

# Effective Laser Luminescence of Nanocomposites $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$ - Polyvinylpyrrolidone

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**Abstract** –Thin films (1-10  $\mu\text{m}$  thickness) of nanocomposites (NC) based on organic coordinated compound (OCC)  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  (where  $\text{TTA}$  is thenoyltrifluoroacetate ( $\text{C}_8\text{H}_5\text{F}_3\text{O}_2\text{S}$ ),  $\text{Ph}_3\text{PO}$  - triphenylphosphine ( $\text{C}_6\text{H}_5\text{PO}$ ) and polymer – polyvinylpyrrolidone ( $(\text{C}_6\text{H}_9\text{NO})_n$ ) (PVP)) were obtained by chemical methods and with different molar ratios into organic polymer matrix. NC have been characterized by measurements of optical transmission, excitation spectra of photoluminescence (PL) and photoluminescence of NC at different concentrations of  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  in NC. In the optical transmission of NC, the characteristic parameters of NC such as threshold absorbance, dependence on the concentration of the organic coordinated compound in NC, etc., have been determined. The displacement of threshold absorption to infrared is observed with increasing of the concentration of the coordination material in NC. The excitation spectrum of photoluminescence of NC led the range from 200 to 400 nm energy at which takes place the photoluminescence in NC. The PL of nanocomposites was detected as specific for internal transitions  $4f \rightarrow 4f$  of the  $\text{Eu}^{3+}$  ion  ${}^5D_0 \rightarrow {}^7F_i$  ( $i = 0, 1, 2, 3$  and 4) centred at 537, 578, 615, 632, 649, 690 and 705 nm, respectively at  $T=300$  K. The dominant PL is in the position to 615 nm and the halfwidth is less than 10 nm and it is attributed to the transition  ${}^5D_0 \rightarrow {}^7F_2$ . The comparison of PL of NC with organic coordinated compounds at equal ultraviolet exciting show the increasing of the external efficiency of NC luminescence. In nanocomposites, the effect of energy transfer from polymer matrix to coordinated molecule with subsequent transfer of them to  $\text{Eu}^{+3}$  ion have been identified. It was proposed some applications of given nanocomposites in optoelectronics and medicine.

**Key words** – nanocomposites, rare earth ion, photoluminescence, polymer, energy transfer, laser emission

## I. INTRODUCTION

Nanocomposites (NC) based on polymers and coordinate complex organic compounds of rare earth metals are excellent materials for a new generation of light emitting devices with high efficiency due to strong luminescence, easy colour tuneable, temperature insensitivity, and high stability. Luminous properties of the complex coordinated compounds and nanocomposites on their basis can be a subject of different applications in medicine, solar cells devices on the flexible substrates, optical signal amplification, etc. For the visible spectrum, more frequently are used the compounds with Europium ( $\text{Eu}^{3+}$ ) and Terbium ( $\text{Tb}^{3+}$ ) ions. Improving of their luminescence properties depends on the type of ligands using for surrounding of the rare earth ions. Photoactive complexes of organic compounds of lanthanides may be used, as an example, like the trivalent ion of Europium chelated with  $\beta$ -diketonates, or the cyclic ligands of carboxylate when the coordination number of  $\text{Eu}^{3+}$  varies in the range from 6 to 9. Future researches should be oriented towards achieving coordinated surrounding of the ion of  $\text{Eu}^{3+}$  in order to improve luminescence efficiency, and to obtain a final stable compound for various practical applications. The fundamental studies of the spectroscopy photophysic of rare earth metals and applications of the technology connected with effective luminescence with the halfwidth of the

luminescence bands less than 10 nm in the visible and near-infrared regions of spectrum at different excitations are of special interest.

Advantage of application of coordinated compounds of rare earth ions with  $\beta$ -diketonates and ligands in nanocomposites is based on the so-called "antenna" effect, or the transfer of excitation energy from outside of the system of  $\text{Eu}^{3+}$  ion towards their energy levels. The population of upper energy levels with subsequent transition to ground states is increased in this case. The intermolecular energy transfer to the  $\text{Eu}^{3+}$  ion takes place via the levels of ligands and their surroundings.

In previous paper we report the investigations of the NC from copolymer butylmetacrylate and styrene in ratio of 1:1 in whose matrix  $\text{Eu}(\text{TTA})_3\text{H}_2\text{O}$ ,  $\text{Eu}(\text{TTA})_3\text{Phen}$  and  $\text{Eu}(\text{DBM})_3\text{Phen}$  were introduced [1-4]. For all investigated materials with NC, photoluminescence levels caused by  $4f \rightarrow 4f$  transitions of  $\text{Eu}$  were identified. The most intensive luminescence band was centered at 615 nm and halfwidth ca 10 nm in all studied cases.

## II. METHODOLOGY

The synthesis of organic coordinated compound of bis(thenoyltrifluoroacetato) bis(triphenyl-phosphine oxide)(mononitrate) europium (III) ( $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$ ) was carried out after the scheme described in [5,6] for analogue compounds. An amount of 4 mmol (0.44 g) of  $\beta$ -diketone and 2 mmol (0.56 g) of neutral ligand were dissolved in 10 ml. of hot 96% ethanol, and 2 ml. of 1N

sodium hydroxide were added. The mixture was stirred, while 1 mmol of Europium nitrate in 5 ml. of water was added dropwise. A type of light cream precipitate formed immediately. The precipitate was filtered off, washed with ethanol, dried thoroughly in air, and the solid of the complex was obtained. Yield was (0.85 g) :

For  $C_{52}H_{38}F_6EuNO_9P_2S_2$  calcd, %:  $C = 51.49$ ;  $H = 3.16$ ;  $N = 1.15$ ;  $S = 5.28$ .

Found, %:  $C = 51.49$ ;  $H = 3.48$ ;  $N = 0.95$ ;  $S = 5.14$ .

The formula of the structure of OCC bis(thenoyltrifluoroacetato)bis(triphenylphosphine oxide) (mononitrate)Europium(III)  $C_{52}H_{38}F_6EuNO_9P_2S_2$  is shown on Fig.1.

Nanocomposites  $PVP/Eu(TTA)_2(Ph_3PO)_2NO_3$  were prepared from chemical solutions of separate components by detailed method of preparation which will be described separately later [7]. Polyvinylpyrrolidone ( $(C_6H_9NO)_n$ ) was used as the polymer with an average molecular weight 1 300 000  $g \cdot mol^{-1}$ , white to light yellow, hygroscopic, amorphous powder (purchased from Aldrich Chemical Company). The Europium complex  $Eu(TTA)_2(Ph_3PO)_2NO_3$  was successfully incorporated with different molar ratios into organic polymer matrix of PVP via sol-gel process. Drop- and spin-coated thin films on optical glass and quartz substrates were obtained. The dried layers with thickness around 1-10  $\mu m$  turn out to be transparent in visible range of spectrum.

The microscopic investigations of the morphology of the NC surface on a microscope MII-4 show that the dimensions of  $Eu(TTA)_2(Ph_3PO)_2NO_3$  particles, incorporated in the polymer matrix are invisible and hence are less than 100 nm. Photoluminescence spectra have been measured using a set-up based on MDR-23 monochromator connected to PC. NC excited with  $N_2$ -laser ( $\lambda = 0.337 \mu m$ ) or Deuterium lamp have generated some sharp emission bands in the spectral range of 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.

### III. EXPERIMENTAL RESULTS

Fig.2a,b shows the surface images of the NC films at different concentration of  $Eu(TTA)_2(Ph_3PO)_2NO_3$  in the nanocomposites under white (Fig. 2a) and UV illumination (Fig. 2b). The photos also reveal that  $Eu(TTA)_2(Ph_3PO)_2NO_3$  complex are dispersed in PVP homogeneously without any phase separation.

Transmission spectra  $T(\lambda)$  of thin layers of NC on quartz substrates in the ultraviolet (UV) show clearly 3 absorption bands with maximums at 3.8, 4.5 and 4.8 eV, and with increasing of the OCC concentration in NC they grow until complete darkening in UV range. The sharp absorption threshold (Fig.3,4) is presented for all concentrations of coordinated compounds of OCC in NC in the range of 370 - 380 nm of spectrum. The absorption spectra ( $\alpha(\lambda)$ ) are calculated from the transmission spectra  $T(\lambda)$  by the formula  $\alpha(\lambda) = -\ln T/d$  (where  $d$  is the thickness of NC,  $\alpha$  – absorption coefficient). The energies of forbidden bands of NC ( $\Delta E_{NL} = LUMO - HOMO$ , where  $HOMO$  is energy of high occupied molecular orbital and  $LUMO$  – low unoccupied molecular orbital) obtained from 80 % of absorption threshold of  $T(\lambda)$  are in the range 3.14 - 3.16 eV. Forbidden band  $\Delta E_{NL} = LUMO - HOMO = 3.15 eV$  are referred to coordinated compounds of

$Eu(TTA)_2(Ph_3PO)_2NO_3$ .

On Fig.5a,5b,5c the spectra of photoluminescence of NC  $Eu(TTA)_2(Ph_3PO)_2NO_3$ -PVP 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, 578, 615 (611, 613, 617, 620), 650 and 702 nm, and can be attributed to the spin forbidden  $4f \rightarrow 4f$  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 others, and its halfwidth is less than 10 nm.

The optimal concentrations of  $Eu(TTA)_2(Ph_3PO)_2NO_3$  in nanocomposite were found in the range of 6 – 11% (Fig.6). There is an almost monotonous increase of intensity of photoluminescence up to some 6 % of the OCC concentration in NC, and this feature is characteristic for all thin film samples at room temperature. The main feature of these 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.

### IV. DISCUSSION

The measuring of PL spectra determine the effective transfer of energy from polymer matrix PVP to energy levels LUMO chelates of the complex  $Eu(TTA)_2(Ph_3PO)_2NO_3$  and subsequent energy transfer to the energetic levels of  $Eu^{3+}$  ion. HOMO and LUMO of complex  $Eu(TTA)_2(Ph_3PO)_2NO_3$  are found to be situated between levels  $S$  and  $T$  of polymer, and this case is similar to the doping case of semiconductor into its forbidden band with particularities of they dimensions.

By comparing the PL of  $Eu(TTA)_2(Ph_3PO)_2NO_3$  complex with PL of NC, the enhancing of the efficiency for photoemission in NC was observed. The enhancing 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  $Eu(TTA)_2(Ph_3PO)_2NO_3$  neighborhood after incorporation process.

The emission spectra of  $PVP/Eu(TTA)_2(Ph_3PO)_2NO_3$  NC and  $Eu(TTA)_2(Ph_3PO)_2NO_3$  powder was studied and analyzed. The emission spectra of NC were similar to that of corresponding  $Eu(TTA)_3Phen$  complex [2], and the halfwidths of the strongest bands of PL were found to be less than 10 nm, but in this case the  $PVP/Eu(TTA)_2(Ph_3PO)_2NO_3$  have most high fluorescence intensity and color purity. 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 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. PVP 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 613 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 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 615 nm peak of NC.

The difference of the photoluminescence of Eu complex in 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 PVP, 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 the spectra of NC (Fig. 5a,b), 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 interdicted under the high symmetry 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 axial symmetry of the inner coordination sphere of central ion  $Eu^{3+}$ .

#### V. CONCLUSION

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 range 200 to 800 nm we have identified the absorption bands with maximums centred at 3.8, 4.5 and 4.8 eV in the UV, and the threshold of absorption forbidden band  $\Delta E_{NL} = 3.15$  eV was estimated. It is shifted slightly in the IR direction of the spectrum with increasing the percentage of  $Eu(TTA)_2(Ph_3PO)_2NO_3$  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, 578, 615 (611, 613, 617, 620), 650 and 702 nm. The halfwidth of PL band at 615 nm is less than 10 nm, which indicates that the nanocomposite exhibits high fluorescence intensity and colour purity.

The positive influence of PVP matrix on the coordinative environment of  $Eu^{3+}$  ions was determined. A possible method of raising the fluorescence of NC  $PVP/Eu(TTA)_2(Ph_3PO)_2NO_3$  is energy transfer from polymer PVP levels and from levels of ligand to internal levels of  $Eu^{3+}$  ion. It was demonstrated the amplification of PL in the NC compared with organic complex compound special.

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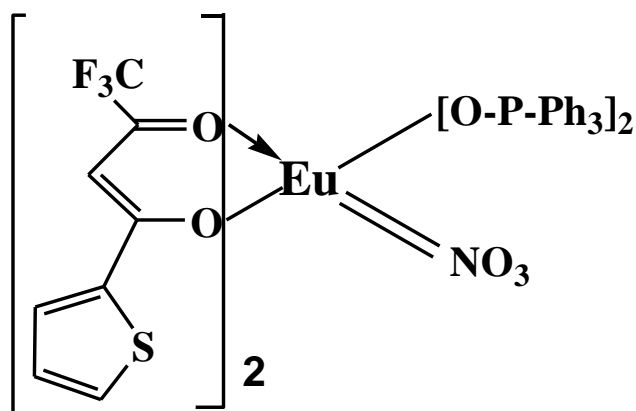
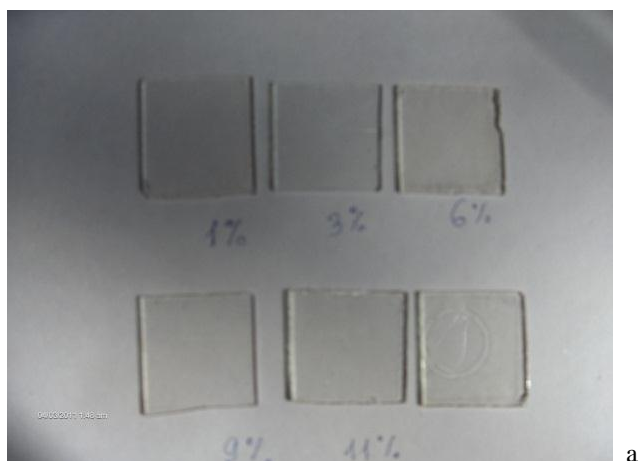
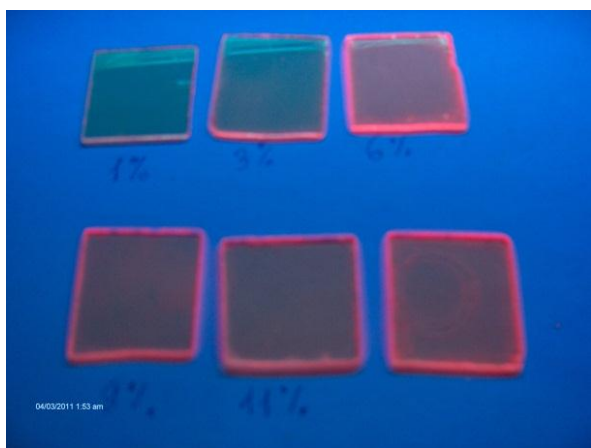


Fig.1. Formula of the structure of bis(thenoyltrifluoroacetato)bis(triphenylphosphine oxide)(mononitrate)Europium(III)  $C_{52}H_{38}F_6EuNO_9P_2S_2$ .



a



b

Fig.2. Samples of thin layers of NC illuminated with visible (a) and UV light (b).

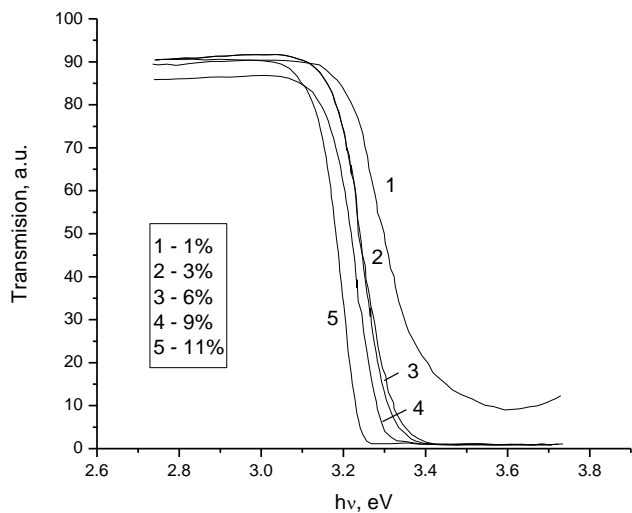


Fig.3. The transmission spectra of samples of thin layers of NC on glass substrates for different concentration of  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  in PVP at room temperature ( $T=293\text{ K}$ ).

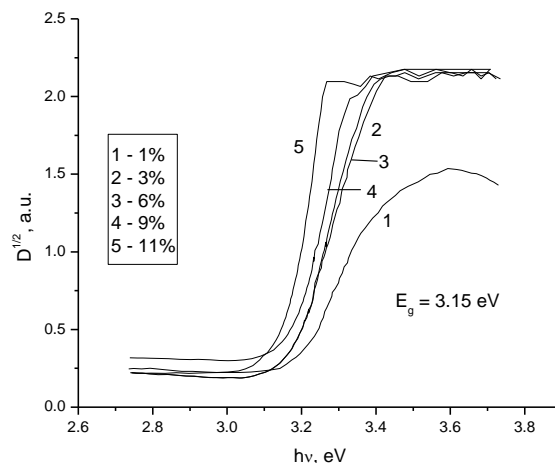


Fig.4. The optical density transmission spectra of samples of thin layers of NC on glass substrates for different concentration of  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  in PVP at room temperature ( $T=293\text{ K}$ ).

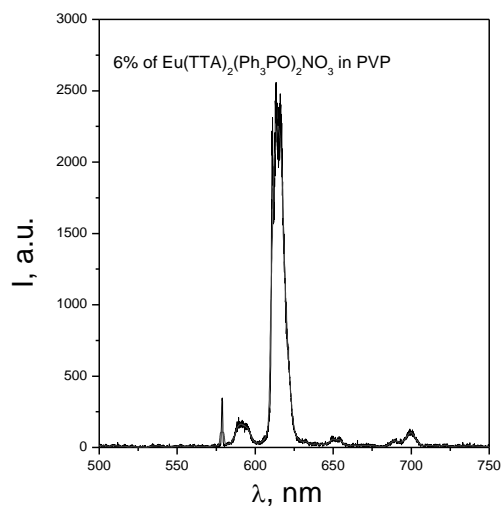


Fig.5a

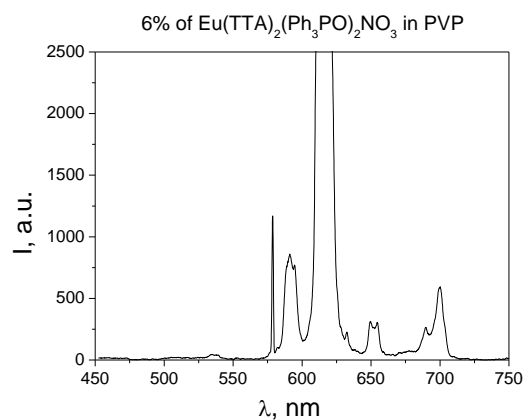


Fig.5b

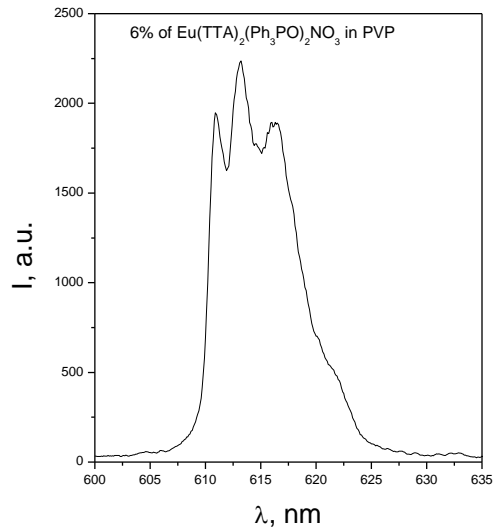


Fig.5c

Fig.5. The photoluminescence spectrum of thin layer of NC  
 PVP/ $Eu(TTA)_2(Ph_3PO)_2NO_3$  10 wt.% of concentration of complex  
 $Eu(TTA)_2(Ph_3PO)_2NO_3$  in NC: a,b – whole spectrum, c – detailed spectrum  
 of main maximum at room temperature ( $T=293$  K).

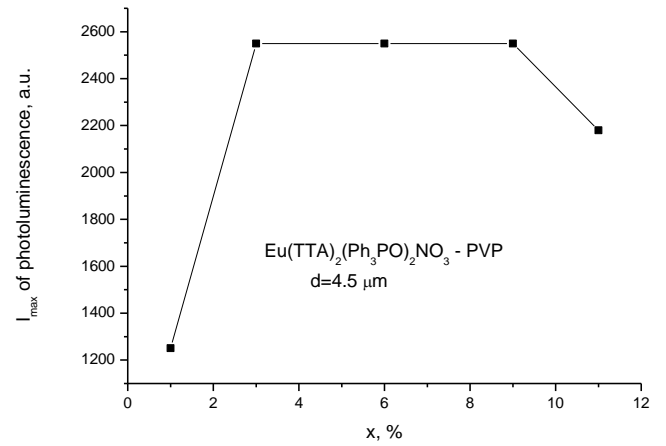


Fig.6. The maximum of intensity of photoluminescence at 615 nm of thin layers of NC versus of concentration  $x$  of  $Eu(TTA)_2(Ph_3PO)_2NO_3$  in NC.