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Preparation and luminescence of silica aerogel composites containing an europium (III) phenanthroline nitrate complex

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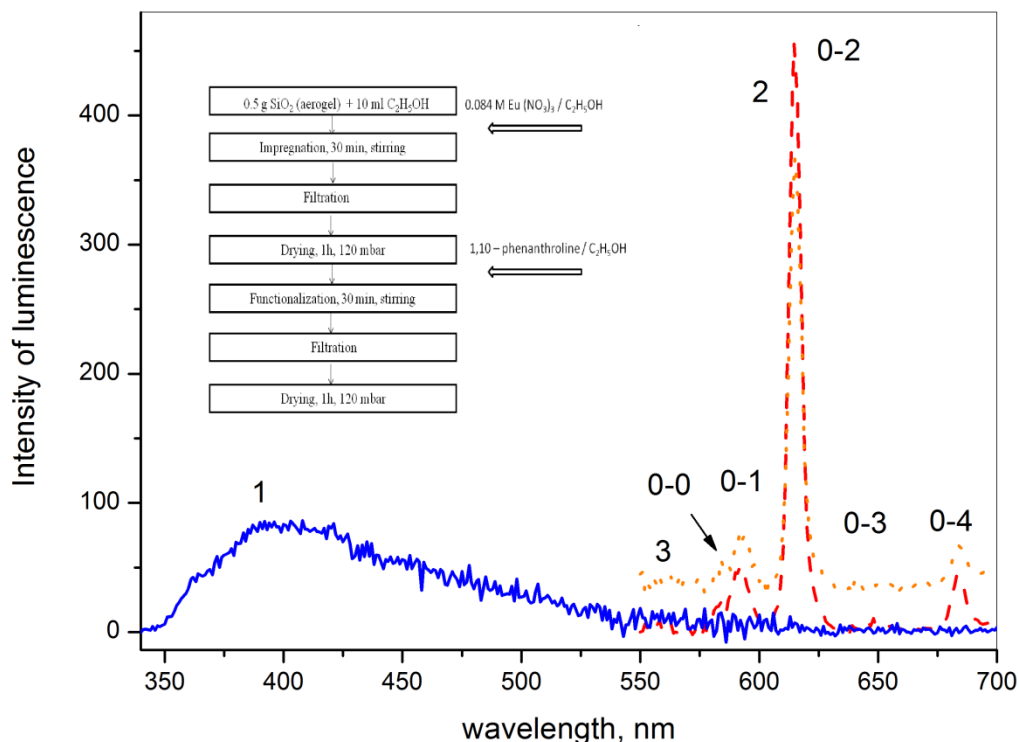
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Abstract

A simple two step procedure for the functionalization of hydrophobic silica aerogel microgranules with europium ions and / or 1,10 - phenanthroline is demonstrated. The activation procedure is based on soaking aerogels in a europium nitrate solution, followed by functionalization with 1,10 – phenanthroline. The functionalized materials display strong red or blue emission at UV-excitation, coming from the formation of $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ or $\text{Si}(\text{IV})$ –1,10-phenanthroline complexes in the porous system of the aerogels. The most probable site symmetry of the europium cation is C_{2v} confirmed by luminescence spectra analysis. Room temperature diffuse reflectance spectra and excitation / luminescence spectra are used to describe the optical properties of the hybrid composites. Excitation spectra prove an efficient energy transfer between 1,10 – phenanthroline and the Eu^{3+} ion.

graphical abstract



An effective activation procedure for functionalization of silica aerogel granules with $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ and/or 1,10 – phenanthroline /phen/ has been demonstrated in order to obtain red or blue emitting materials. Luminescence spectra (excitation at 355 nm) of functionalized aerogel granules: 1 – $\text{SiO}_2:0.18\text{phen}$; 2 – $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$; 3– $\text{SiO}_2:0.007\text{Eu}(\text{phen})_2(\text{NO}_3)_3$. The Eu^{3+} f-f $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1,2,3,4}$ emission transitions are denoted as 0-0, 0-1, 0-2, 0-3, 0-4. The most probable site symmetry of Eu^{3+} ion is C_{2v} .

Keywords: europium, silica aerogels, luminescence, composites

Introduction

Silica aerogels are advanced amorphous materials with promising physical properties: extremely low thermal conductivity, density and 90-98% porosity. There are a few different physico-chemical techniques for the preparation of aerogels: a) supercritical drying of oxide gels obtained via classic sol-gel method. b) subcritical drying of hydrophobic aerogels c) preparation

of hydrophobic aerogel at ambient temperature and pressure using trifunctional precursor or surfactant reagent during sol-gel synthesis [1]. A potential application of aerogel matrices is to fill their pore volume with a suitable dopant having applicable optical, electrical or magnetic properties. Using the soaking or co-gelation techniques, silica aerogel composites containing NiO, ZnSO₄, Co(NO₃)₃, Fe(NO₃)₃ or EDTA have been designed [2, 3, 4, 5]. Despite of numerous investigations the question about incorporation strategies of lanthanide complexes in hydrophobic aerogel granules has not been investigated. On the other hand, aerogels possess a high potential to be a matrix containing efficient complexes suitable for light production and optical sensor applications.

There are some different approaches for functionalization of dense sol-gel materials with hybrid complexes: a) doping during the sol-gel process with a solution of the hybrid complex; b) surface functionalization of pure gels with a solution of the hybrid complex; c) incorporation of hybrid nanocrystals in to the sol-gel network; advantages and disadvantages of these methods are discussed in [6]. In our recent papers we also described a new “in situ” approach for functionalization of previously doped with Eu³⁺ silica or zirconia sol-gel micropowders with 1,10 – phenanthroline solution. The sol-gel materials prepared in this way display a strong, red luminescence, coming from f-f transitions in the Eu³⁺ cations [7].

The aim of the present contribution is to find efficient conditions for the functionalization of hydrophobe silica aerogels with [Eu(phen)₂](NO₃)₃ in the framework of designing luminescent composite materials. Here, [Eu(phen)₂](NO₃)₃ is used as a model for a hybrid complex displaying strong red luminescence with a quantum yield of 35-40% at UV – excitation, due to the f-f luminescent transition of the Eu³⁺ ion [6,8]. Two different physicochemical techniques for functionalization are used in the present contribution in order to compare their efficiency: A) Doping with europium ions of containing sol-gel silica powders followed by hydrophobization and functionalization with 1,10-phenanthroline which is the common way for dense oxide sol-gel materials and B) soaking of hydrophobe millimeter scaled aerogel granules with a bulk density around 0.1 g/cm³ described in [9] with a Eu(NO₃)₃ solution followed by drying and functionalization with 1,10 – phenanthroline.

Materials and methods

For the preparation of silica aerogel composites, containing $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ the following chemicals have been used: 98% TEOS / Tetraethoxysilan, Aldrich/, 99.8% Ethanol, Ridel de Haën and Eu_2O_3 , Ridel de Haën. For the aerogel drying a vacuum furnace NÜVE model EV018 with volume $V = 15 \text{ l}$ and a Labor port diaphragm pump (delivery 30 l min^{-1} , power 300W, ultimate vacuum 100 mbar) was constructed. The preparation of silica aerogel granules with a bulk density approximately 0.1 g / cm^3 at 0.5 atm and 40°C followed exactly the scheme already published in [9]. We realized two schemes given in figures 1. and 2. for the functionalization of silica aerogel granules with 1,10-phenanthroline /phen/, described in details bellow:

- A) Doping of sol-gel silica with europium ions followed by hydrophobization and functionalization with 1,10-phenanthroline. The doping with Eu^{3+} ions has been performed during the sol-gel process. The molar ratio of starting reagents was: $n_{\text{TEOS}} : n_{\text{EtOH}} : n_{\text{H}_2\text{O}} : n_{\text{HCl}} = 1 : 1 : 3 : 0.007$. After solvent exchange in ethanol, the europium doped silica aerogel-like powders with a bulk density 0.3 g/cm^3 have been surface modified in 10 vol% of a TMCS solution in hexane. Finally the aerogels have been functionalized with a 1,10 – phenanthroline solution in ethanol. The as prepared functionalized powders did not luminescence at UV – excitation and have a bulk density of about 0.4 g / cm^3 .
- B) Soaking of hydrophobic aerogel granules with a bulk density around 0.1 g/cm^3 described in [9] with a $\text{Eu}(\text{NO}_3)_3$ solution followed by drying and hydrophobization with 1,10 – phenanthroline. The initial aerogel granules have been prepared following the procedure described in [9]. After drying the impregnated aerogel granules were functionalized with a 1,10 – phenanthroline solution in ethanol, followed by filtering and drying. The impregnation condition was $n_{\text{phen}}/n_{\text{SiO}_2} = 0.18$. The as prepared aerogel like granules with a bulk density 0.35 g/cm^3 displayed strong red luminescence at UV excitation. Using the same preparation scheme, aerogel powders functionalized with 1,10-phenanthroline were obtained. Here, the prepared hydrophobe silica aerogel granules have been functionalized with a 1,10 – phenanthroline solution in ethanol leading to the formation of blue emitting aerogel-like granules, SiO_2 :1,10 – phenanthroline.

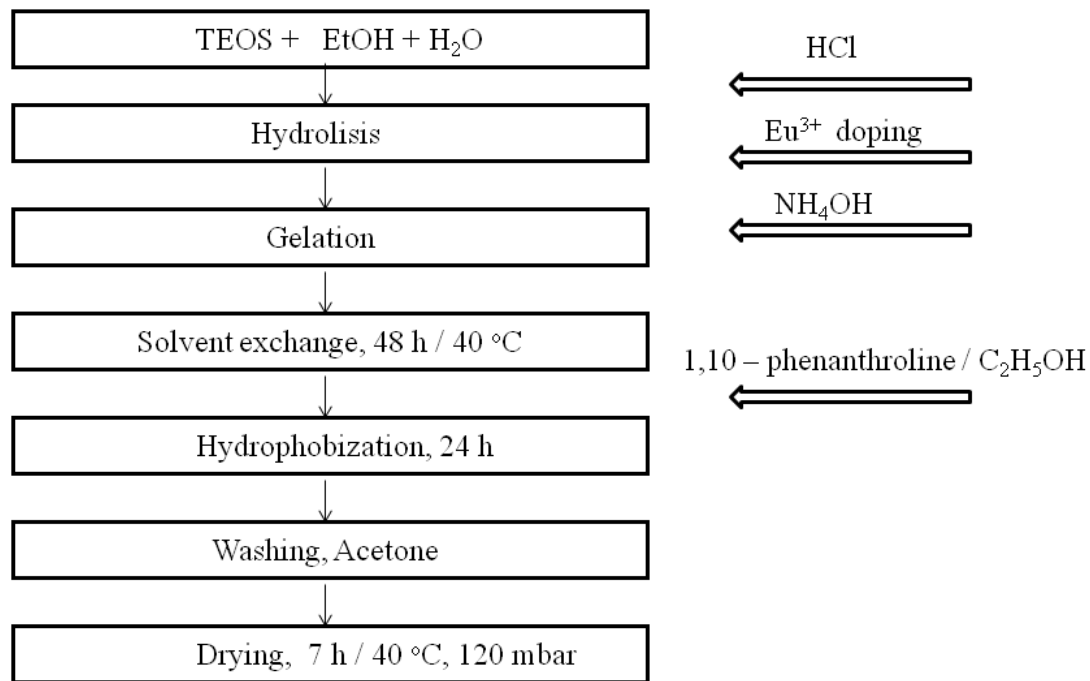


Figure 1. Preparation scheme A leading to europium doped aerogel granules. The functionalization with 1,10 – phenanthroline results in composites with a very low Eu³⁺ luminescence.

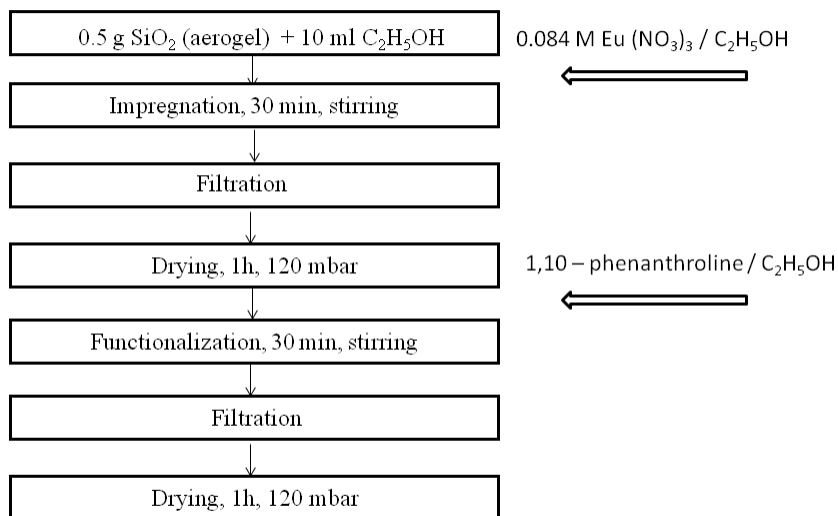


Figure 2. Preparation scheme B consisting of functionalization with 1,10 – phenanthroline of micropowders, impregnated with Eu^{3+} . The composites obtained display a strong red luminescence

Experimental

The chemical composition of the composites was checked by ICP Ultima 2 Horiba – Jobin Yvon unit. Bulk density of gels has been determined densimetrically. Room-temperature UV-Vis transmittance and diffuse reflectance spectra of solutions and powdered species were measured on a Perkin Elmer (Waltham, MA, USA) Lambda 35 spectrophotometer with a deuterium lamp for the UV region. Diffuse reflectance spectra from powdered gels were obtained with a specular reflectance accessory (RSA-PE-20, Labsphere, North Sutton, NH, USA) between 250 and 900 nm. The powders were placed in a black vertical sample holder made in-house from POLIPOM [10]. The f-f transitions of Ho_2O_3 were used as a reference; both peak positions and intensities were in agreement with theory between 250 nm and 900 nm [10]. The Kubelka – Munk function $F(R)$ was calculated from diffuse reflectance $R(\%)$ [11]. Room temperature excitation and luminescence spectra of powders were measured on a standard Varian

Cary Eclipse spectrophotometer with the same sample holder as in the case of the diffuse reflectance measurements.

The calculation of integrated luminescence intensities and second derivative emission spectra follows the procedure of Gaussian deconvolution published in [12]. The calculation of x and y values were performed by homemade program able to read the raw data file as it comes out from the instrument, based on the procedure published in [13]. The data points were validated through OSRAM Sylvania Color Calculator program [14]. All the luminescent composites were investigated with X-Ray diffraction (XRD) using a PANalytical Empyrean powder diffractometer working with $\text{Cu}_{k\alpha}$ radiation.

Results

In figure 3 diffuse reflectance spectra of functionalized and non-functionalized aerogel materials are given. The spectra of gels, functionalized with 1, 10 – phenanthroline are close to that of the hybrid $\text{SiO}_2:\text{[Eu(phen)}_2\text{]}\text{(NO}_3\text{)}_3$ samples [7]. The peak maxima in figure 3 correspond to well known absorption transitions in 1,10 – phenanthroline and Eu^{3+} f-f transitions in inorganic gels [15, 16, 17]. The spectrum of aerogel composites containing only 1,10 – phenanthroline is given for comparison. Diffuse reflectance spectra of non – doped aerogels are discussed in [9]. The weak peak color of the powders is attributed to optical transitions in the 1,10 - phenanthroline molecule in the visible spectral region.

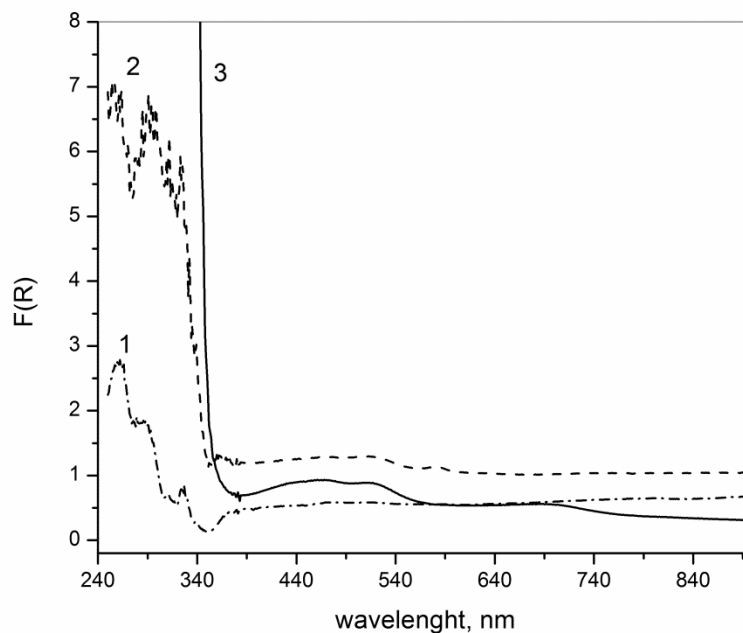


Figure 3. Diffuse reflectance spectra of aerogel composites. Notations: 1 - $\text{SiO}_2:0.007\text{Eu}(\text{phen})_2(\text{NO}_3)_3$, 2 - $\text{SiO}_2:0.001\text{Eu}(\text{phen})_2(\text{NO}_3)_3$, 3 - $\text{SiO}_2:0.18\text{phen}$. Spectra are vertically shifted.

Preparation conditions, sample chemistry and quantification of emission optical properties are summarized in tables 1. and 2. Table 1. displays the sample chemistry, results of chemical analysis and the scheme used for the preparation of the aerogel composites. Luminescence spectra of functionalized aerogel granules prepared using different sol-gel techniques and solid $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ are presented in figure 4.

Table 1 Sample chemistry, preparation conditions and optical properties of aerogel composites functionalized with $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$. The chemistry of the investigated samples is expressed through ICP obtained europium content in the gels in % and the molar ratio $n_{\text{Eu}} / n_{\text{Si}}$.

Sample	Chemistry	Eu % Gel	$n_{\text{Eu}} / n_{\text{Si}}$ Gel	$n_{\text{Eu}} / n_{\text{Si}}$ Sol	Preparation scheme -
Ra3	SiO ₂ :0.001Eu(phen) ₂ (NO ₃) ₃	0.45	0.001	0.0017	B
Ra4	SiO ₂ :0.0072Eu(phen) ₂ (NO ₃) ₃	1.72	0.0072	0.0094	B
Ra5	SiO ₂ :0.007Eu(phen) ₂ (NO ₃) ₃	1.70	0.007	0.0065	B
RaZ31	SiO ₂ :0.003Eu(phen) ₂ (NO ₃) ₃	0.79	0.003	-	A
Eu(phen) ₂	[Eu(phen) ₂](NO ₃) ₃	12.7	-	-	Ref. [18]
Ra0	SiO ₂ :0.18phen	-	-	-	B

Table 2. Emission properties of aerogel composites functionalized with [Eu(phen)₂](NO₃)₃. Notations: I₀₋₂ – relative intensity of the Eu³⁺ ⁵D₀→⁷F₂ transition, I – integral luminescence intensity, X,Y – CIE 1931color coordinates. Sample notations are the same as in table 1.

Sample	I ₀₋₂ %	I a.u.	X	Y
Ra3	70±3	5702±507	0.6044	0.3949
Ra4	70±3	4765±470	0.6260	0.3734
Ra5	75±4	6255±625	0.6425	0.3571
RaZ31	75±4	214±20	0.5661	0.4329
Eu(phen) ₂	79±4	6948±690	0.6539	0.3458
Ra0	-	9862±980	0.1816	0.1551

In table 2. the overall luminescence intensity of the aerogel composites investigated is given. For Eu(III) containing materials the luminescence intensity between 550 nm and 720 nm is taken into account, all the spectra are measured under equal spectroscopic conditions. SiO₂:1,10 – phenanthroline samples display a broad peak with a maximum at 390 nm [15].

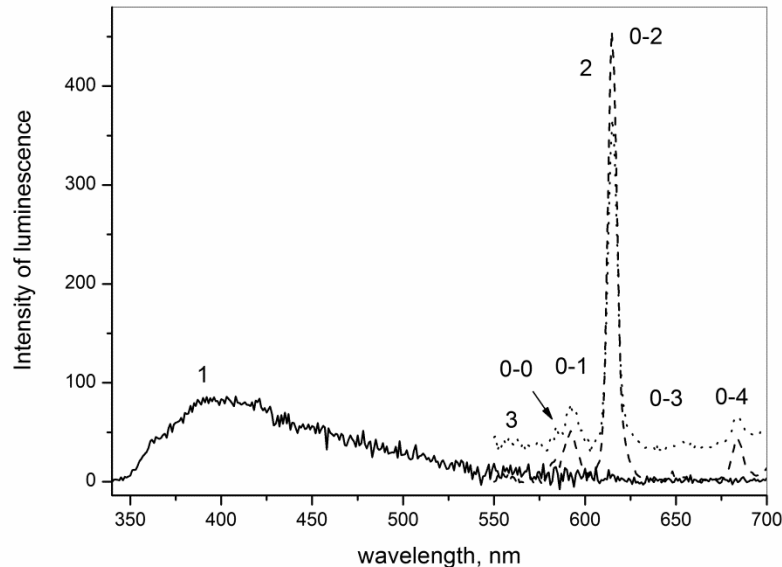


Figure 4. Luminescence spectra (excitation at 355 nm) of functionalized aerogel granules. Sample notations: 1 – $\text{SiO}_2:0.18\text{phen}$; 2 – $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$; 3– $\text{SiO}_2:0.007\text{Eu}(\text{phen})_2(\text{NO}_3)_3$. Spectra are vertically shifted. The Eu^{3+} f-f ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,1,2,3,4}$ emission transitions are denoted as 0-0, 0-1, 0-2, 0-3, 0-4.

In Figure 5 the CIE 1931 X-Y color coordinates of the investigated functionalized composites are presented. The results are compared with our recent studies involving multicolor emitting $\text{ZrO}_2\text{-SiO}_2:[\text{Eu}(\text{phen})_2]\text{NO}_3$ sol-gel powders [18] and red emitting sol-gel materials: $\text{SiO}_2:[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$, $\text{ZrO}_2:[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ and pure solid $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$. All the europium containing powders in this study Ra3, Ra4, Ra5 and RZ31 belong to red emitting materials.

CIE 1931

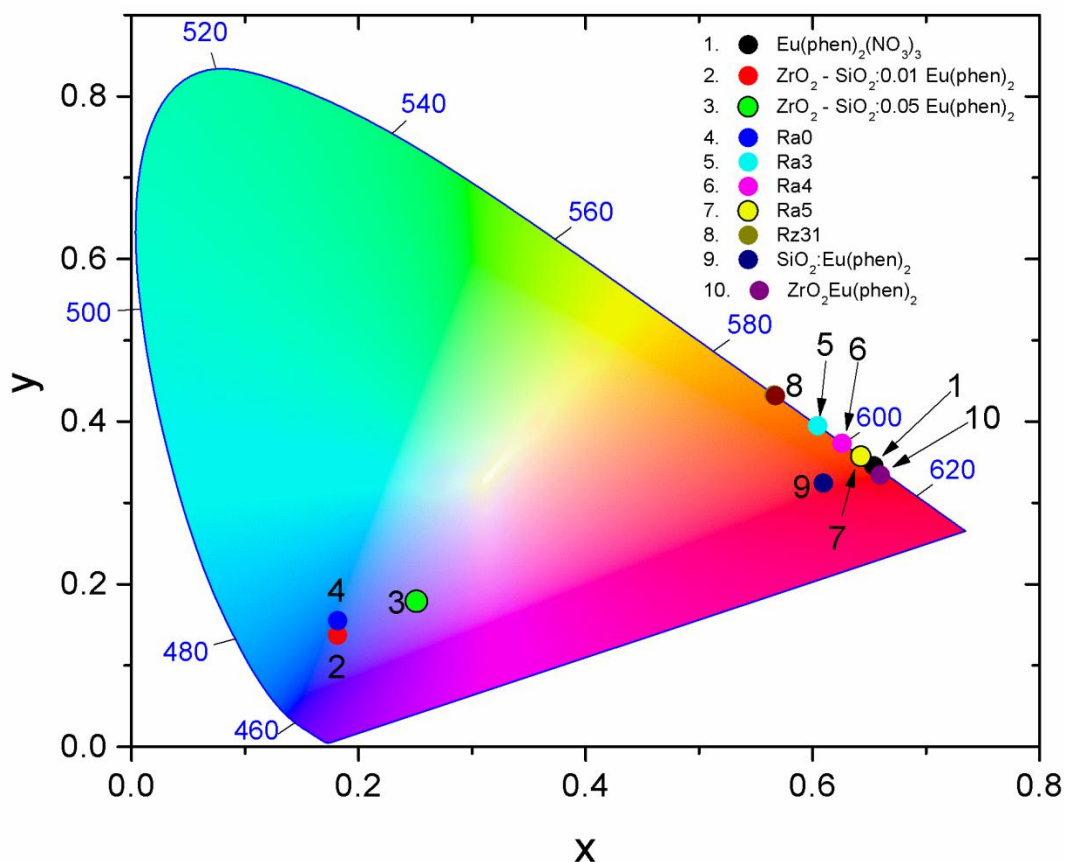


Figure 5. CIE – 1931 Color coordinates of the functionalized aerogels are compared to color coordinates of red and multicolor emitting SiO_2 , ZrO_2 and $\text{SiO}_2 - \text{ZrO}_2$ samples containing $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$. Sample notations: Ra0 – $\text{SiO}_2:\text{SiO}_2:0.001\text{Eu}(\text{phen})_2(\text{NO}_3)_3$, Ra4 – $\text{SiO}_2:0.0072\text{Eu}(\text{phen})_2(\text{NO}_3)_3$, Ra5 – $\text{SiO}_2:0.007\text{Eu}(\text{phen})_2(\text{NO}_3)_3$, RaZ31 – $\text{SiO}_2:0.003\text{Eu}(\text{phen})_2(\text{NO}_3)_3$.

Figure 6 presents excitation spectra of the investigated aerogel composites. Excitation spectra maxima are in a good agreement with the diffuse reflectance spectra and prove that an effective energy transfer to the Eu^{3+} ion takes place through the molecules of 1,10 – phenanthroline.

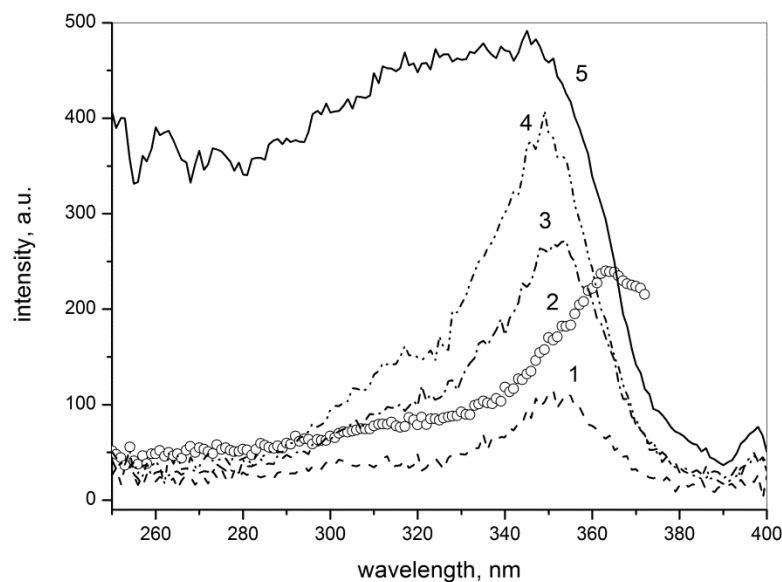


Figure 6. Excitation spectra of aerogel like micropowders monitoring the 615 nm emission maximum. Sample notations: 1 – $\text{SiO}_2:0.001\text{Eu}(\text{phen})_2(\text{NO}_3)_3$; 2 – $\text{SiO}_2:0.18\text{phen}$; 3 – $\text{SiO}_2:0.0072\text{Eu}(\text{phen})_2(\text{NO}_3)_3$; 4 – $\text{SiO}_2:0.007\text{Eu}(\text{phen})_2(\text{NO}_3)_3$; 5 – $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$. The spectrum of $\text{SiO}_2:0.18\text{phen}$ is measured monitoring the 400 nm maximum

Our diffraction data unambiguously prove that the red emitting powders are luminescent composites containing $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ [17,23], while blue emitting gels containing a Si(IV) – 1,10 phennathroline complex are amorphous.

Discussion

Both luminescence intensity and europium emission spectra are indicators for the efficiency of activator incorporation into the amorphous, highly porous silica network. It is visible that preparation scheme (A) represented by sample RaZ31, tables 1. and 2., dealing with preparation of europium doped aerogel granules, leads to a very low luminescence intensity, about 5% of that of the pure europium complex. Possible reasons for the observed low luminescence intensity could be a reaction of the europium nitrate during hydrophobization with TMCS. On the other hand, (B) preparation leads to strong emitting aerogel powders with a luminescence intensity comparable to that of pure $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ powders, which display a

quantum yield of 35% [15]. Here, the initial powders are porous aerogel granules. The high luminescence intensity is a result of a two – step process of incorporation of the activator ions: physical adsorption followed by a chemical reaction between $\text{Eu}(\text{NO}_3)_3$ and 1,10 – phenanthroline taking place in the porous network of aerogels. The chemistry of the sol and gel, represented by the ration $n_{\text{Eu}}/n_{\text{Si}}$ in the gels and before soaking are very close. Such an observation gives a possible explanation for the incorporation mechanism of the europium activator in the aerogel matrix: first, the soaking solution enters the porous matrix of aerogels, followed by solvent release during drying and a chemical reaction between $\text{Eu}(\text{NO}_3)_3$ and 1,10 – phenanthroline.

The relative intensity I_{0-2} of the color giving $\text{Eu}(\text{III})$ $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 615 nm, in respect to the overall $^5\text{D}_0 \rightarrow ^7\text{F}_j$ luminescence intensity between 550 nm and 720 nm, is in the range of 75%. The values are close to that of pure $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ and dense silica and zirconia xerogels containing $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ [18]. The intensity ratios $I_{^5\text{D}_0-^7\text{F}_2} / I_{^5\text{D}_0-^7\text{F}_1}$ of the europium functionalized aerogels are in the range of 5.7, lower than the value of pure $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ powders which is about 6.8.

The relative intensity of the forbidden $^5\text{D}_0 - ^7\text{F}_0$ transition at 584 nm is about 1.5% from that of the overall $^5\text{D}_0 - ^7\text{F}_j$ emission intensity. According to [8] the most probable site symmetry of the Eu^{3+} cations in the investigated microcomposites is C_{2v} , while intensity ratios and relative intensities indicate the presence of a structural disorder in the optical centers formed in the porous system of aerogels. The site symmetry C_{2v} also has been confirmed using second derivatives of the luminescence spectra of solid $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ and $\text{SiO}_2:\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ in the region of the $^5\text{D}_0 - ^7\text{F}_0$ transition [6,8]. Two kinds of low-symmetry Eu^{3+} optical centers exist in the functionalized aerogels, which leads to maxima at 582 nm and 584 nm in the region of the $^5\text{D}_0 - ^7\text{F}_0$ transition, visible in the second derivative emission spectra.

There are small, but essential differences between the emission color of functionalized aerogels, xerogels and pure solid europium(III) phenanthroline nitrate, probably coming from different sites in the porous architecture of aerogels. In [19] small deviations of X-Y coordinates in europium doped inorganic oxides with a different doping concentration have been presented. Samples, functionalized with 1,10 –phenanthroline only emits in the blue spectral region. It is visible that a mixture of different activated aerogel like powders could be a source of white light under UV – excitation [20, 21]. A possibility for the explanation of the intense blue

luminescence coming from samples SiO₂: 1,10 – phenanthroline is the surface formation of Si(IV)– 1,10-phenanthroline complexes, as discussed in [22].

There are significant differences in the excitation spectra of the pure [Eu(phen)₂](NO₃)₃ complexes and the functionalized aerogel composites. The main energy transfer channel of aerogel is about 330 - 350 nm, while the pure complex is effectively excited in a broad spectral region between 250 nm and 350 nm. The excitation spectrum of the blue emitting aerogel containing 1,10 – phenanthroline has a maximum at about 370 nm, while the spectra of samples doped with [Eu(phen)₂](NO₃)₃ have a maximum at 350 nm. The relative reflectance intensities published in this study differ from that of solid 1,10 – phenanthroline powders indicate a [Eu(phen)₂](NO₃)₃ complex formation during functionalization. The diffuse reflectance spectra (fig 3) are in agreement with the excitation spectra of functionalized aerogel composites (fig 6).

Conclusions

Hydrophobic silica aerogels are a suitable matrix for the preparation of efficient emitting hybrid composites. An effective, simple low temperature procedure for functionalization of silica aerogel granules with [Eu(phen)₂](NO₃)₃ has been demonstrated. The functionalized aerogel composites display a bright red Eu³⁺ f-f luminescence suitable for UV – light sensor applications or light production. The Eu³⁺ ion has a site symmetry C_{2v} in the hybrid composites, excitation spectra prove the presence of an effective energy transfer 1,10 – phenanthroline → Eu³⁺. Samples, functionalized only with 1,10 – phenanthroline emits in the blue spectral region due to surface formation of Si(IV)– 1,10-phenanthroline complexes. Optical spectra and color coordinates analysis of the functionalized composites display the formation of different optical centers during functionalization.

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