

Europium dibenzoylmethane complexes in SiO₂-based matrix

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The complex of europium with dibenzoylmethane and mixed-ligand complex containing 1,4-diphenyl-1,10-phenanthroline is entrapped in SiO₂-based sol-gel produced immobilization matrices. The IR spectra, thermochemical behavior, photoluminescence properties of the obtained composites and the influence of the synthetic conditions (composition of the sol, pH, presence of contaminant ions, ageing and films/membrane drying conditions) are studied and some recommendations to synthetic procedure are given.

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1. Introduction

The Ln³⁺-ions (Ln = lanthanides) display narrow-line fluorescence (originating from intra-4f electron transitions), relatively insensitive to material of the immobilization matrix. The organic ligands in lanthanoid complexes can serve as an energy absorption antenna and in this way significantly increase otherwise low absorption ability of rare earths. In such a case Ln³⁺ show intense emission. Such a type of complexes of lanthanides with β – diketonates (incl. with dibenzoylmethane, HDBM) are used as an active component of organic LED, in some biomedical investigations and have potential application as high density recordable optical materials, etc.

Recently the chemistry and application of the lanthanide diketonates and their application have been an object of excellent reviews [1 - 3]. Some peculiarities of the lanthanide dibenzoylmethanates synthesis have been discussed in [4].

The potential usage of the studied complexes requires their immobilization in suitable matrices. The latter have to ensure a uniform distribution of the optically active dye, its proper entrapping as to prevent the leaching and in the same time they have to preserve the complex optical properties. The effect of the chemical nature of the ligands, co-ligands and matrix is discussed in a review [5] considering Eu-complexes entrapped in different matrices (including SiO₂-based one). A strong dependence (for the studied system) of the matrix material nature on the emission lifetime is shown. The coligands nature influences the same parameter due to their specific interactions with the matrix and with the main ligand.

It is revealed that the surface coating of Eu chelates by sol-gel glasses is an effective way of inorganic-organic hybridization for high-stability of chelate bonding against free oxygen and water [6].

The comparison between matrices based on pure SiO₂, ZrO₂, mixed oxides (SiO₂ + TiO₂), organically modified

gels with 3-glycidoxypropyl trimetoxysilane (Glymo) is made [5,7]. Lifetimes of the excited states of Eu³⁺ and Tb³⁺ oxides, sulfides and some complexes entrapped in ZrO₂ or ZrO₂ - Glymo matrices are reported in [8].

The quenching, taking place in sol-gel produced matrices is decreased by the association of the Eu-complexes with polyethylene glycol [9].

Wang et al. [10] report the immobilization of the Ln(DBM)₃ in SiO₂-based sol-gel produced matrix. The sol ageing is done at 40 °C in sealed vessel followed by a stay for 4-5 weeks at ambient conditions.

Review of the complexes immobilization in monolith matrices is made by Meng et al. [11]. In the same time the authors report the spin-coating deposition of films using Eu(DBM)₃ or Eu(DBM)₃.phen (phen – 1,10-phenanthroline) solutions in a mixture of ethanol and dimethylformamid (DMF). The complexes fluorescence spectra are presented and their photo and thermal stability are studied. Despite of efforts devoted to incorporate lanthanide complexes in silica matrix [12, 13] the films produced have a short-term stability [14].

In a previous paper [4] some peculiarities observed in the course of application of the methods proposed for synthesis of Eu-complexes with HDBM or HDBM and 4,7-diphenyl-1,10-phenanthroline (dpp) and influence of the synthetic method on composition, structure and optical properties were discussed. In the present paper the entrapping of complexes produced by different synthetic routes in SiO₂-based sol-gel produced immobilization matrices is studied. The attention is devoted to the elucidation of the synthesis and immobilization impact on the photoluminescence properties of the materials prepared and for the first time data are reported on the SiO₂-based composite containing ternary complex with HDBM and dpp.

2. Experimental

2.1 Materials

HDBM (purum, > 98 %, supplied by Fluka), dpp (>98 %, Alfa Aesar) and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (>99 %, Fluka) as starting materials, ethanol (96 % or p.a., >99.7 %), acetone (p.a.) and dimethylformamide (DMF, p. a. LAB-SCAN) as solvents were used as starting materials for complexes production and dissolving. Tetraethoxysilane (TEOS, >99%, Fluka) and ethanol (96 %) were used for matrix preparation. Films were produced on polished microscopic slides. Before deposition the slides were cleaned by 15 min treatment in ultrasound bath consequently with distilled water, methanol, acetone and finally with distilled water.

2.2 Synthesis of the complexes

The complexes were synthesized by the methods applied and discussed in [4]:

a) Method of Khomenko and Kuznetsova [15]. To 10 cm^3 ethanol solution of HDBM (0.5 M), containing 26 mg NaOH, 2 cm^3 ethanol solution of EuCl_3 (0.3 M) was added. The mixed solution exhibits (under UV illumination) red fluorescence, characteristic for the Eu-complexes and the crystals were formed just after mixing of the mentioned solutions. After stirring for 4 h at room temperature the crystals were filtered, recrystallized from ethanol (the raw product is not completely dissolving in ethanol) and dried at ambient conditions.

b) Method of Melby et al. [16]. To 48 cm^3 ethanol solution containing 6 mmol HDBM, 12 cm^3 0.5 M NaOH and 10 cm^3 EuCl_3 aqueous solution (2 mM) were added. The solution was heated at reflux (60 °C) and stirred for 4 h. The formed crystals were dried at 110 °C for 7 h under reduced pressure and were stored in vacuum dessicator.

c) Methods of Meng et al. [11]. Saturated ethanol solutions of EuCl_3 and of HDBM were mixed at HDBM: EuCl_3 mole ratio 3 and 0.5 M aqueous solution of NaOH was added adjusting pH = 6. The solution was stirred at ambient conditions for 4 h; the crystals formed were filtered, washed with absolute ethanol and dried at room temperature. Ethanol solutions of dpp was added to the crystals (mole ratio Eu^{3+} :dpp = 1), the suspension was stirred for 4 h, filtered, the separated crystals were washed with absolute ethanol and dried in desiccator over silica gel at reduced pressure.

2.3 Sol and films/membrane preparation

At magnetic stirring, to ethanol-DMF solution (volume ratio 14) of the complex (2.5 g/dm^3) TEOS was added drop wise in such an amount as the mole ratio ethanol:TEOS = 4 to be adjusted. After that water (with pH 8, adjusted by aqueous ammonia solution) was added in the same manner, this way reaching mole ratio ethanol:TEOS:water = 16:1:4. Experiments with ratios 8:1:4 and 4:1:4 were also performed. After 2 h stirring the so obtained sol was undergone to ageing at 50-70 °C for

different time. At some experiments sonication of the fresh sol was done for 30 min in ice-water ultrasound bath.

From the prepared gels films (typical thickness of ~300 nm) were produced by dip-coating using a device described in [17] at one immersion with withdrawn speed of 0.2 mm/s. Membranes (1-2 mm in thickness) were prepared casting of the gel in Teflon® mould.

The influence of the temperature (ambient to 70 °C) and time (3 h to 4 weeks) of the ageing of the sol before films/membranes preparation and of their drying on the photoluminescence properties is discussed in the Results.

2.4 Analysis and characterization

The IR spectra of the materials were taken by FTIR Bruker-spectrometer in KBr pellets. The DTG and TG curves of the produced composites were recorded by Paulic-Paulic-Erdey derivatograph. Approx. 0.1 g of the studied sample was heated in synthetic corundum crucible in static air at heating rate of 5 °C/min.

The photoluminescence was qualitatively evaluated at excitation with UV lamp Sylvania TLD 18 W/0.8. The excitation and emission photoluminescence spectra and the lifetime of the excitation states were recorded by Cary Eclipse fluorescence spectrometer (Varian) in solid state.

The films thickness was measured by a Talystep profilometer.

3. Results

3.1 Composite synthesis

- *Influence of the pH.* As it was mentioned the water with pH=8 (adjusted with concentrated aqueous ammonia solution) has to be used for the alkoxide hydrolysis and so pH=6.5 of the sol is set up. Such a value ensures the stability of the complex. The addition of distilled water (instead of such with pH=8) leads to sol pH of ~5 and, judging from the photoluminescence, the complex suffers destruction.

- *Sol preparation.* Few mole ratios TEOS: $\text{C}_2\text{H}_5\text{OH}$: H_2O were tested for the preparation of the starting sol applying water with pH = 8. At a mole ratio 1:4:4 the hydrolysis is very fast. The increase of the ethanol content to 1:8:4 leads again to weak but visible hydrolysis immediately after solutions mixing. Clear starting sol was obtained at 1:16:4 mole ratio.

The introducing of the complex in the sol has to be done as ethanol-DMF solution. However, a higher content of DMF in the solution (for example at volume ratio ethanol/DMF = 6÷7) results in appearance of opalescence after 6 weeks storage of the composite and change in the composite optical properties.

Ultrasonic treatment of the sol (at the conditions described in the Experimental) leads to decrease of its photoluminescence signal.

- *Thermal treatment.* Disappearance of the photoluminescence is detected if the sol is aged at 70 °C

for ~3 h or for ~24 h at 60 °C. Aging for ~5 h at 50 °C in a case films will be deposited or for

~15 h when membrane (~1 mm in thickness) will be produced does not leads to measurable decrease of the photoluminescence intensity.

The drying of films/membranes at room temperature does not ensure final solidification even after 4 weeks and leads to decrease of the photoluminescence signal. The increase of the temperature above 40 °C also leads to quenching of the fluorescence. Drying of the films for 72 h at 40 °C and of membranes for 90 h at 40 °C was found as optimal. Complete solidification of the specimens is

reached after approx. 2 weeks storage at ambient temperature in vacuum dessicator.

3. 2. Composite's properties

No significant differences in the composite properties were observed depending on the complexes synthesis method but Eu(DBM)₃ produced by the method of Melby [16] shows a little higher thermal stability.

2.1. *IR spectrum.* The IR spectrum of the composites along with that of the pure Eu(DBM)₃ and pure sol-gel produced matrix is shown on Fig. 1 and band positions are summarized in Table 1.

Table 1. Bands (cm⁻¹) in the IR spectra of the studied samples*.

Eu(DBM) ₃	Complex-free matrix	Composites with Eu(DBM) ₃	Composites with Eu(DBM) ₃ .dpp	Eu(DBM) ₃	Complex-free matrix	Composites with Eu(DBM) ₃	Composites with Eu(DBM) ₃ .dpp
3420	3420	3420	3420	1022			
3060							
	2985vw	2980vw	2980vw				
2920vw	2920vw		2933vw				
	1658vw	1658vw	1658vw			969	966
1595		1598 vw	1598vw	940	947		
1550		1551vw	1551vw	785vw	790	790	794
1521		1525vw	1525vw	755		755	755
1477		1480vw	1480vw	721			
1454							
1398		1394vw	1394vw	687		687	687
1311		1311vw	1311vw	608		608vww	608vww
1287			1226		576		576vww
1222	1208		1222				
1183vw	1162	1162	1162				
	1159	1167	1160	520			
1069	1075	1095	1095		460	460	460

*vw - very weak

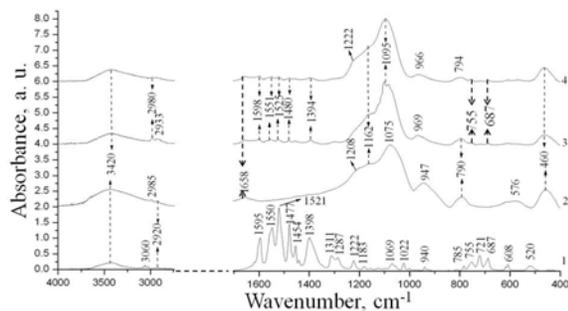


Fig. 1. IR spectra of Eu(DBM)₃ (produced by the method described in paragraph 2b of the Experimental (1), complex-free sol-gel produced matrix (2) and composites containing Eu(DBM)₃ (3) and Eu(DBM)₃.dpp (4).

3.3. Thermal decomposition.

The thermal decomposition of the Eu(DBM)₃-containing composite proceeds in five consecutive exothermic stages (Fig. 2.1). The first one (40 °C - 140 °C) leads to mass loss of 3 %. In the second one (140 °C - 260 °C) the mass loss is 7 % and it increases with the increase of the DMF relative content in the solution, suggesting DMF release in this temperature interval.

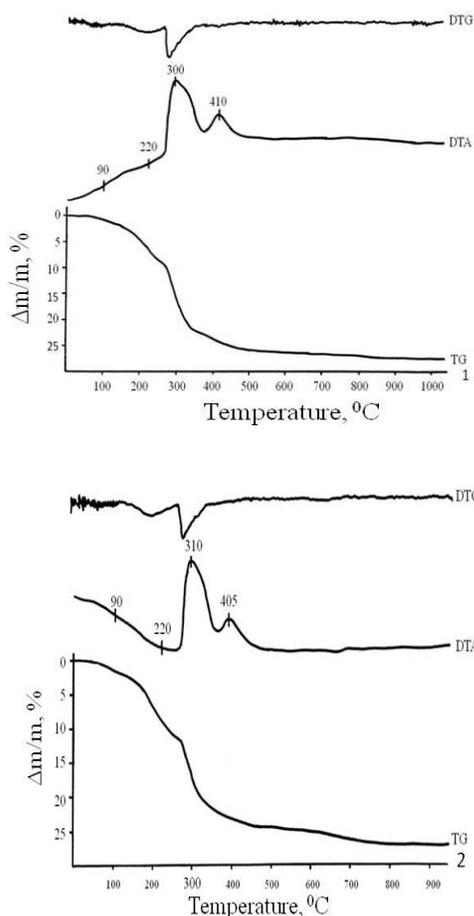


Fig. 2. DTG, DTA and TG curves of composites containing $\text{Eu}(\text{DBM})_3$ (1) and $\text{Eu}(\text{DBM})_3.\text{dpp}$ (2).

The main mass loss is observed at 260 °C - 355 °C (12 %). Considering the final two stages with mass loss of 5 % one can calculate 27 % mass loss in total. The thermochemical behavior of the opalescence material (prepared when the complex is introduced in the starting sol as solution with higher DMF relative content) is similar to that of the standard one but the overall mass loss is higher.

The general pattern of DTA, DTG and TG curves of the composite containing the ternary complex $\text{Eu}(\text{DBM})_3.\text{dpp}$ is practically the same as of the composite with $\text{Eu}(\text{DBM})_3$. The only differences is observed in the first stages of the process up to 280 °C. In the binary complex the mass-loss of 10 % is accompanied with exoeffect where the mass-loss of 12 % in the case of ternary complex is accompanied with endoeffect (Fig.2.2).

The overall mass-loss is 27 %, very close (as to be expected) to that for the composite with $\text{Eu}(\text{DBM})_3$.

3.4 Excitation spectra

The excitation spectra are shown on Fig. 3 and are compared (Table 2) with the spectra of the pure complexes. The main excitation band of the $\text{Eu}(\text{DBM})_3$ -composite is shifted to the longer wave lengths compared with the pure complex ($\lambda_{\text{max}} = 350 \text{ nm}$), appears in the interval 390-450 nm with a maximum at 417 nm (probably with some weaker superimposed bands) and becomes slightly narrower.

No significant shift in the main excitation band is observed (Table 2) in the composite with $\text{Eu}(\text{DBM})_3.\text{dpp}$ compared with the pure complex (Fig. 3.3).

3.5 Emission spectrum.

The emission spectra of the pure complexes and the obtained composite materials (in the form of membrane) are shown on Fig. 4.1,2 and a comparison is made in Table 2. The spectra exhibit typical ligand-sensitized emission of Eu^{3+} ions. The bands of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition are not broadened comparing with the pure complex and the number of Stark components is preserved confirming the relatively ordered environment of the Eu^{3+} in the immobilization matrix.

In the emission spectrum of the composite with $\text{Eu}(\text{DBM})_3.\text{dpp}$ bands bellow 560 nm (some of which are hinted only in the pure complexes spectra and in the spectrum of the $\text{Eu}(\text{DBM})_3$ -containing material) are well expressed (Fig. 4.4, Table 2)

Table 2. Maxima (nm) in the excitation and emission spectra of pure complexes [4] and of the respective microcomposites*

Sample ¹	Excitation	Emission
$\text{Eu}(\text{DBM})_3$ (DMF solution)	350	484, 566, 580, 585, 595, 612, 618, 625, 651, 700
$\text{Eu}(\text{DBM})_3$ in composite	372vw, 381vw, 417, 443sh	567, 580, 593, 612, 618, 625, 653, 705
$\text{Eu}(\text{DBM})_3.\text{dpp}$ (solid)	355, 362, 386, 400	580, 585, 597, 612, 618, 625, 651, 704
$\text{Eu}(\text{DBM})_3.\text{dpp}$ in composite	375 vw, 401, 415sh, 443	460, 485, 488, 490, 530, 535, 540, 565, 580, 590, 595, 612, 618, 625, 651, 702

* vw - very weak, sh – shoulder

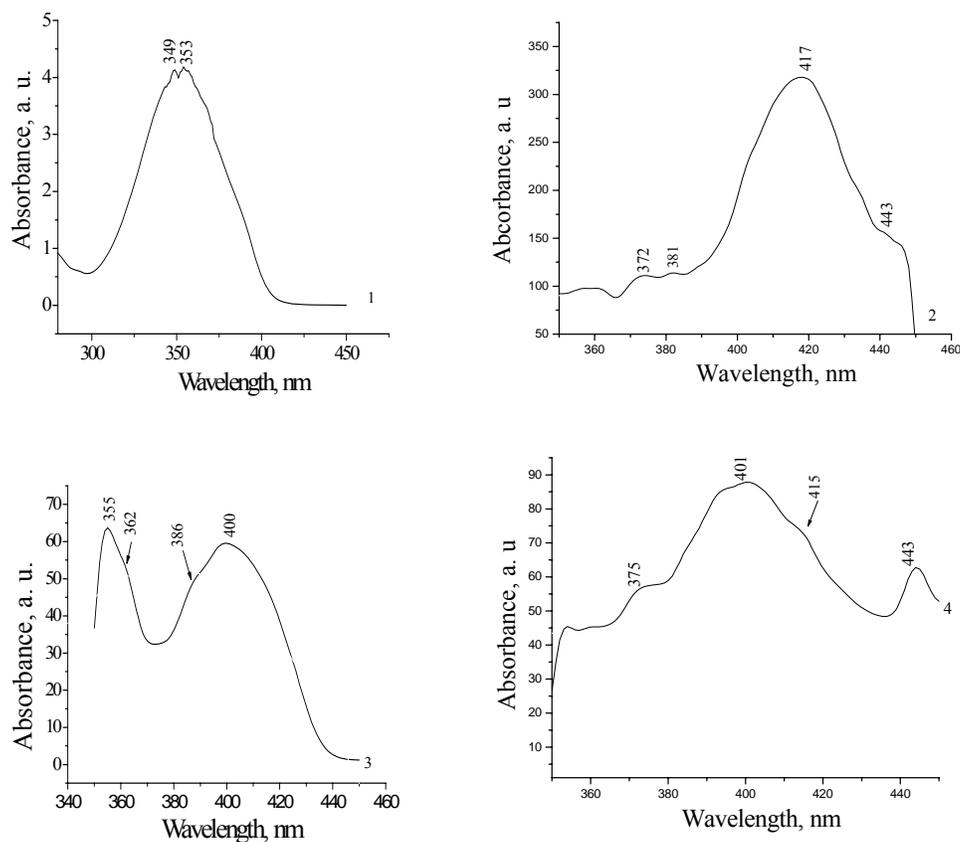


Fig. 3. Excitation spectra of DMF-solution of $\text{Eu}(\text{DBM})_3$ (1), composite containing $\text{Eu}(\text{DBM})_3$ (2), $\text{Eu}(\text{DBM})_3$.dpp in solid state (3) and composite containing $\text{Eu}(\text{DBM})_3$.dpp (4).

3.6 Luminescence lifetime

Luminescence lifetime decay curves of the complexes and of the composites were satisfactorily fitted with first order exponential functions with excited states decay half life (ms) for complexes in solid state 82 ($\text{Eu}(\text{DBM})_3$) and 326 ($\text{Eu}(\text{DBM})_3$.dpp) and 527 and 506 for the composites with the respective complexes.

3. Discussion

As can be seen from Fig.1 the composites IR spectra contain mainly the bands characteristic for the pure matrix. Absorption bands around 3400 cm^{-1} related mainly to the hydroxyl groups, left over in the silica structure, are observed. Bands around to 1088 cm^{-1} [33], 460 cm^{-1} and 793 cm^{-1} are typical for Si-O-Si bonds (asymmetric stretching, Si-O-Si rocking and in-plane bending, respectively) while the one at $965\text{--}970\text{ cm}^{-1}$ can be associated with Si-OH bonds. The weak band at 1660 cm^{-1} in the spectrum of the complex-free matrix is due to the bending mode of water showing not complete drying of this particular sample.

Bands of the complexes, nevertheless very weak, are registered for the first time in this system spectrum – they have not been found at all in the same system (no data are reported for the complex relative content in the matrix) [18] and for Ru(II)-complex incorporated in the same type of matrix ($2.5\text{ g complex/dm}^3\text{ sol}$) [19]. Besides the low content of the complexes in the composite samples, another reason for their bands absence could be [18] the hindered vibration of the complexes ligands by the surrounding matrix structure. The data in Table 1 suggest that the composite spectrum is superposition of the matrix and of immobilized complex spectra without significant shifts of the bands.

The thermochemical behavior of microcomposites based on SiO_2 , similar to the studied in this work, is investigated in details in [20].

Due to the low relative content, the embedded complex has not a significant influence on the thermally induced changes in the microcomposite. Following the findings in [20] and in the present work it can be accepted that in the $40\text{--}140\text{ }^\circ\text{C}$ interval (Fig. 2.1) traces of ethanol (used as solvent and produced as a result of hydrolysis) are released leading to small mass changes, very weak

disturbance in DTG curve at 90 °C and to slight exoeffect due to their burning.

As it was mentioned the DMF left from the synthetic procedure is evolved between 140 °C and 260 °C. In samples with higher DMF-content (not shown in the paper) a strong DTG peak at 160 °C is seen. It is proven [20] that above 205 °C in the complex-free SiO₂-based matrix condensation processes takes place with exoeffects around 300 °C and 430 °C and DTG peak at 410 °C.

Almost the same effects are observed for the material studied in the present work (Fig. 2.1). Overall mass-losses in the both above mentioned materials are also the same (27 % in the present system and 27.2 % found in [20]). This result confirms the formula Si₄O₅(OH)_{5/2} proposed in the latter work as a constructive unit of matrix Si-O-Si network, leading to theoretically expected mass-loss of 26.8 % for the complex-free matrix.

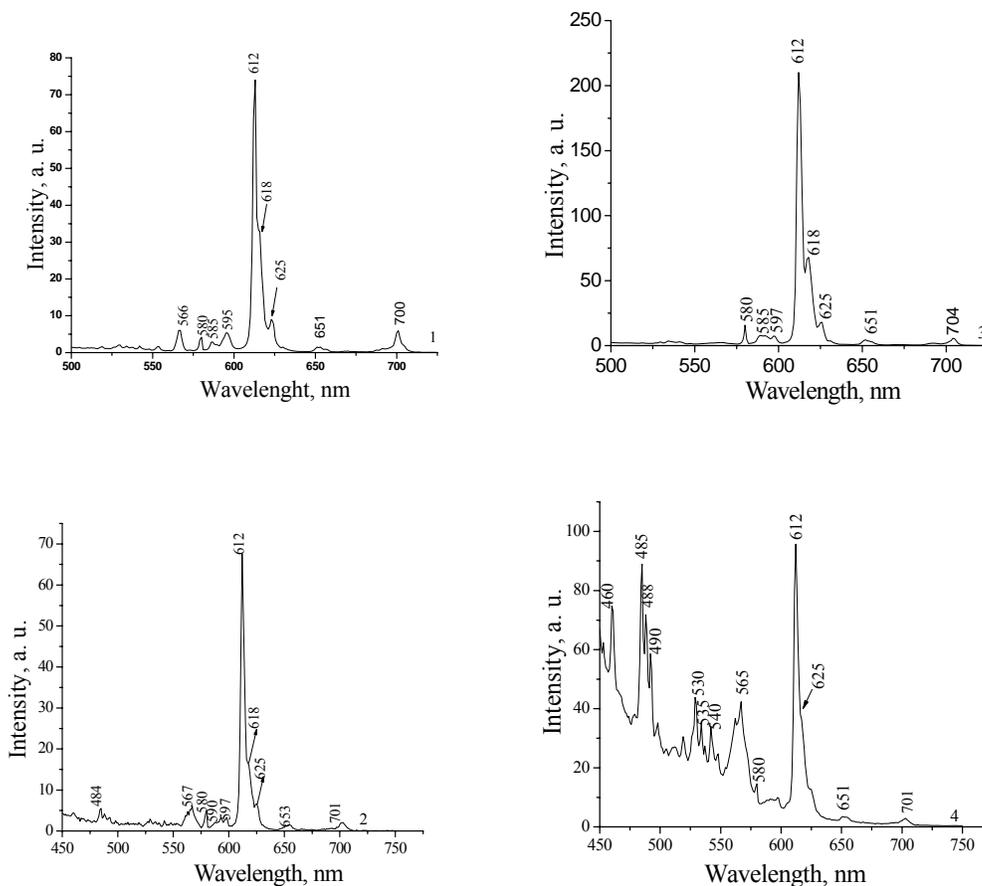


Fig. 4. Emission spectra of $\text{Eu}(\text{DBM})_3$ (1) and $\text{Eu}(\text{DBM})_3,\text{dpp}$ (3) and composites containing $\text{Eu}(\text{DBM})_3$ (2) and $\text{Eu}(\text{DBM})_3,\text{dpp}$ (4).

The only difference between the composites containing the two complexes is the opposite thermal effect of the process taking place to 280 °C. It could be supposed that the exoeffect at the composite containing ternary complex is caused by the separation of the neutral ligand, taking place [21] in the interval 200-300 °C.

The optical properties of the composite are significantly influenced by the synthesis conditions.

- The reported results confirm the thermal instability of the complexes requiring precise setting of the conditions for composite production. The temperatures for aging of the sol and drying of the films or membranes have to be limited to 40 °C for thin films and 50 °C for the thicker membranes. The temperature increase above these values leads to destruction of the complex and decrease of

the fluorescence intensity. The $\text{Eu}(\text{DBM})_3,\text{dpp}$ is thermally little more stable than the binary complex, losing more slowly its fluorescence with time of heating at the above mentioned temperatures. Its fluorescence is preserved (but significantly decreased) after heating at 50 °C for 24 h. In the same time drying at ambient temperature does not allow complete solidification of the specimens even for a prolonged period.

- Despite the positive effect of the sonication [22] on the uniform distribution of the complex in the immobilization matrix it causes quenching of the photoluminescence probably due to some destruction of the complexes and is not to be recommended.

- Due to lower solubility of the complex in the ethanol, the usage of DMF (or similar) as solvent

combined with ethanol is practically unavoidable. However the relative content of the DMF has to be limited. The appearance of opalescence after 6 weeks storage of the composite and change in its optical properties when larger amounts of DMF is introduced is probably due to the disturbance of the Eu³⁺ coordination shell caused by the strong donor ability of the DMF.

- The presence of contaminant ions (using NaOH instead of NH₄OH for adjusting of pH of the water added for alkoxide hydrolysis) strongly decreases the excitation states life-time to 31 μs for Eu(DBM)₃- and to 19 μs for Eu(DBM)₃.dpp- containing composites compared with 82 μs and 318 [4] - 324 μs for the respective pure complexes.

The immobilization of the complex in the supporting matrix leads to:

- Slightly expressed narrowing of the Eu(DBM)₃ excitation band, observed also in a mesophase thin film doped with in-situ formed Eu(DBM)₃.1,10-phenantroline [23]. Our results show that the matrix effect on the coordination shell of the Eu³⁺ as well as the energy transfer between ligands and Eu³⁺ ions is also realized when the latter is introduced in the matrix as finished product. The appearance of band at 443 nm in the composite with Eu(DBM)₃.dpp (revealed as shoulder in the composite with the binary complex) has to be attributed to some specific interaction of the ligands (mainly the neutral one) with the matrix.

- Red shift of the excitation main band in the composite spectrum (417 nm) compared with the one of the pure complex solution s (350 nm) is observed also in [24, 25] and is attributed to a saturation occurring in the crystal [24, 26].

- Preservation of the Eu³⁺ excites state single order exponential decay pattern, suggesting a single average site distribution (a uniform surrounding environment) of Eu³⁺ ions in both complexes and composites and existence of only one type emission centre in the matrices. This result differs from the finding in [10, 11, 18] and is in agreement of the results reported in [23].

- An increase of the luminescence lifetime of both complexes after their embedding in the matrices. Such an effect is observed for Eu-DBM-1,10-phenantroline complex [18] and for Eu(DBM)₃.3H₂O [10] immobilized in sol-gel produced matrices, confirming the general conclusions made in [5]. The increase is ascribed to less efficient non-radiative ⁵D₀ relaxation process due to the decrease of number of OH groups coordinated to lanthanoide ion [10]. Accounting for rather low content of H₂O in the pure complex, used in the present paper, more probably the effect can be explained with the restriction of ligand vibrations when embedded in the rigid structure of silica gel [18].

4. Conclusion

The sensitivity of studied complexes to thermal influences as well as the interaction between the complex and the components of the immobilization matrix taking place in the process of composite preparation imposes

some limitations on the composite preparation mode as to preserve the composites optical properties:

- Methods of Melby [16] and of Meng [11] are recommended for preparation of Eu(DBM)₃ and Eu(DBM)₃.dpp complexes, respectively.

- Clear starting sol for composite preparation can be produced at mole ratio TEOS:C₂H₅OH:H₂O = 1:16:4, pH = 6.5 and 2.5 g complex/dm³ sol.

- The relative content of DMF if used at the composite preparation for complex dissolving has to be limited to ethanol/DMF volume ratio 14. The higher concentrations lead to decrease of the fluorescence signal of the composite during its storage.

- The aging of the sol has to be performed at 50 °C for 5-15 h depending thin films or thicker membranes will be produced. The final products drying are to be done at 40 °C for 72 h for films and at 40 °C for 90 h for membranes. At higher temperature the complexes color disappears despite that the complex itself preserved the fluorescence up to 110 °C.

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