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Optical and photoluminescence characteristics of amorphous nanocomposites containing organic compounds with Eu^{+3} and polymers

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Thin films (1-10 µm thickness) of nanocomposites (NC) based on polymers and organic coordinated compounds (OCC) $Eu(TTA)_3H_2O$, $Eu(TTA)_3Phen$, $Eu(DBM)_3Phen$, $Eu(TTA)_2(Ph_3PO)_2NO_3$ (where *TTA* is thenoyltrifluoroacetonate ($C_8H_5F_3O_2S$), Ph_3PO – triphenylphosphine oxyde (C_6H_5PO) and polymer – polyvinylpyrrolidone ($(C_6H_9NO)_n$) (*PVP*) and copolymer styrene-butylmethacrilate (SBMA)) were obtained by chemical methods. NC were characterized by measurements of optical transmission, and photoluminescence (PL) at different concentrations of OCC in NC. It was established that the excitation spectrum of the photoluminescence covers the range of wavelength from 200 to 410 nm. All types of NC show similar characteristics of the photo luminescence and absorption. PL bands centred at 580, 590, 612 - 615, 651, and 700 nm, have been detected that that correspond to the radiative transitions between the energy levels of the Europium ions and it can be attributed especially to internal *4f-4f* transitions $^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4), respectively. This has been explained from the viewpoint of the surrounding environment of Eu^{3+} ion and removal of internal interdiction for transitions in electronic shields of Eu^{3+} ion as a result of ligands interactions. The dominant maximum of PL is in the range to 612-615 nm with halfwidth less than 10 nm and its intensity is about 20 times higher than intensity of maxima of other bands. The optimal concentrations of OCC in NC for maximum of PL efficiency were in the range 6 - 12%. It was found that there is an effective transfer of energy from polymer matrix to ligands of the OCC complex on their energetic levels HOMO and LUMO, and subsequent energy transfer to the Eu^{3+} ion. HOMO and LUMO of the OCC complex are found to be situated between levels *S* and *T* of the polymer, and they are higher than the energy of $^5D_0 \rightarrow {}^7F_i$ transitions in Eu^{3+} ion.

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1. Introduction

Lanthanides and their compounds possess a number of unique properties for practical applications in science, medicine and technique. They are excellent materials for a new generation of optoelectronic devices with advanced functional capabilities. Among various applications of lanthanides compounds we may mention light emitting devices with high efficiency of luminescence and temperature insensitivity, ferromagnetic materials, high-temperature superconducting materials, etc. Novel functional properties of NC are determined in a considerable extent by 4f electrons that are partially shielded by outer electrons $5s^25p^66s^2$.

Most commonly used materials for visible light sources are compounds with Europium (Eu^{3+}) and Terbium (Tb^{3+} ions. Improving their luminescence properties depends on the type of ligands used for surrounding of the rare earth ions. For example, photoactive complexes of organic compounds of lanthanides may be used, like the trivalent ion of Europium chelated with β-diketonates, or the cyclic ligands. The coordination number of Eu^{3+} ion varies in this case in the range from 6 to 9.

Many research efforts are made towards achieving of surrounding of the Eu^{3+} ion in order to improve the luminescence efficiency, and to obtain a final stable compound for various practical applications.

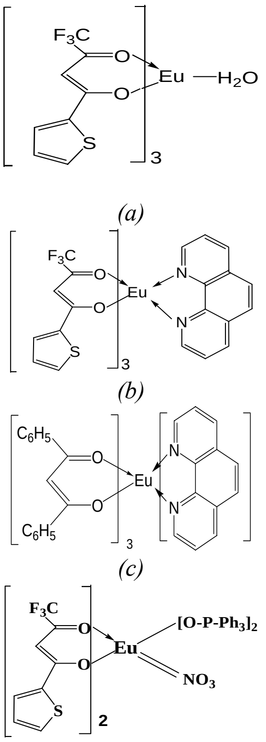
The results obtained through spectroscopic investigation of the nanocomposites are very important for application of OCC compounds from lanthanides materials. One of the advantages of application of organic coordinated compounds of rare earth ions with β-diketonates and ligands in nanocomposites is based on the so-called "antenna" effect, i.e. the transfer of excitation energy from outside of the system of Eu^{3+} ion towards its energy levels. In this case the population of the upper energy levels is increased with subsequent transition to the ground states. The intermolecular energy transfer to the Eu^{3+} ion occurs via the energetic levels of ligands and their surroundings.

In the previous paper we reported preliminary investigations of the NC based on copolymer butylmetacrylate and styrene at the ratio 1:1 in whose matrix $Eu(TTA)_3H_2O$, $Eu(TTA)_3Phen$ and $Eu(DBM)_3Phen$ [1-4] were introduced, and NC based on polymer polyvinylpirrolidone with $Eu(TTA)_2(Ph_3PO)_2NO_3$ [5]. For all investigated materials with NC, photoluminescence levels caused by *4f - 4f* transitions of *Eu* were identified.

The most intensive luminescence band was centred at 612 - 615 nm and it halfwidth was less than 10 nm in all studied cases.

2. Methods of experiments

It is very interesting to examine the influence of each organic coordinated compound on optical and luminescence properties in NC. In the previous paper [4] we have presented new type of NC based on OCC with trivalent *Eu* of different coordination numbers ($Eu(TTA)_3H_2O$, $Eu(TTA)_3Phen$, $Eu(DBM)_3Phen$, $Eu(TTA)_2(Ph_3PO)_2NO_3$) (Fig.1). Details of the technology for preparation of OCC were presented in [1-5] and were similar of those described in [6-7]. The OCC-Europium complexes were successfully incorporated into organic matrixes of copolymer *SBMA* (1:1) and polyvinylpyrrolidone via sol–gel process. NC were obtained from chemical solutions and at different molar ratios of OCC into polymer matrix.



(a)

(b)

(c)

(d)

Fig.1. Structure formulas of OCC: (a) $Eu(TTA)_3H_2O$, (b) $Eu(TTA)_3$ Phen, (c) $Eu(DBM)_3$ Phen, (d) $Eu(TTA)_2(Ph_3PO)_2NO_3$.

Drop- and spin-coated thin films deposited on optical glass and quartz substrates were obtained [1-5]. The dried layers with thickness around 1-10 μm turn out to be transparent in the visible range of spectrum. The microscopic investigations of the morphology of the NC films on a microscope MII-4 shows that the dimensions of OCC particles, incorporated in the polymer matrix are invisible and hence are less than 100 nm and they are dispersed homogeneously in the polymers matrix.

Thin films of NC have been characterized by measurements of optical transmission and photoluminescence at different concentrations of OCC in NC.

Photoluminescence spectra have been measured using a set-up based on MDR-23 monochromator connected to PC. NC samples have been excited with a N_2-laser (λ = 0.337 μm) or Deuterium lamp. The PL emission spectra exhibit several sharp emission bands in the spectral range 300 – 800 nm. For optical transmission investigations a Specord UV/VIS (300÷800 nm) CARL ZEISS Jena unit was used. Absorption and luminescence properties of powder of Europium complex and NC were measured on each step of technology.

3. Experimental results

Fig. 2 shows the room temperature transmission spectra $T(\lambda)$ of thin nanocomposite layers of different OCC deposited on glass substrates at 6% concentration of OCC in NC. PL measurements in NC films have been carried out at identical excitation conditions. Transmission spectra measurements $T(\lambda)$ of thin layers of NC *PVP-*$Eu(TTA)_2(Ph_3PO)_2NO_3$ deposited on quartz substrates at different concentration of OCC in the NC are presented on Fig. 3. The spectral distribution T(λ) of all investigated NC are similar. NC thin layers deposited on quartz substrates clearly show 4 absorption bands in the ultraviolet (UV) with maximums at 3.0 - 3.15, 3.8, 4.5 and 4.8 eV, while with increasing of the OCC concentration in NC they grow until complete darkening in UV range.

The sharp absorption threshold is presented for all concentrations of coordinated compounds in NC in the range of 370 - 380 nm of the spectrum. The absorption spectra ($\alpha(\lambda)$) are calculated from the transmission spectra $T(\lambda)$ through the relation $\alpha(\lambda) = - lnT/d$ (where *d* is the thickness of the NC, α – the absorption coefficient) (Fig. 4). The energies of forbidden band gaps in the NC ($\Delta E_{HL}= LUMO - HOMO$, where *HOMO* is the energy of highest occupied molecular orbital and *LUMO* – is the energy of lowest unoccupied molecular orbital) obtained from 80 % of the absorption threshold of the spectral distribution $T(\lambda)$ are in the range 2.9 eV for NC *SBMA-*$Eu(TTA)_3H_2O$ *and SBMA-*$Eu(DBM)_3Phen$; and 3.2 eV for NC SBMA-*PVP-*$Eu(TTA)_3Phen$ and $Eu(TTA)_2(Ph_3PO)_2NO_3$.

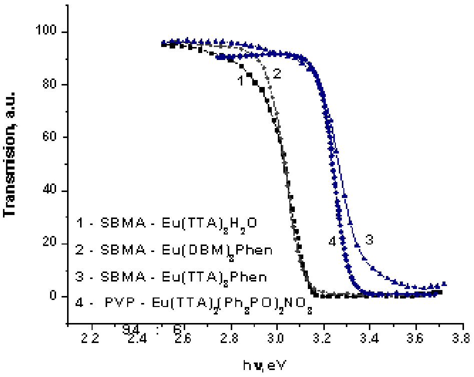


Fig. 2. The transmission spectra of thin layers deposited on glass substrates of different NC and at 6% of OCC (T=293 K).

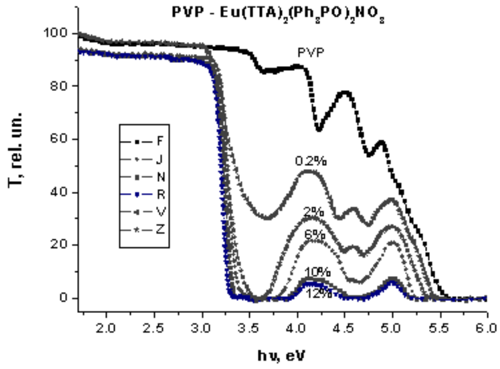


Fig. 3. The transmission spectra of thin layers deposited on quarz substrates of NC PVP-$Eu(TTA)_2(Ph_3PO)_2NO_3$ at different concentration of OCC in NC.

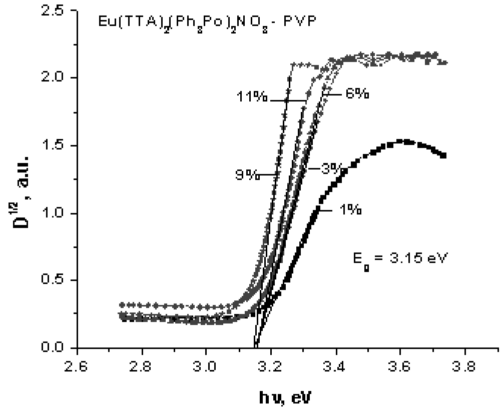


Fig. 4. The absorption spectra of thin layers of NC PVP-$Eu(TTA)_2(Ph_3PO)_2N$ at different concentration of OCC in NC plotted as $(\alpha d)^{1/2}$ vs *hν.*

On Fig. 5 (a), (b) the spectra of photoluminescence of NC PVP-$Eu(TTA)_2(Ph_3PO)_2NO_3$ films under excitation by N_2 laser are presented. The detected fluorescence bands correspond to the radiative transitions between the energy levels of the Europium ions centred at 537, 580, 615, 650 and 702 nm, and can be attributed to the spin forbidden *4f* - *4f* transitions $^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4), respectively. The most effective luminescence has the maximum at 615 nm at temperature 293 K which is about 20 times higher than the luminescence maximum of other bands, and its halfwidth is less than 10 nm.

The optimal concentrations of $Eu(TTA)_2(Ph_3PO)_2NO_3$ in nanocomposite were found to be in the range of 6 – 12 % (Fig. 6). This is roughly true for all examined NC samples. There is an almost a monotonous increase of intensity of photoluminescence vs OCC concentration in NC up to some 10% of OCC in NC, and this feature is characteristic for all thin film samples at room temperature. The main feature of PL characteristics is a quite low signal of photoluminescence in liquid solution samples, while thin film samples exhibits a significant grow of the intensity of photoluminescence. The effective excitation of PL of the organic coordinated compound with Eu^{3+} ion in NC thin films was attained. The results indicate that due to decreased symmetry in the composites the excitation bands are split into two different components, peaking at ~246 and ~336 nm, respectively, while the ratio of the electronic dipole $^5D_0$-$^7F_2$ transitions to the magnetic dipole $^5D_0$-$^7F_1$ ones in the emission spectra becomes a little larger. The photoluminescence intensity of NC at 612 - 615 nm is about 2 times higher than the value of intensity of PL of $Eu(TTA)_2(Ph_3PO)_2NO_3$ powders at equal conditions of excitation.

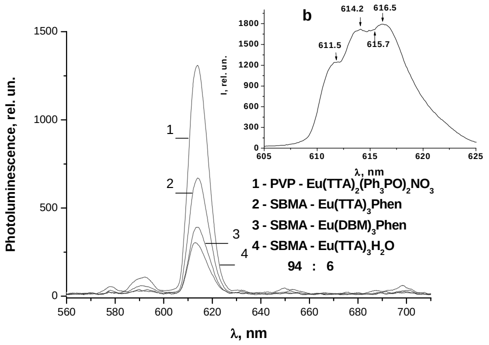


Fig. 5. The photoluminescence spectra of thin layer of NC PVP-$Eu(TTA)_2(Ph_3PO)_2NO_3$ at 6 wt.% of concentration of complex OCC in NC: a – whole spectrum, b – detailed maximum at room temperature (T=293 K).

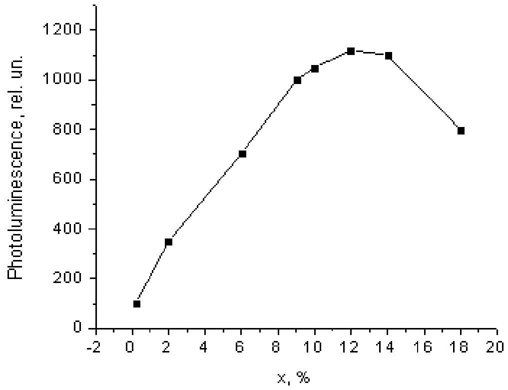


Fig. 6. The maximum of intensity of photoluminescence at 615 nm of thin layers of NC versus of concentration x of PVP-$Eu(TTA)_2(Ph_3PO)_2NO_3$ (T=293 K).

4. Discussion

Rare-earth based NC show high photoluminescence efficiency with sharp emission bands involving electrons associated with inner *4f* orbitals of the central rare-earth metal ions. We consider that the enchancing of PL in NC is determined by the effective transfer of energy from polymer matrix to chelates of the complex OCC and subsequent energy transfer to the energetic levels of Eu^{3+} ion. HOMO and LUMO energy levels of complexes are found to be situated between singlet S and triplet T levels of polymer, and this case is similar to the doping case of semiconductor into its forbidden band with particularities of their dimensions. The enhancing of PL can be explained by the coordination ability of the organic counterpart of the host structure of polymer, which is strong enough to stabilise the position of chelates in *Eu-OOC* neighbourhood after the incorporation process. Nanocomposites display a bright and narrow Eu^{3+} ion emission, which is due to the so-called "antenna" effect, defined as a light conversion process via an absorption energy transfer-emission sequence involving distinct absorption by a polymer and ligand and their energy transfer to Eu^{3+} ions with subsequent and later their emission.

The experimental data of photoluminescence can be explained from the viewpoint of the surrounding environment where the Eu^{3+} ion resides. Polymers and OCC significantly affected the strength of the hypersensitive transitions ($^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4) for Eu^{3+}) of the complexes and the maximum of PL intensity at 612-615 nm.

For the Europium complex, the intensity of the transitions of $^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4) increases in the nanocomposite with grows of the concentration of OCC in NC. When $Eu(TTA)_2(Ph_3PO)_2NO_3$ complexes were incorporated into *PVP*, the complexes exhibited disorder. Under the influence of the electric field of the surrounding ligands, the distortion of the symmetry around the lanthanide ion by the capping *PVP* due to the polarization of Eu^{3+}, which increases the probability for electric dipole allowed transitions. The influence of *PVP* on the coordinated environment of Europium ions changes the energy-transfer probabilities of electric-dipole transitions, accounting for the increase in luminescent intensity of 612 - 615 nm maxima of NC.

The different PL intensity of *Eu* complex in 4 different nanocomposites can be interpreted as follows: when *Eu* complexes are introduced into the *PVP*, the molecular motion is restricted and the stretching and bond vibration are weakened by the polymer, both of which decrease the non-radiative transition. These results show that the nanocomposites could provide a relatively stable environment for lanthanide complexes and improve their luminescence properties.

We suppose that the interaction of macromolecular ligands at high concentrations of Eu^{3+} ion leads to partial formation of coordinated unsaturated complexes and ionic aggregates, leading to the quenching of luminescence. From these positions, the resulting polymer composites open the most promising way to neutralize the coordinated complexes and to obtain structurally homogeneous materials with desired properties. From PL spectra of the NC (Fig. 5) we can also suppose a low local symmetry of ligand field of ion Eu^{3+} observed line transition $^5D_0 \rightarrow {}^7F_0$, which is forbidden under the high asymmetry of the luminescence centre. The intensity of the transition $^5D_0 \rightarrow {}^7F_0$ is comparable with intensities of $^5D_0 \rightarrow {}^7F_1$, indicating also a significant asymmetry around of rare-earth ions. The presence of splitting of the transition line $^5D_0 \rightarrow {}^7F_1$ on three components and of the transition line $^5D_0 \rightarrow {}^7F_2$ on five components indicates the absence of spherical symmetry.

5. Conclusions

The nanocomposites $PVP/Eu(TTA)_2(Ph_3PO)_2NO_3$ were obtained by the method of chemical solutions.

From transmission spectra of NC measured in the range 200 to 800 nm we have identified the absorption bands with maximum positions centred at 3.8, 4.5 and 4.8 eV in the UV. The threshold of absorption forbidden band for different NC was estimated at ΔE_{HL} = 2.9 – 3.2 eV. It is shifted slightly in the IR direction of the spectrum with increasing the percentage of *OCC* concentration in NC.

The photoluminescence spectra of NC was attributed to the internal of transition of Eu^{3+} ion $^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4) centred at 537, 580, 612 - 615, 650 and 702 nm. The halfwidth of PL band at 612 - 615 nm is less than 10 nm, which indicates that the nanocomposite exhibits high fluorescence intensity and colour purity.

The positive influence of *PVP* and SBMA polymers matrixes on the coordinative environment of Eu^{3+} ions was determined. A possible method of raising the fluorescence of NC are energy transfer from polymers *PVP* and *SBMA* levels and from levels of ligand to internal levels of Eu^{3+} ion. It was demonstrated PL amplification in the NC compared with organic complex compound samples.

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