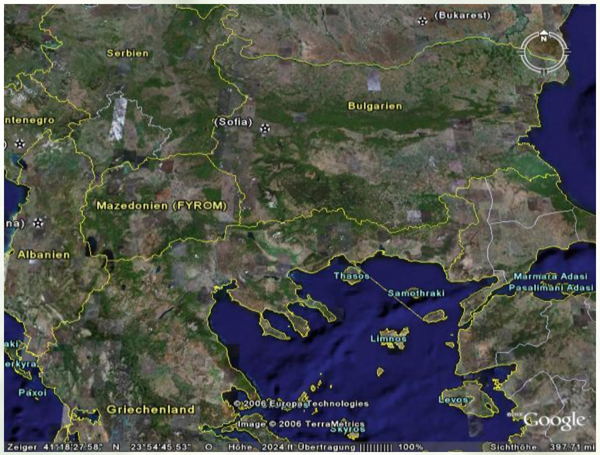
Preparation and optical properties of sol-gel matrices doped with lanthanides



Sofia, Bulgaria

Sofia University "St. Kliment Ohridski"

1. ***Sol-gel chemistry: conditions, doping, examples***
2. ***Inorganic materials doped with rare earth ions***
3. ***Hybrid optical materials: preparation and properties***

Functional Optical Materials

www.uni-sofia.bg/index.php/eng/faculties/faculty_of_chemistry_and_pharmacy/structures/departments/physical_chemistry/functional_optical_materials

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Research interests

- Optical materials
- Hybrid materials
- Sol-gel chemistry: Zirconia, Silica doped with Eu, Tb, Ho, Sm

Teaching

- Physical Chemistry (I, II)
- Ceramic materials, Luminescent materials

Equipment

- Electrochemical workstation CH Instrument
- Laboratory equipment – sol-gel chemistry, solid state
- Laboratory furnaces (1200 °C)
- UV/Vis Perkin Elmer transmission / reflectance spectrophotometer

Characterization methods

- SEM, AFM
- UV/Vis, Luminescence
- XRD
- DSC / TG

Current Projects

- **TK 02/26 – 2009** Preparation, structure and optical properties of new hybrid materials, Bulgarian National Science Fund; Coordinator: S. Gutzov
- **FP7 EFFiHEAT** The overall objective of the proposed project is to develop and validate cost - efficient based on Stirling engine of novel design geothermal heat pump technology with 25% higher COP10 comparing to technologies in operation. WP4 /SOFIA/ regenerator materials, aerogels

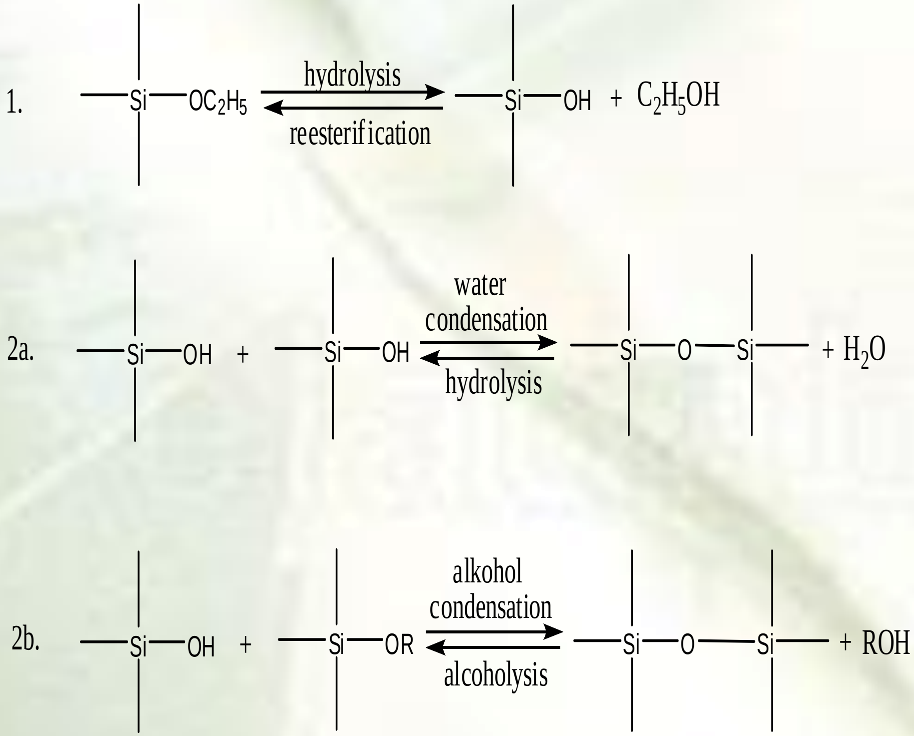
Sol – gel chemistry

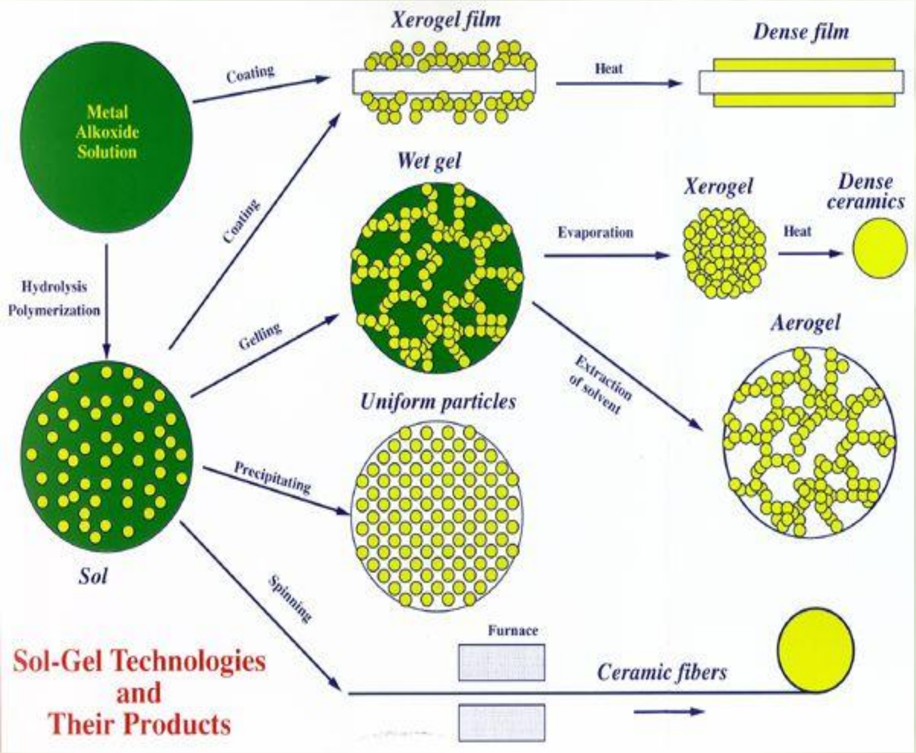
Sol-gel chemistry offers a possibility for the ambient preparation of optical materials like xerogels or layers doped with rare earth ions. In the same way a wide range of useful ceramic materials like Al_2O_3, ZrO_2 , SnO_2, SiO_2, Al_2O_3 can be easily prepared.

Gels are solids confining a solvent in a three-dimensional network. The solvent may be enclosed as quasi-liquid in a pore system. In this state, the gels are called hydrogels (water as solvent) or alcogels (alcohol as solvent) etc. If the network has nano-dimensions or is index-matched, the gel looks transparent. If the solvent is removed without destruction of the network, the resulting body is called a xerogel ("dry gel"). If the pores then are filled simply with air, it is an aerogel.

The advantages of sol-gel technologies are low synthesis temperatures, possibilities for preparation of rare chemical compositions, formation of transparent materials or aerogels depending on the drying conditions. Sol-gel technologies, however, need long duration times of each preparation step as well as individual preparation procedures for each material.

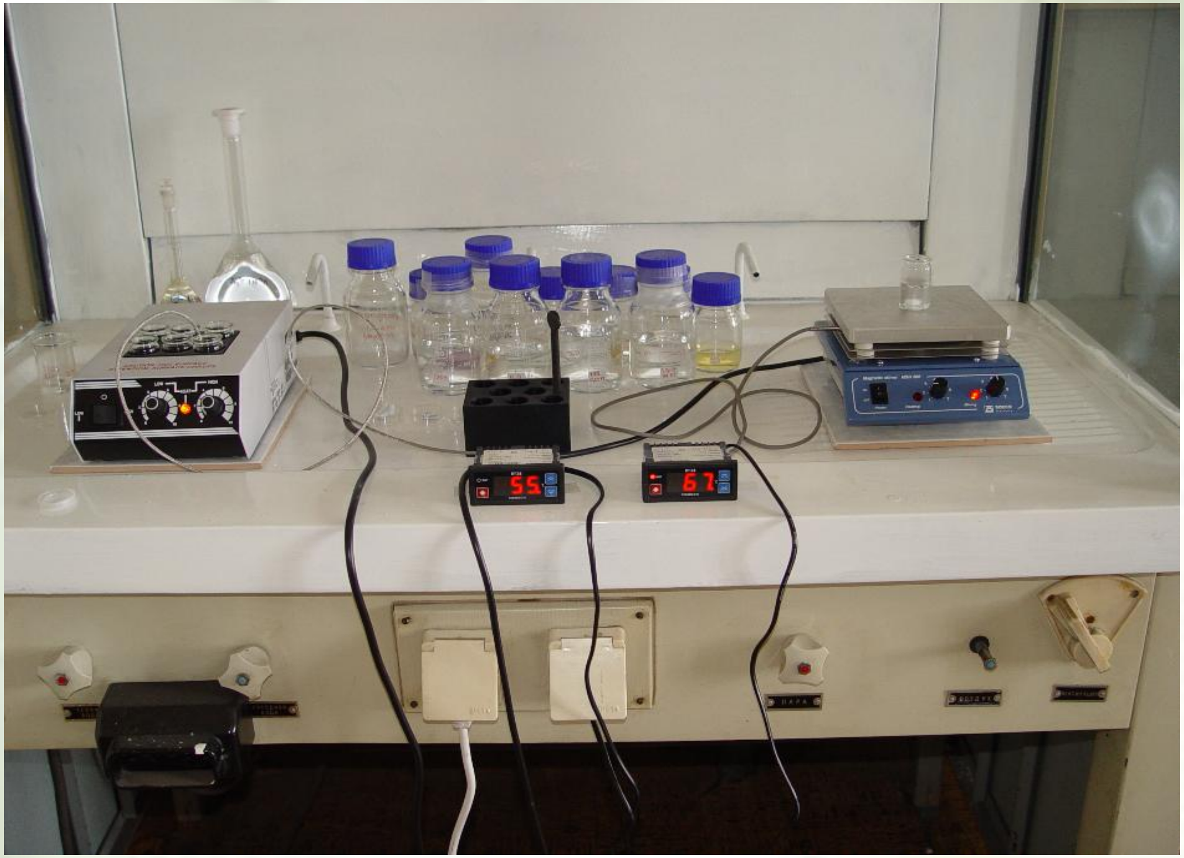
$$Si(OEt)_4 + 4H_2O \rightarrow Si(OH)_4 sol + EtOH \rightarrow SiO_2.nH_2O gel$$





C. J. Brinker, G. W. Scherer, Sol-Gel Science, Academic Press, 1990.

Preparation of rare earth ion doped materials using sol-gel chemistry



$T_{hydrolisis}$ °C

pH

n_{Si} / n_{H2O}

n_{Si} / n_{EtOH}

n_{Si} / n_{H2O}

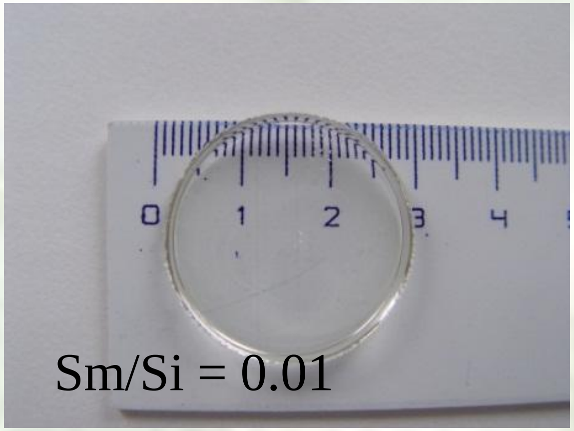
V_{drying}, T_{drying} °C

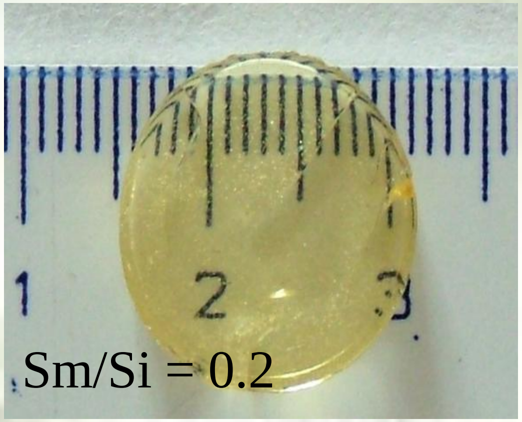
$\mathbf{n_{Ln} / n_{Si}}$

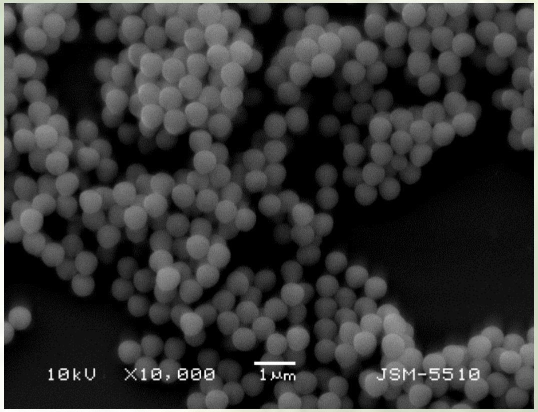
Characterization methods

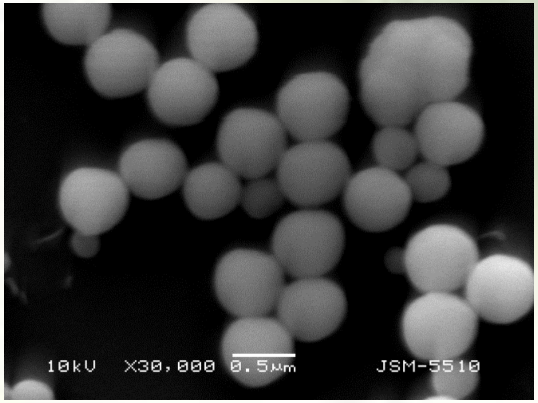
UV/Vis, luminescence, SEM, AFM, IR, XRD, DSC / TG

Inorganic SiO_2 materials doped with Tb, Sm, Ho. Control of transparency: nanophases, nanopores. Sizes depend on sol-gel conditions: n_{Si} / n_{H2O}, n_{NH3} / n_{Si}, pH, drying





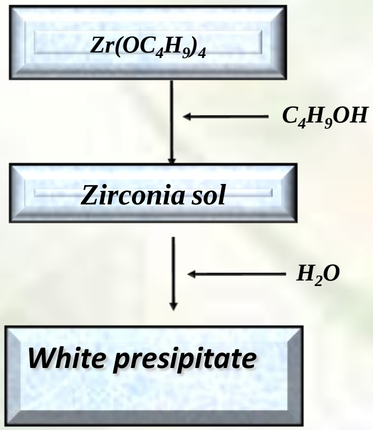




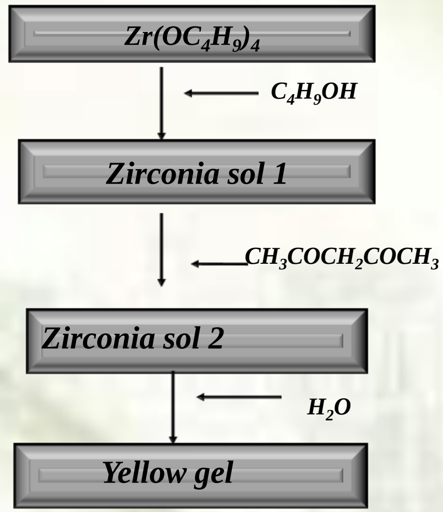
Dr Gulay Ahmed, PhD (2009), U Sofia

Preparation of transparent zirconia sol-gel materials using protection agents: acethylacetone and acetic acid

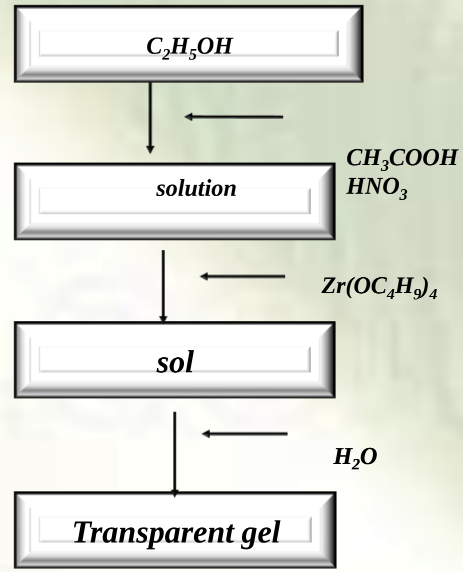
Without protection

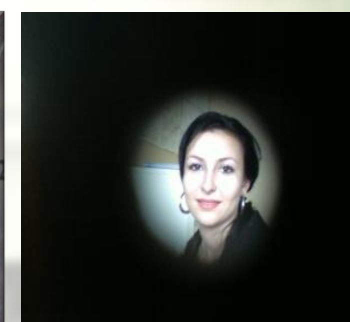


Acethylacetone (AcAc)



Acetic acid (AA)





Dr Nina Danchova, PhD (2012) U Sofia

Silica materials for thermal superinsulation with a porous nanostructure (FP7 Project EFFiHEAT)

Chemical Prepared Aerogel Granules (SOFIA)

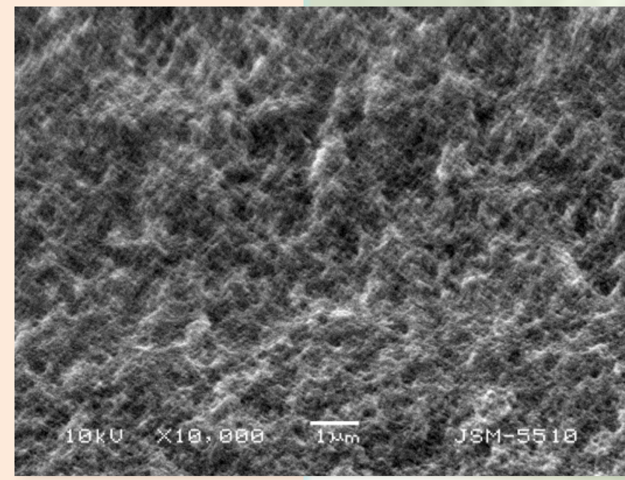
- Tetraethoxysilane (TEOS)
- C_2H_5OH
- H_2O
- HCl
- NH_4OH

1.5h hydrolysis time

λ<0.1 W/m·K
ρ = 0.1 g/cm^3
Cp = 700 - 950 J/kg·K
α =4÷6·10^{-6} K^{-1}
granules

Gelation — 24h

Solvent exchange in ethanol — 5 days



Surface **modification with** TMCS (trimethylclorsilane) solution in hexane → Washing with acetone → Drying of gels at subcritical condition: 0.5 atm T= 70° C — 24 h

Optical properties of lanthanide (Ln) ions. Spectra – structure correlation

- Weak, forbidden electric dipole (ED) or magnetic dipole (MD) **f-f** transitions ($^{2S+1}L_J$) in the UV/Vis and NIR spectral region
- MD transitions $\Delta J=1$: $I_{MD}>I_{ED}$ and Ln occupies a center of symmetry (CS).
- ED transitions $I_{ED}>I_{MD}$, $\Delta J=2, 4, 6$. $f_{ED}>f_{MD}$, ED transitions are responsible for luminescence properties of rare earth ions.
- $\Delta J=2$ ED hypersenstive transitions, very sensitive for structural changes, $^5D_0$-$^7F_2$ Eu^{3+} . Absorption / emission peak number is related to site symmetry.

Optical spectra measurements of doped sol-gel materials

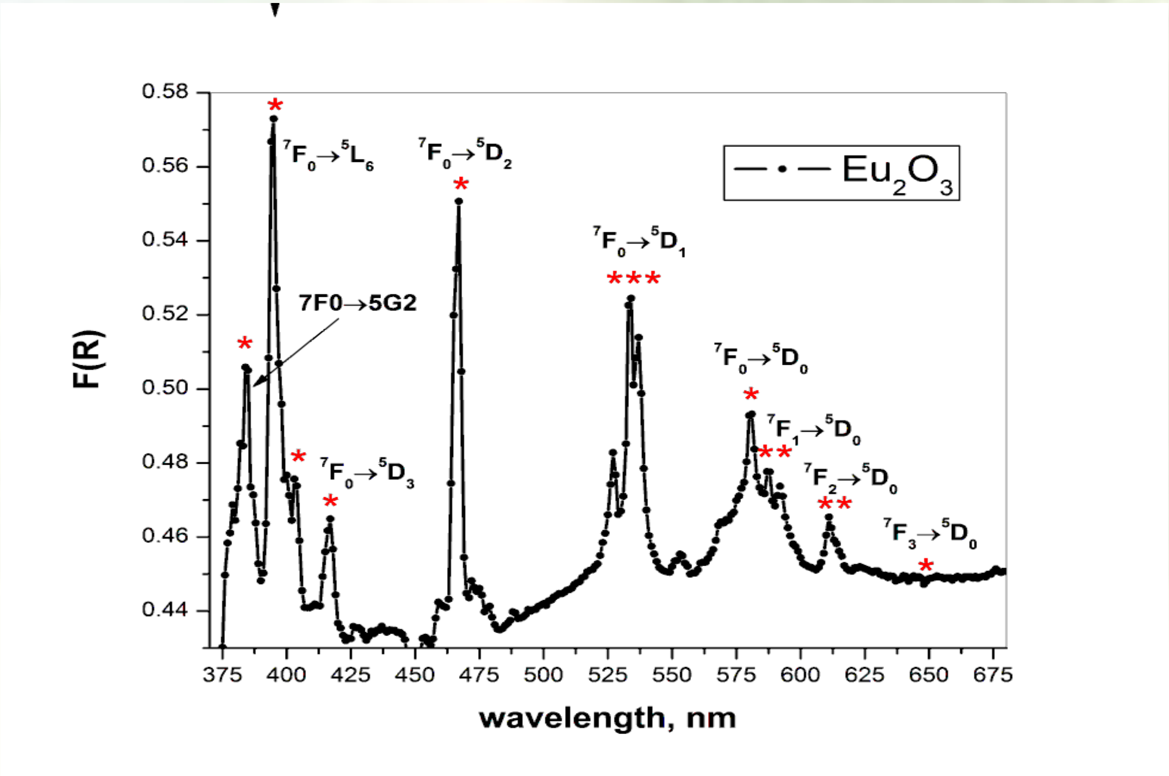
Transmission measurements

$$f = 4.32 \cdot 10^{-9} \cdot \frac{A_{int}(\tilde{v})}{c \cdot d}$$

Diffuse reflectance measurements:
Labsphere PSA-PE-20 200 – 900 nm

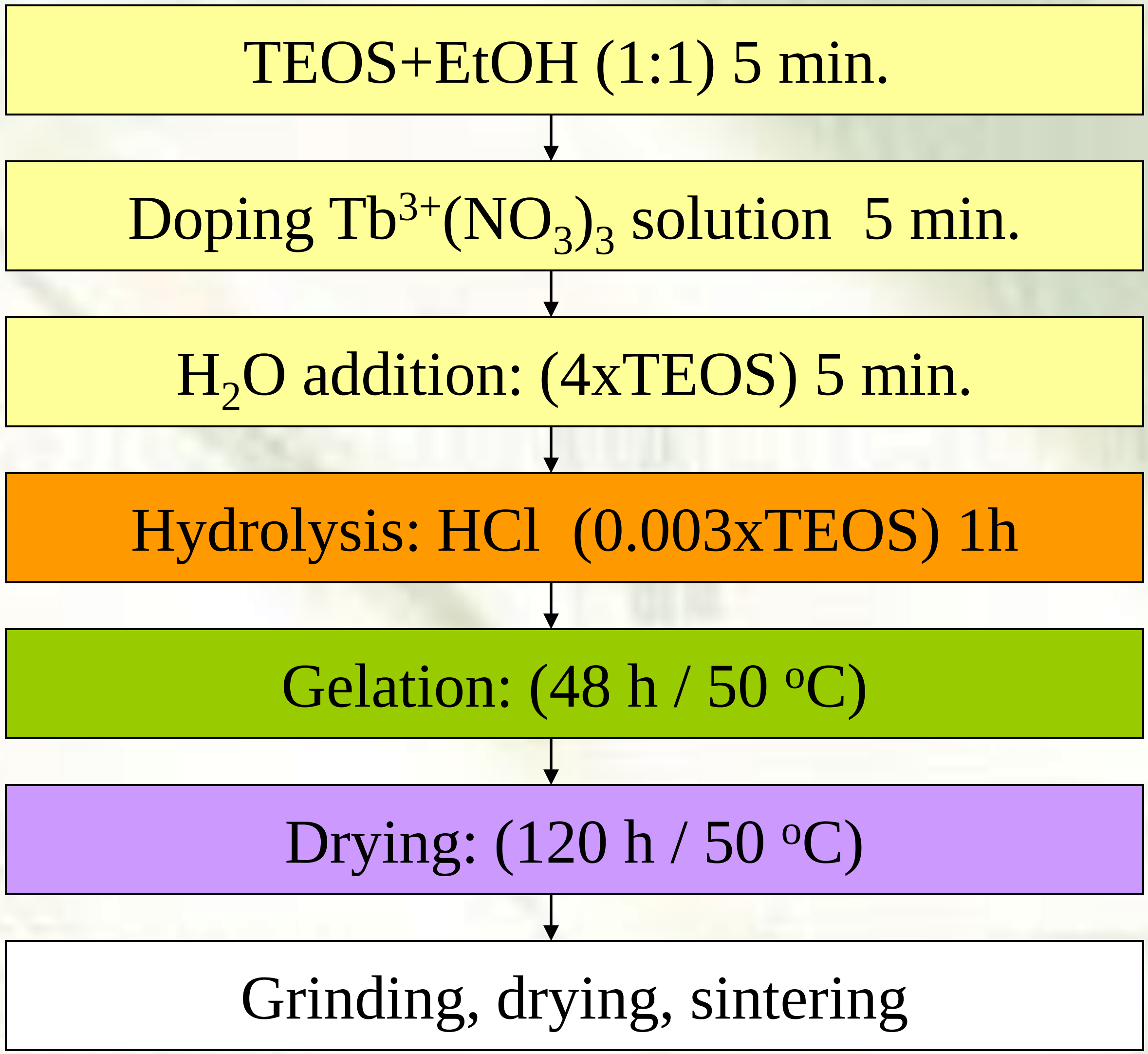
$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R}$$

Eu^{3+} optical transitions: spectra-structure correlation. Site symmetry determination from optical measurements

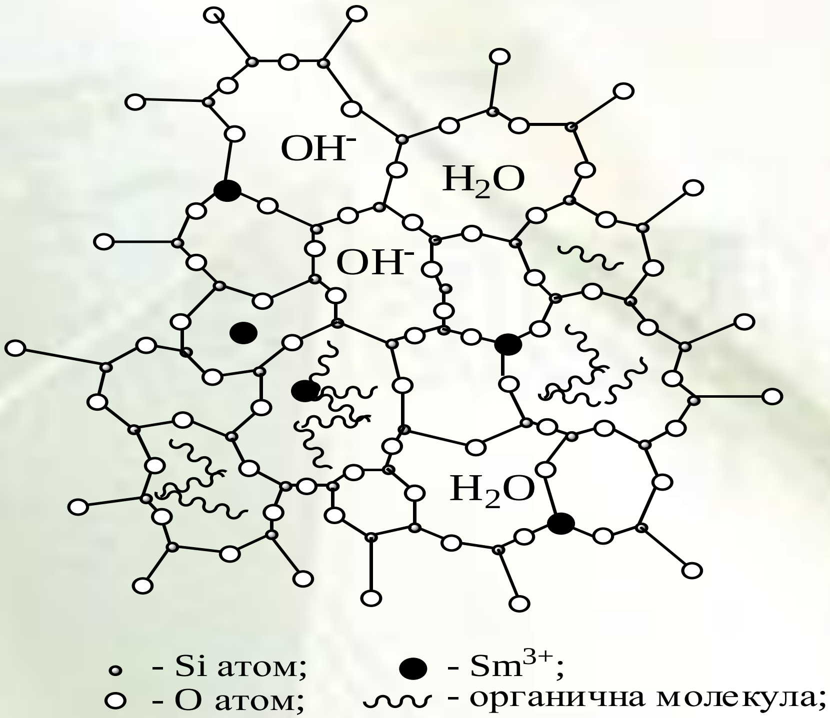


G. Blasse (1968): Intensity ratio $I_{5D0-7F2} / I_{5D0-7F1}$ luminescence spectra
J. Peterson et al (1994): Analysis of number of luminescence peaks
K. Binnemans et al (1996): Complex analysis of number of absorption peaks

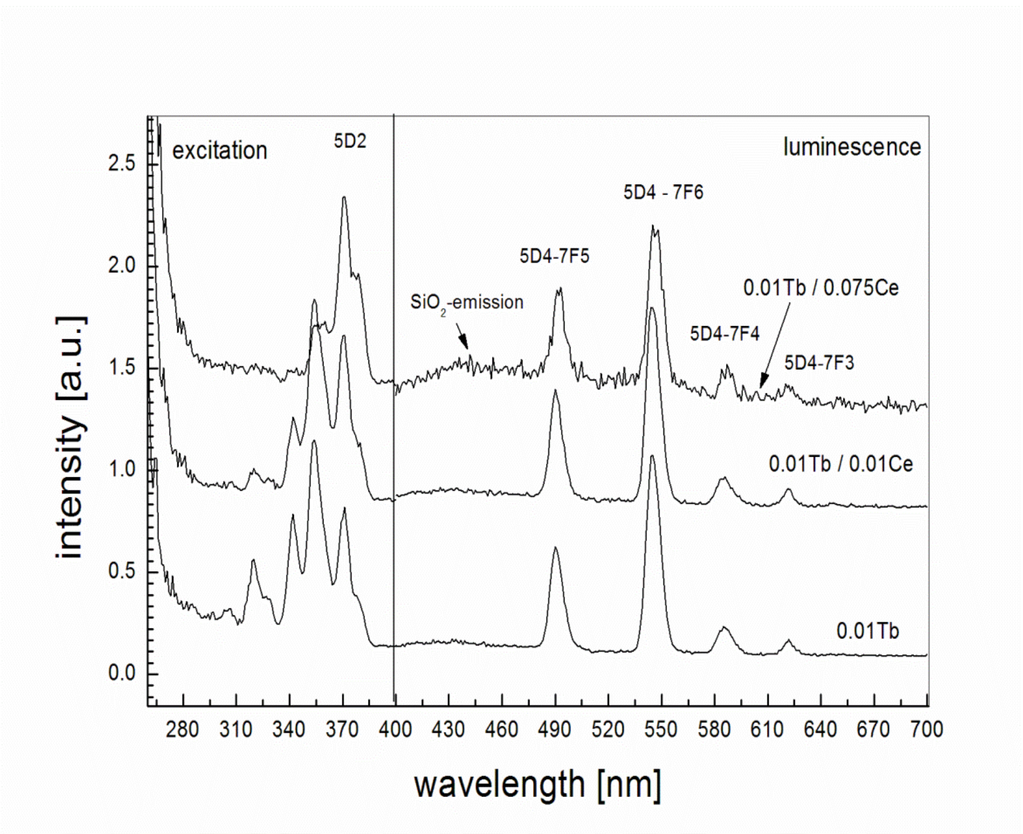
M. Bredol, S. Gutzov, Effect of Germanium codoping on the luminescence of Terbium doped silica xerogels, Opt. Mater 20 (2002) 233-239.



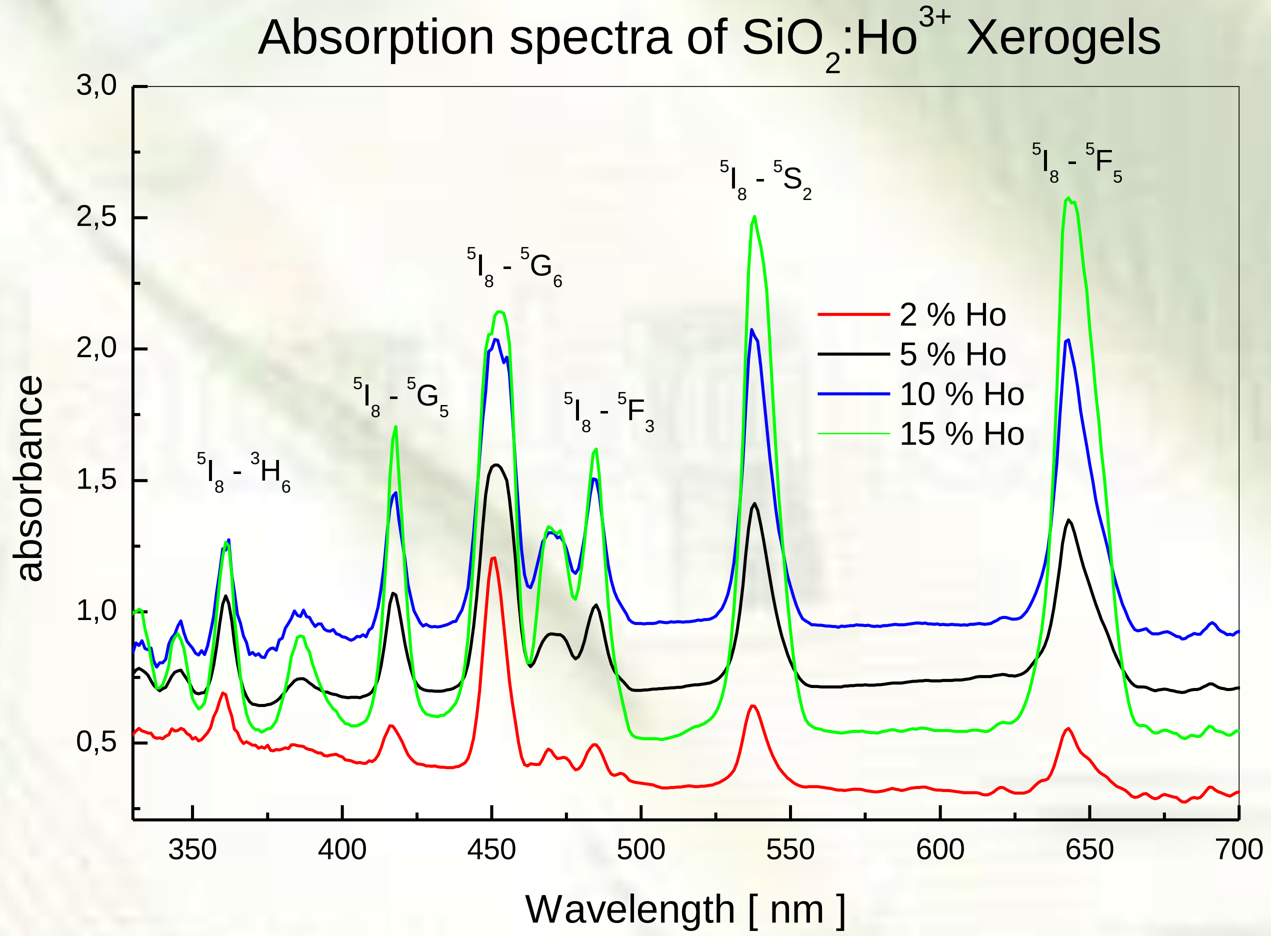
Sol-gel materials are amorphous solids with different doping agents: ions, nano – or microphases, organic molecules, complexes. Optical propreties can be controlled by preparation conditions and dopands.



SiO_2:Tb,Ce

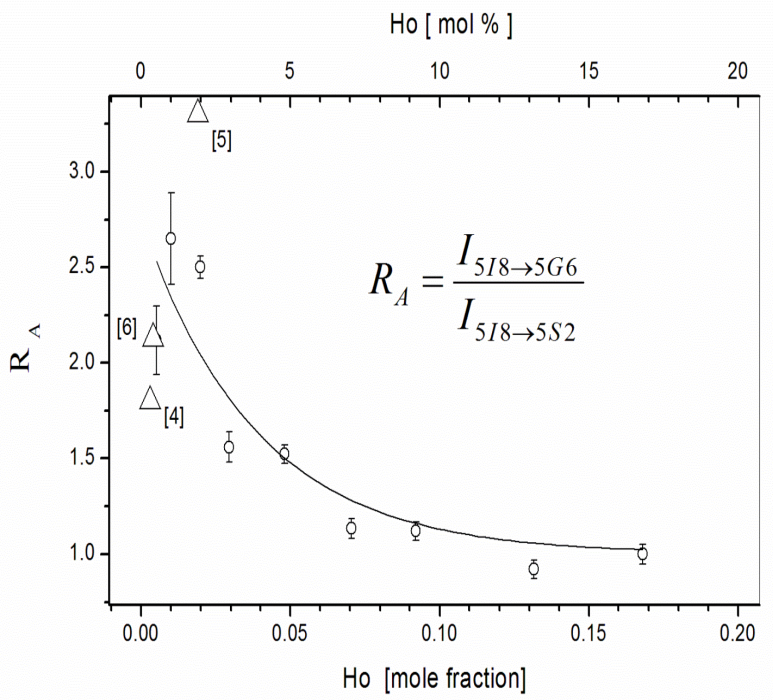


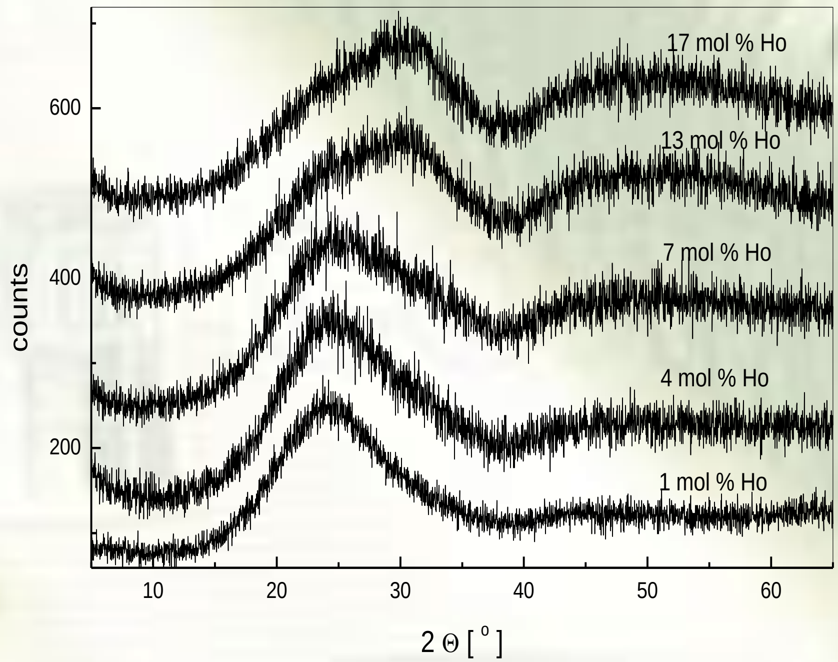
S. Gutzov , C. Berger , M. Bredol , C. L. Lengauer, Preparation and Optical Properties of Holmium Doped Silica Xerogels, J. Mater. Sci. Letters 21 (2002) 1105-1107.



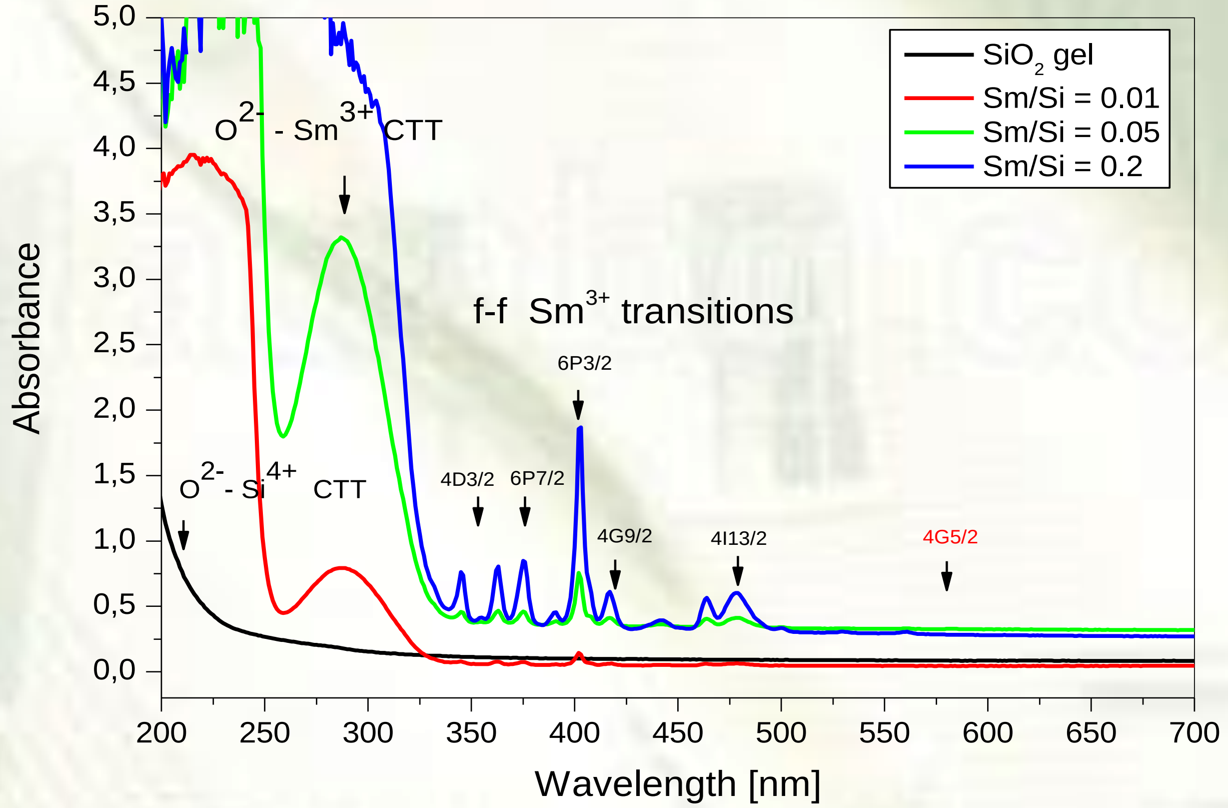
Ho – nitrate nanophase formation in silica at Ho > 10%

$^5I_8 \rightarrow {}^5G_6$ is a hypersensitive electric-dipole transition, the decrease of R_A indicates the formation of centrosymmetric Ho sites with increasing Ho content. Therefore absorption spectra may be used for describing of Ho short-range changes in solids.

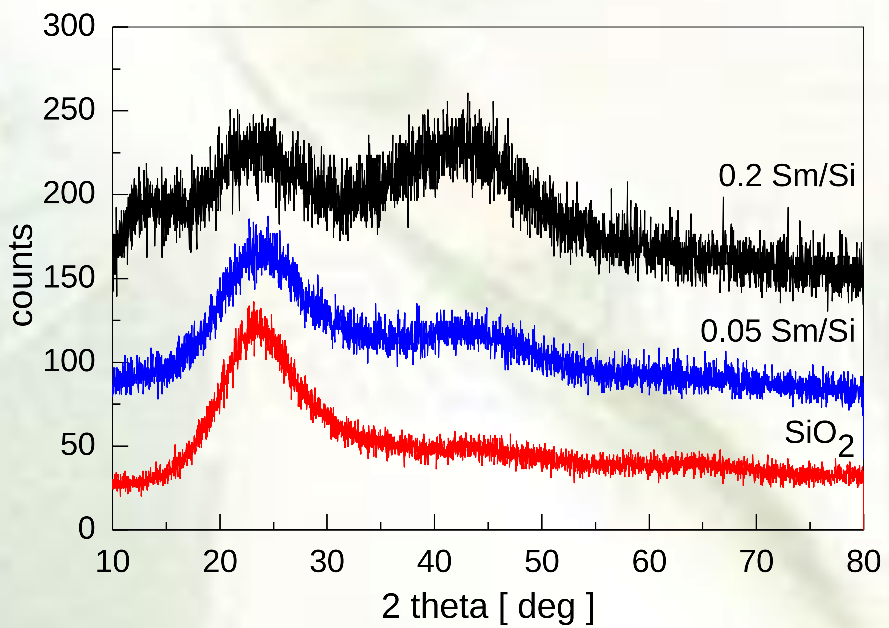


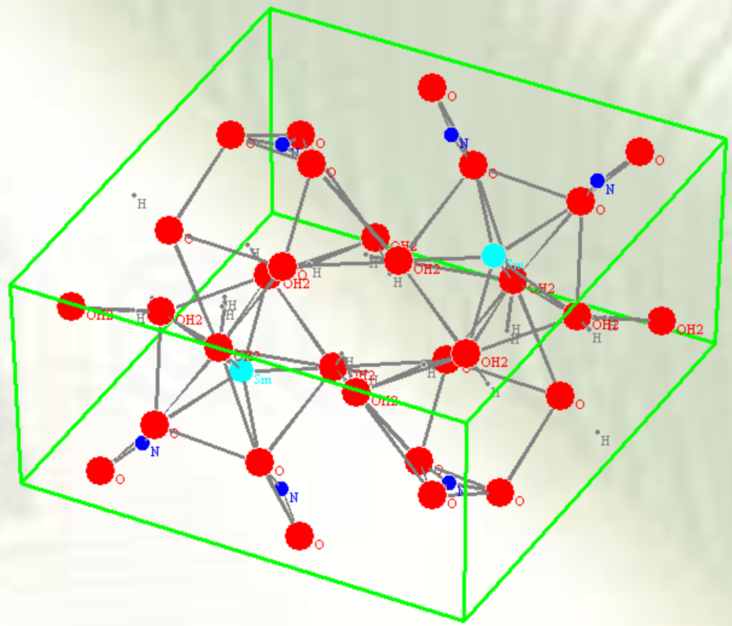


Materials for UV – powder protection coatings: SiO_2:Sm^{3+} Here, the intensity of the 280 nm CTT transition depends on sol-gel preparation scheme. Sample shape is controlled by drying conditions.



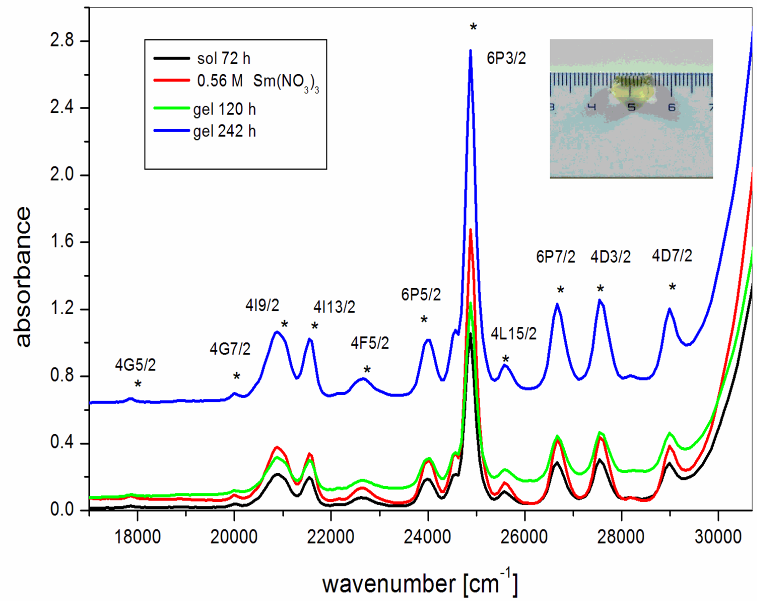
Formation of samarim nitrate nano – microphases at high doping content. Transparent gels became translucent.

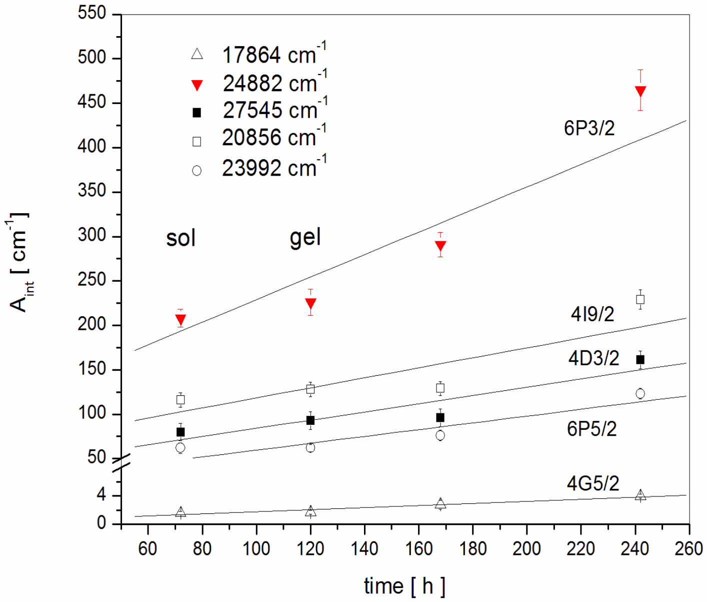




Increasing level of doping leads to formation of a micro-phase of $Sm(H_2O)_6(NO_3)_3$

Absorption spectra vs. time: calculation of the rate of densification of gels from UV/Vis – data.

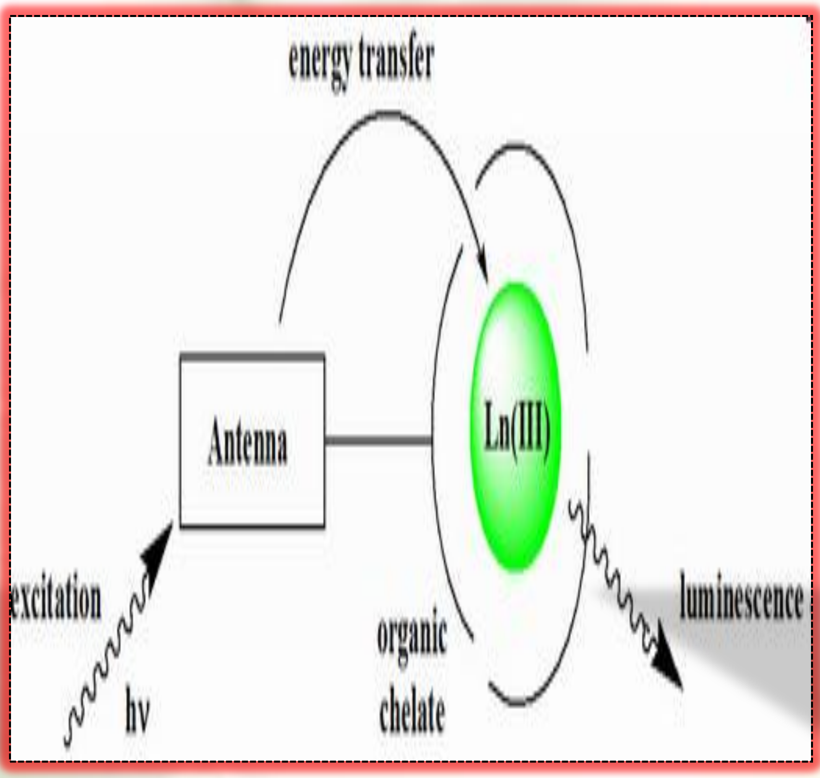


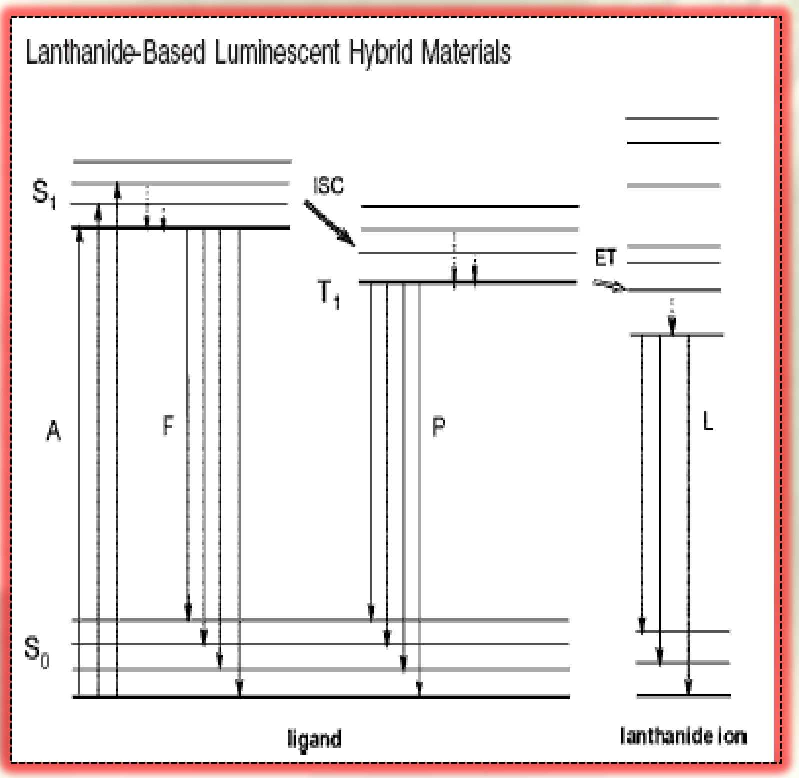


$$A_{\text{int}}(\tilde{\nu}) = \int A(\tilde{\nu})d\tilde{\nu} = \varepsilon_{\text{int}} \cdot C \cdot d \quad \longrightarrow \quad A_{\text{int}}(\tilde{\nu})_t = \varepsilon_{\text{int}} \cdot v \cdot t + A_{\text{int}}(\tilde{\nu})_{t0}$$

$$v \approx 1.77 \pm 0.25 \text{ mmol/cm}^{-2} \cdot h.$$

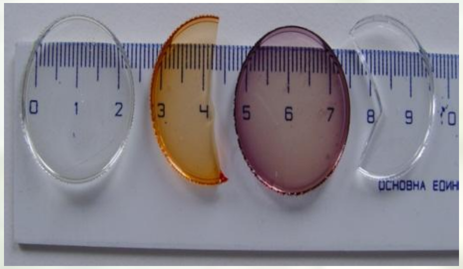
Hybrid optical materials: high quantum efficiency, low rare earth content, energy transfer

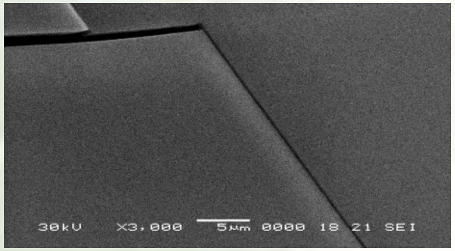




Svetlana V. Eliseeva, Jean-Claude G. Bunzli, Chem. Soc. Rev. 39 (2010) 189–227.
Koen Binnemans, Chem. Rev. 109 (2009) 4283-4374.

Preparation of Sm^{3+} - coumarin doped gels. The sol-gel scheme need a "gelation window" to incorporate organic components without decomposition depending on chemistry of organic components.

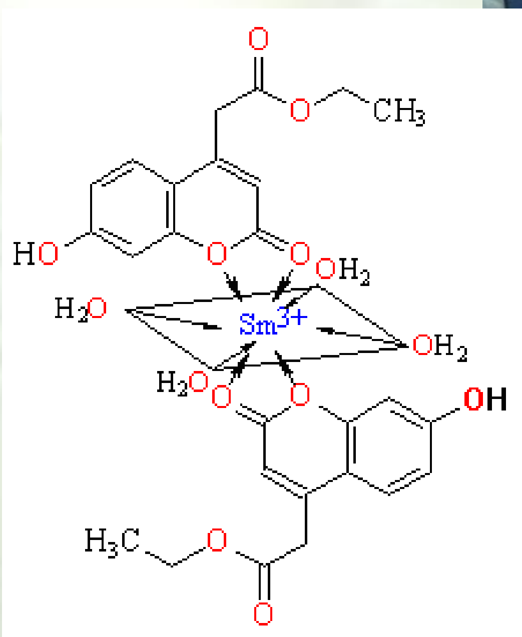


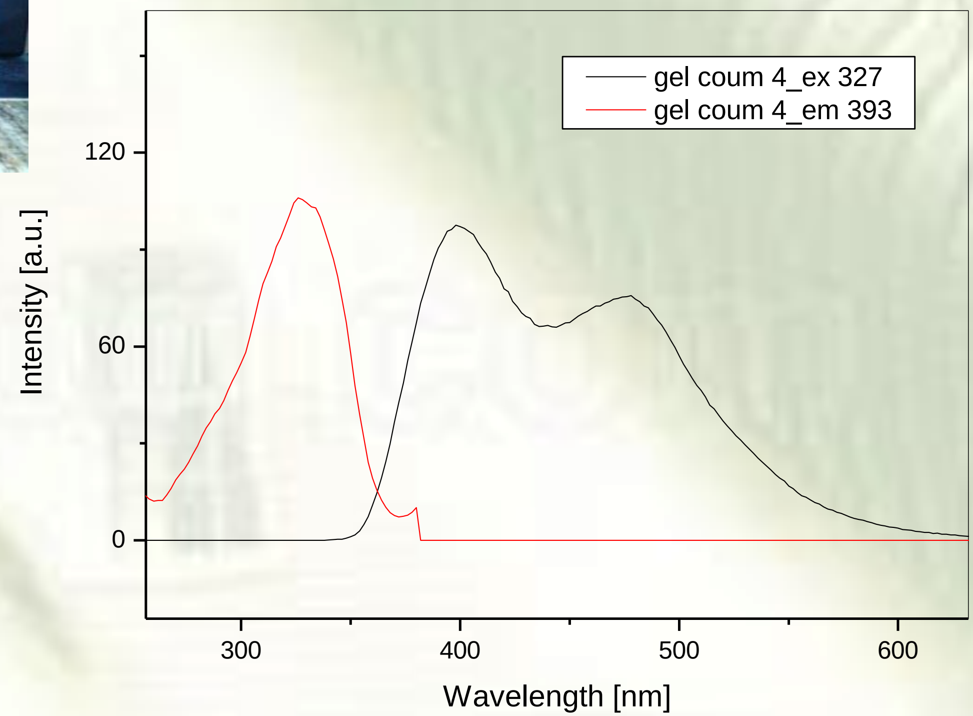


5ml TEOS + 1.3 ml EtOH (1:1) 5 min.	*pH=6.8*
Sm^{3+} doping (0.57 mol/l solution)	
1.58 ml H_2O (4xTEOS) 5 min.	*pH=6.7*
HCl-Hydrolisis: $n_{HCl} = 0.003 \cdot n_{TEOS}$	*pH=2*
NH_3 addition $6/5 * n_{HCl}$	*pH=6.3*
Coumarin Doping: 1 ml 1.10^{-4} M	
Gelation – 30 min	
Drying (168 h / 20 °C)	*ρ_{gel} =1.3 g.cm^{-3}*

G. Ahmed, B. Koleva, S. Gutzov, I. Petkov, *J Incl. Phenom. Macro.* (2007),
DOI: 10.1007/s10847-007-9309-0.

Luminescence properties of hybrid gels: the samarium luminescence is not visible, the complex formed display a strong blue emission, different from that of coumarin.





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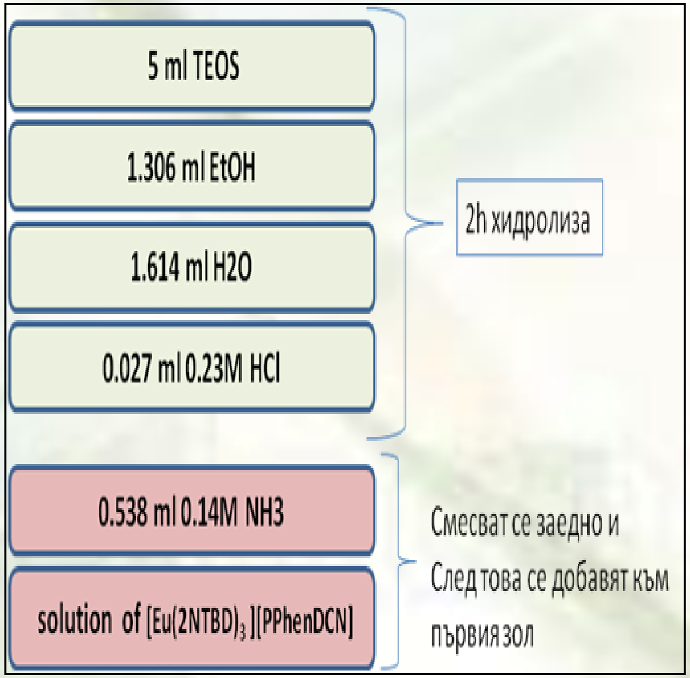
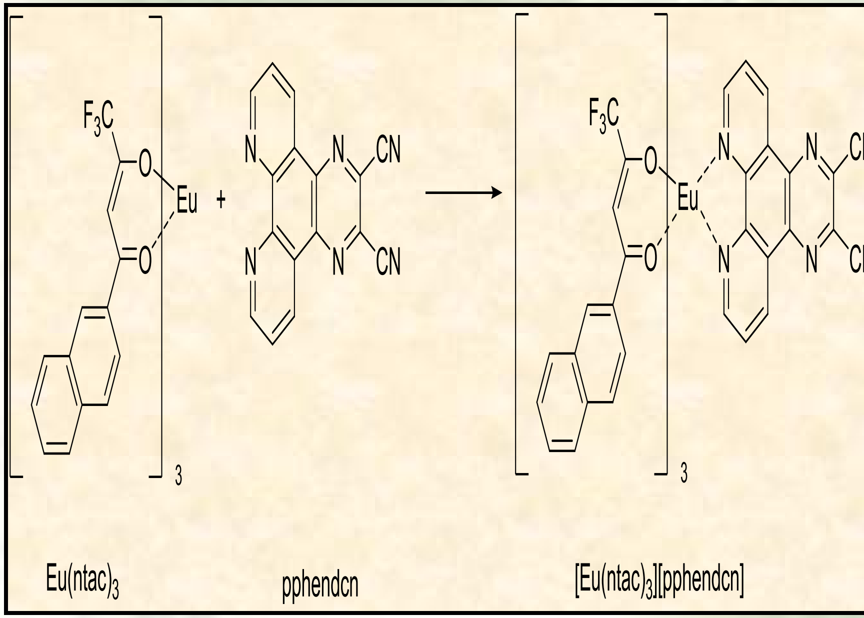
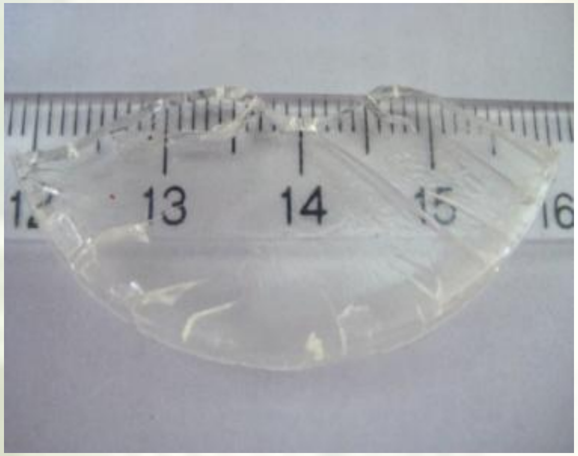
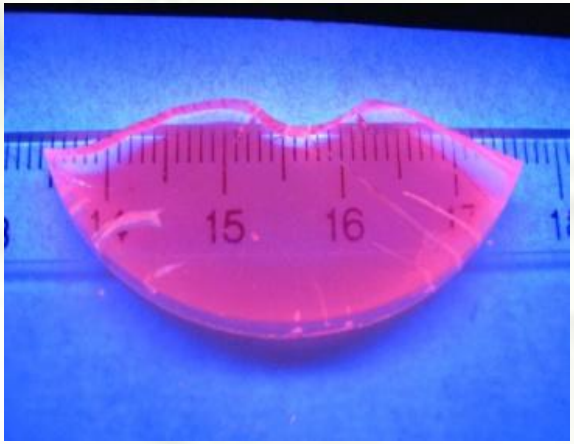
Doping of SiO_2 with [Eu(ntac)$_3$][PPhenDCN]

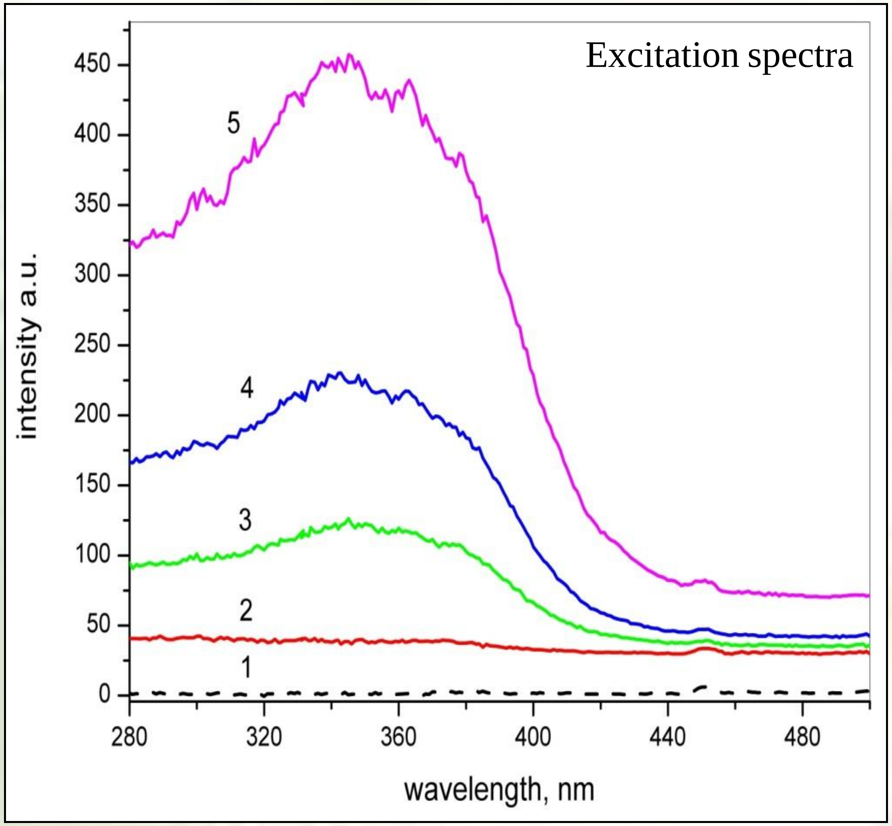


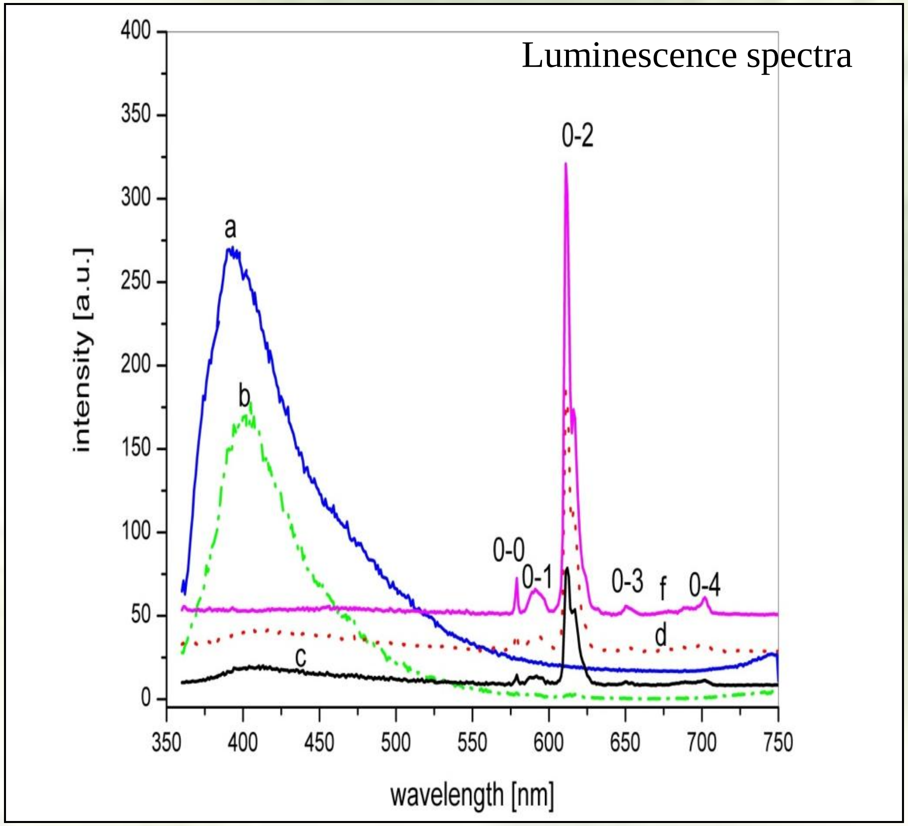






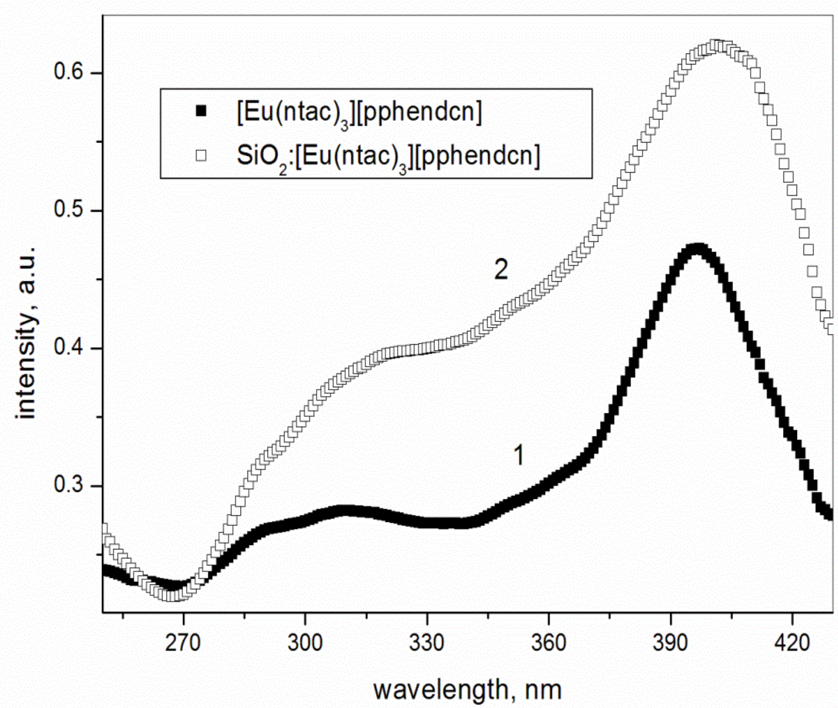
The as prepared sol–gel materials SiO_2:[Eu(ntac)$_3$][pphendcn] display a strong red Eu(III) luminescence even at low doping concentrations due to an effective energy transfer from the organic ligands to the Eu(III) ion. The site symmetry of the Eu(III) ion in the new complex and is C_2 or lower. An additional blue emission at 400 nm appears in the doped gels, most probable coming from decomposition of the Eu(III) complex during time in the silica matrix.



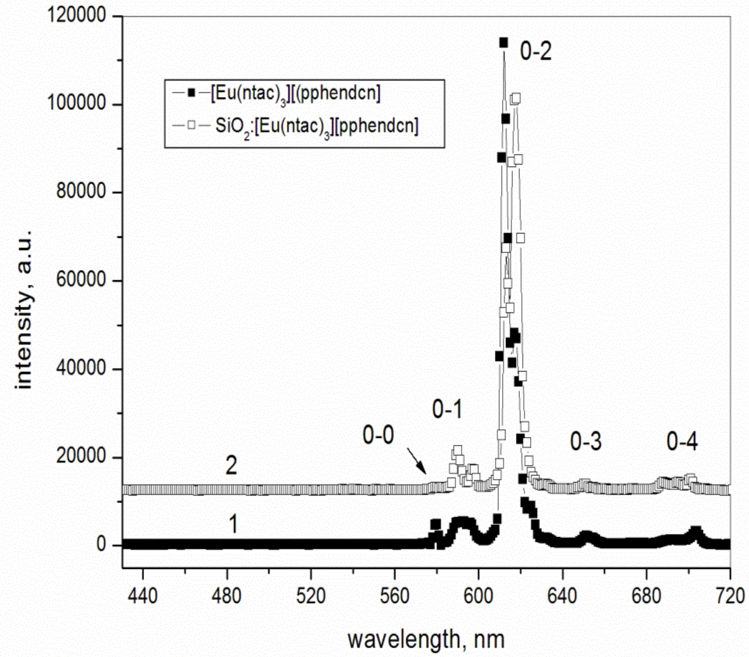


Functionalization of silica sol-gel microparticles with a [Eu(ntac)$_3$][pphendcn] solution: stable in time, red emission without additional blue luminescence.

Excitation spectra

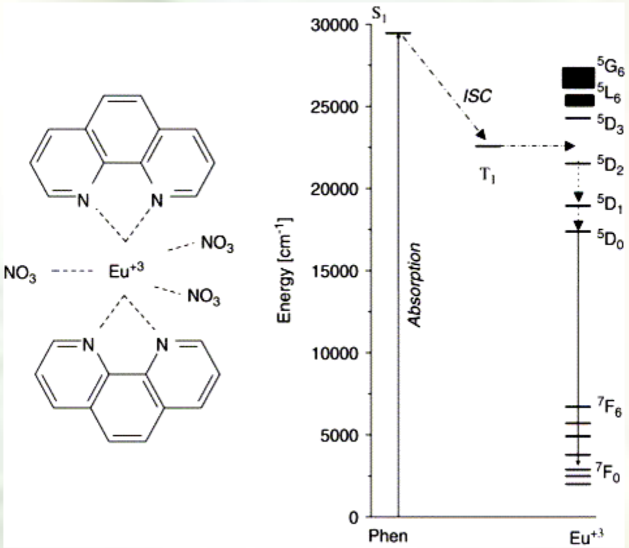


Luminescence spectra



The $^5D_0$-$^7F_0$ transition (0-0) suggests a symmetry / chemical change as a result of surface incorporation of Eu(III) complex

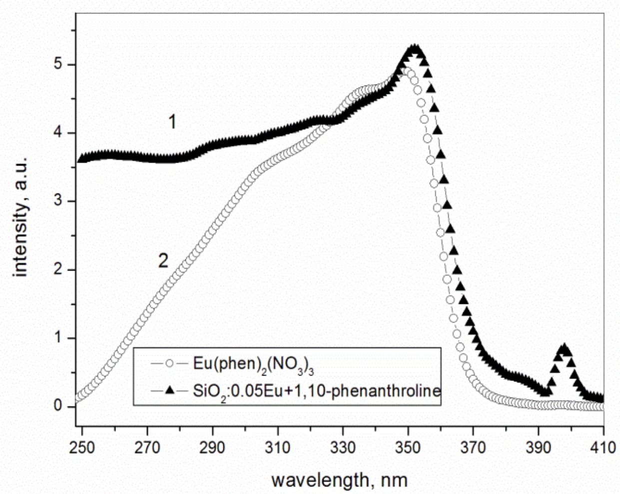
Functionalization of SiO_2:Eu and ZrO_2:Eu micropowders using absorption of a $[Eu(phen)_2](NO_3)_3$ solution



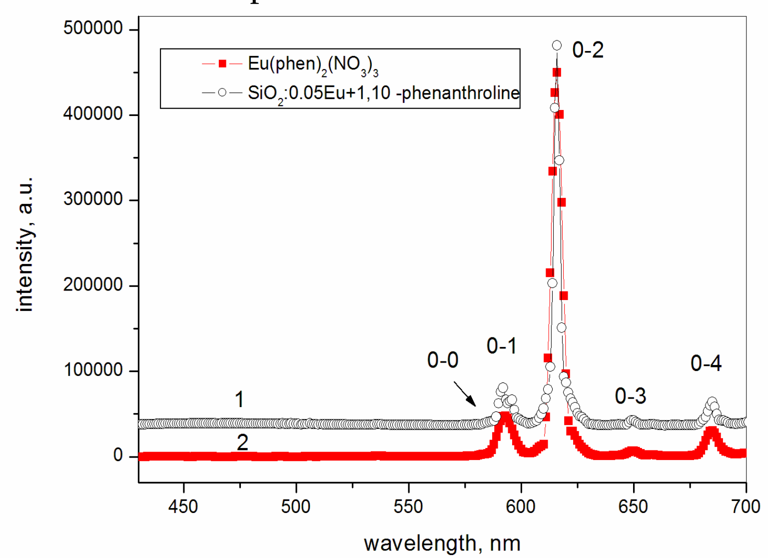
Functionalization of Ln - doped sol-gel oxides

- ***Synthesis of Eu*** $^{3+}$ ***doped transparent sol-gel oxide materials (SiO_2:Eu, ZrO_2:Eu). Homogenization of the gels in a mortar to obtain Eu***$^{3+}$ ***doped microparticles.***
- ***Impregnation of micro particles with ethanol solution of 1.1 M 1,10-phenanthroline in ethanol (48 h at room temperature).***
- ***Washing the micropowders with absolute ethanol to remove the excess amount of ligand.***

Excitation spectra



Luminescence spectra



Quantum yields of functionalized sol-gel materials

Sample / Chemistry	Excitation [nm]	QY [%]	Eu [%]
SiO_2:[Eu(ntac)$_3$][pphendcn]	400	17.4±1.7	0.1±0.001
SiO_2: [Eu(phen)$_2$](NO$_3$)$_3$	352	39.6±3	5.4±0.005
[Eu(ntac)$_3$][pphendcn]	396	10.8±1.8	11.4±0.11
[Eu(phen)$_2$](NO$_3$)$_3$	352	35.4±3.5	12.7±0.13

Excitation wavelengths, quantum yields and europium content of the investigated samples.

Two complexes [Eu(ntac)$_3$][pphendcn] and [Eu(phen)$_2$](NO3)$_3$ and silica samples, obtained by functionalization using surface adsorption of these complexes are described. A successful method for functionalization of europium doped silica with 1,10–phenanthroline is demonstrated. All the samples show a pure, stable in time Eu – luminescence with quantum yield 10 – 40% due to energy transfer from organic ligands. Eu^{3+} spectra structure correlation could be useful for studying processes of functionalization of microparticles.

Acknowledgments

- ✓ ***Dr Nina Danchova, Dr Gulay Ahmed***
- ✓ ***MSc Jaklin Missirian, BSc Stefka Stancheva, Petia Stoyanova***
- ***Bulgarian National Science Fund Project TK 02/26 (2009)***
- ***FP7-REGPOT-2011-1 BeyondEverest***