

Optical characterization of a new nanocomposite *SBMA/Eu(TTA)₃(Ph₃PO)₂*

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Abstract: We describe a new nanocomposite material based on the copolymer of styrene with butyl methacrylate (1:1) (*SBMA*), and coordinating compound of Europium(III) $Eu(TTA)_3(Ph_3PO)_2$. The $SBMA/Eu(TTA)_3(Ph_3PO)_2$ nanocomposite was prepared by a simple technology and can be obtained in the form of optical fibers, thin films and planar waveguides on various substrates with large area. Experimental results on optical transmission and photoluminescence spectroscopy are presented. The nanocomposite exhibits a strong photoluminescence emission in the range 560-750 nm, with the main photoluminescence band at 613 nm.

Keywords: rare earth, $Eu(TTA)_3(Ph_3PO)_2$, nanocomposite, photoluminescence, absorption.

1. INTRODUCTION

Nanocomposite materials (NC) with coordination compounds of rare earth elements (RE) have been attracted much attention because of their various applications in science, medicine, engineering, etc. [1,2]. The main advantages of the lanthanides are determined by high luminescence efficiency of their organic compounds with ligands and polymer matrix. These lanthanides complexes present also a lot of interest because of their potential applications in planar waveguide amplifiers, lasers, light emitting diodes, etc. [3,4].

Specific properties of lanthanides are determined by their optically active $4f$ electrons which form a compressed electronic shell, shielded by the outer two completed shells $5s$ and $5p$, that usually prevent any strong interaction of $4f$ electrons with the environment [5]. For this reason intraconfigurational $4f$ optical transitions are characterized by atomic-like narrow absorption and emission lines. Consequently, $4f$ optical transitions are not affected by nonradiative transitions caused by molecular thermal vibrations. On the other hand the structure and spherical symmetry of the rare earth ion forbids direct optical transitions to $4f$ and $5d$ levels. For this reason a free lanthanide ion does not exhibit any luminescence and absorption of light and therefore the fluorescence of RE ions is quite weak due to a forbidden electronic transition.

The formation of organic compounds on the Eu^{3+} ions base leads to a larger distortion of spherical symmetry because of stronger interactions of Eu^{3+} ions with the neighbor ligands. In this case, unlike the common fluorescence and phosphorescence in compounds, the complexes with rare-earths exhibit high luminance efficiency with sharp emission bands [6-10]. Application of the complex compounds of lanthanide ions with various organic ligands allows sensitization of the central ion luminescence. An important advantage of the lanthanides is also their property to coordinate with a large number of homo- and hetero- ligands to form organic coordination compounds. Various anionic and cationic ligands allow obtaining compounds that are soluble in polar or nonpolar solvents. This gives the possibility to apply different technologies for deposition of thin film layers and to select the appropriate and compatible polymer as a matrix for a coordination lanthanide compounds.

One of goals when preparing the lanthanide compounds based composites is to increase the main ligand hydrophobicity by direct synthesis in order to avoid coordinative attachment of H_2O molecules or other solvents that can attenuate luminescence. For this purpose it is necessary to introduce more ligands in the molecule with RE that will make the RE ion more distant from the outer environment and from influence of organic solvents.

It has been proved that the next ligand plays an important role in Europium complexes, the synergistic complexation of the second ligand can not only lead to the construction of efficiently emitting Europium(III) complexes, but also improve the volatility and electron-transporting ability of the complex [11-12]. Therefore for practical application it is important to design Europium(III) complexes with new ligands.

Photoluminescence excitation in composite structures with rare earths elements occurs not only as a result of light absorption by the Eu^{3+} ion, but also as a result of light absorption by the organic moiety of organic coordinative complex and polymeric matrix [13]. When absorbing a photon the molecule of polymer or organic compound is excited from the ground state to the singlet state (S_1). From this state the molecule can be deactivated through radiative transition to the ground state S_0 (ligand luminescence), or it can nonradiatively relax to the triplet state T_1 with longer life time. The excited molecule can relax from the T_1 level to the ground state ($T_1 \rightarrow S_0$, molecular phosphorescence), and if the energy of the T_1 level of the ligand ($E(T_1)$) is greater than or equal to the energy of lanthanide resonant level, then the excitation energy $E(T_1)$ can be transferred to RE resonant level. In this case the ion of RE is promoted to an excited state with subsequent radiative transition and emission of a photon. Surrounding of Eu^{3+} ions by ligands leads, on the one hand, to reduction of nonradiative energy losses due to exclusion of the vibrational coupling, and, on the other hand, increases the Eu^{3+} ions transfer of energy through the „antenna effect”. The organic ligands absorb the light energy and transfer it to the central metal of lanthanide, which results in a narrow emission band in the visible region [13].

Organic copolymer made of styrene and butylmethacrylate attract particular interest as a polymer matrix for its low optical absorption in visible range, refractive index depending on molecular mass, simple technology, and low cost [14]. These characteristics of *SBMA* make it attractive as a host material for rare earth coordinative compounds and organic dyes. Incorporation of organic nanoparticles into a polymer matrix proved to be an effective method for improving the performances of polymer NC materials and for obtaining structures with novel physical properties [13]. Rare earth compounds on the Eu^{3+} ion base exhibits a strong emission line at 613-615 nm, which coincides with the region of low optical loss in *SBMA*-based optical fiber, and has a large energy gap between the emissive state and the next lower level [6-7].

In the present work we investigated the organic coordination compound of the Eu^{3+} ion, surrounded by anionic ligands tris(thenoyltrifluoroacetato) (*TTA*) and triphenylphosphine oxide (*Ph₃PO*) in the matrix of *SBMA* with the goal to investigate the luminescence process and energy transfer to Eu^{3+} ion.

2. PREPARATION AND EXPERIMENTAL DETAILS

The nanocomposites *SBMA/Eu(TTA)₃(Ph₃PO)₂* was prepared from organic luminophore compound *Eu(TTA)₃(Ph₃PO)₂*, and organic copolymer based on styrene ($C_6H_5CH=CH_2$) and butylmethacrylate ($C_8H_{14}O_2$) as described elsewhere [15].

Synthesis. 0.66 g (3 mmol) of thenoyltrifluoroacetone and 0.56 g (2 mmol) of triphenylphosphine oxide were dissolved in 10 ml of warm 96 % ethanol and 3 ml of 1N solution of sodium hydroxide was added. The mixture was stirred, while 1 mmol of Europium chloride in 5 ml of water was added dropwise. A type of light pink precipitate formed immediately. The precipitate was filtered off, washed with small portions of ethanol and diethyl ether, dried thoroughly in air, and the solid of the complex was obtained. Yield was 0.68 g.

For $C_{60}H_{42}F_9EuO_8P_2S_3$ calcd, %: C = 52.53; H = 3.09.

Found, %: C = 52.37; 52.28; H = 3.18; 2.98. Molecular structure of tris(thenoyltrifluoroacetato)bis(triphenylphosphine oxide)Europium (III) [*Eu(TTA)₃(Ph₃PO)₂*] [8] is represented in Fig. 1.

Organic coordination compound *Eu(TTA)₃(Ph₃PO)₂* was dissolved in toluene (9.3 mg/ml), while *SBMA* was dissolved in dimethylformamide (*DMFA*) at room temperature (111.67 mg/ml). After complete dissolution of organic compound in toluene we prepared 5 composite solutions with different concentration of *Eu(TTA)₃(Ph₃PO)₂* in the *NC* (9.3%, 4.75%, 1.18%, 0.59%, 0.14%). The solutions were mixed thoroughly by ultrasonic method. The final composite solution was deposited on quartz substrates by spin-coating method for obtaining thin films homogeny with thickness ~ 1 μ m (Fig. 3). The films were dried out at 80°C for 2 hours for subsequent optical characterization.

Microscopic investigations of the morphology of the films surface were carried out with transmission electron microscope (TEM) EM 410 and optical microscope MIK-4. Photoluminescence spectra excited by a N_2 -laser ($\lambda = 337$ nm) or a diode laser ($\lambda = 405$ nm) have been measured using a set-up based on MDR-23 spectrophotometer connected to