

Photoluminescence of composites based on Eu^{3+} /TTFA and polymer SBMA

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

^aMoldova State University

^bInstitute of Chemistry of the Academy of Sciences of Moldova

New composite material on the base of thienyltrifluoroacetate (TTA) coordinated with trivalent europium ions without and with polymer from styrene and butylmethacrylate (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 ($\lambda=0.33 \mu\text{m}$). 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 ${}^5\text{D}_0 \rightarrow {}^7\text{F}_i$ ($i = 0, 1, 2, 3$ and 4), respectively.

(Received July 3, 2007; accepted October 1, 2007)

Keywords: Composites, Polymer, Rare-earth ion, Thin film, Optical absorption, Fluorescence

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 $1.5 \mu\text{m}$ "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(methyl 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 [11-14]. 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 $\text{Eu}(\text{III})$ with TTA from β -diketonate row:

tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanediono)aqueuropium $\text{Eu}(\text{III})\cdot\text{H}_2\text{O}$ ($\text{Eu}(\text{TTA})_3\cdot\text{H}_2\text{O}$).

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 $\text{Eu}(\text{TTA})_3\cdot\text{H}_2\text{O}$ ($T_{\text{melt}}\sim 120^\circ\text{C}$).

2. Experimental

The fluorescence compound $\text{Eu}(\text{TTA})_3\cdot\text{H}_2\text{O}$ and the composition ($\text{Eu}^{3+}\text{TFTBA}$) were prepared from thenoyltrifluoroacetate ($\text{C}_8\text{H}_5\text{F}_3\text{O}_2\text{S}$) and organic composites based on styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$) and butylmetacrylat ($\text{C}_8\text{H}_{14}\text{O}_2$) doped with Eu^{3+} using the method described in [15,16], respectively. As a polymer was used the polymer based on styrene and butylmetacrylat (100:100), synthesized in the Moldova State University. For preparation of butylmetacrylat and styrene activated complex copolymer, the needed amount of copolymer was dissolved in benzene, the solution was kept 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 $\text{Eu}(\text{III})$ 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 $L\sim 10 \mu\text{m}$.

The compound $\text{Eu}(\text{TTA})_3\cdot\text{H}_2\text{O}$ (*Tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanediono)aqueuropium(III)*) was prepared by using the method described in [15] 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.

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 spectra of spectra of the Eu³⁺TFTBA composites thin films. The investigated composites are high transparent (T~90 %) at the wavelength $\lambda \geq 450$ nm. A wide absorption band can be observed in the spectrum of 500-600 nm.

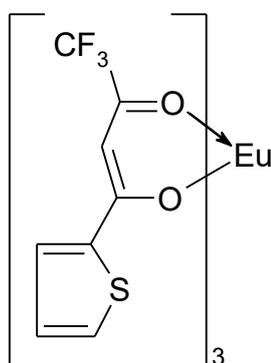


Fig.1a. Europium complex used for doping the TFTBA copolymers.

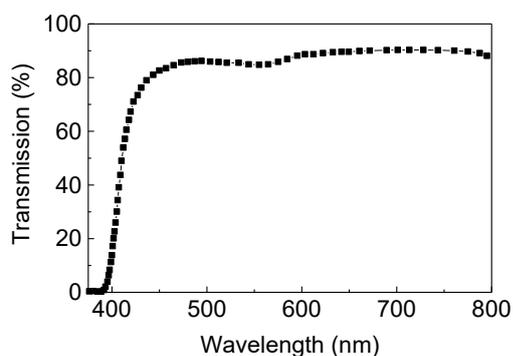


Fig.1b. The transmission spectra of the Eu³⁺(TFTBA)-SBMA composites thin films.

The strong absorption with bands characteristic the presence of Eu³⁺ ions in the Eu³⁺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 ⁷F₀ and from the low level ⁷F₁ to the Stark components of the Eu³⁺ ion: ⁷F₀→⁵D₄, ⁷F₀→⁵G₄, ⁷F₀→⁵G₂, ⁷F₁→⁵L₇, ⁷F₁→⁵L₆ (Fig.2).

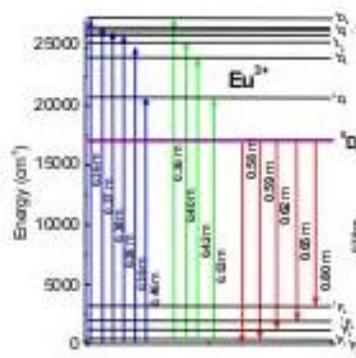


Fig. 2. The absorption (blue and green arrows) and emission (red arrows) transitions in the Eu³⁺ ion.

The photoluminescence spectra of Eu³⁺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 ⁵D₀ to the ⁷F₀, ⁷F₁ and ⁷F₂ levels of the Eu³⁺ ion: ⁵D₀→⁷F₀ (580 nm), ⁵D₀→⁷F₁ (590 nm), and ⁵D₀→⁷F₀ (620 nm).

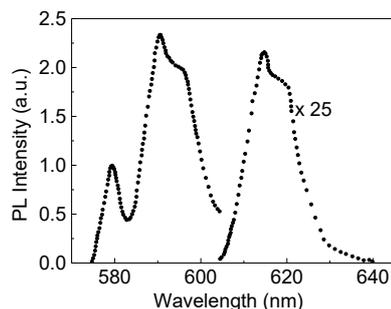


Fig.3a. The PL spectra of the Eu³⁺TFTBA compound (powder) at room temperature (T=293 K).

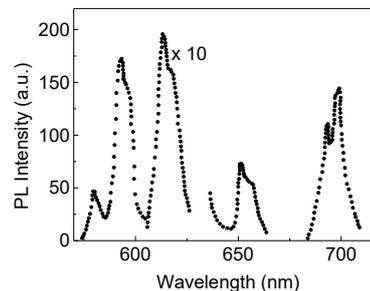


Fig.3b. The PL spectra of the Eu³⁺TFTBA compound (powder) at nitrogen temperature (T=78 K).

The photoluminescence spectra measured at nitrogen temperature T=78 K (Fig.3b) in the region 550÷720 nm manifest additional emission at 650 nm and around 700 nm. The photoluminescence band situated at 650 nm corresponds to radiative transition from the excited state ⁵D₀ to the ⁷F₃ level of the Eu³⁺ ion. At low temperature (T=78 k) the intensity of photoluminescence increase essentially.

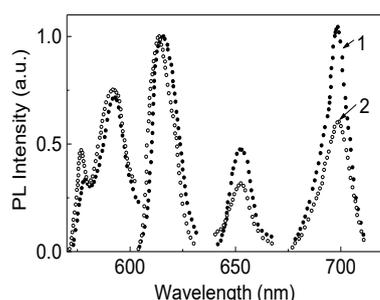


Fig.4a. The emission spectra of the Eu^{3+} (TFTBA)-SBMA composites at $T=78\text{ K}$ (1) and $T=293\text{ K}$ (2). Sample 1.

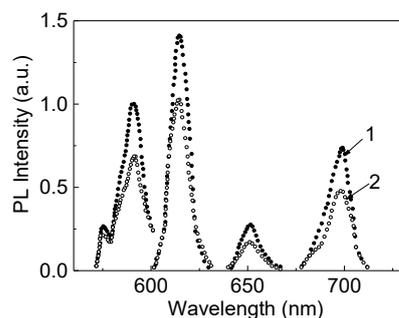


Fig.4b. The emission spectra of the Eu^{3+} (TFTBA)-SBMA composites at $T=78\text{ K}$ (1) and $T=293\text{ K}$ (2). Sample 2.

The Fig.4a and 4b represent the photoluminescence spectra the Eu^{3+} (TFTBA)-SBMA composites at $T=78\text{ K}$ (1) and $T=293\text{ K}$ (2) for two the sample 1 and the sample 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. For the sample 2 with higher concentration of Eu^{3+} we can observe the increasing 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 consists about $2\div 5\text{ nm}$.

The energy of the excited –state rare-earth ion may be radiatively and non-radiatively and depend 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 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.

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 $T=78\text{ K}$. The observed photoluminescence bands are associated with the radiative transitions from the excited state $^5\text{D}_0$ to the $^7\text{F}_3 - ^7\text{F}_0$ levels of the Eu^{3+} ion. Lowering of the temperature increasing the intensity of the photoluminescence bands in the Eu^{3+} (TFTBA)-SBMA composite.

Acknowledgments

This work is supported by the Supreme Council for Science and Technological Development of the Academy of Sciences of Moldova (Project 06.408.012F)

References

- [1] M. Koppe, H. Neugebauer, N. S. Sariciftci, *Mol. Cryst. Liq. Cryst.*, **385**, [221]/101 (2002).
- [2] S. -G. Roh, N. S. Baek, K. -S. Hong, H. K. Kim, *Bull. Korean Chem. Soc.* **25**, 343 (2004).
- [3] H. K. Kim, J. B. Oh, N. S. Baek, S. -G. Roh, M. -K. Nah, Y. H. Kim, *Bull. Korean Chem. Soc.* **26**, 201 (2005).
- [4] Properties, Processing and Applications of Glass and Rare Earth Doped Glasses for Optical Fibers, Ed. D.Hewak, INSPEC, London, UK, 1998.
- [5] Z. Andric, M. D. Dramicanin, V. Jokanovic, T. Dramicanin, M. Mitric, B. Viana, *J. Optoelectron. Adv. Mater.* **8**, 1457 (2006).
- [6] I. Sajo, K. Papp, P. Baranyai, M. Pavai, F. Kormos, E. Kalman, *Digest Journal of Nanomaterials and Biostructures* **1**, 115 (2006).
- [7] J. Gordon, J. Ballato, J. Jin, D. W. Smith Jr., *J. of Polymer Science: Part B, Polymer Physics* **44**, 1592 (2006).
- [8] M. M. Silva, V. Z. Bermudez, L. D. Carlos, A. P. P. Almedia, M. J. Smith, *J. Mater. Chem.* **9**, 1735 (1999).
- [9] E. Cordoncillo, B. Viana, P. Escribano, C. Sanchez, *J. Mater. Chem.* **8**, 507 (1998).
- [10] R. F. Sosa, M. H. Flores, R. T. Rodriguez, A. F. Munoz, *Revista Mexicana de Fızica* **49**, 519 (2003).
- [11] M. S. Iovu, A. M. Andriesh, S. A. Buzurniuc, V. I. Verlan, E. P. Colomeico, St. V. Robu, *J. Optoelectron. Adv. Mater.* **8**(1), 257 (2006).
- [12] M. S. Iovu, A. M. Andriesh, S. A. Buzurniuc, V. I. Verlan, *Digest Journal of Nanomaterials and Biostructures* **2**, 2001 (2007).
- [13] A. M. Andriesh, M. S. Iovu, *J. Optoelectron. Adv. Mater.* **8**(6), 2080 (2006).
- [14] M. S. Iovu, N. N. Syrby, Yu. S. Tver'yanovich, G. J. Adriaenssens, *J. Optoelectron. Adv. Mater.* **8**(4), 1341 (2006).
- [15] L. R. Melty, N. J. Rose, E. Abramson, J. C. Caris, *J. Amer.Chem.Soc.* **86**, 5117 (1964).
- [16] G. N. Marcenco, D. G. Batir, G. A. Safonov, G. I. Ershova, *High-molecular Compounds* **A17**, 2086 (1975) (In Russian).

*Corresponding author: miovu@asm.md