission bands located at 5795, 590, 596, 615 and 620 nm at T=300 K, and at 580, 593, 595, 614, 618, 651, 656, 694, 698, and 700 nm at T=78 K were detected. The emission bands centered at 580, 590, 615, 651, and 700 nm can be attributed to the spin forbidden f-f transitions $^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4), respectively.. New composite material on the base of thienyltrifluoroacetonate (TTA) coordinated with trivalent europium ions without and with polymer from styrene and butylmethacrilate (1:1) (SBMA) was prepared. The visible emission spectra of the composites at room temperature and at T=78 K when excited with Ar-laser (λ=0.33 µm). For the Eu^{3+}/TTA composite material some sharp emission bands located at 5795, 590, 596, 615 and 620 nm at T=300 K, and at 580, 593, 595, 614, 618, 651, 656, 694, 698, and 700 nm at T=78 K were detected. The emission bands centered at 580, 590, 615, 651, and 700 nm can be attributed to the spin forbidden f-f transitions $^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4), respectively.

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1. Introduction

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: waveguide optical amplifiers, solar cells, light emitting diodes, gas selective sensors, etc. [1-3].

For rare-earth doped optical waveguide amplifiers of inorganic materials (silica and chalcogenide glasses) there are limitations of doping due to the concentration quenching effects: for silica glasses the doping level is limited up to 0.1 mole percent [4]. At higher doping levels, clustering of the rare earth-ions causes increasing of optical losses and quenching of the luminescence. This problem is easy solving by using for this purpose organic systems. The polymer matrices can be doped to much higher concentrations than silica glasses, using different lanthanide complexes. The rare-earth doped polymers especially are attractive for optical waveguide amplifiers operating at 1.5 µm "third telecommunication window". Some Eu^{3+}doped polymer composites were prepared by different methods and investigated its optical and luminescence properties [5-10]. The fluorescence in the visible region was obtained for Eu^{3+} doped polymer of poly(metal methacrylate) (PMMA) [7,10].

In our previous papers we have reported some results on new composite materials from polymers and chalcogenide glasses doped with rare-earth ions [11,12]. In this paper we propose a new method of preparation of fluorescence composite materials, excluding the presence of chalcogenide glass. For this purpose we have used the complex of coordinated compound of Eu(III) with TTA from β-diketonate row:

tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanediono)aquaeuropium Eu(III)·H_2O (Eu$(TTA)_3 \cdot H_2O$).

The main goal of the present investigation is to demonstrate the possibility of fabrication of fluorescence thin films and optical fibres from the above mentioned complex in conjugation with polymers having near or similar melting temperature of $Eu(TTA)_3 \cdot H_2O$ (T_{melt}~120 ^{0}C).

2. Experimental

The fluorescence compound $Eu(TTA)_3 \cdot H_2O$ and the composition (Eu^{3+}TFTBA) were prepared from thenoyltrifluoroacetonate ($C_8H_5F_3O_2S$) and organic composites based on styrene ($C_6H_5CH{=}CH_2$) and butilmetacrylat ($C_8H_{14}O_2$) doped with Eu^{3+} using the method described in [13,14], respectively. As a polymer was used the polymer based on styrene and butilmetacrylat (100:100), synthesized in the Moldova State University. For preparation of butilmetacrylat and styrene activated complex copolymer, the needed amount of copolymer was dissolved in benzene, the solution was keep for 1 hour, and another hour was mixed. After that in the mixture was introduced the Europium complex, also preliminary dissolved in benzene and the solution was mixed during 30 min. The obtained mixture, consisted from polymer, solvent and complex of Eu(III) was deposited on the clean optical glass. After the evaporation of the mixture, the transparent achromatic films were obtained. The thickness of the composite films consists L~10 μm.

The compound Eu(TTA)$_3$·H$_2$O (*Tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanediono)aquaeuropium(III)*) was prepared by using the method described in [13] by interaction of europium nitrate (the ratio 1:3) in the presence of sodium hydroxide. The purification was carried out by dissolution in benzene, with the sequential precipitation of hexane. On the Fig. 1a is presented Europium complex used for doping the TFTBA.

For optical transmission investigations a UV/VIS (300÷800 nm) Specord CARLZEISS Jena production was used. The luminescence spectra were measured at room temperature and at nitrogen temperature when excited with Ar$^+$-laser.

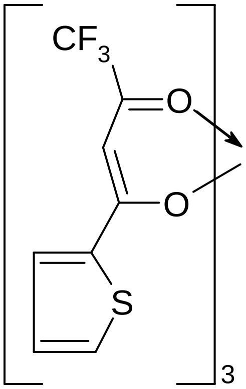

Fig. 1a. Europium complex used for doping the TFTBA copolymers.

3. Results and discussion

The spectroscopic investigations show, that the composition and the structure of the composite are not changed after incorporation into the polymer. Fig.1b represents the transmission spectrum of the Eu^{3+}TFTBA composite thin films. The investigated composite is high transparent (T~90 %) at the wavelength λ≥450 nm. A wide absorption band can be observed in the spectrum of 500-600 nm.

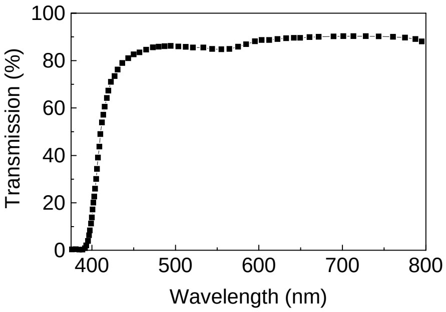

Fig. 1b. The transmission spectrum of the Eu^{3+}(TFTBA)-SBMA composite thin film.

The strong absorption with bands characteristic the presence of Eu^{3+} ions in the Eu^{3+}TFTBA composite was detected in the high energy region (350÷400 nm). According to [10], this absorption bands is attributed to the electron transitions from the ground state $^7F_0$ and from the low level $^7F_1$ to the Stark components of the Eu^{3+} ion: $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_4$, $^7F_0 \rightarrow {}^5G_2$, $^7F_1 \rightarrow {}^5L_7$, $^7F_1 \rightarrow {}^5L_6$ (Fig.2).

The photoluminescence spectra of Eu^{3+}TFTBA composite powder at room temperature (T=293 K) and at nitrogen temperature (T=78 K) are presented at in the Fig.3a and Fig.3b, respectively. The room temperature T=273 K photoluminescence bands situated in the region 550÷630 nm correspond to radiative transitions from the excited state $^5D_0$ to the $^7F_{0'}$ $^7F_1$ and $^7F_2$ levels of the Eu^{3+} ion: $^5D_0 \rightarrow {}^7F_0$ (580 nm), $^5D_0 \rightarrow {}^7F_1$ (590 nm), and $^5D_0 \rightarrow {}^7F_0$ (620 nm).

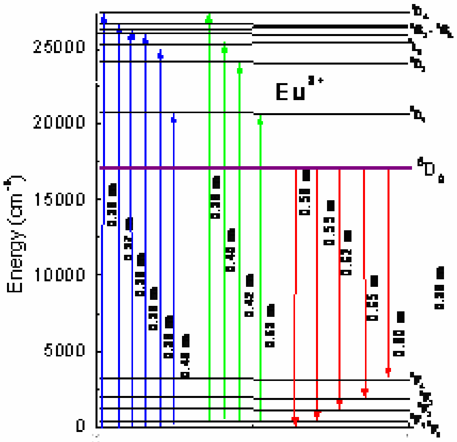

Fig. 2. The absorption (blue and green arrows) and emission (red arrows) transitions in the Eu^{3+} ion.

The photoluminescence spectrum measured at nitrogen temperature T=78 K (Fig. 3b) in the region 550÷720 nm manifests additional emission at 650 nm and around 700 nm.

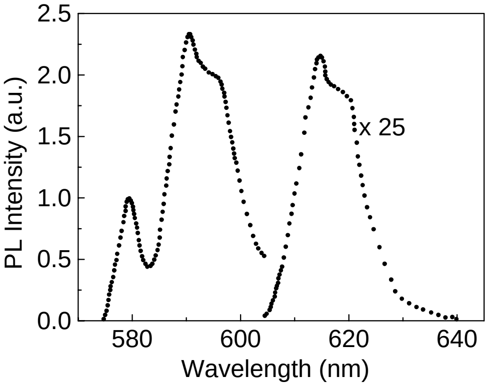

Fig. 3a. The PL spectrum of the Eu^{3+}TFTBA compound (powder) at room temperature (T=293 K).

The Fig. 4a and 4b represent the photoluminescence spectra the Eu^{3+}(TFTBA)-SBMA composites at T=78 K (1) and T=293 K (2) for two samples: 1 and 2. The sample 2 was characterized with higher concentration of Eu^{3+} ions. For both samples the lowering of the temperature lead to increasing the photoluminescence intensity of the bands situated at 650 and 700 nm.

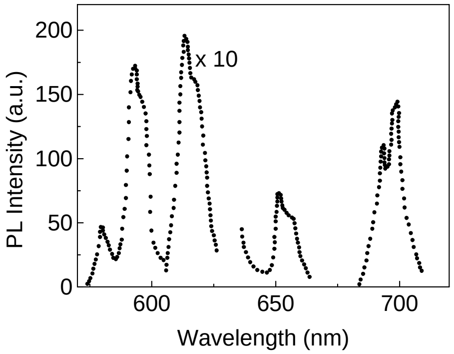

Fig. 3b. The PL spectrum of the Eu^{3+}TFTBA compound (powder) at nitrogen temperature (T=78 K).

The photoluminescence band situated at 650 nm corresponds to radiative transition from the excited state $^5D_0$ to the $^7F_3$ level of the Eu^{3+} ion. At low temperature (T=78 k) the intensity of photoluminescence increase essentially.

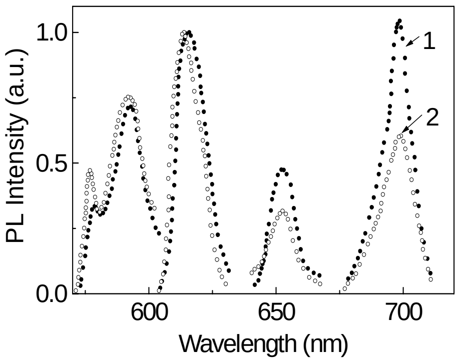

Fig. 4a. The emission spectra of the Eu^{3+}(TFTBA)-SBMA composites at T=78 K (1) and T=293 K (2). Sample 1.

For the sample 2 with higher concentration of Eu^{3+} we can observe the increase of the photoluminescence intensity also for the bands situated at 580, 590 and 620 nm. Increasing of the temperature lead to the shift of the photoluminescence bands located at 650 and 700 nm to lower energies, while the photoluminescence bands situated at 580, 590 and 620 nm are shifted to higher energies. In both cases this shift is about 2÷5 nm.

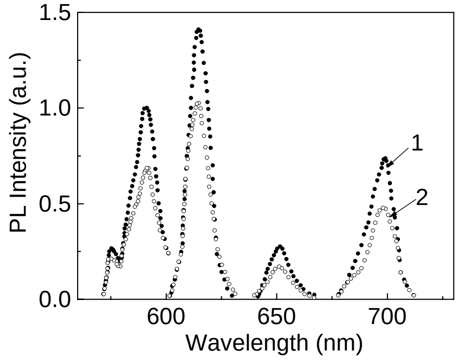

Fig. 4b. The emission spectra of the Eu^{3+}(TFTBA)-SBMA composites at T=78 K (1) and T=293 K (2). Sample 2.

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 composites with respect to other lanthanides (Sm^{3+}, Tb^{3+}, Dy^{3+}, Yb^{3+}) is due to the fact that the emitting level ($^5D_0$) 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.

4. Conclusions

A fluorescent Eu^{3+}(TFTBA)-SBMA composite was prepared and investigated. The photoluminescence spectra of Eu^{3+}(TFTBA)-SBMA composite were investigated at room temperature and at T=78 K. The observed photoluminescence bands are associated with the radiative transitions from the excited state $^5D_0$ to the $^7F_3$ - $^7F_0$ levels of the Eu^{3+} ion. Lowering of the temperature increases the intensity of the photoluminescence bands in the Eu^{3+}(TFTBA)-SBMA composite.

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[*] Corresponding author: miovu@asm.md