СУ “Св. Климент Охридски”
Катедра “Физикохимия”

доц д-р Стоян Гуцов

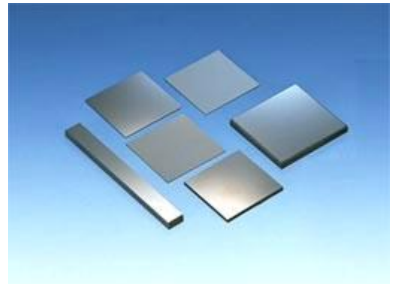
Зол-гелните технологии като метод за получаване на наноматериали

1. ***Керамични материали***
2. ***Зол-гелни технологии***
3. ***Нанопорьозни суперизолациони материали***
4. ***Хибридни оптични материали***
5. ***Материали за UV – филтри и защитни покрития***

www.chem.uni-sofia.bg/depart/pchem/main/SPGroup.htm

GUTZOV

Керамични материали



C

TiC, ZrC

MoC, TaC, MoC

SiC, B_4C

TiB_2

BN, TaN, Si_3N_4

ZrN, TiN, AlN

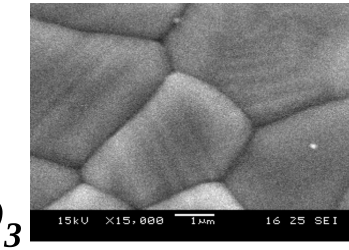
Si_2N_2O

Zr – O – N

Zr – Mg – O – N

Ta – O – N, La – Ta – O – N,

La – Ca – Ta – O - N



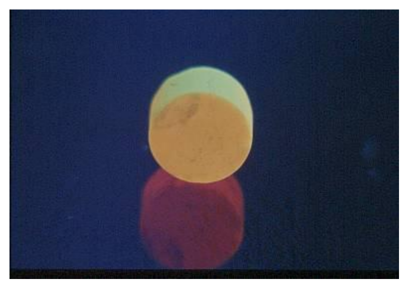
SiO_2

$SiO_2 – Al_2O_3$

$SiO_2 – Al_2O_3$ - MgO

$SiO_2 – Al_2O_3$ - MgO

SiO_2 – MgO



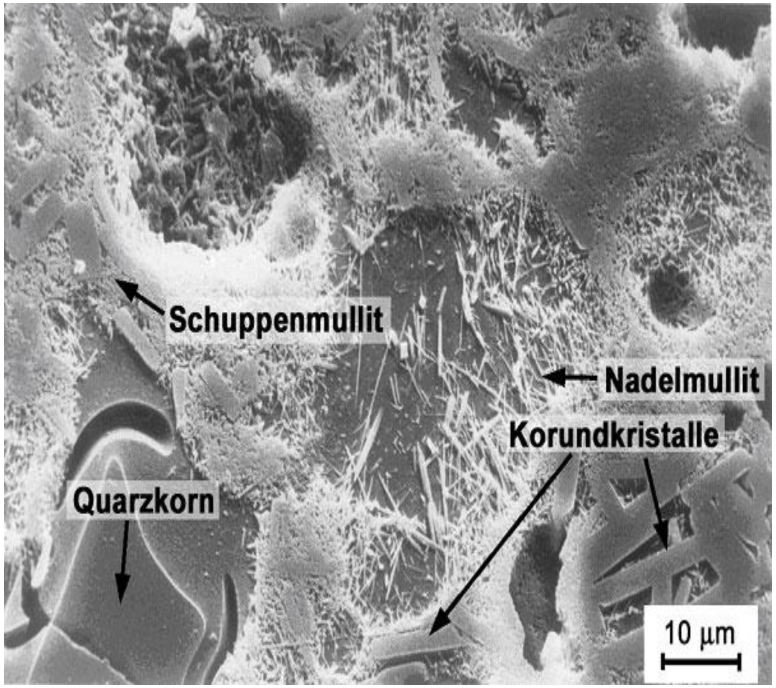
Al_2O_3, MgO, ZrO_2

SnO_2, TiO_2, $BaTiO_3$

Y_2O_3:Eu, $(Y,Gd)_2O_3$:Eu

$GdSiO_5$:Tb

Porzellan in Braunschweig, 2006



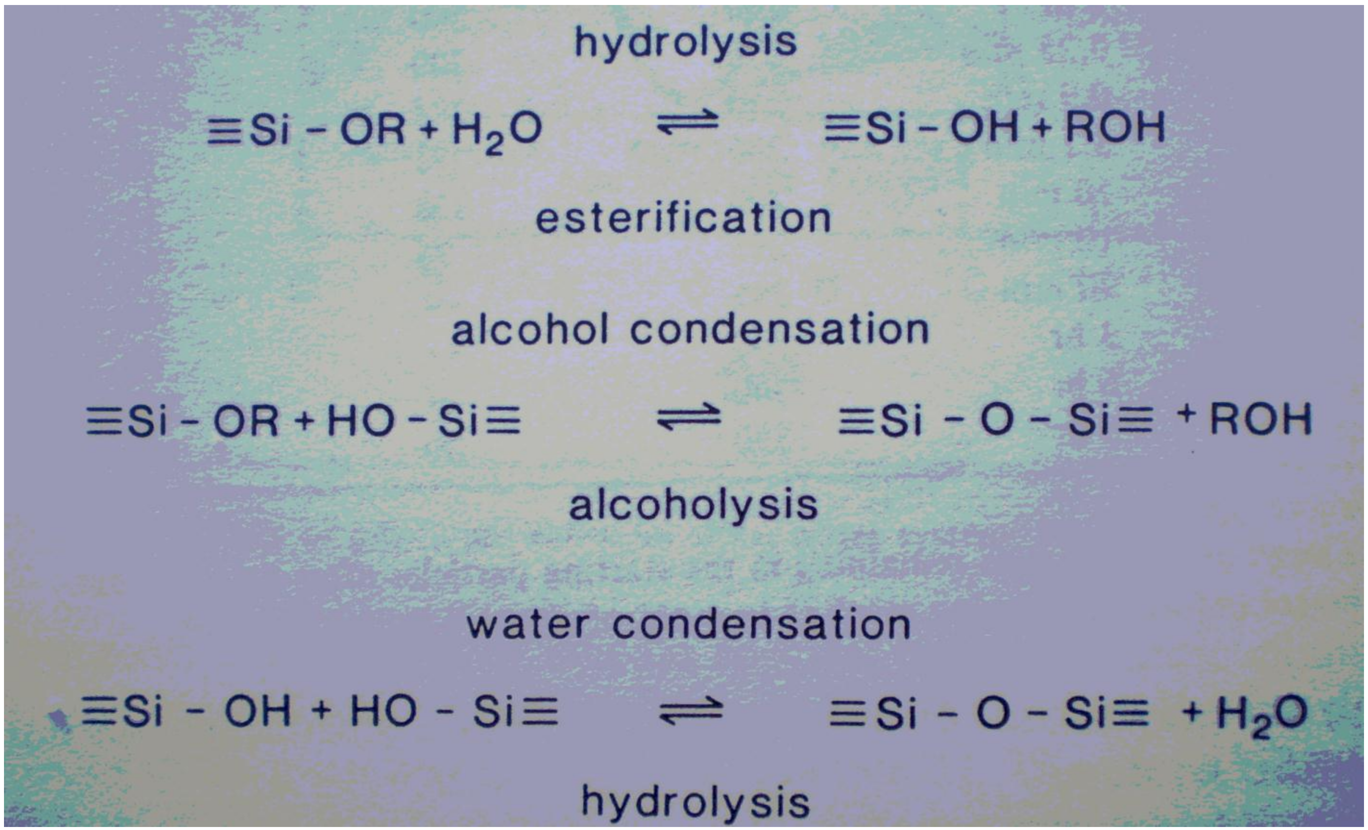
Sol-gel chemistry offers a possibility for the ambient preparation of optical materials like xerogels or layers doped with rare earth ions. In the same way a wide range of useful ceramic materials like Al_2O_3, ZrO_2 , SnO_2, SiO_2, Al_2O_3 can be easily prepared.

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.

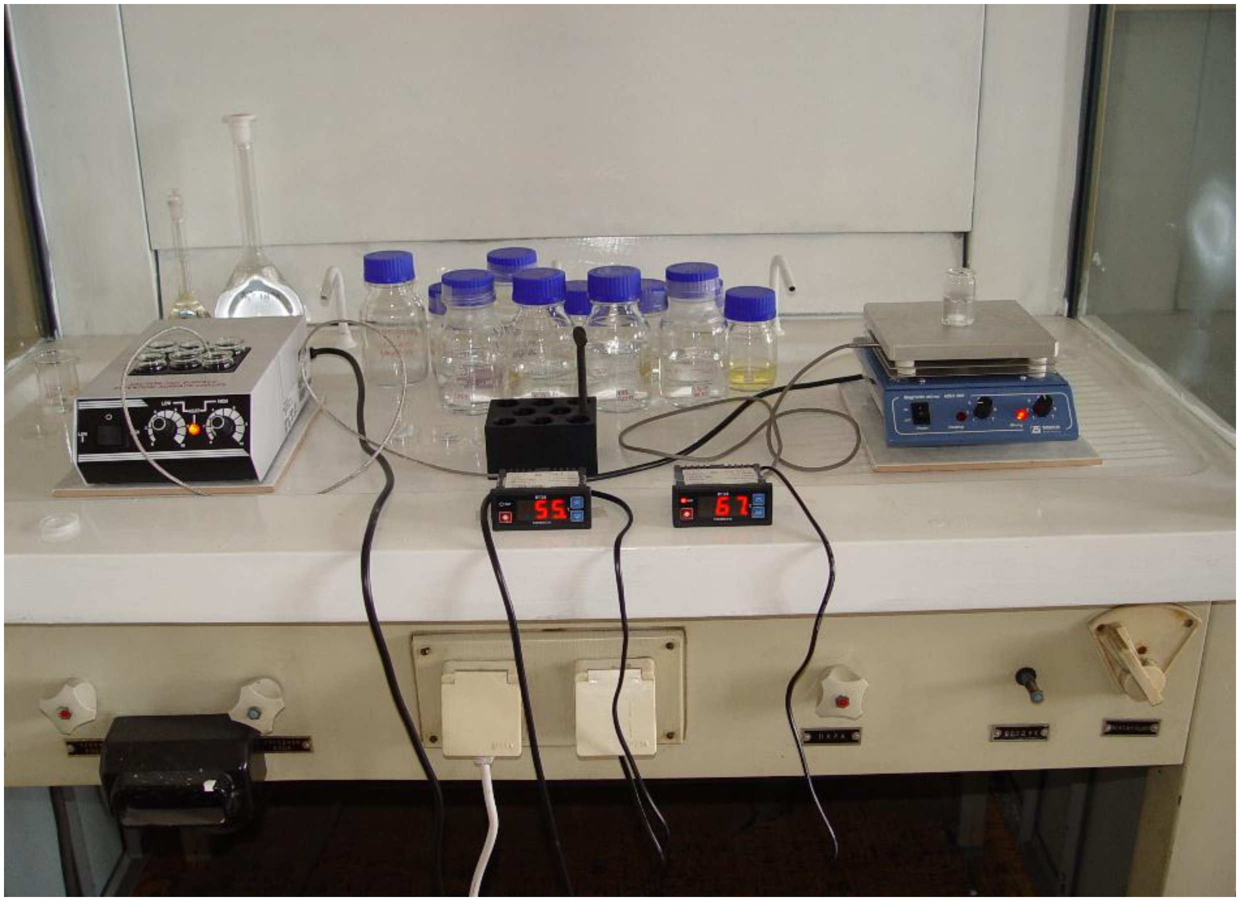
Sol-Gel Science, C. J. Brinker, G. W. Scherer, Academic Press, 1990.

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



Оксидни материали по зол-гел метода:

лаб. 543, кат. Физикохимия (проект ВУХ 08/05)



T_{hyd} ^{o}C

pH

n_{Si} / n_{H2O}

nSi / n_{EtOH}

n_{Si} / n_{H2O}

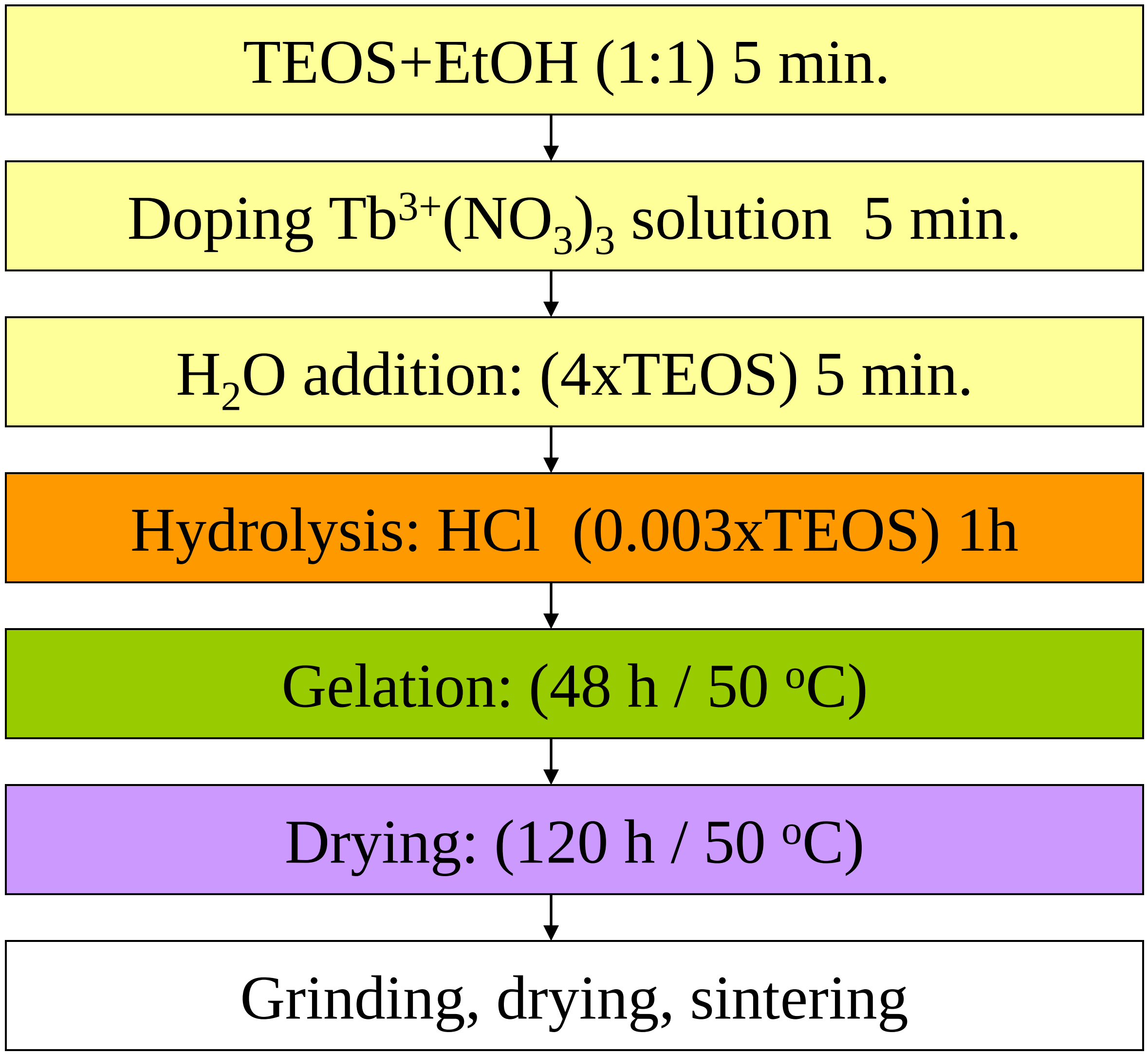
n_{Si} / n_{H+}

n_{Si} / n_{OH-}

v_{drying}

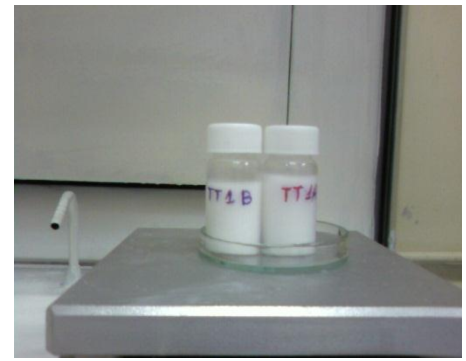
T_{drying} ^{o}C

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



Нанопори и нанофази в зол-гелни материали

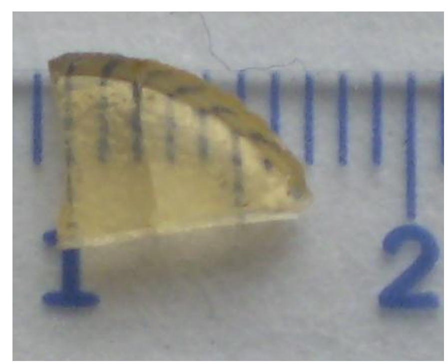
Hydrolisis ***Gelation*** ***Ceramic method***



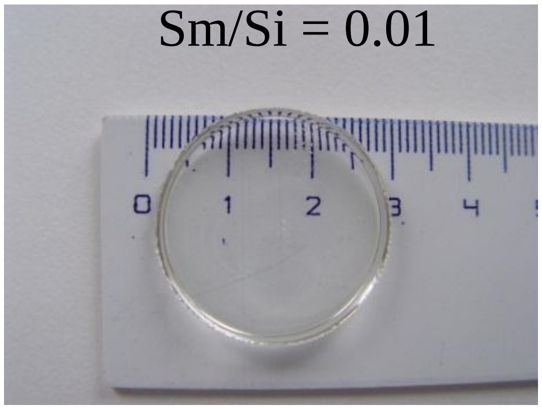
TEOS + H_2O + 0.5 M $Al(NO_3)_3$ ***SiO_2+ 0.5 M $Al(NO_3)_3$***

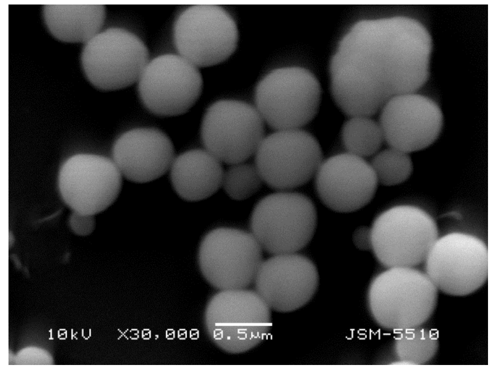
Aging & index matching of doped gels (0.05-0.5 Sm/Si)

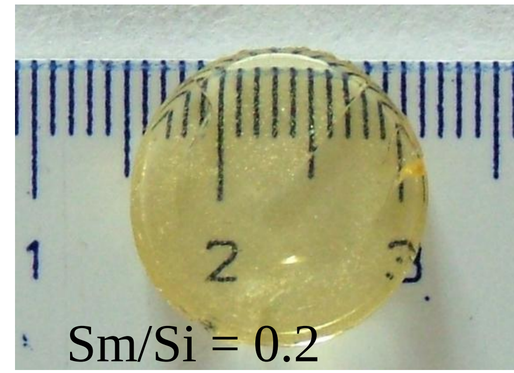
+ H_2O =

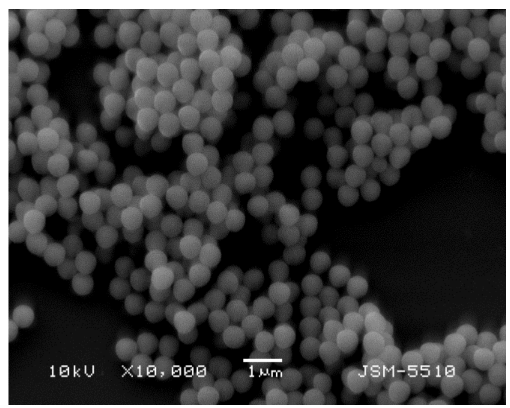


Неорганични SiO2 материали с оптично активни компоненти: Tb, Sm, Ho. Контрол на прозрачността чрез получаване на микро- и нанофази на дотиращия оксид. Контрол на размерността чрез катализатори.



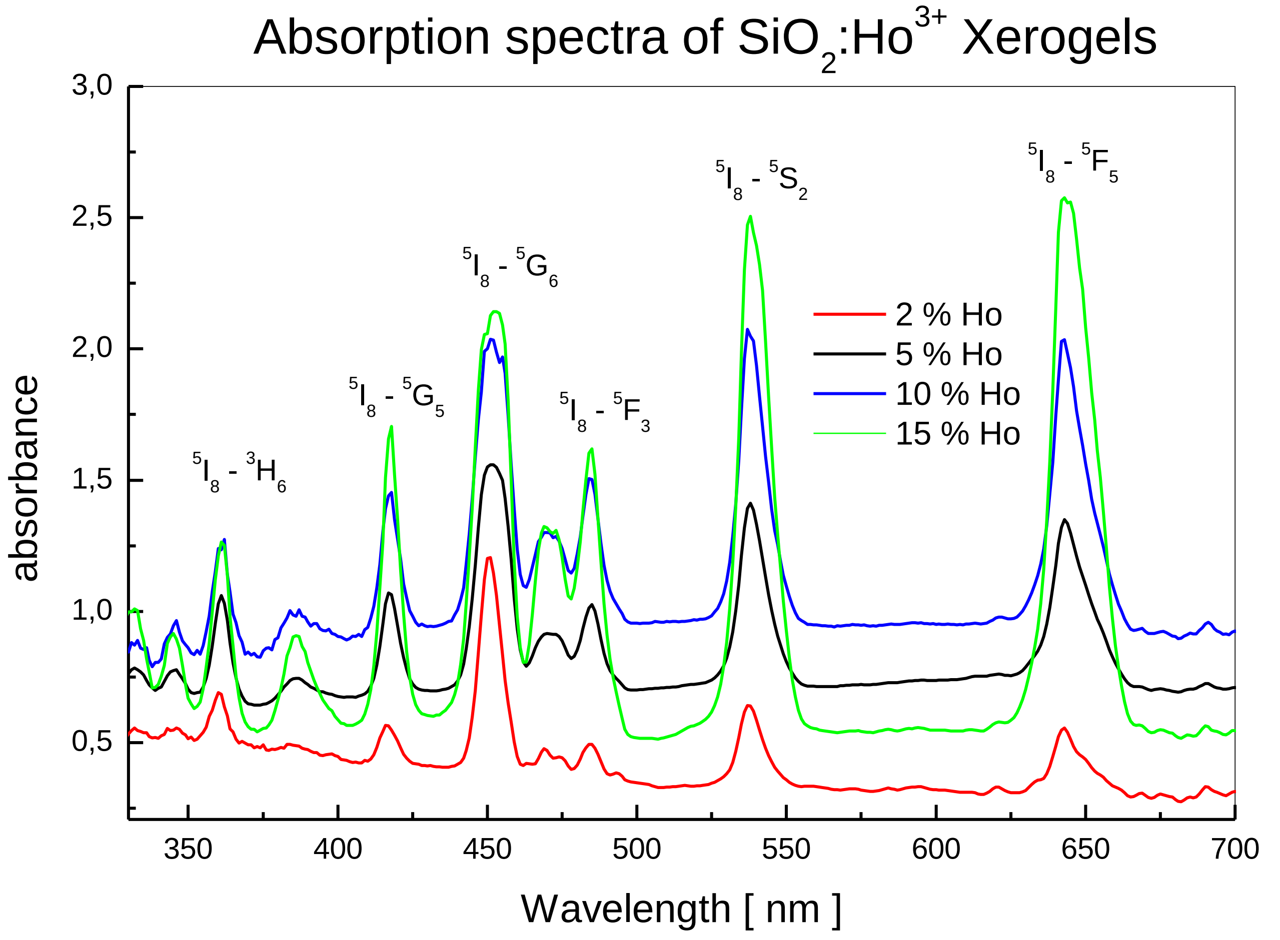






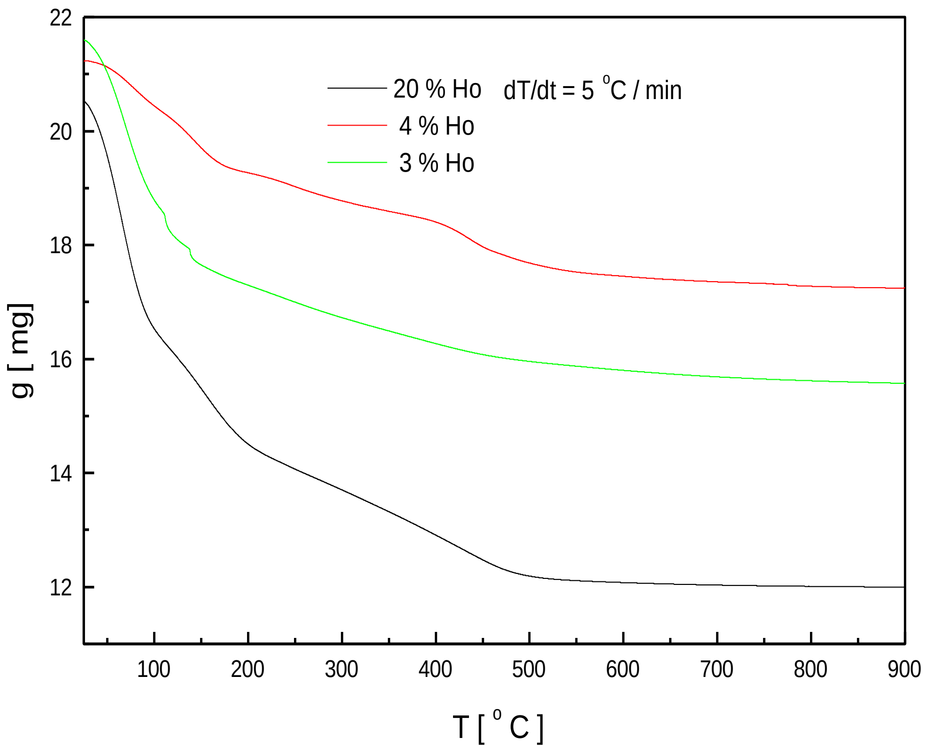
SiO2

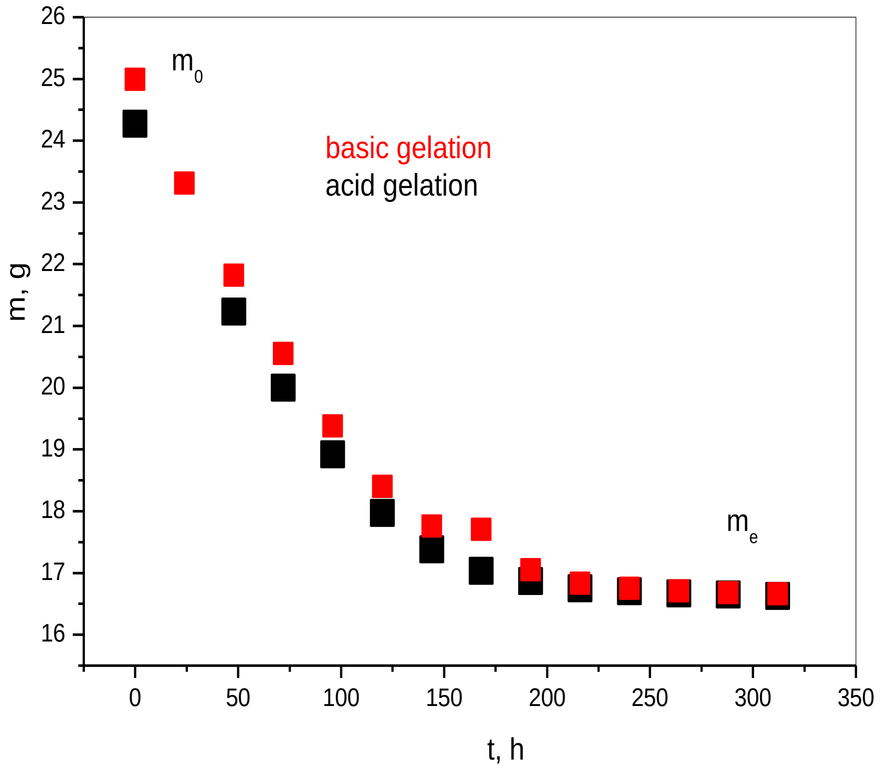
S. Gutzov , C. Berger , M. Bredol , C. L. Lengauer, Preparation and Optical Properties of Holmium Doped Silica Xerogels, J. Mater. Sci. Letters 21 (2002) 1105-1107.



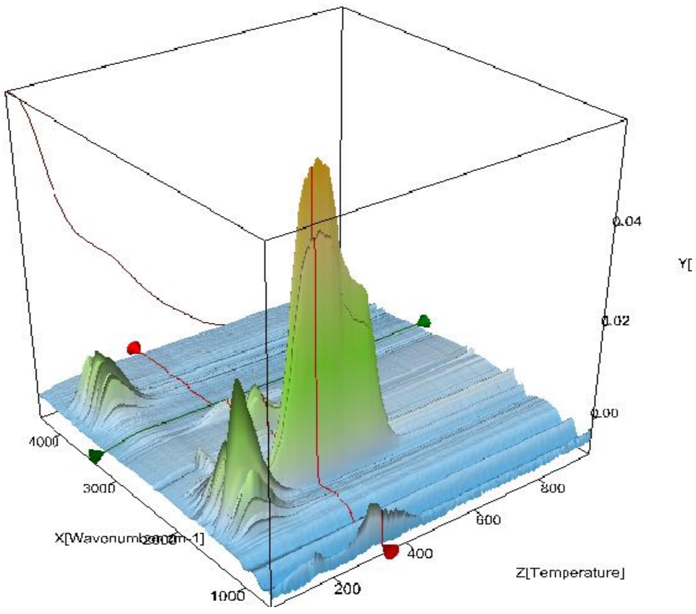
Ho – nitrate nanophase formation in silica at Ho > 10%

Термична стабилност – зависи от дотирането, наличието на нано – и микрофази, пори





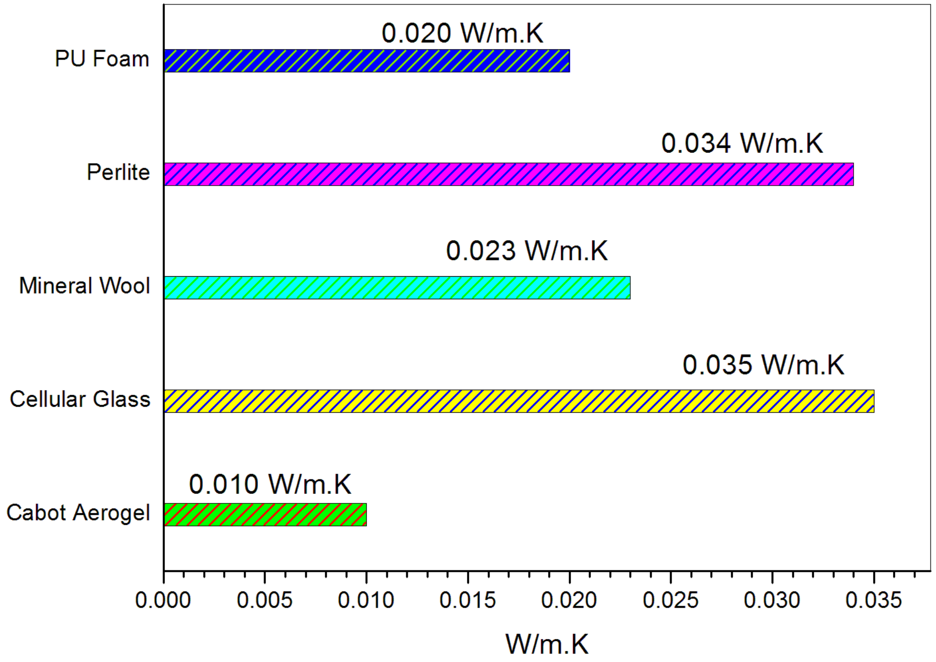
TG/FTIR анализ на гел съдържащ 0.05 Sm/Si

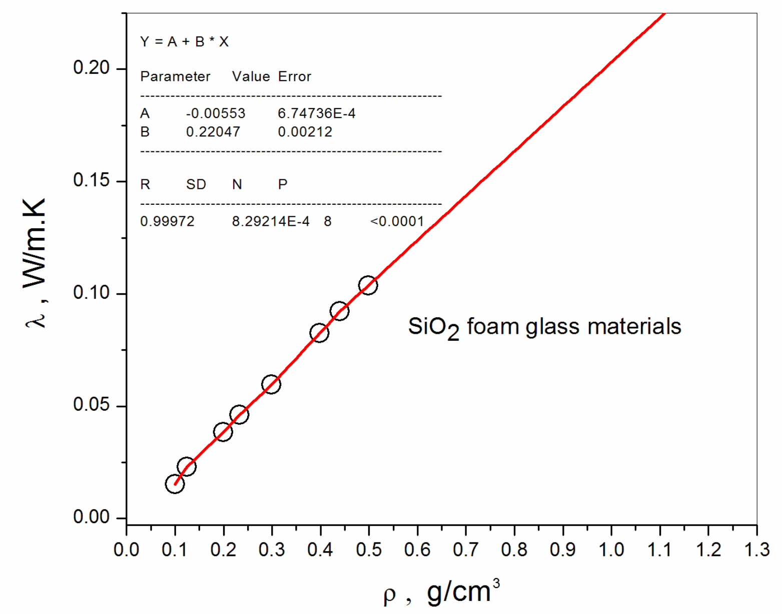


NETZSCH TG 209 ***F1*** coupled with FTIR Bruker TENSOR 27

TG/FTIR анализ на гел съдържащ 0.05 Sm/Si., Фирма NETZSCH, Germany, Dr. E. Füglein

Нанопорьозни суперизолациони материали

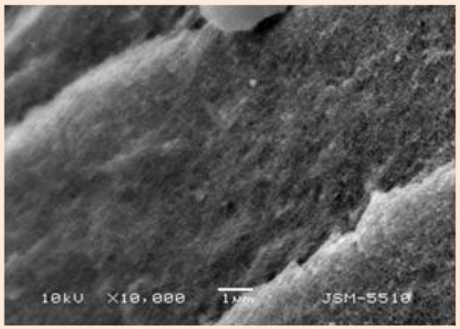


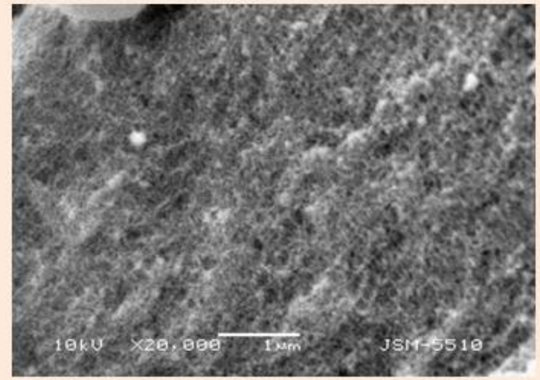


$$\dot{Q} = -\lambda \cdot A \cdot \frac{T_2 - T_1}{\Delta x}$$

Cabot Granulated Nanogels

- One of the best insulation materials in the world produced at subcritical drying. Nano size pores (20 - 40nm), hydrophobic network.





$\lambda = 0.01$ W/m·K

$C_p = 700 - 1150$ J/kg·K

$\rho = 0.03$ g/cm^3

$\alpha = 2.0 \div 4.0 \cdot 10^{-6}$ K^{-1}

Granules

1l = 45 $

Supercritical Drying

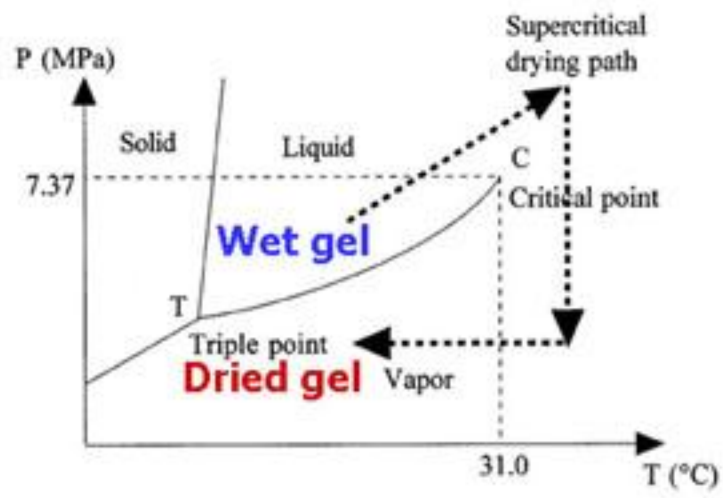


Table Critical Points of Various Fluids

Fluid	T_c (℃)	P_c (MPa)
Water H_2O	374.1	22.04
Carbon dioxide CO_2	31.0	7.37
Freon 116 $(CF_3)_2$	19.7	2.97
Acetone $(CH_3)_2O$	235.0	4.66
Nitrous oxide N_2O	36.4	7.24
Methanol CH_3OH	239.4	8.09
Ethanol C_2H_5OH	243.0	6.3

The solvent in a wet gel is replaced by a supercritical fluid, and then depressurize it to obtain a dried gel. Surface tension of the supercritical fluid is nearly zero, so the weak structure in the wet gel is maintained.

Critical point of a fluid is usually high pressure and sometimes high temperature. So SCD should be avoided as far as possible.

Optimization of materials, required for efficient heat machine operation (case materials).

Chemical Prepared Aerogel Granules (SOFIA)

Tetraethoxysilane (TEOS)

C_2H_5OH

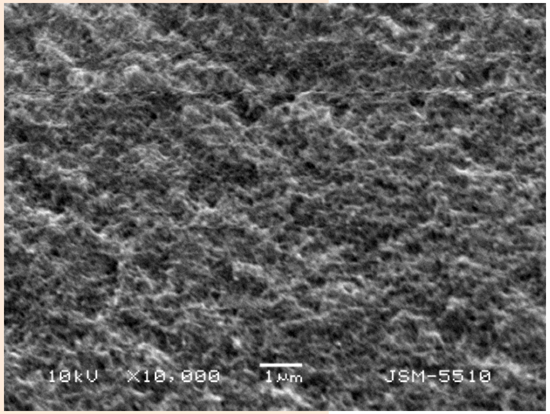
H_2O

HCl

NH_4OH

1.5h hydrolysis time

λ<0.1 W/m·K
ρ = 0.1 g/cm³
Cp = 700 - 950 J/kg·K
α =4÷6·10⁻⁶ K⁻¹
granules

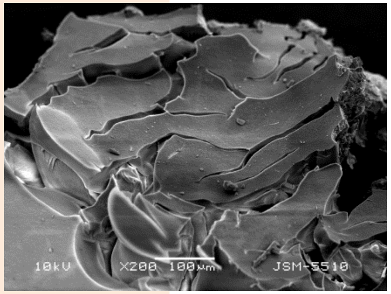


Gelation

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

Multipore Xerogel Granules by Silicon Bulk Hydrophobisation

TEOS

PS-21

NH_4OH

H_2O

HNO_3

Gelation — 48 h

Solvent exchange in ethanol, five times (once per day in the next 5 days)

Drying at subcritical conditions: 0.5 atm and temperature 70° C — 24h

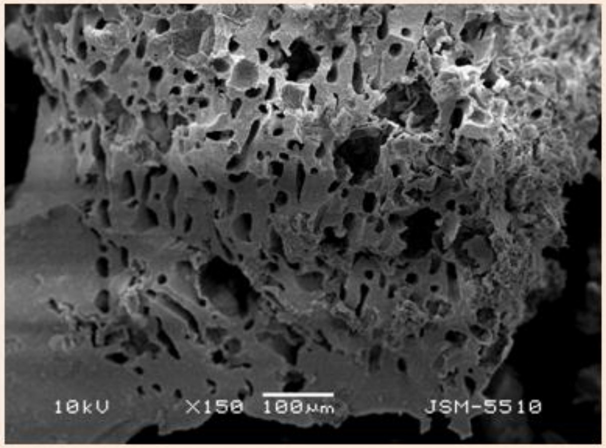
$\lambda < 0.1$ W/m.K

$Cp = 800 \div 900$ J/kg·K

$\rho = 0.4$ g/cm^3

$\alpha = 4 \div 6 \cdot 10^{-6}$ K^{-1}

Granules



Surface Modified Freeze Dried Xerogel Granules

- TEOS
- EtOH
- H_2O
- HCl

1.5 h

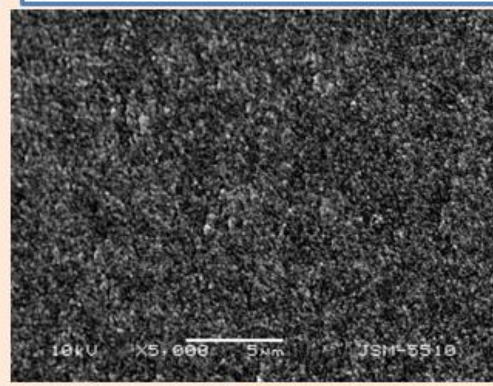
- NH_4OH

Gelation and ripening at -20 °C — 24 h

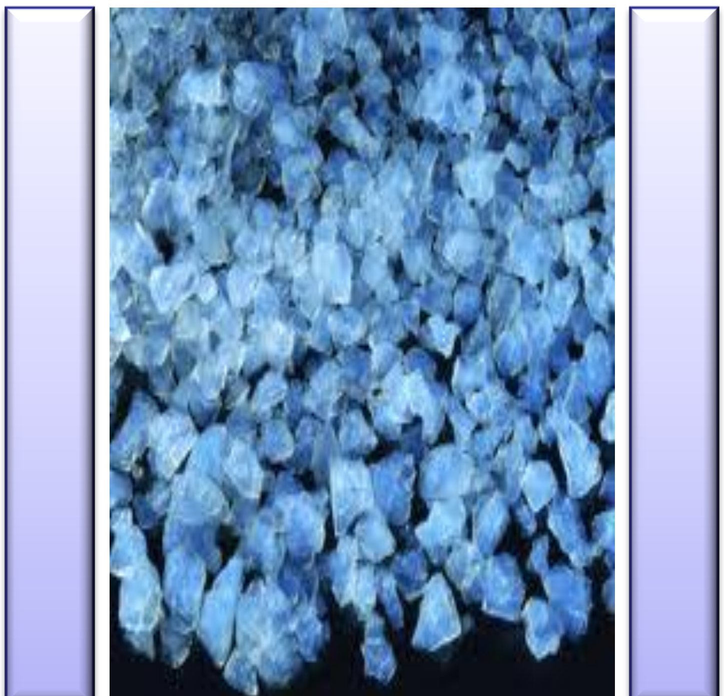
Solvent exchange in ethanol, five times (once per day) — 5 days

Surface modification with a TMCS (trimethylchlorsilane) solution in hexane → Washing the gels with acetone → Drying at subcritical condition: 0.5 atm and temperature 70° C — 24 h

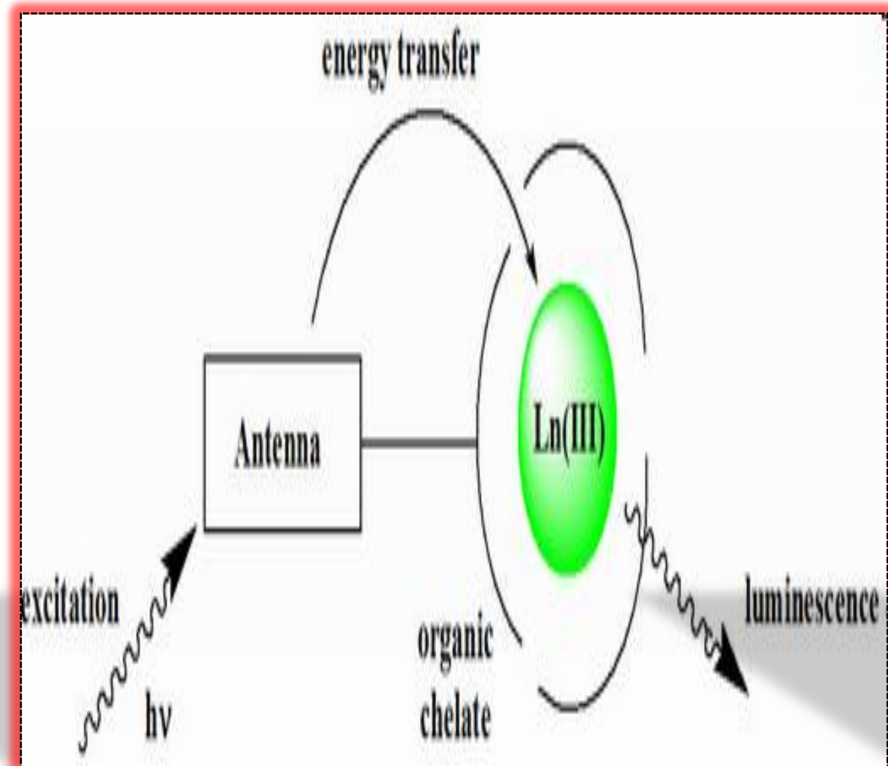
λ<0.2 W/m·K
ρ = 0.45 g/cm3
Cp = 700 – 840 J/kg·K
$\alpha = 4 \div 6 \cdot 10^{-6}$ K^{-1}
granules

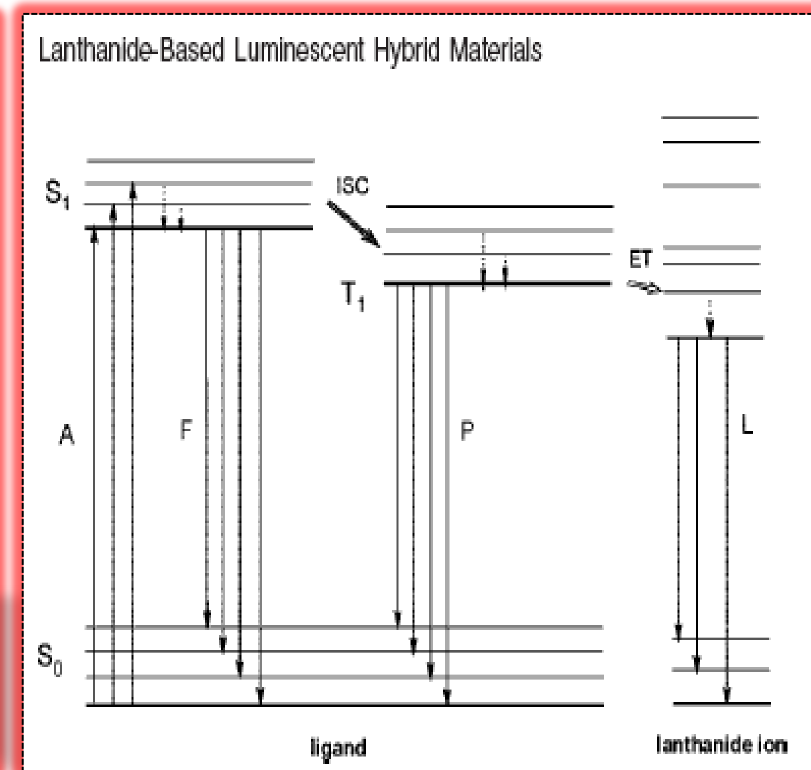


***SUMMARY*: Aerogel granules posses perfect insulation properties, they have to be incorporated into a panel for effective case insulation.**



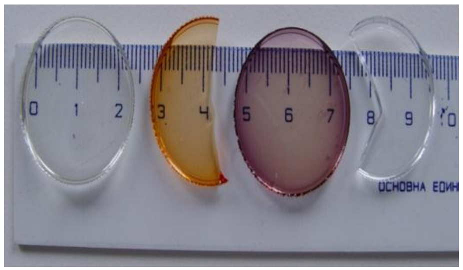
Хибридни оптични материали

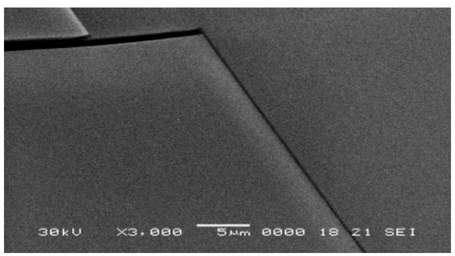




ЛУМИНЕСЦЕНТНИ СВОЙСТВА НА КОМПЛЕКСИ НА ЛАНТАНИДНИ ЙОНИ

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





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

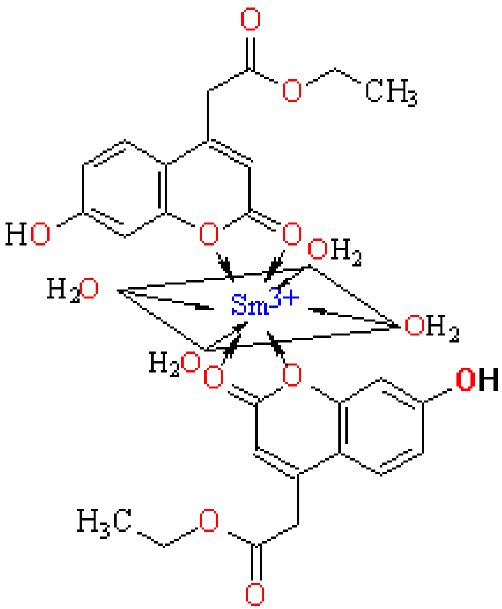
↓

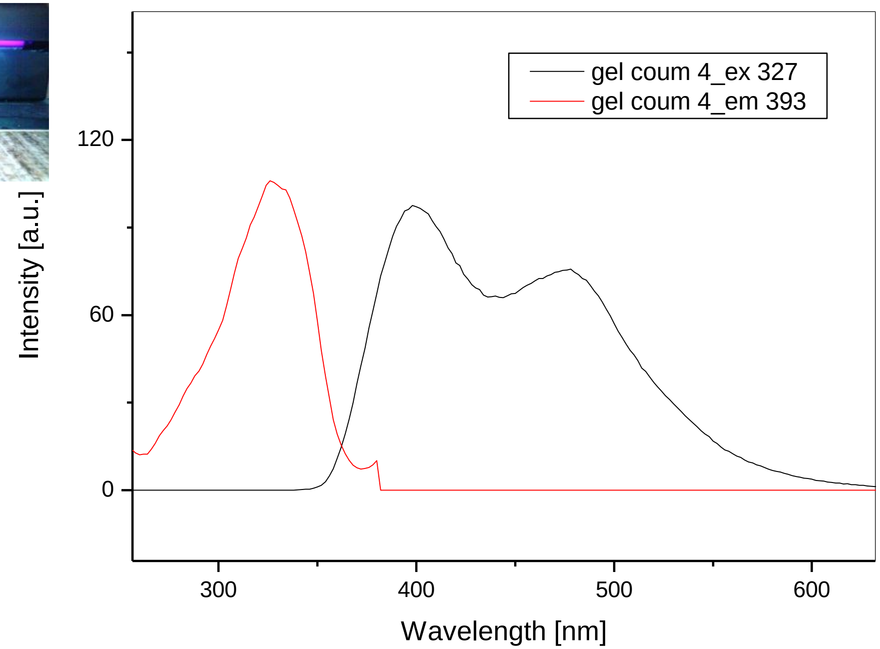
Gelation – 30 min

↓

Drying (168 h / 20 ^{o}C) — $\rho_{gel} = 1.3\ g.cm^{-3}$

Luminescence of hybride materials doped with coumarin and Sm^{3+}: G. Ahmed, B. Koleva, S. Gutzov, I. Petkov, *J Incl. Phenom. Macro.* (2007), DOI: 10.1007/s10847-007-9309-0.





*Л*уминесценция на гелове, дотирани с

етил 2-(7-хидрокси-кумарин-4-ил) ацетат

Измерване на спектри в режим трансмисия и дифузно отражение

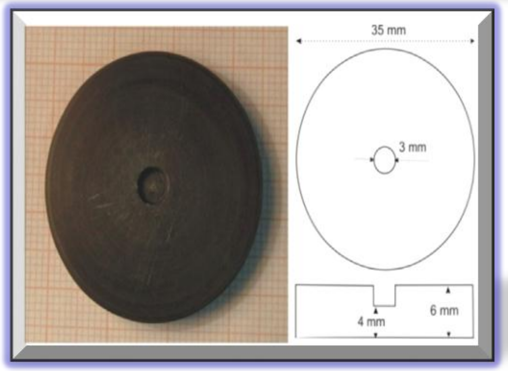
кварцови кювети
200 – 900 nm

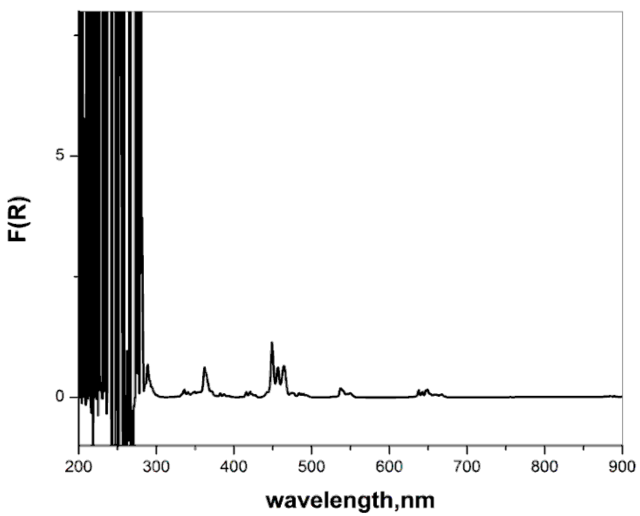
$$f = 4.32 \cdot 10^{-9} \cdot \frac{A_{int}(\tilde{v})}{c \cdot d}$$

интегрираща сфера Labsphere PSA-PE-20
200 – 900 nm

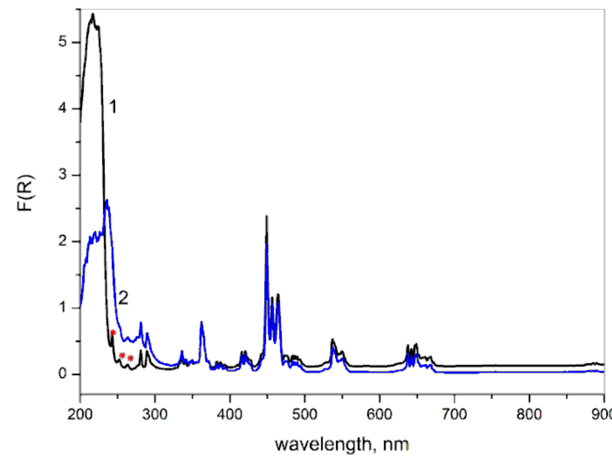
$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R}$$

Разработване на нови държатели с различни геометрии и размери на базата на полицетал Polipom POM ®, съвместими с интегриращата сфера модел Labsphere PSA-PE-20





Дифузно - отражателен спектър на холмиев оксид, покрит с предметно стъкло



Съпоставка между дифузно - отражателни спектри на холмиев оксид, измерен директно (1) и с покритие от кварцово стъкло (2) .

Получаване на ZrO_2 по зол-гелна технология

Without protection

$Zr(OC_4H_9)_4$

↓ ← C_4H_9OH

Zirconia sol

↓ ← H_2O

White presipitate

Acethylacetone (AcAc)

$Zr(OC_4H_9)_4$

↓ ← C_4H_9OH

Zirconia sol 1

↓ ← $CH_3COCH_2COCH_3$

Zirconia sol 2

↓ ← H_2O

Yellow gel

Acetic acid (AA)

C_2H_5OH

↓ ← CH_3COOH, HNO_3

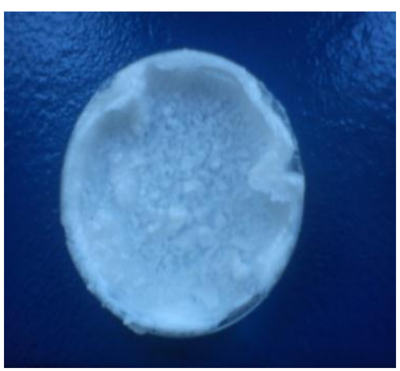
solution

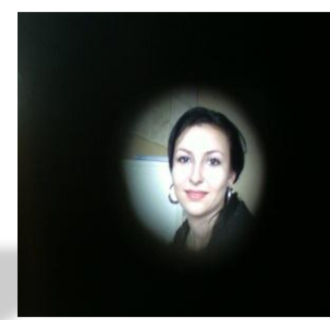
↓ ← $Zr(OC_4H_9)_4$

sol

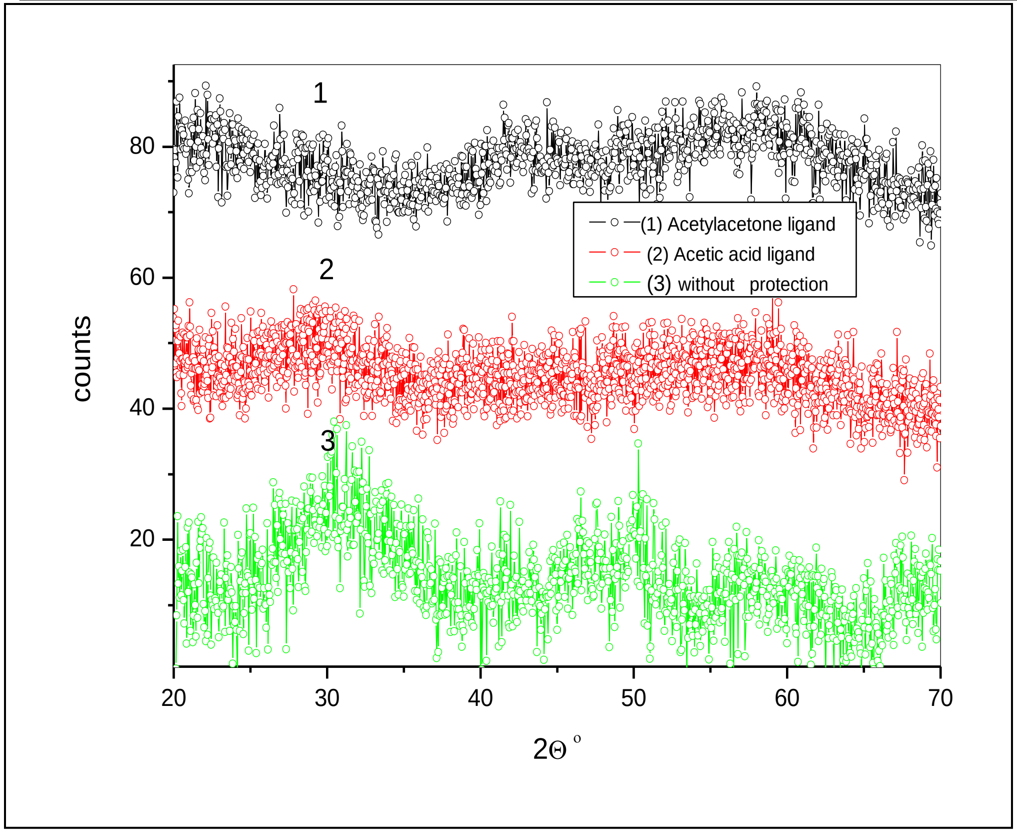
↓ ← H_2O

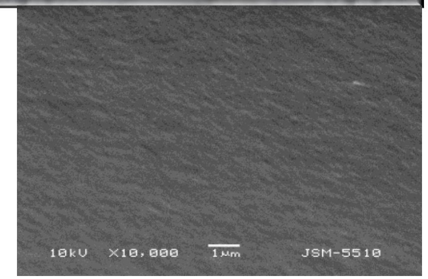
Transparent gel



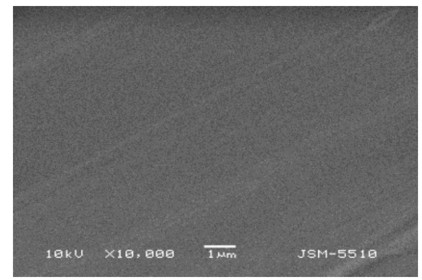


Рентгеноструктурен анализ
СЕМ микроскопия

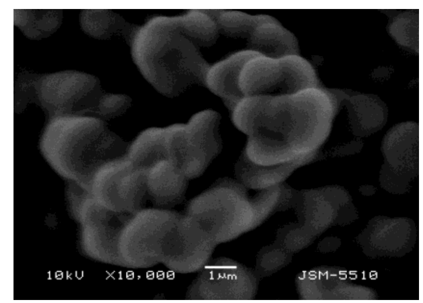




1



2



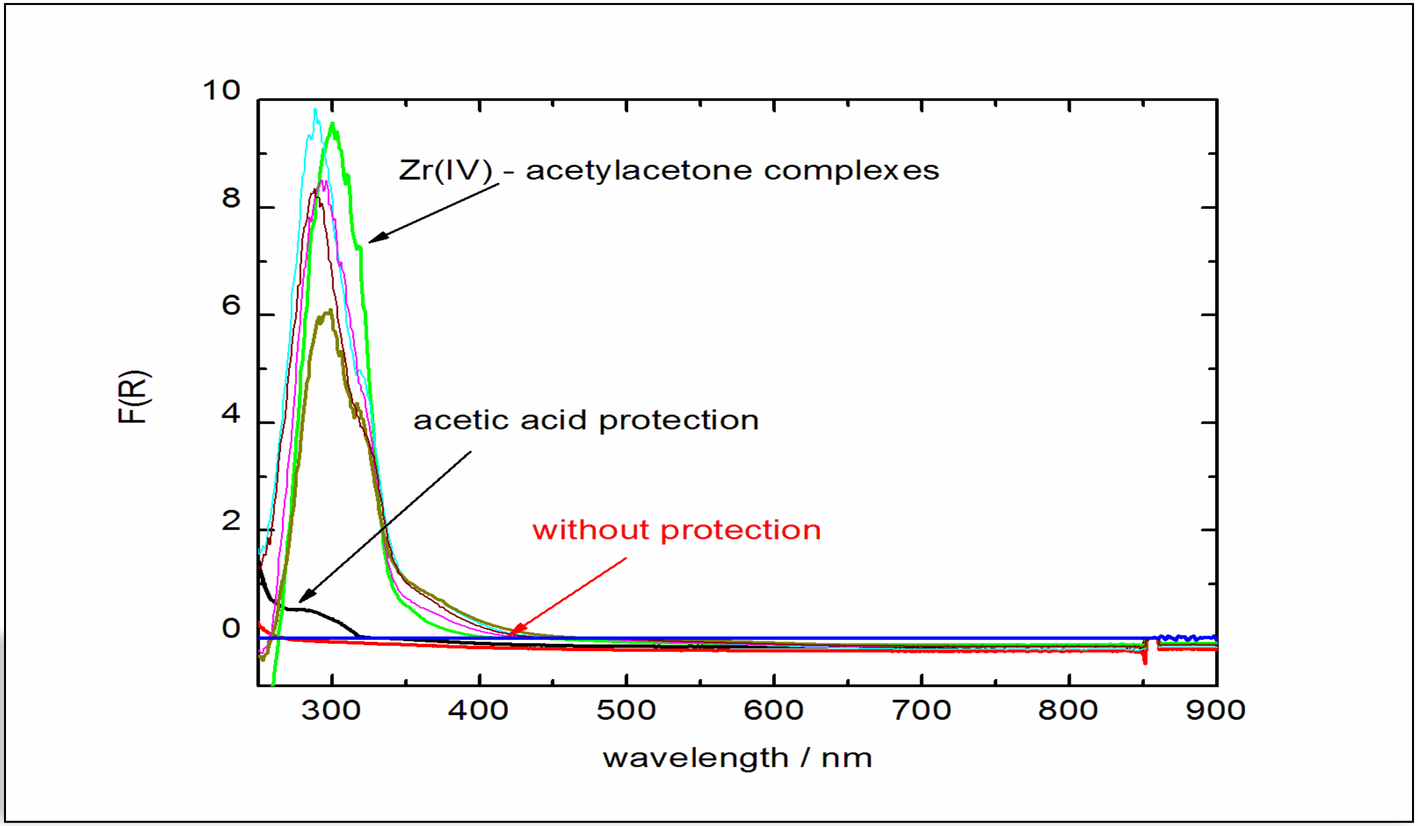
3

1 - Гелове, синтезирани с ацетилацетон като модифициращ агент

2 - Гелове получени с оцетна киселина като протектиращ лиганд

3 - Гелове получени без протекция на алкоксида

UV/VIS РЕФЛЕКСИОННА СПЕКТРОСКОПИЯ



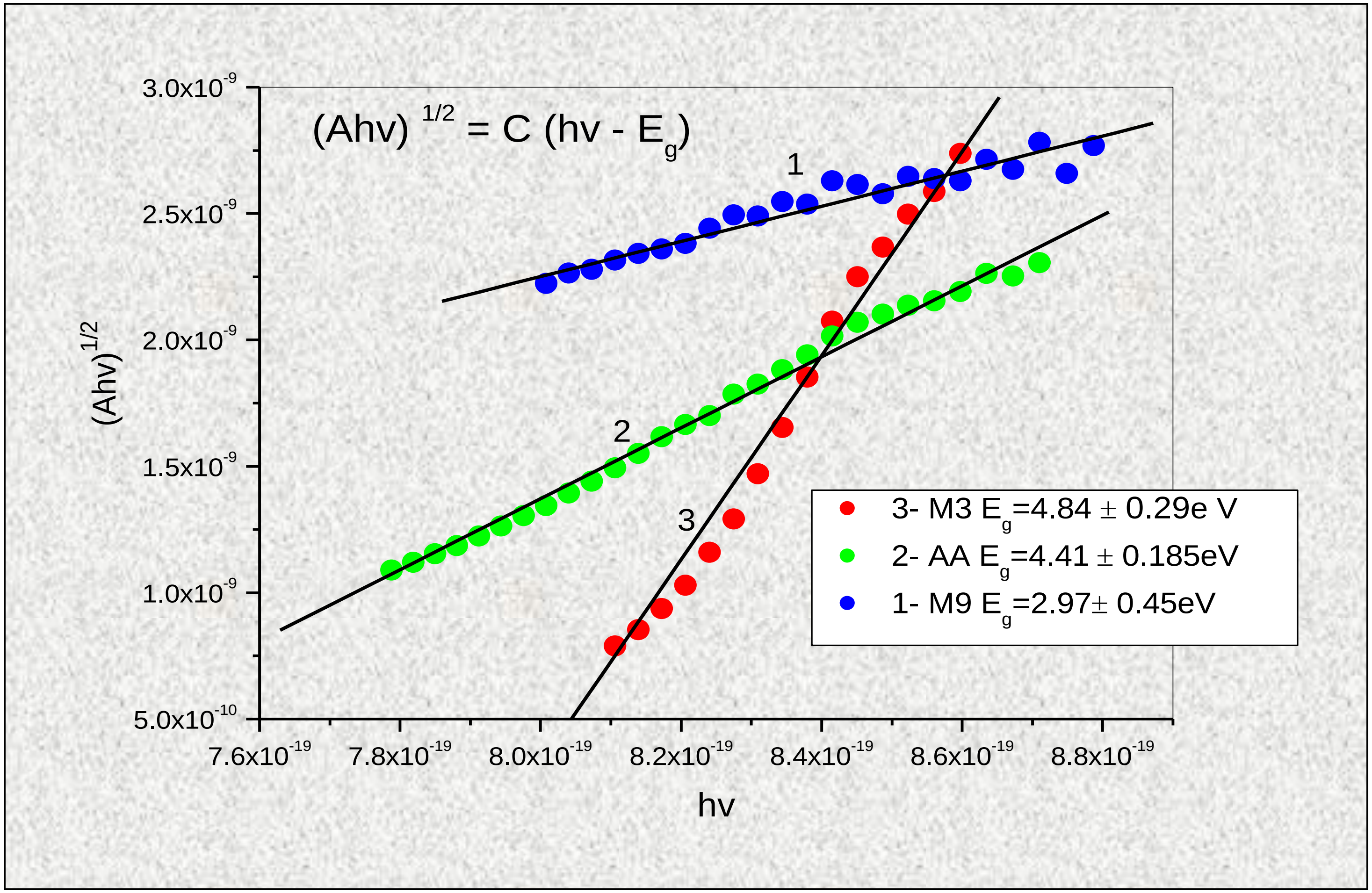
UV/Vis спектри на отражение на циркониеви зол-гел материали. За референтен спектър е използван KCl

1 – Гел, получен без протекция на началния прекурсор;

2-Гел, протектиран с оцетна киселина като протектиращ лиганд;

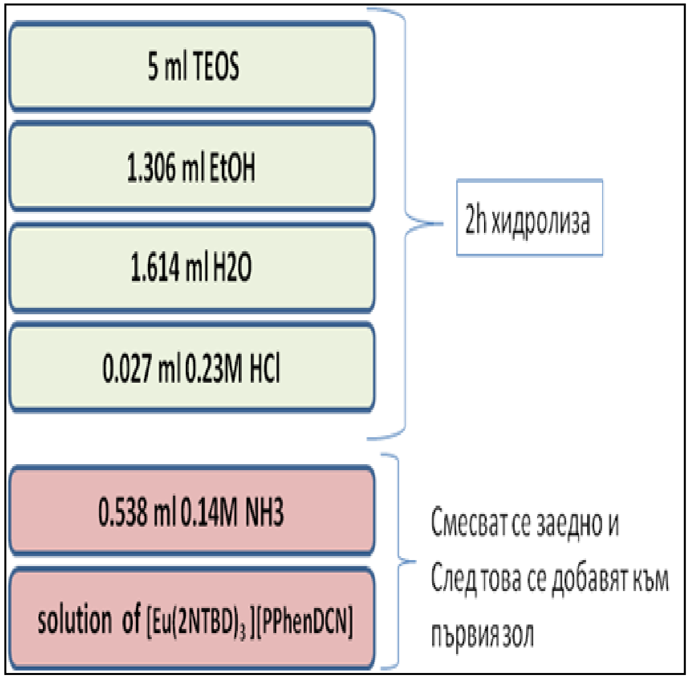
3,4,5- Гелове получени с оцетна киселина като модифициращ лиганд.

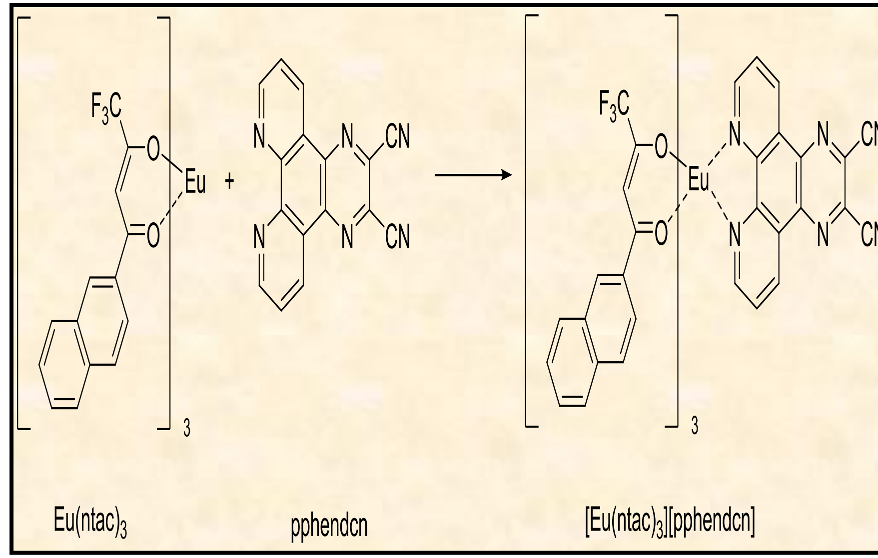
ОПТИЧНА ШИРИНА НА ЗАБРАНЕНАТА ЗОНА

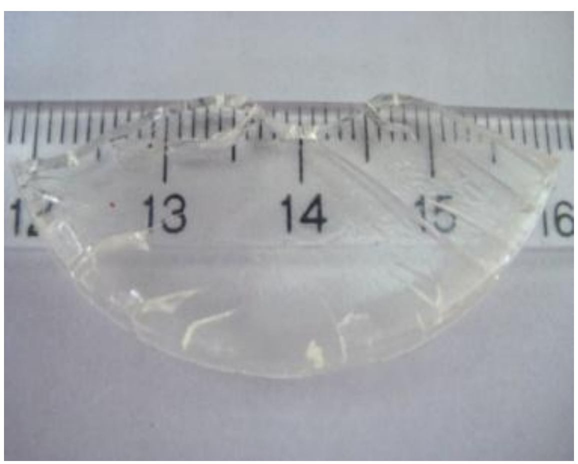


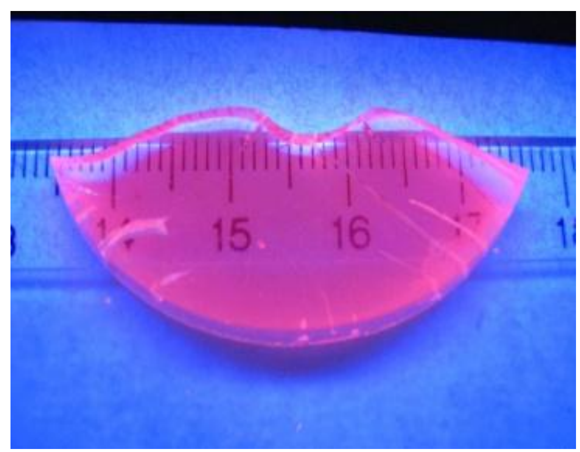
1 - гел синтезиран с ацетиалацетон Eg=2.97±0.45eV r = 0.97
2 - гел с оцетна киселина Eg=4.41±0.185eV r = 0.99
3 - бърза хидролиза на прекурсора Eg=4.84±0.29eV r = 0.99

Дотиране на SiO_2 с $Eu[ntac]_3[PPhenDCN]$

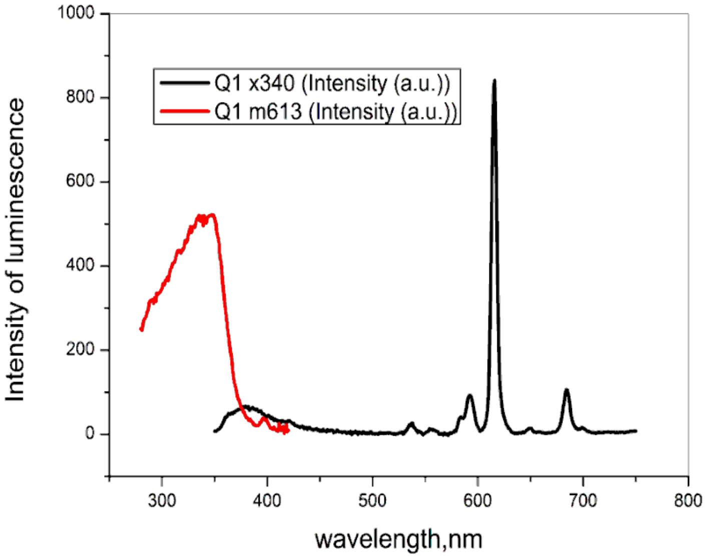


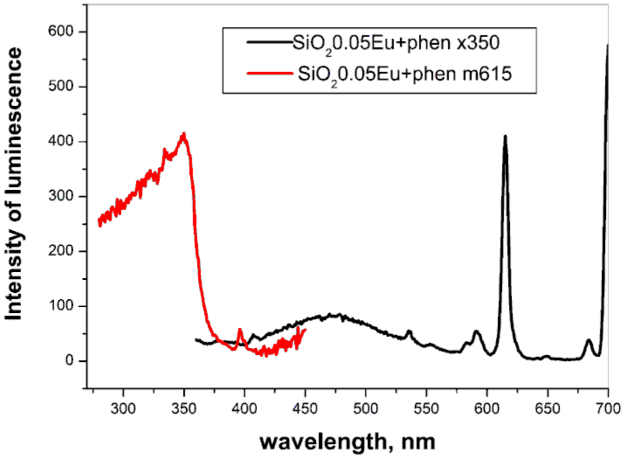


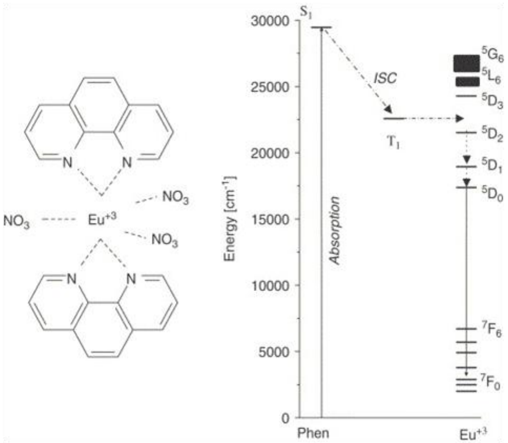


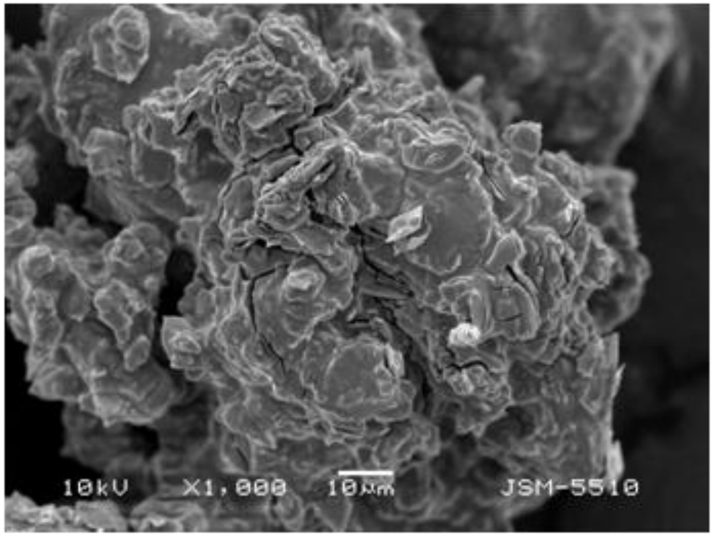


Хибридни микро – и нанопрахове: $SiO2$ и ZrO_2 получен по зол-гел метода с $[Eu(phen)_2](NO_3)_3$









Квантов добив

QY= брой емитирани фотони / брой абсорбирани фотони

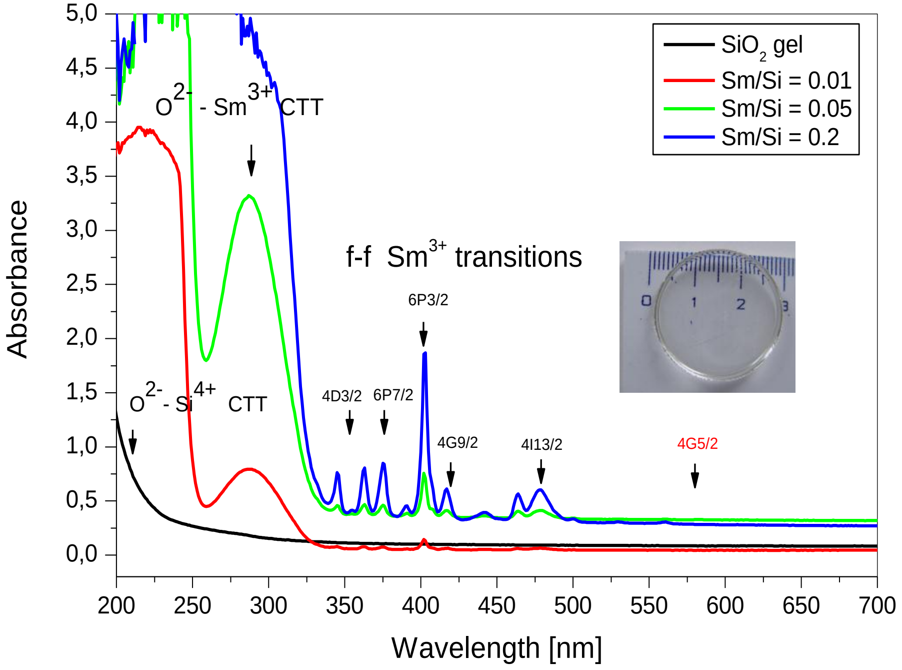
$$QY_{Samp} = QY_{Ref} \frac{Int_{samp} \cdot Abs_{Ref}}{Int_{Ref} \cdot Abs_{Samp}} \cdot 100\%$$

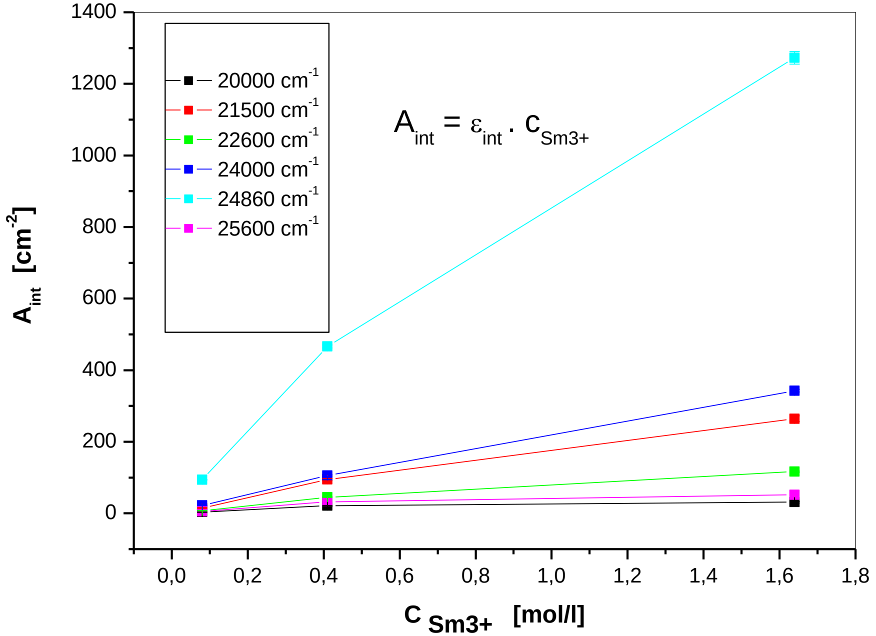
Проба	**описание**	**$\lambda_{exc,}$nm**	**QY, %**	**n_{Eu}/n_{Si} ; n_{Eu}/n_{Zr}**
$[Eu(ntac)_3][PPhenDCN]$	Багрило	396	10.8 ± 1.8	-
SiO_2:Eu[$(ntac)_3$(pphenDCN)]	Импрегнирана	400	17.4 ± 1.74	$3.18 \cdot 10^{-4}$
ZrO_2:[Eu$(phen)_2$]$(NO_3)_3$	Дотирана зол-гел	350	48.2 ± 4.8	$9 \cdot 10^{-3}$
SiO_2 0.05Eu + phen	Функционализиране	352	39.57 ± 3.9	$5 \cdot 10^{-2}$

В аморфни неорганични системи при тези условия QY ≈ 1-2%

Материали за UV – филтри и защитни покрития

$SiO_2:Sm^{3+}$

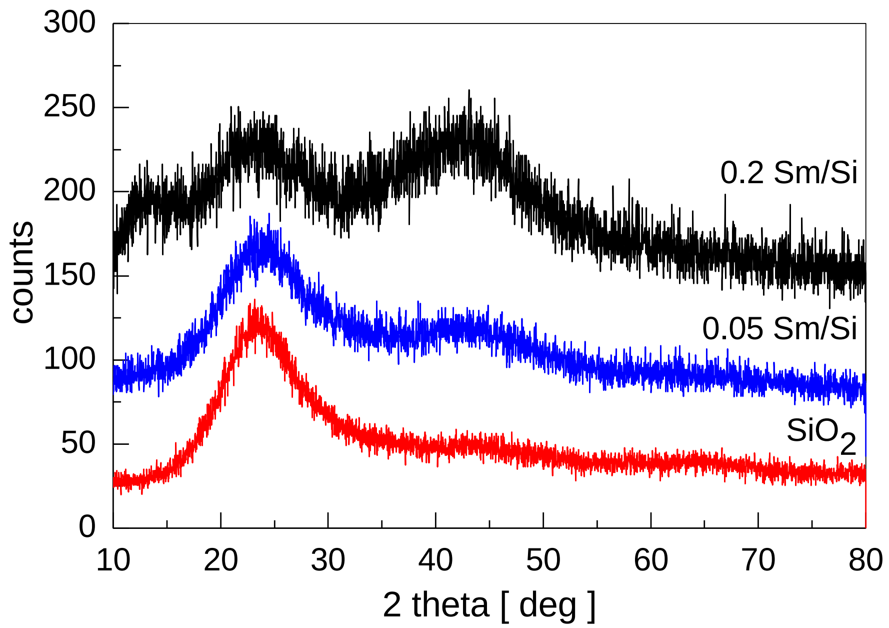




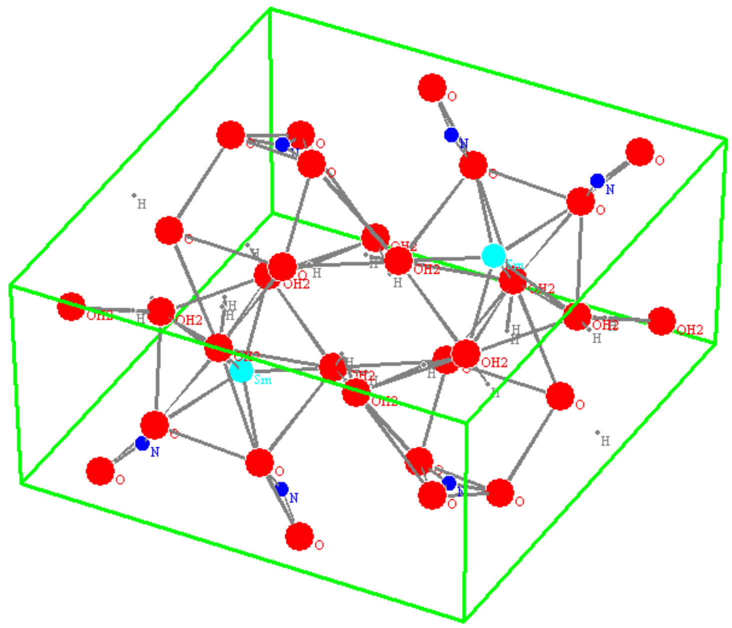
UV/Vis спектри на гелове, модифицирани с различно количество Sm^{3+}, и гел без модифициране.

Зависимост на абсорбцията на от концентрацията

Рентгеноструктурен анализ на гелове дотирани със самарий

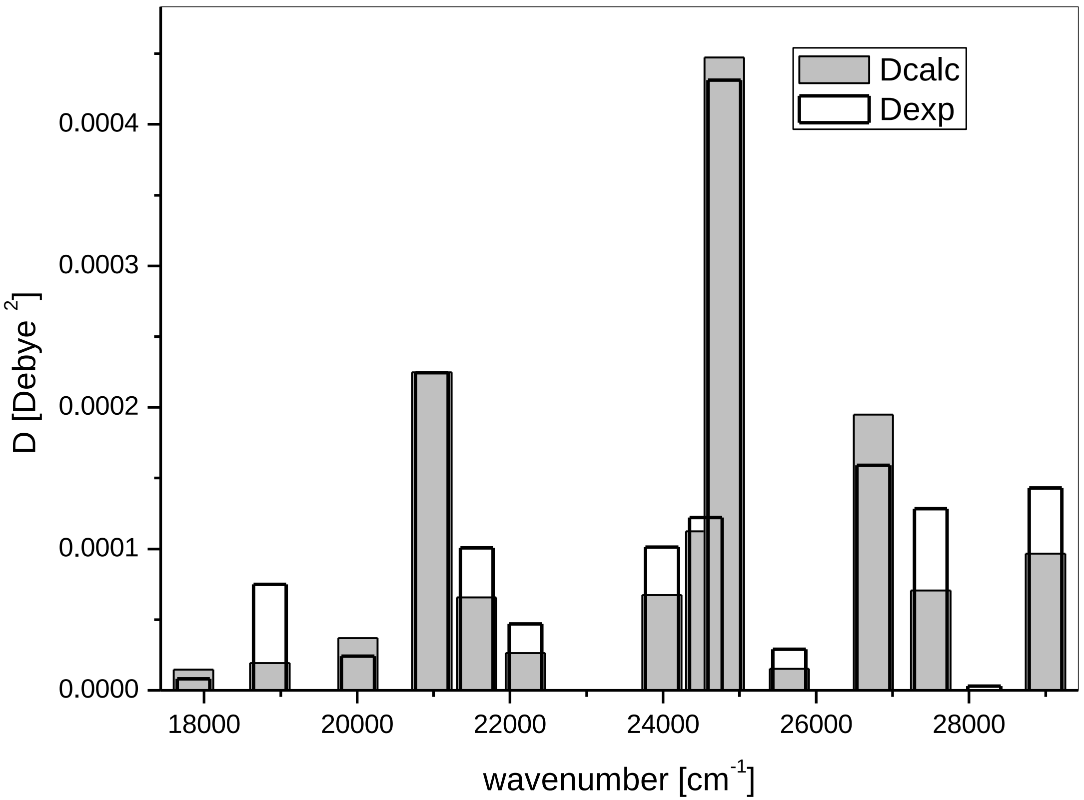


Рентгенограма на гелове, дотирани с различно количество Sm.



Нанокристална фаза от $Sm(H_2O)_6(NO_3)_3$ в гел, съдържащ 20 и повече молни % Sm.

Calculations vs. measurements



$$D_{calc} = \frac{1}{2J+1} \cdot \frac{(n^2+2)^2}{9n} e^2 \sum_{k=2,4,6} \Omega_k \left| \left\langle J \middle\| U^{(k)} \middle\| J' \right\rangle \right|^2$$

$$D_{\exp} = \frac{1}{108.9 \cdot C \cdot d} \int \frac{A(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu}$$

Preparation of $SiO_2:Sm^{3+}$

Basic gelation scheme.

TEOS

↓

Ethanol

↓

0.55M $Sm(NO_3)_3$

↓

H_2O, 2h at room temperature

↓

0.23M HCl pH≈2

↓

0.14M NH_3 pH≈6-7

nTEOS: nC_2H_5OH:nH_2O: nHCL= 1:1:4:0.003

Acid gelation scheme.

TEOS

↓

Ethanol

↓

0.55M $Sm(NO_3)_3$

↓

H_2O, 2h at room temperature

↓

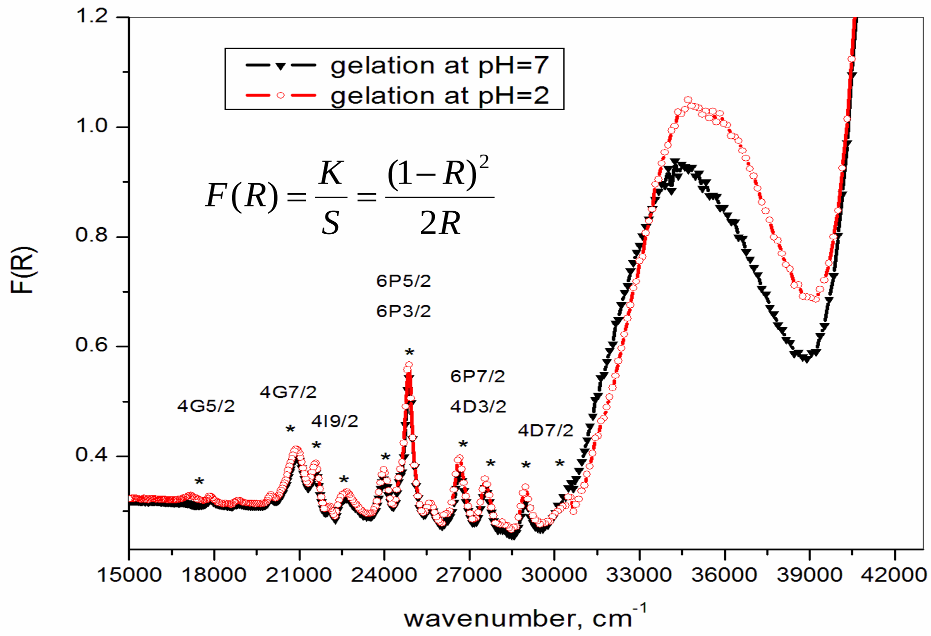
0.23M HCl pH≈2

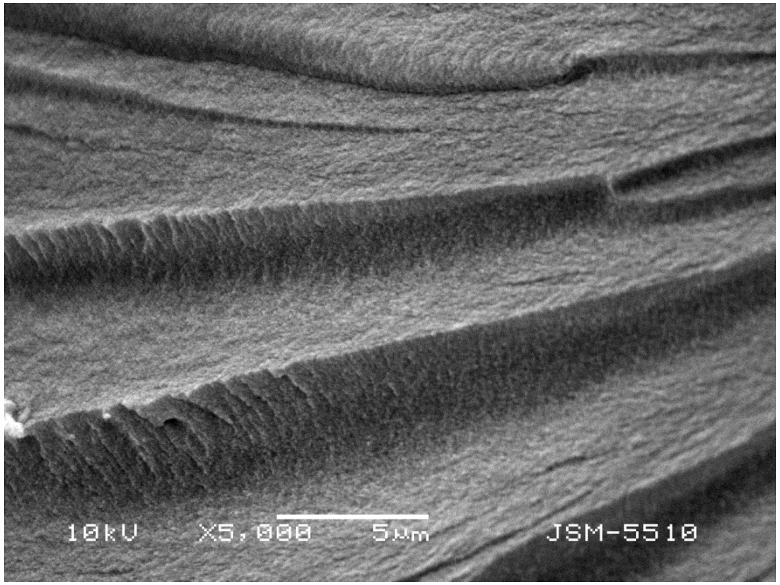
↓

Gelation 48h at 50°C

nTEOS: nC_2H_5OH:nH_2O: nHCL= 1:1:4:0.003

UV/Vis diffuse reflectance spectra of Sm doped silica gels

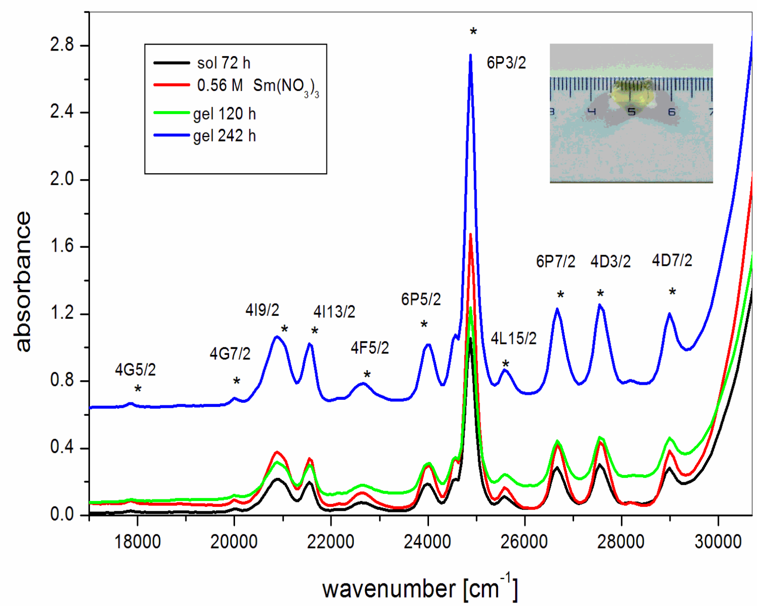


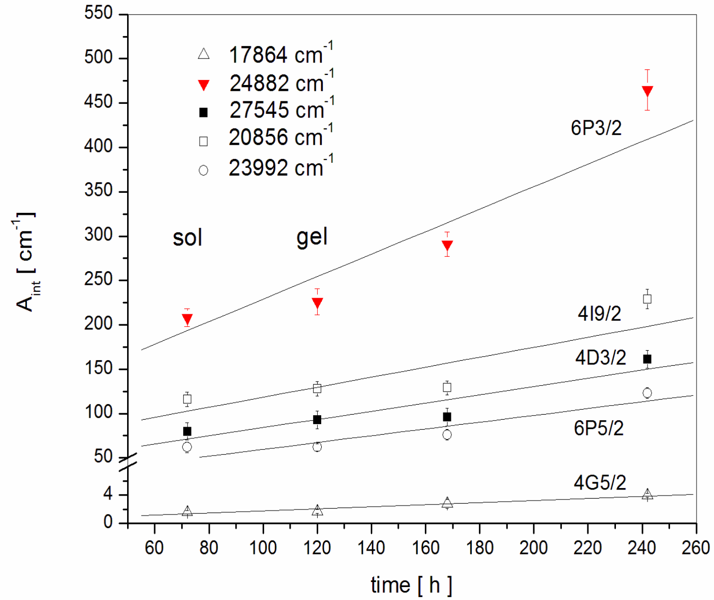


Our results suggest that acid gelation conditions increase the UV – absorption intensity of doped silica gels.

Application: powder coatings for UV - protection

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





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

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

Благодарности

- ***Нина Данчова, Гюляй Ахмед, Жаклин Мисирян, Стефка Станчева, Петя Стоянова, Станимир Стоянов (СУ - ФХФ)***
- ***E. Füglein (NETSCH GmbH), M. Bredol (FH Münster), T. Schmidt (TIGER Coatings AG).***
- ***НФНИ – проекти ВУХ 08/05, ТК 02/26***
- ***FP7 EFFiHEAT, FP7 BeyondEverest***