Люминесцентные материалы

Заключительная лекция

План лекции

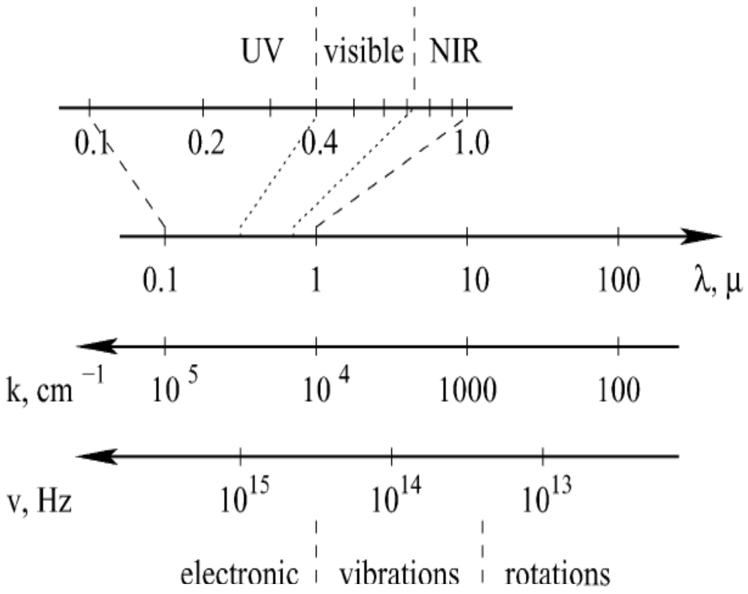
- Фотолюминесценция
- Люминофоры для белых светодиодов
- Наноразмерные люминофоры

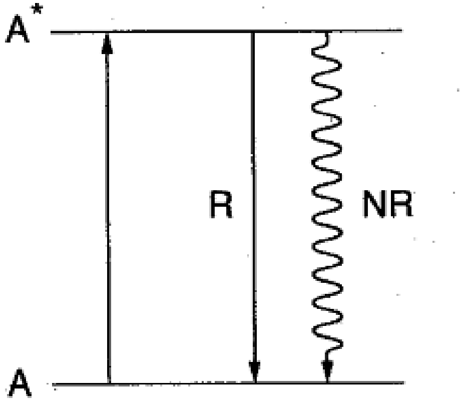
Оптическая спектроскопия

$$E\ (\mathrm{eV}) = \frac{1240}{\lambda\ (\mathrm{nm})} = 1.24 \times 10^{-4}\bar{\nu}\ (\mathrm{cm}^{-1})$$

$$\bar{\nu}\ (\mathrm{cm}^{-1}) = \frac{10^7}{\lambda\ (\mathrm{nm})} = 8064.5E\ (\mathrm{eV})$$

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \qquad h = 6.62 \times 10^{-34}\ \mathrm{J\ s}$$





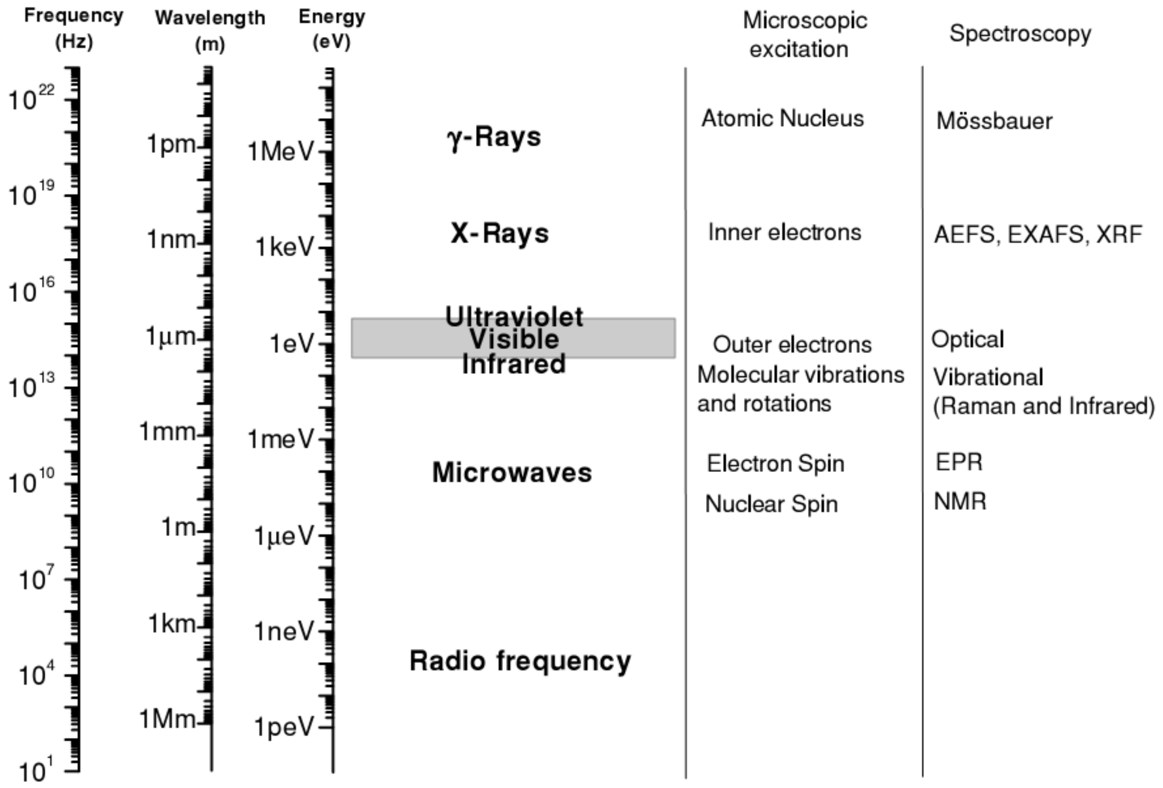
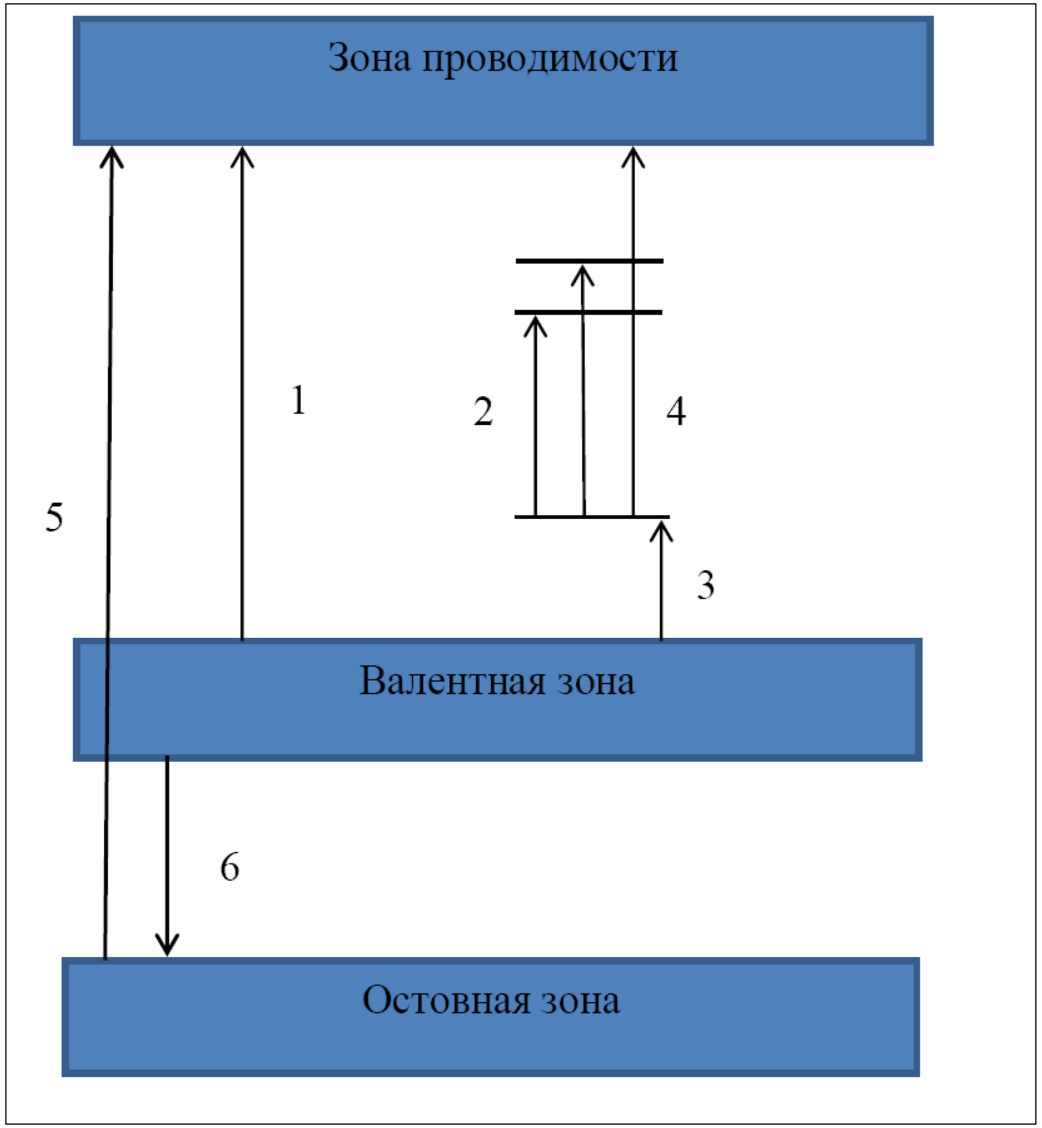


Figure 1.1 The electromagnetic spectrum, showing the different microscopic excitation sources and the spectroscopies related to the different spectral regions. XRF, X-Ray Fluorescence; AEFS, Absorption Edge Fine Structure; EXAFS, Extended X-ray Absorption Fine Structure; NMR, Nuclear Magnetic Resonance; EPR, Electron Paramagnetic Resonance. The shaded region indicates the optical range.

Типы переходов в кристаллах

Основные типы переходов в диэлектрических кристаллах.
1 – межзонные переходы,
2 – внутрицентровые переходы,
3 – переходы с переносом заряда,
4 – фотоионизация,
5 – переходы с верхней остовной зоны в зону проводимости,
6 – кросслюминесценция (остовно-валентные переходы)



Двухуровневый центр в конденсированном веществе

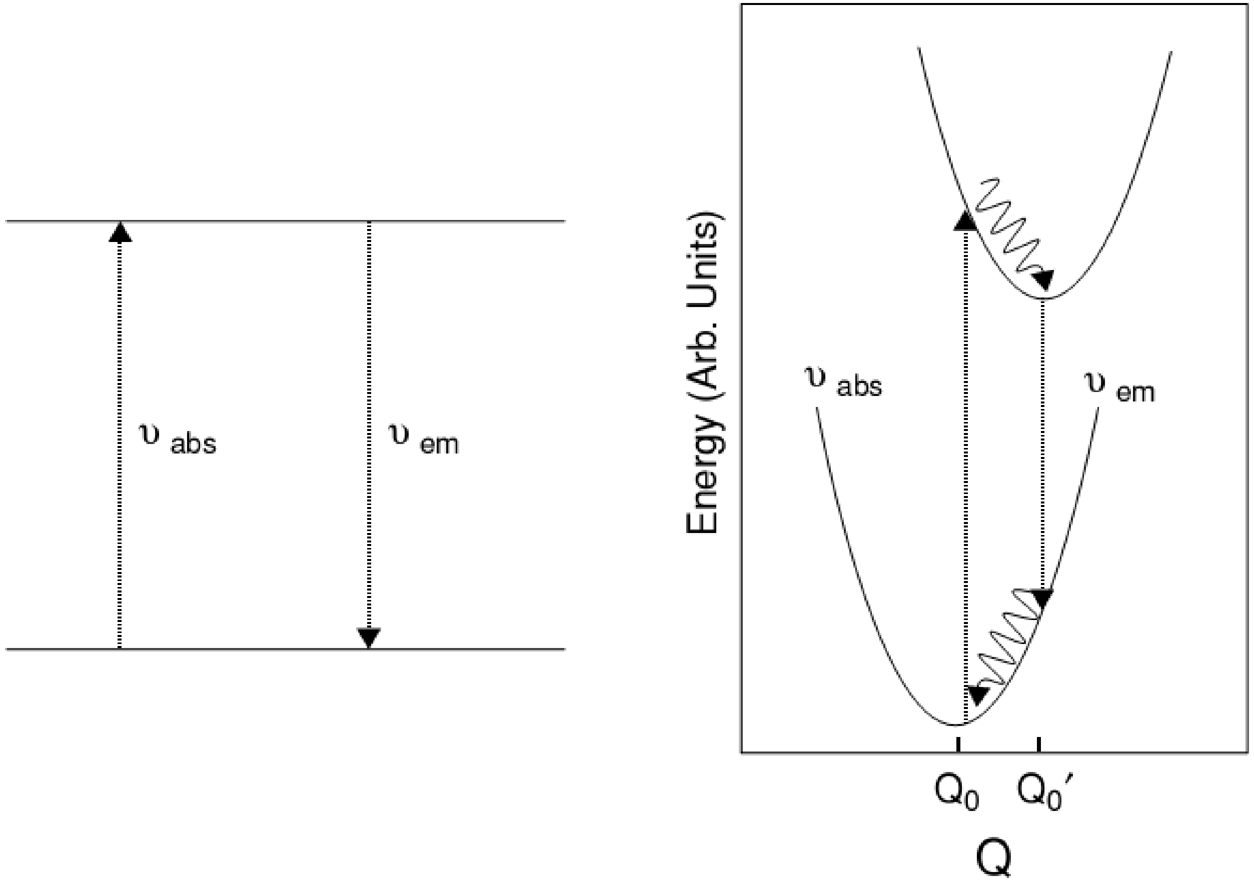


Figure 1.10 (a) The absorption and emission energies for a two-level system (rigid lattice). (b) The absorption and emission energies showing the Stokes shift (vibrating lattice).

Люминесценция

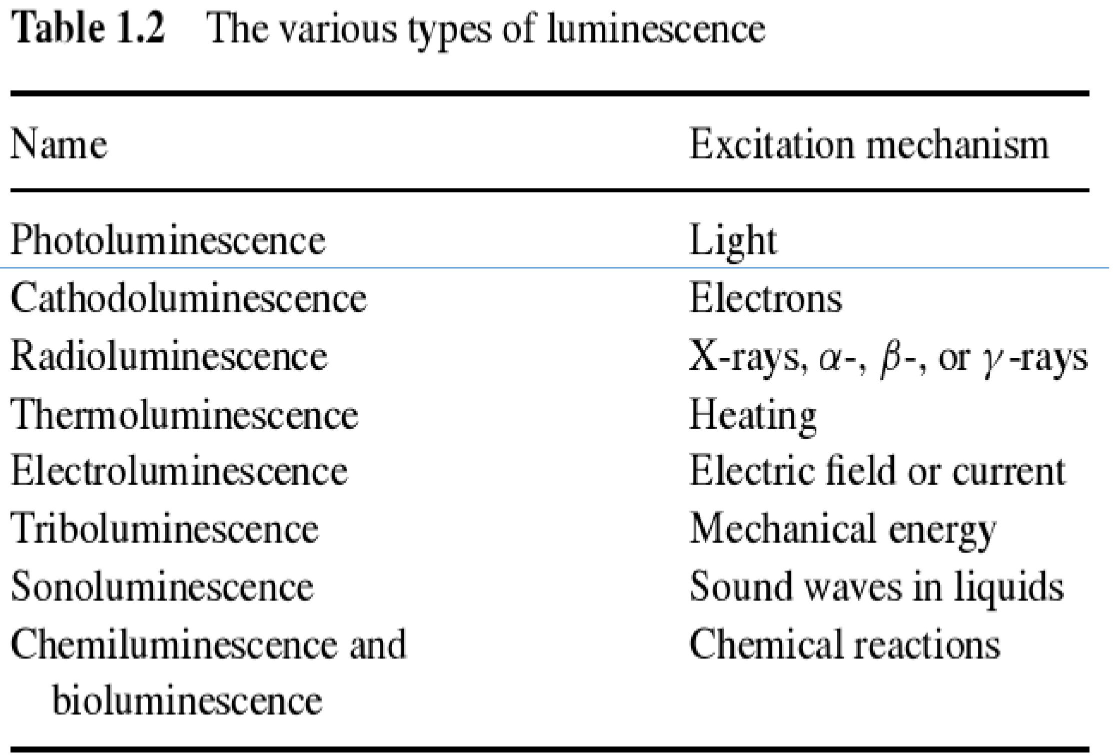
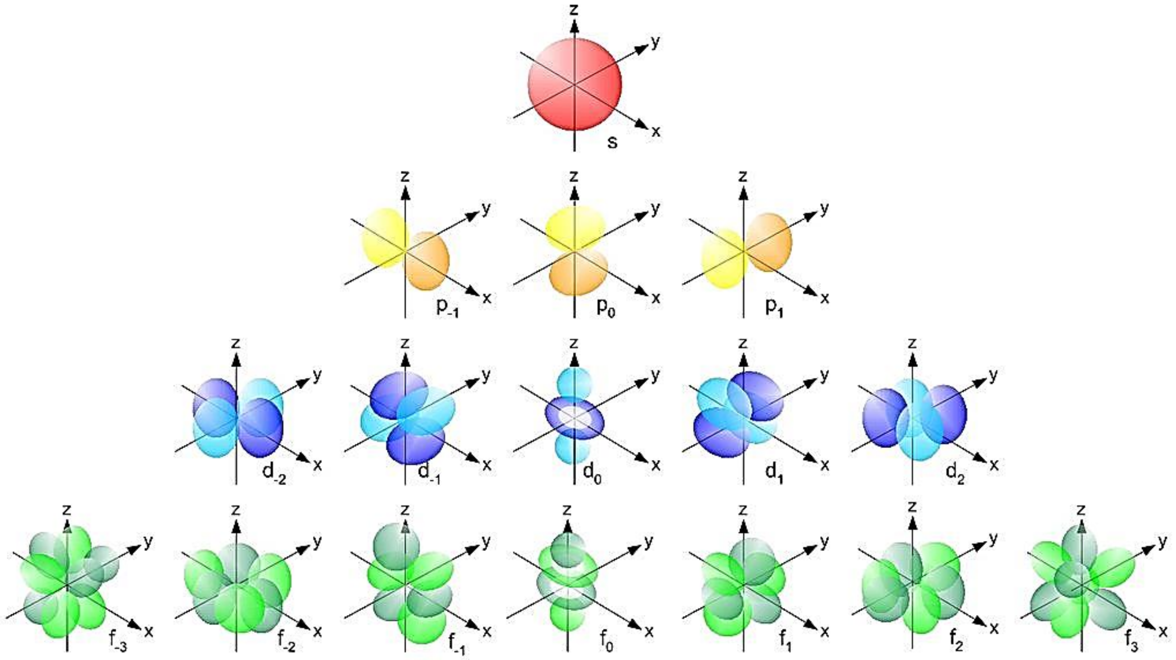


Table 1.2 The various types of luminescence

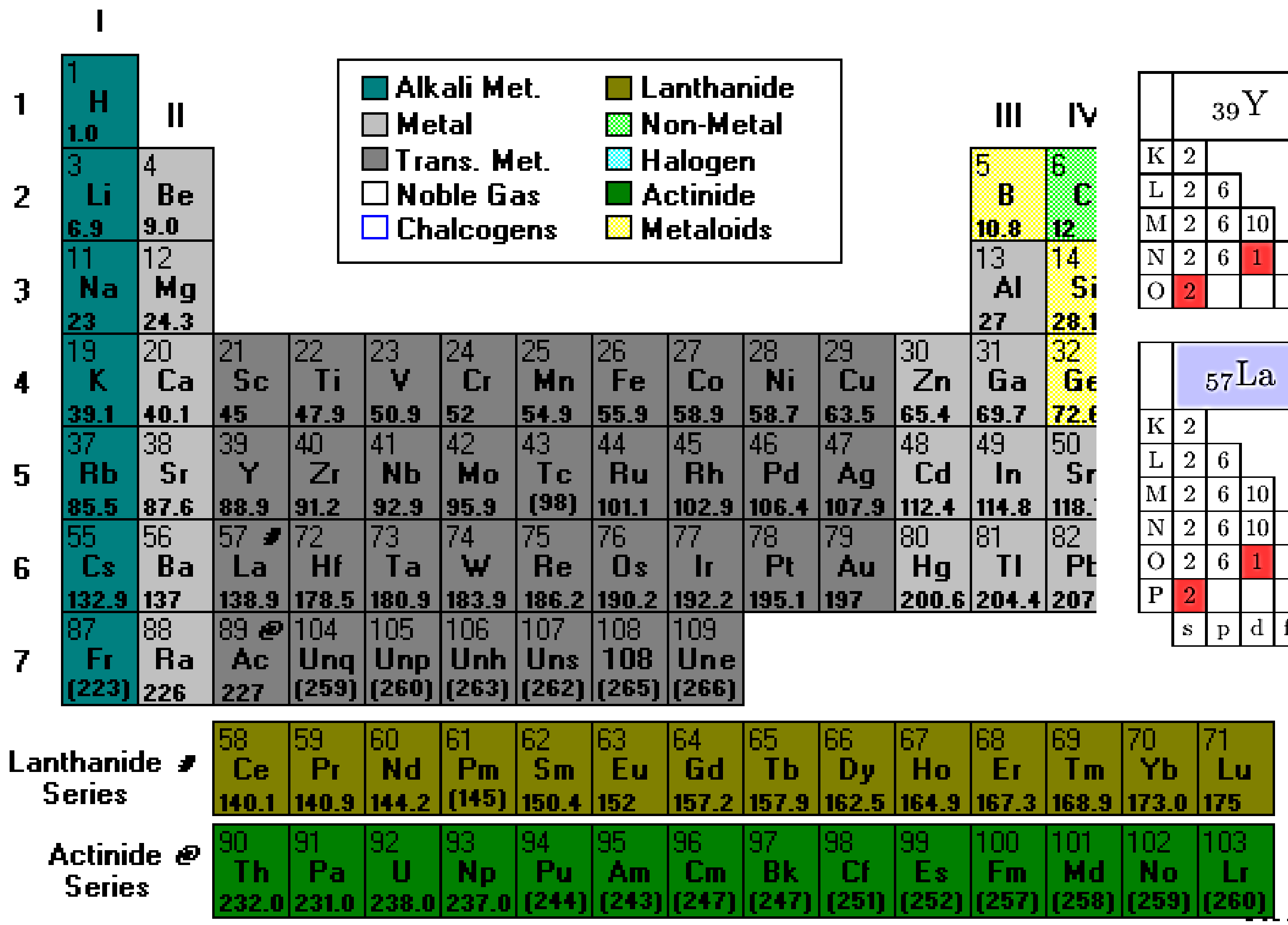
Name	Excitation mechanism
Photoluminescence	Light
Cathodoluminescence	Electrons
Radioluminescence	X-rays, α-, β-, or γ-rays
Thermoluminescence	Heating
Electroluminescence	Electric field or current
Triboluminescence	Mechanical energy
Sonoluminescence	Sound waves in liquids
Chemiluminescence and bioluminescence	Chemical reactions

Атомные орбитали



Формы s-, p-, d-, f- орбиталей в атоме водорода

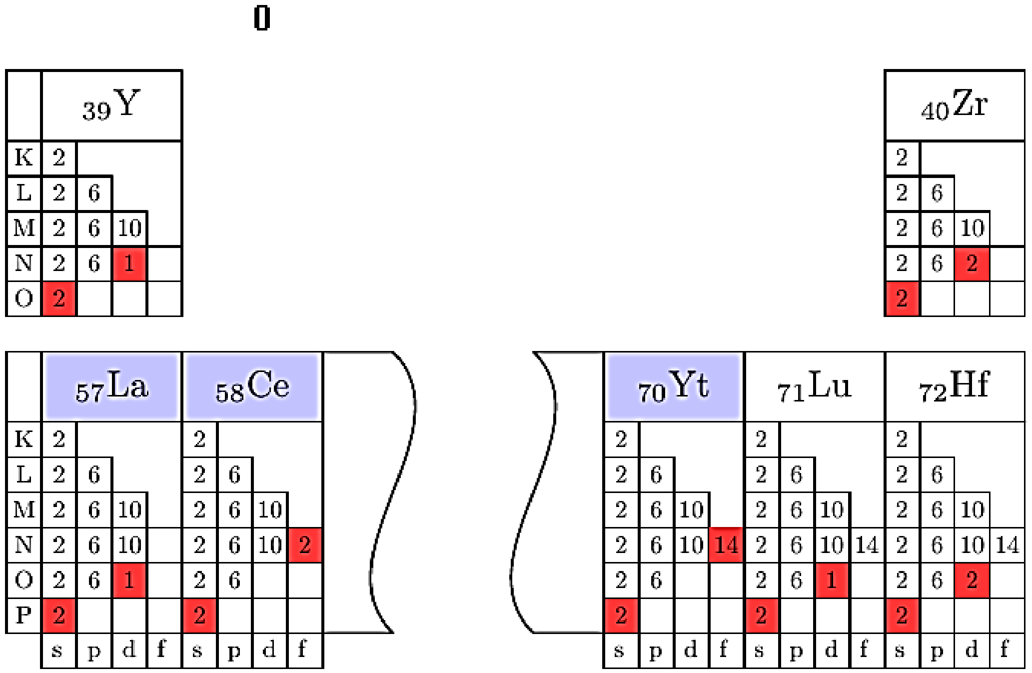
Люминофоры для белых светодиодов



	I	II											III	IV
1	1 H 1.0													
2	3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12
3	11 Na 23	12 Mg 24.3											13 Al 27	14 Si 28.1
4	19 K 39.1	20 Ca 40.1	21 Sc 45	22 Ti 47.9	23 V 50.9	24 Cr 52	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6
5	37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.
6	55 Cs 132.9	56 Ba 137	57 ✱ La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197	80 Hg 200.6	81 Tl 204.4	82 Pb 207
7	87 Fr (223)	88 Ra 226	89 @ Ac 227	104 Unq (259)	105 Unp (260)	106 Unh (263)	107 Uns (262)	108 108 (265)	109 Une (266)					

Lanthanide ✱ Series	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152	64 Gd 157.2	65 Tb 157.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175
Actinide @ Series	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

- 🟦 Alkali Met.
- ⬜ Metal
- ⬛ Trans. Met.
- ☐ Noble Gas
- ☐ Chalcogens
- 🟫 Lanthanide
- 🟩 Non-Metal
- 🟦 Halogen
- 🟩 Actinide
- 🟨 Metaloids



	$_{39}$Y			
K	2			
L	2	6		
M	2	6	10	
N	2	6	1	
O	2			

$_{40}$Zr			
2			
2	6		
2	6	10	
2	6	2	
2			

	$_{57}$La				$_{58}$Ce			
K	2				2			
L	2	6			2	6		
M	2	6	10		2	6	10	
N	2	6	10		2	6	10	2
O	2	6	1		2	6		
P	2				2			
	s	p	d	f	s	p	d	f

$_{70}$Yt				$_{71}$Lu				$_{72}$Hf			
2				2				2			
2	6			2	6			2	6		
2	6	10		2	6	10		2	6	10	
2	6	10	14	2	6	10	14	2	6	10	14
2	6			2	6	1		2	6	2	
2				2				2			
s	p	d	f	s	p	d	f	s	p	d	f

Люминофоры для белых светодиодов

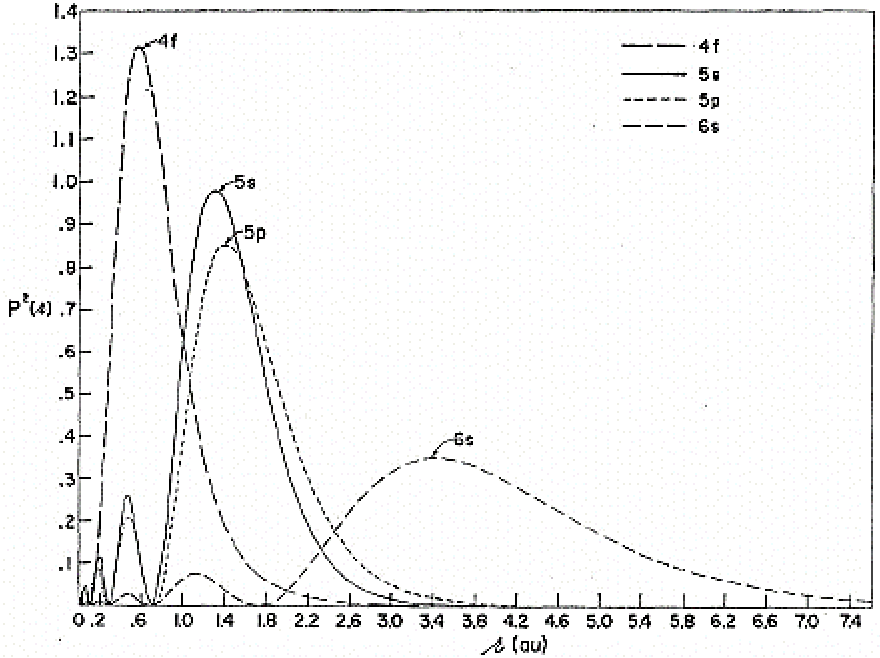
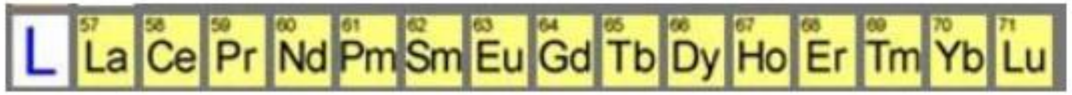


Figure 3.2: A theoretical prediction of the radial distribution of the orbitals of a rare-earth ion (Gd^+). The $4f$ orbital is seen to lie inside the $5s$ and $5p$ orbitals. Illustration from Ref. [28].

Редкоземельные ионы в материалах имеют валентность 2+, 3+ и 4+. Происходит заполнение экранированной 4f оболочки.

В трехвалентном состоянии La и Lu имеют закрытую f-оболочку

$[Xe]\ 4f^N\ 5s^2\ 5p^6;$

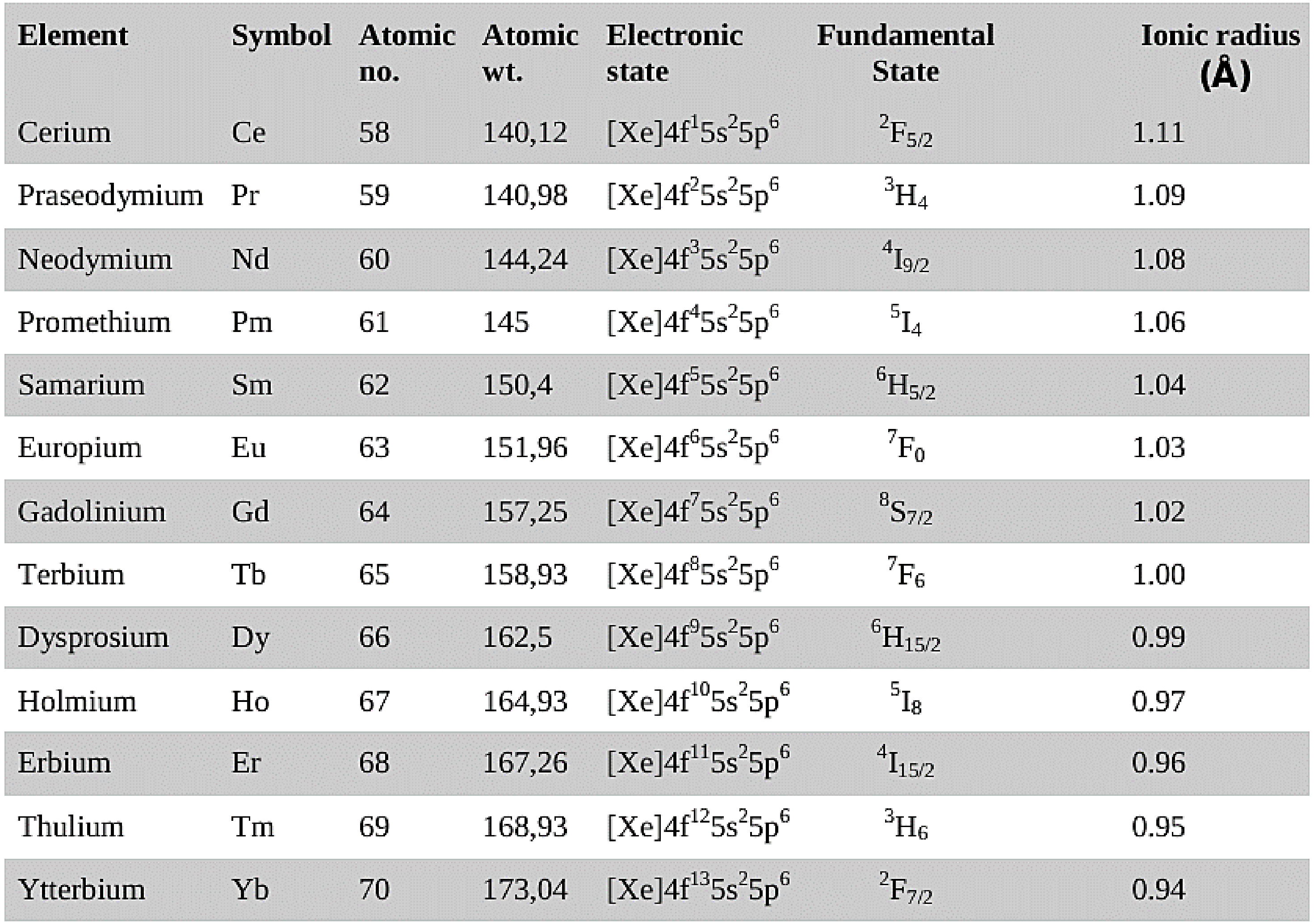


L	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

- La and Lu – closed outer shell (N = 0 and 14)

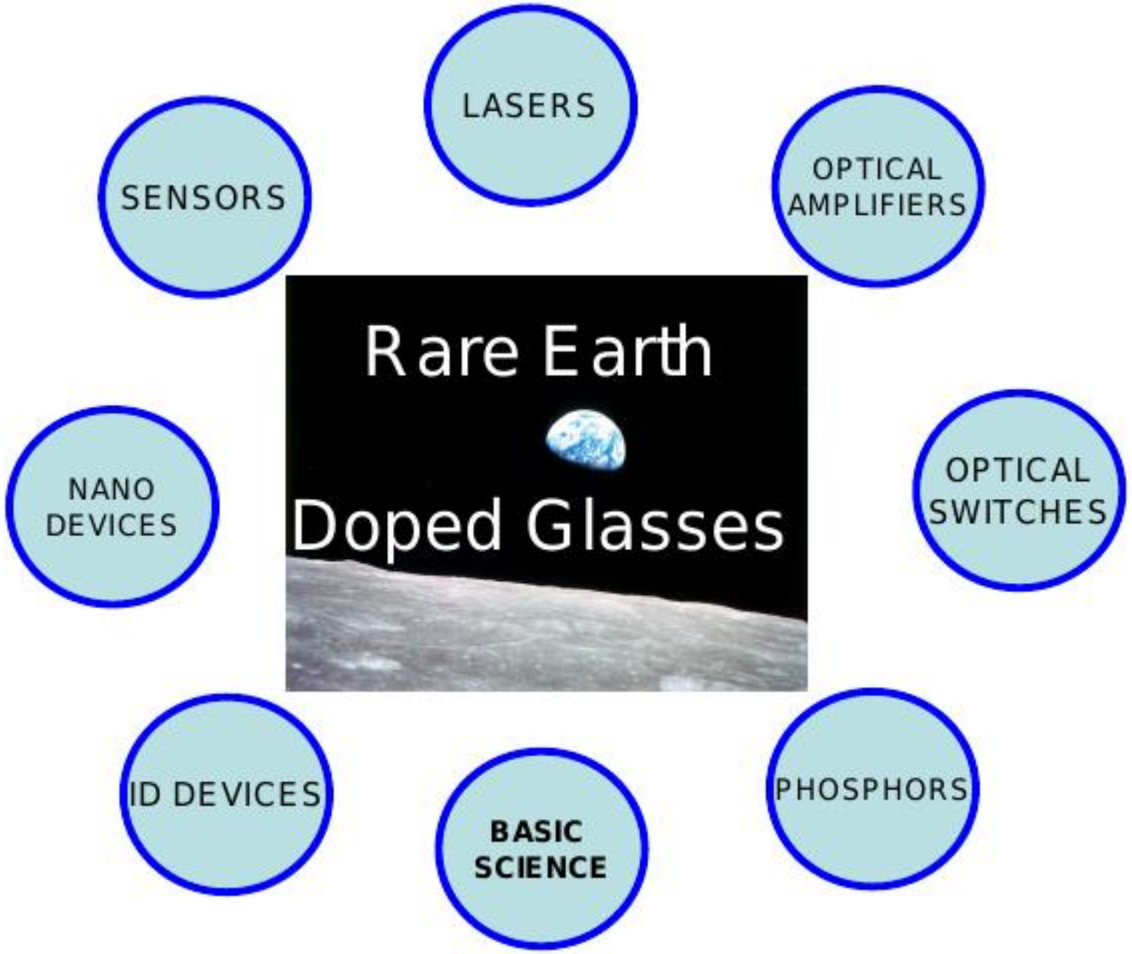
- All the others – outer shell 4f partially filled

Люминофоры для белых светодиодов

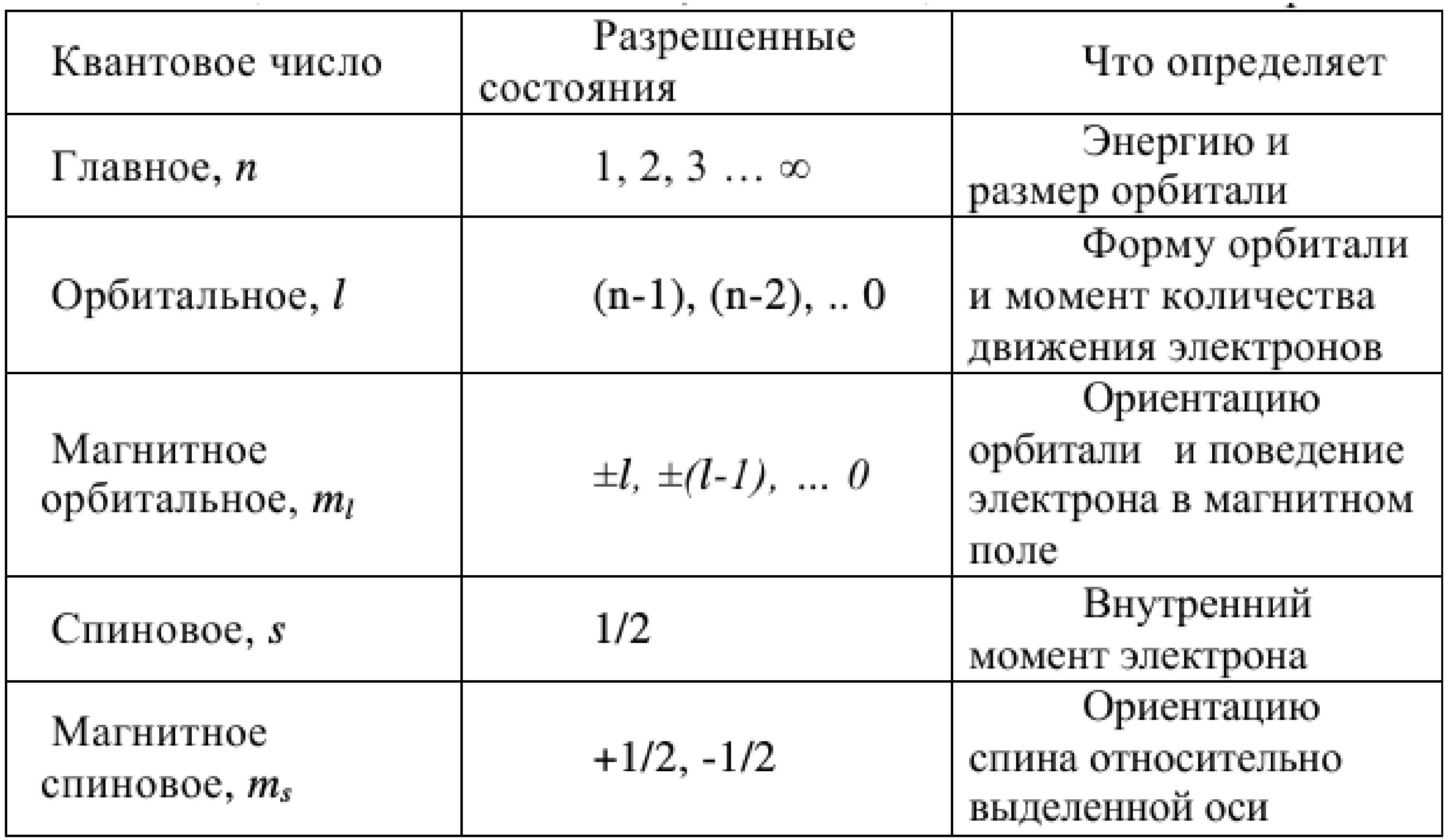


Element	Symbol	Atomic no.	Atomic wt.	Electronic state	Fundamental State	Ionic radius (Å)
Cerium	Ce	58	140,12	$[Xe]4f^1 5s^2 5p^6$	$^2F_{5/2}$	1.11
Praseodymium	Pr	59	140,98	$[Xe]4f^2 5s^2 5p^6$	$^3H_4$	1.09
Neodymium	Nd	60	144,24	$[Xe]4f^3 5s^2 5p^6$	$^4I_{9/2}$	1.08
Promethium	Pm	61	145	$[Xe]4f^4 5s^2 5p^6$	$^5I_4$	1.06
Samarium	Sm	62	150,4	$[Xe]4f^5 5s^2 5p^6$	$^6H_{5/2}$	1.04
Europium	Eu	63	151,96	$[Xe]4f^6 5s^2 5p^6$	$^7F_0$	1.03
Gadolinium	Gd	64	157,25	$[Xe]4f^7 5s^2 5p^6$	$^8S_{7/2}$	1.02
Terbium	Tb	65	158,93	$[Xe]4f^8 5s^2 5p^6$	$^7F_6$	1.00
Dysprosium	Dy	66	162,5	$[Xe]4f^9 5s^2 5p^6$	$^6H_{15/2}$	0.99
Holmium	Ho	67	164,93	$[Xe]4f^{10} 5s^2 5p^6$	$^5I_8$	0.97
Erbium	Er	68	167,26	$[Xe]4f^{11} 5s^2 5p^6$	$^4I_{15/2}$	0.96
Thulium	Tm	69	168,93	$[Xe]4f^{12} 5s^2 5p^6$	$^3H_6$	0.95
Ytterbium	Yb	70	173,04	$[Xe]4f^{13} 5s^2 5p^6$	$^2F_{7/2}$	0.94

Люминофоры для белых светодиодов. Редкоземельные элементы



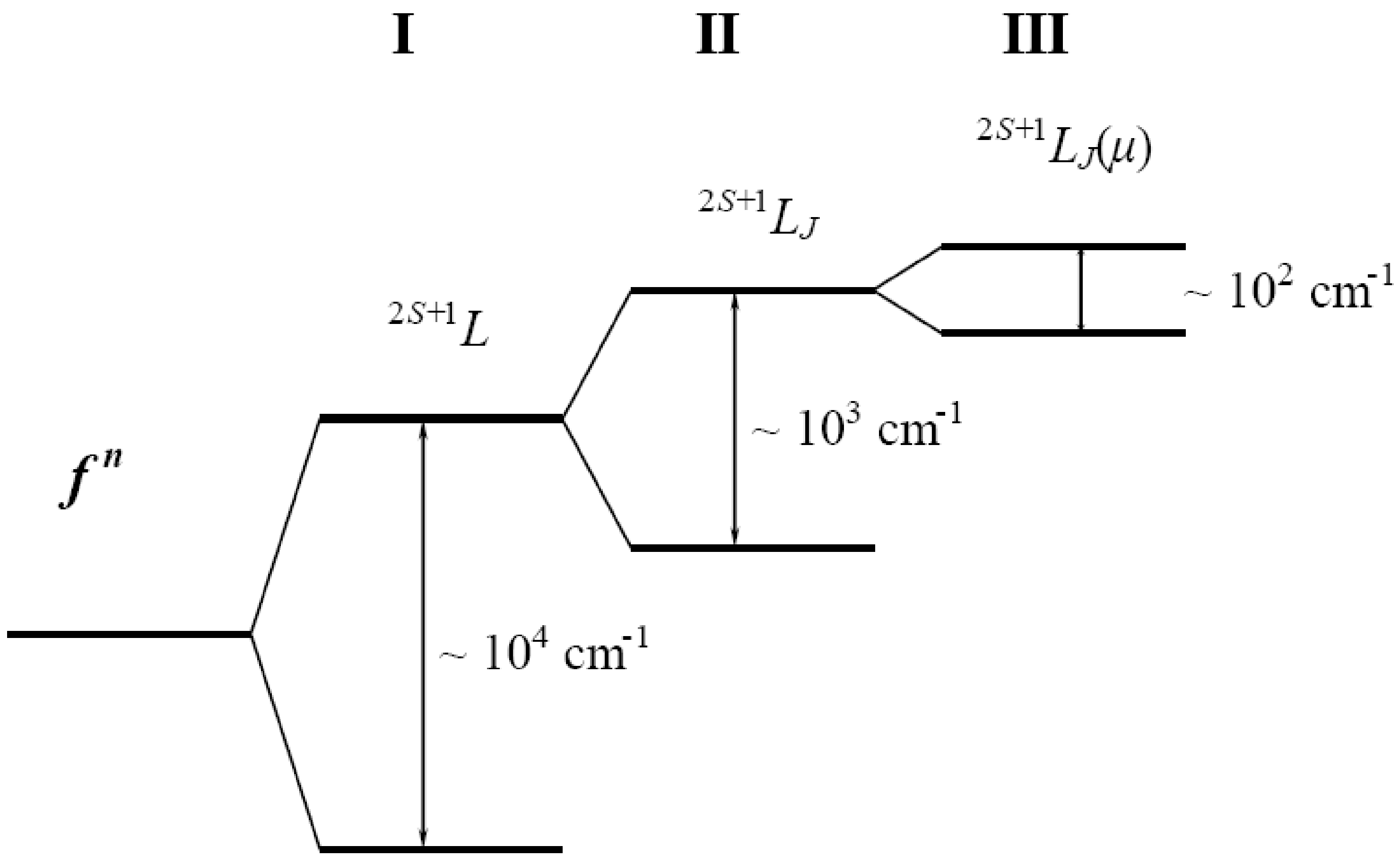
Квантовые числа



Квантовое число	Разрешенные состояния	Что определяет
Главное, n	1, 2, 3 … ∞	Энергию и размер орбитали
Орбитальное, l	(n-1), (n-2), .. 0	Форму орбитали и момент количества движения электронов
Магнитное орбитальное, m_l	$\pm l, \pm(l-1), \ldots 0$	Ориентацию орбитали и поведение электрона в магнитном поле
Спиновое, s	1/2	Внутренний момент электрона
Магнитное спиновое, m_s	+1/2, -1/2	Ориентацию спина относительно выделенной оси

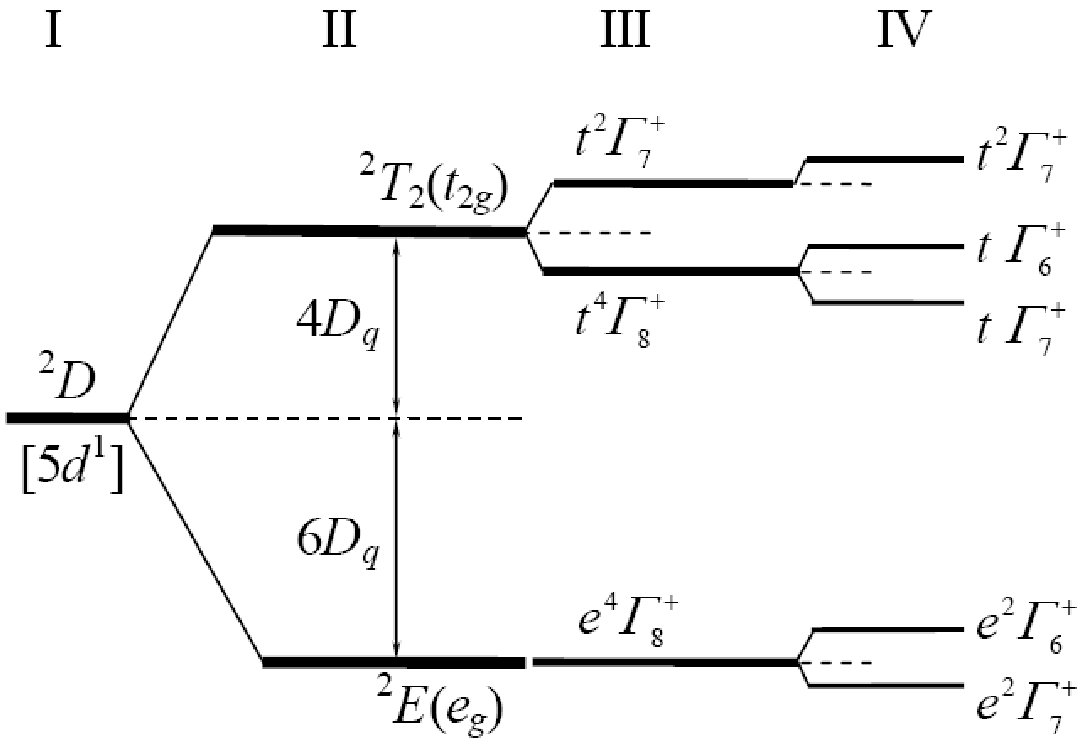
Расщепление 4f уровней

Splitting of energy levels of 4f^n electronic configuration due to: I – Coulomb interaction; II – spin-orbit interaction; III – crystal-field interaction



Crystal field splitting for 4f^{n-1}5d electronic configuration

The 5*d* electrons are not effectively shielded by other electrons, and the crystal field influence on the energy levels of 4f^{n-1}5d electronic configuration is **strong**. Accordingly, crystal field splitting of 5*d* levels is large and the energies of levels within 4f^{n-1}5d electronic configuration can strongly differ for different crystal hosts.



Crystal-field splitting of 5d^1 configuration for tetragonal Ce^{3+} center:
I – free ion, II – O_h, III – O_h + spin-orbit, IV – C_{4V}

Спин-орбитальное взаимодействие. Расщепление f-состояния

G. H. Dieke and
H. M. Crosswhite
Appl. Opt. 2, 675 (1963)

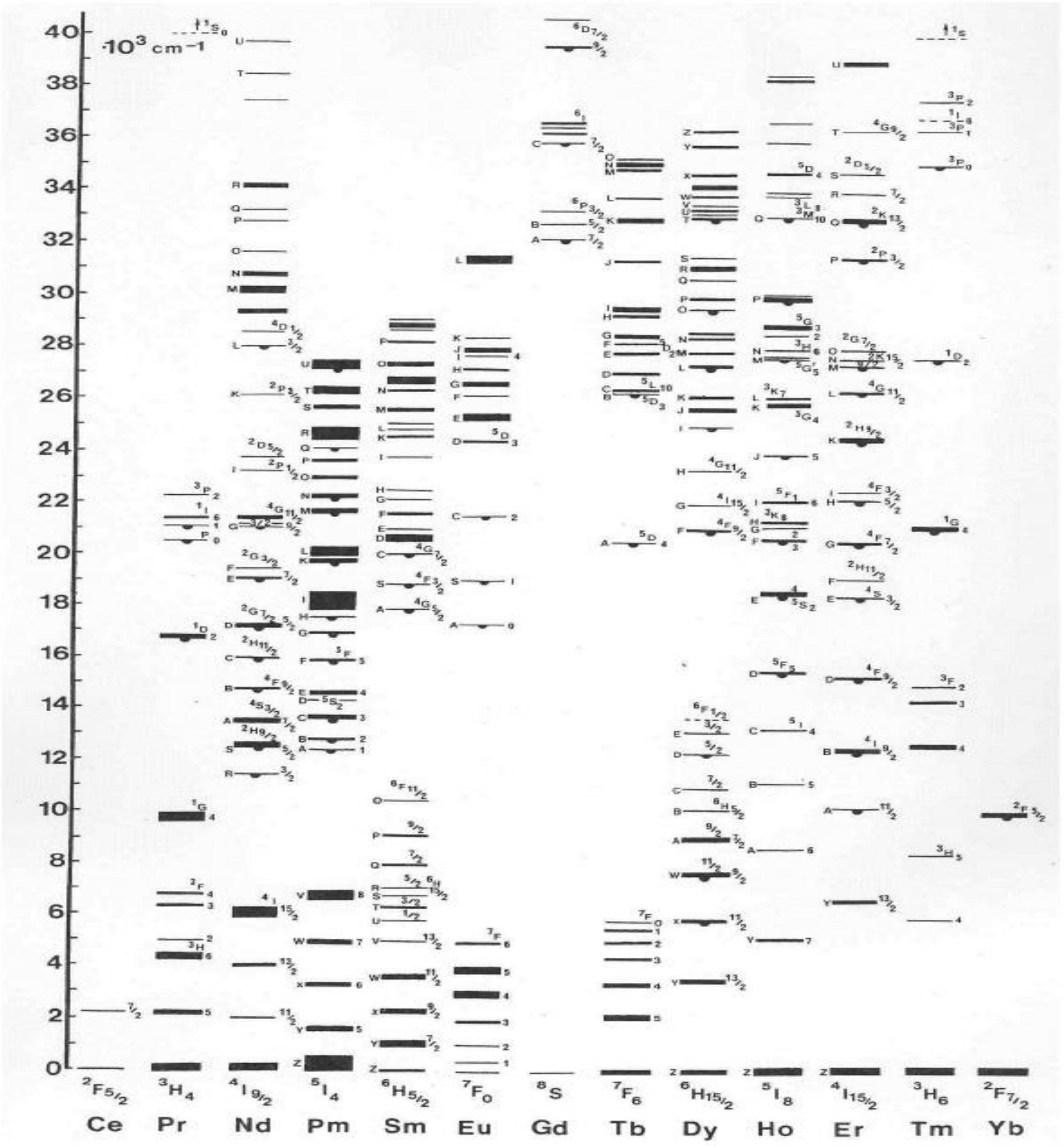
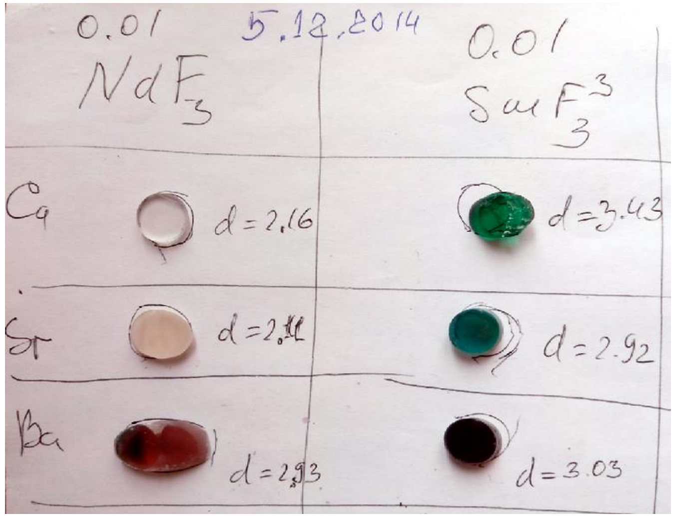


Рис.4.10. Диаграмма уровней энергии трехвалентных лантаноидов. Знаком полукруга под уровнем обозначены состояния с которых наблюдалось свечение.

Спектры RE^{2+}



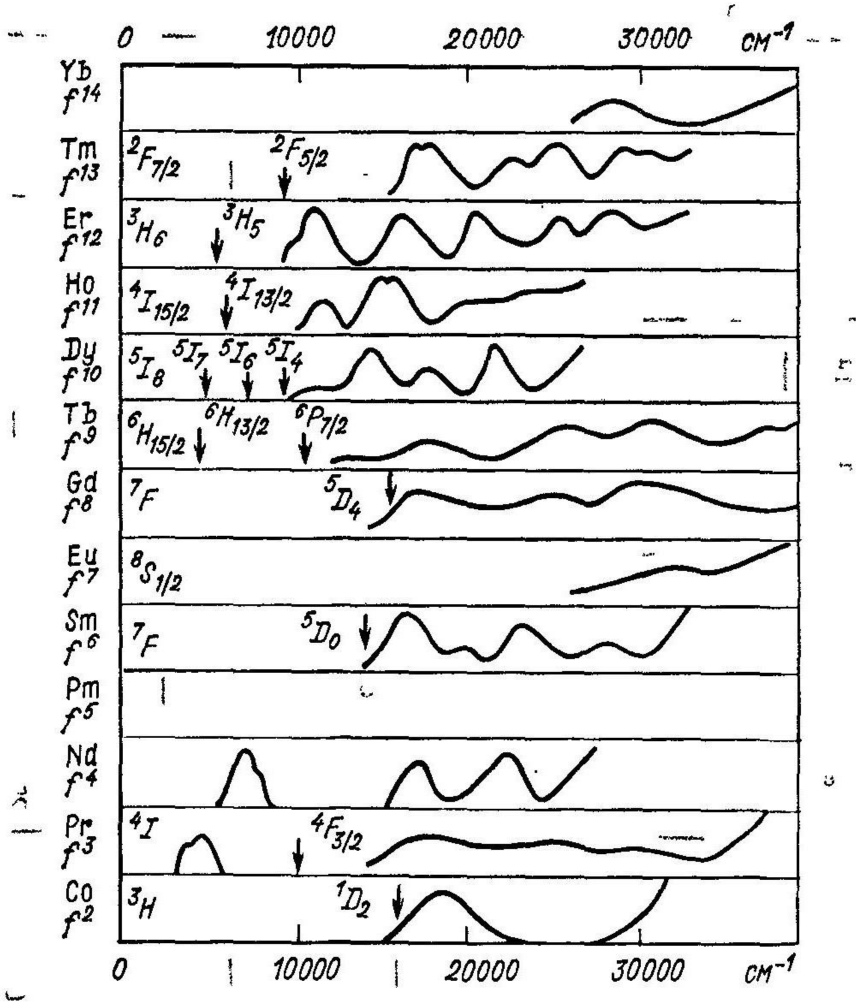
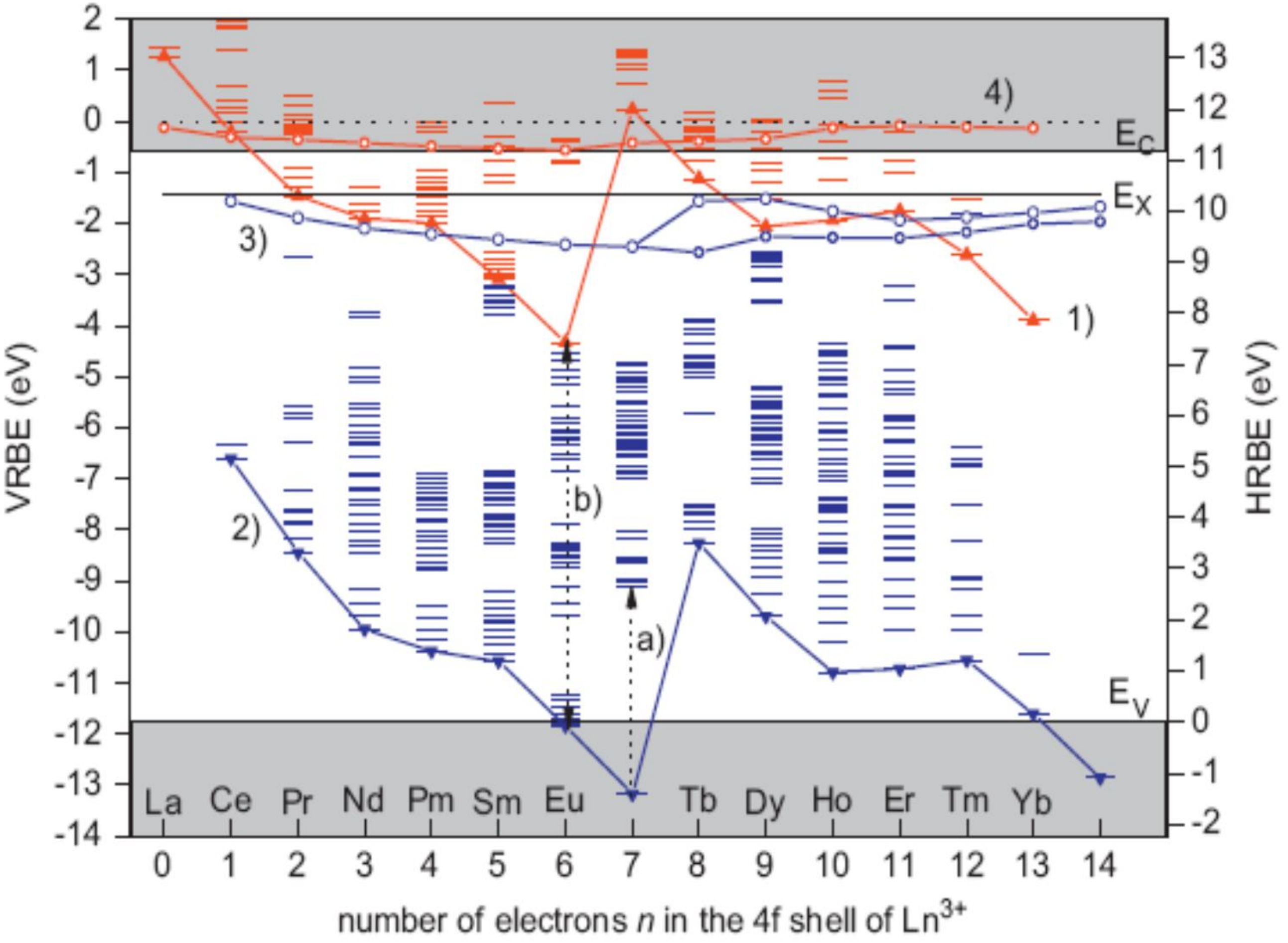


Рис. 33.41. Спектры поглощеиия ионов двухвалентных редкоземельных элементов в кристалле CaF$_2$ [6]. Положение переходов $f \rightarrow f$ указано стрелкой.

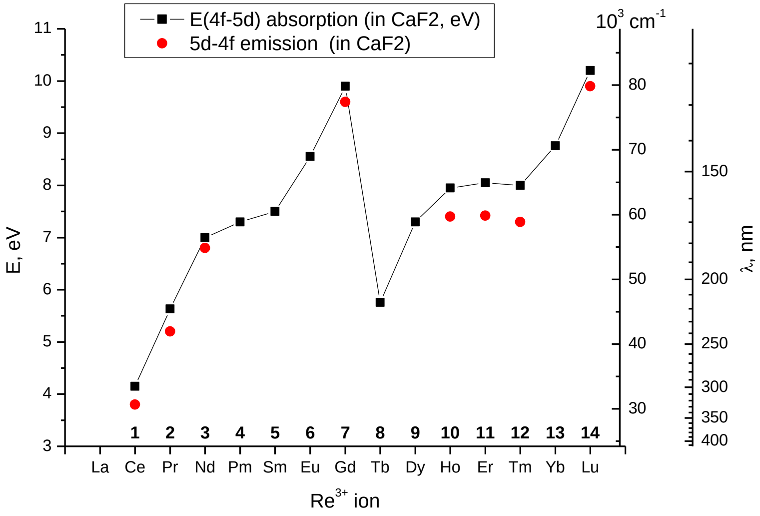
Уровни лантаноидов в кристалле

Положение основных 4f уровней и наинизших возбужденных 5d-уровней редкоземельных трехвалентных (RE^{3+}) и двухвалентных (RE^{2+}) ионов в зонной схеме кристалла фторида лантана. Верхняя зона – зона проводимости, нижняя зона – валентная зона.

P.Dorenbos, J. luminescence, 2013, 135, 93-104



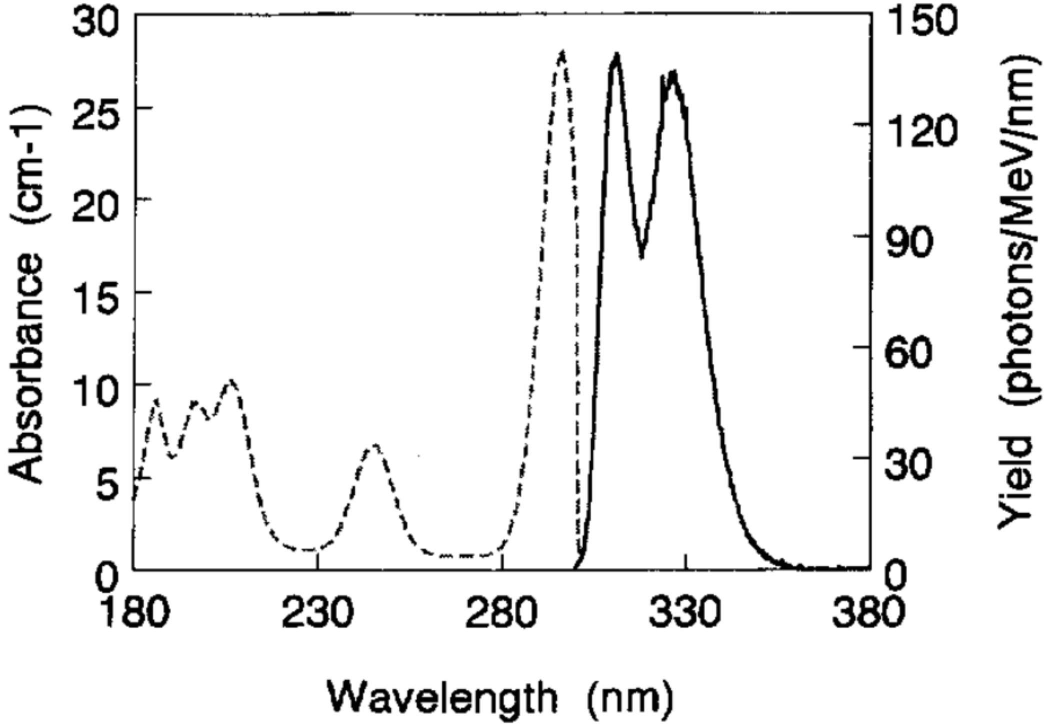
Свечение Re^{3+} в щелочно-земельных фторидах

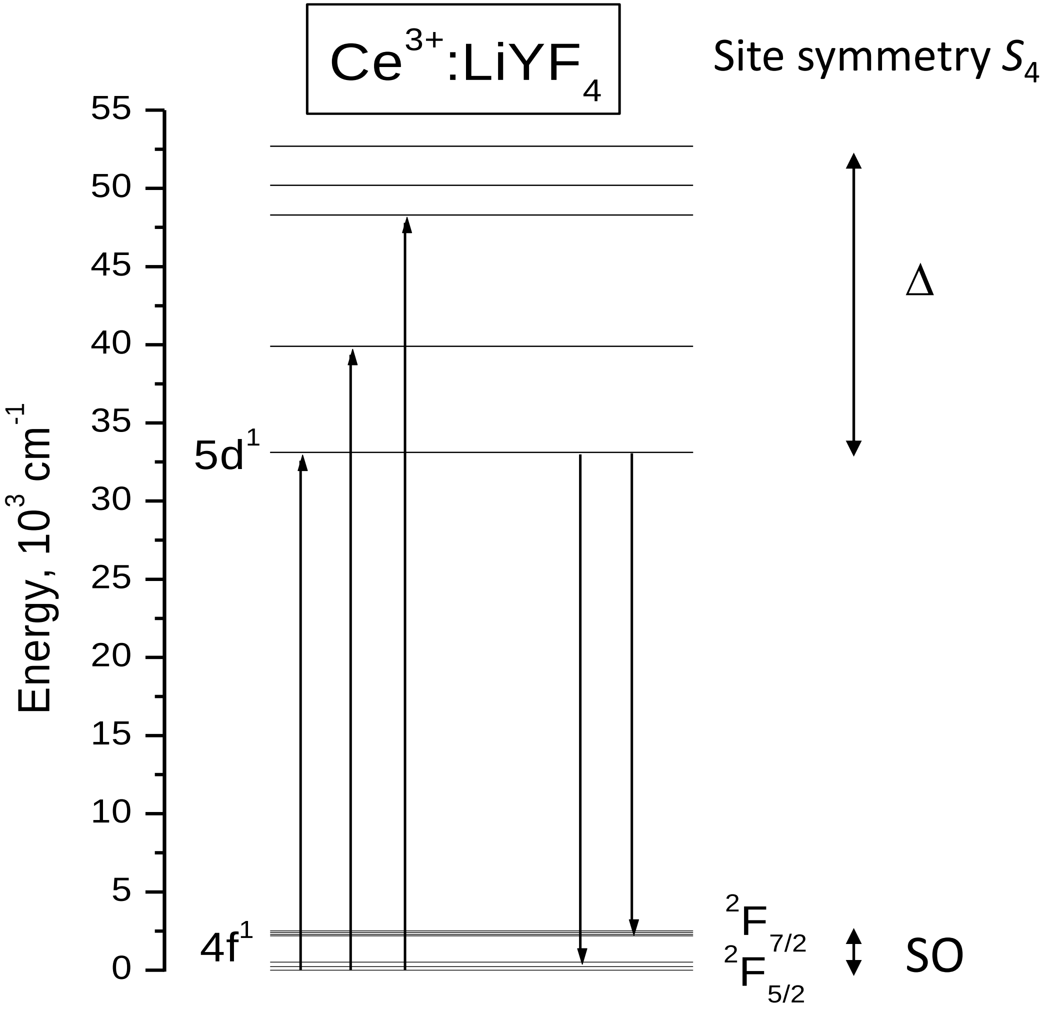


Crystal	Tm (5d→ $^3H_6$), nm	Er (5d→$^4I_{15/2}$), nm	Nd (5d→$^4I_{9/2}$), nm	Gd (5d→$^4I_{9/2}$), nm	Ho (5d→$^4I_{9/2}$), nm	Sm (5d→$^4I_{9/2}$), nm
CaF_2	168,4	166,0	183,9 17.7 ns	128.9 129 [2]	168.5	171.1
SrF_2	166,4 167 HS[1]	164,2 164.5 HS[1]	180,0 15.3 ns	No	167.2	172.0
BaF_2	164,6	163,7	179,2 12.3 ns	No	165.9	174.1

1 Ivanovskih et al Journal of Luminescence 122–123 (2007) 28–31
2 V.N.Makhov et.al. ФТТ (2008) 50 1565

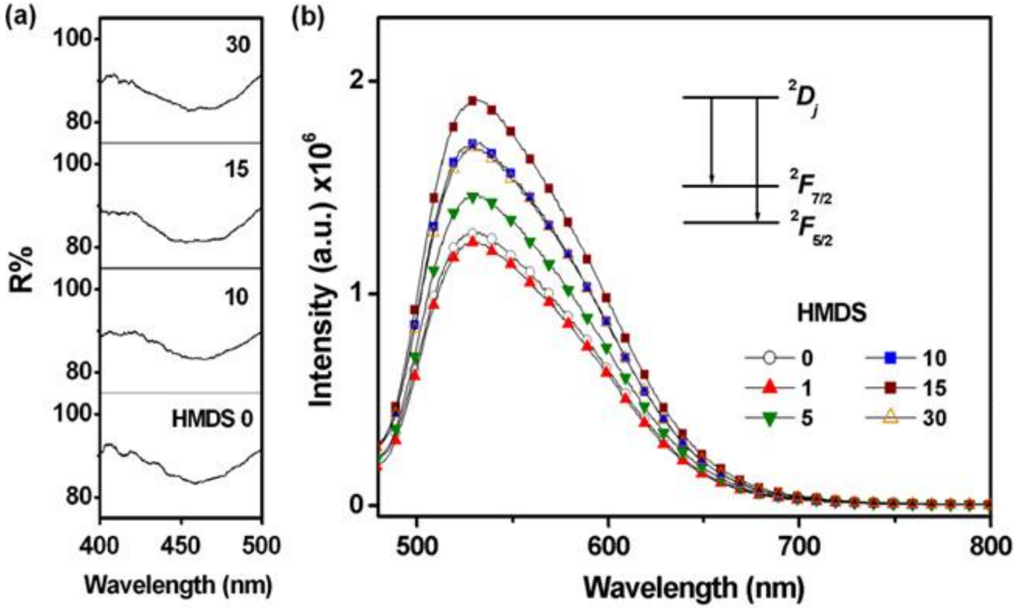
4f and 5*d* уровни ионов Ce^{3+} в тетрагональном окружении



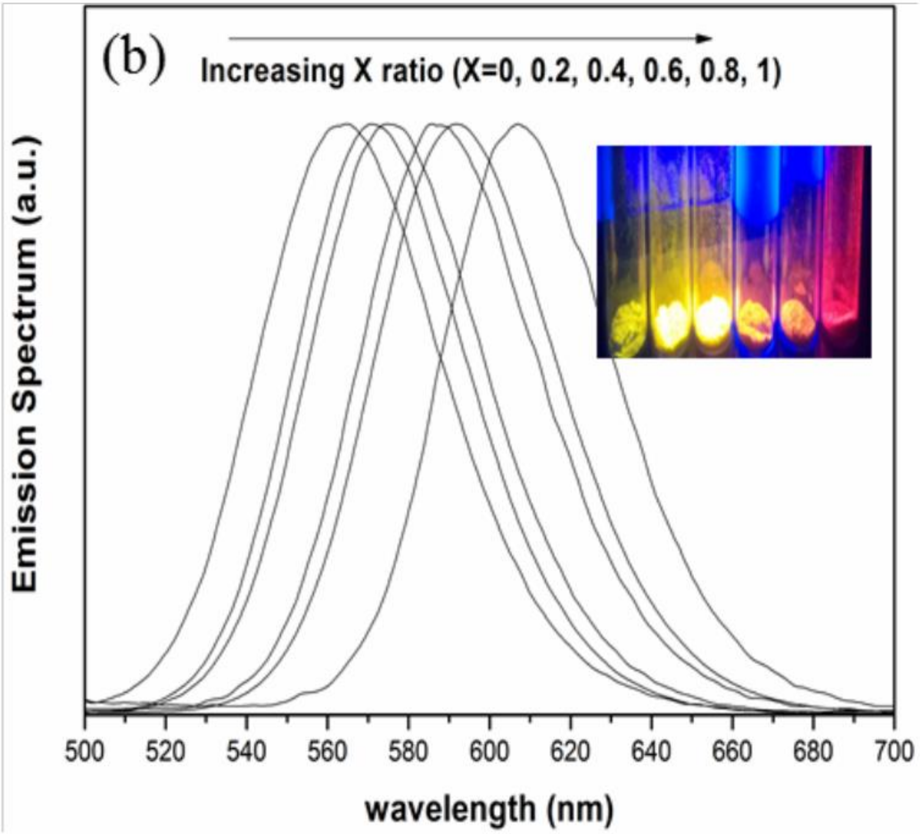


Люминофоры с редкоземельными ионами

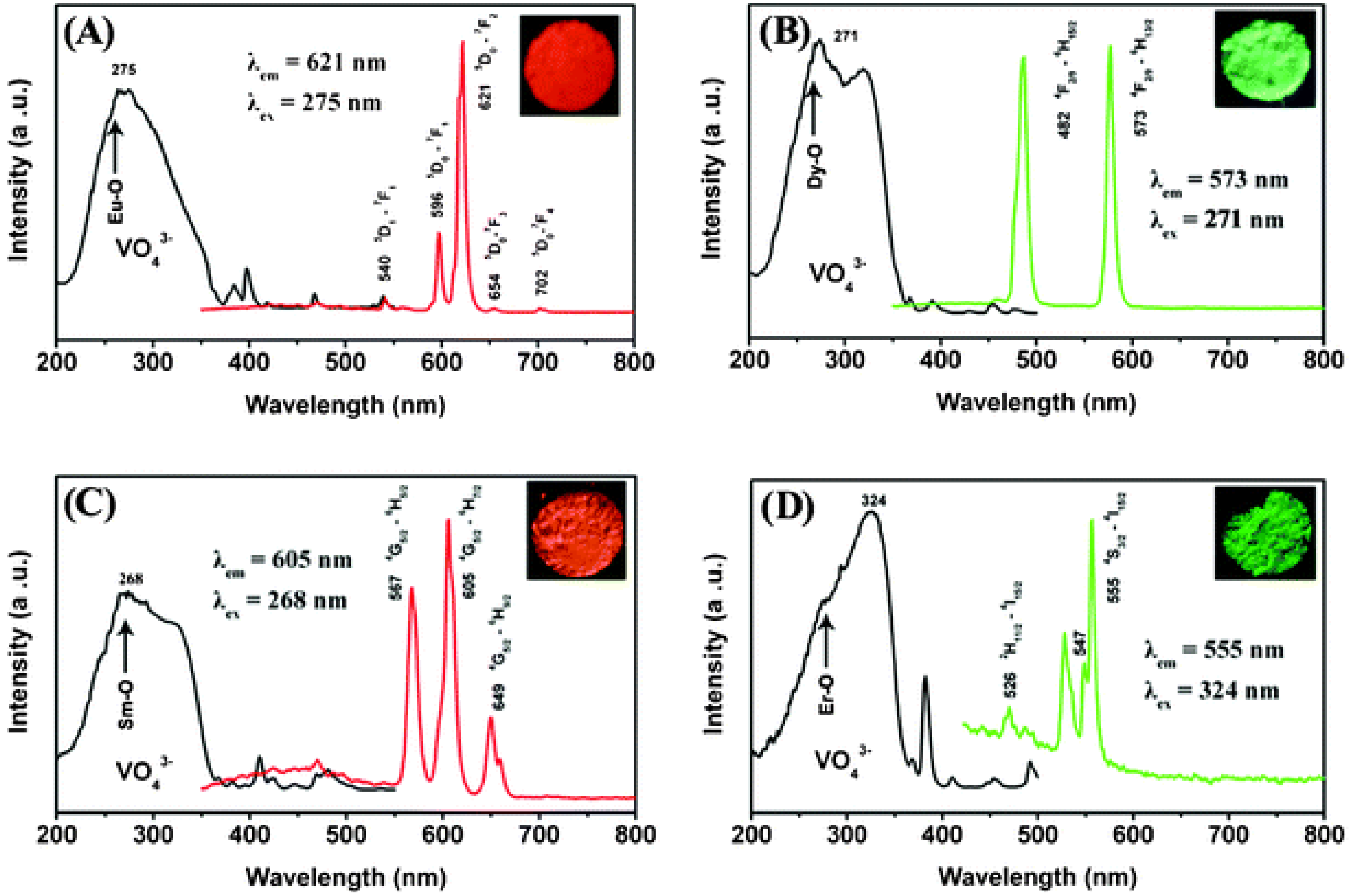
Ионы церия



$Sr_{1-x}Ca_xSe:Eu^{2+}$

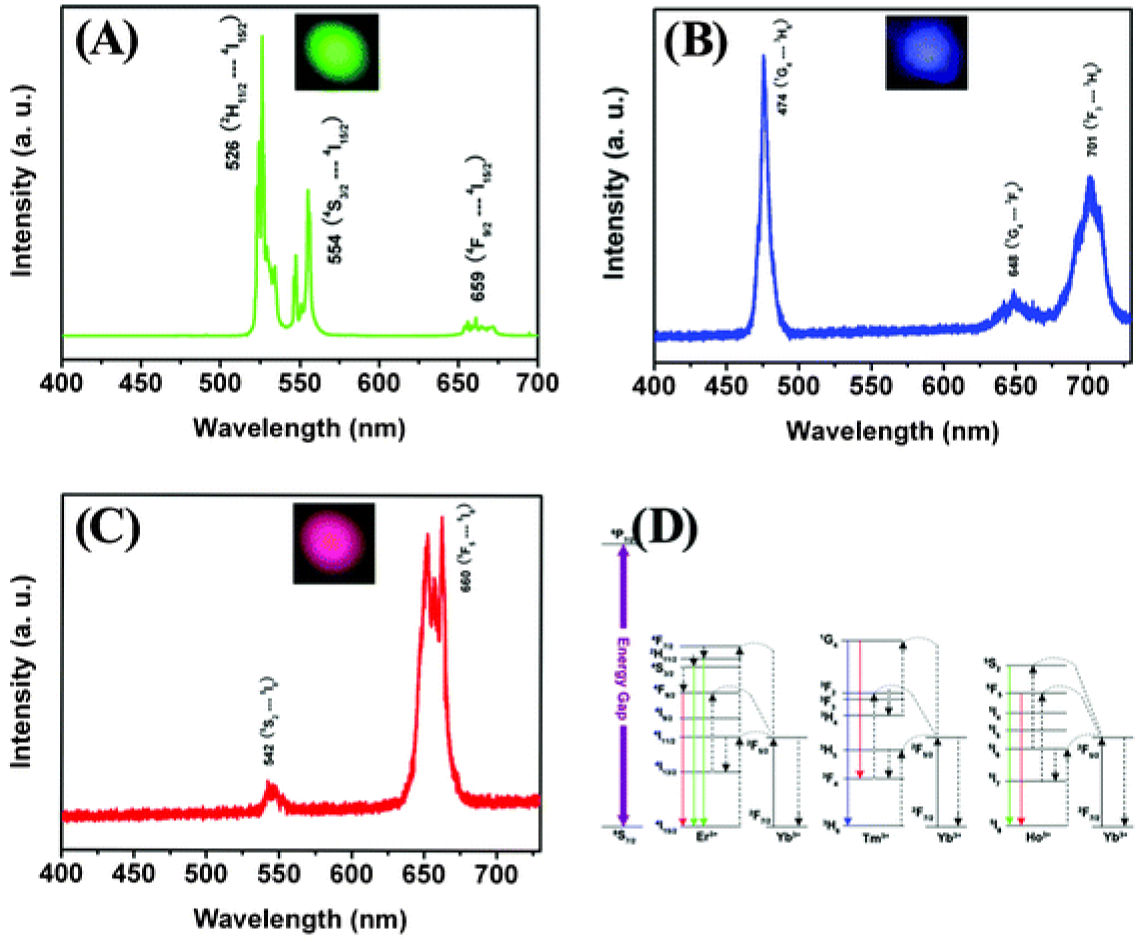


Люминофоры с редкоземельными ионами



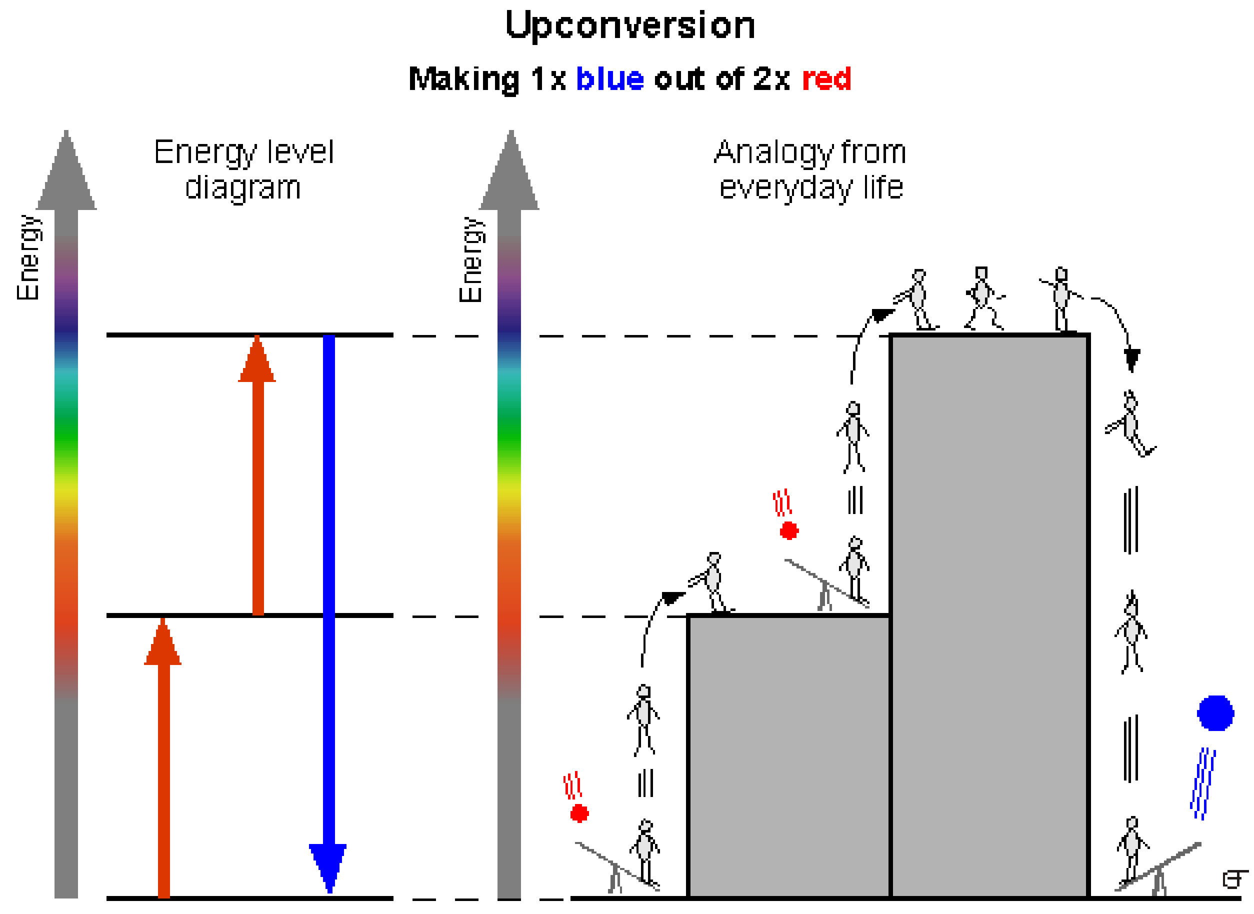
Excitation and emission spectra of LuVO4:5 mol% Eu3+ (A), LuVO4:5 mol% Dy3+ (B), LuVO4:5 mol% Sm3+ (C), and LuVO4:5 mol% Er3+ (D). The insets are the corresponding luminescence photographs of the samples upon excitation at 254 nm with a UV lamp.

Люминофоры с редкоземельными ионами

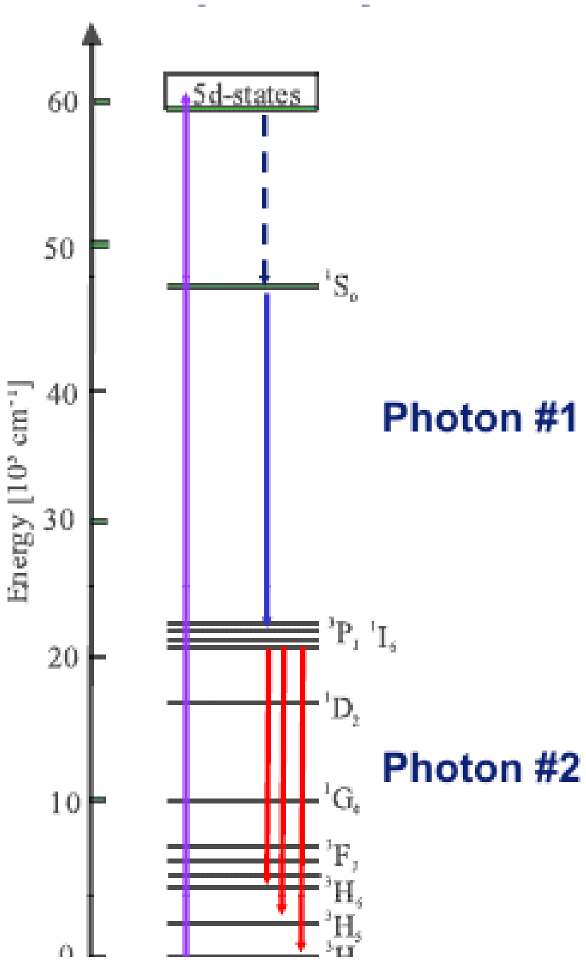


NIR-to-visible UC emission spectra of LuVO4:Yb3+/Er3+ (A), LuVO4:Yb3+/Tm3+ (B), and LuVO4:Yb3+/Ho3+ (C) under 980 nm laser excitation. (D) The proposed energy transfer mechanisms under 980 nm diode laser excitation in LuVO4:Yb3+/Er3+, LuVO4:Yb3+/Tm3+, and LuVO4:Yb3+/Ho3+. The insets are the corresponding luminescence photographs of the samples upon excitation at 980 nm light.

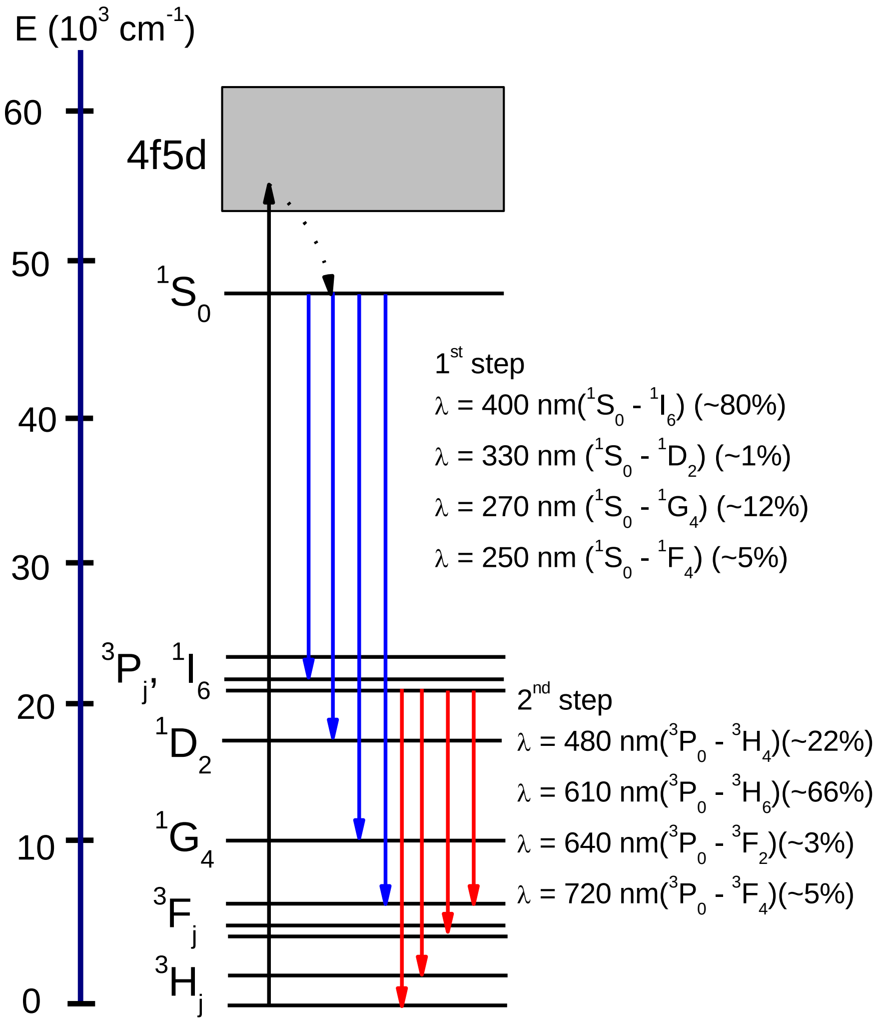
Люминофоры с редкоземельными ионами. Upconversion and cascade emission



Квантовый выход больше 1



Каскадное свечение Pr^{3+} в кристалле YF_3



Pr^{3+} ion

Configuration – $4f^2$

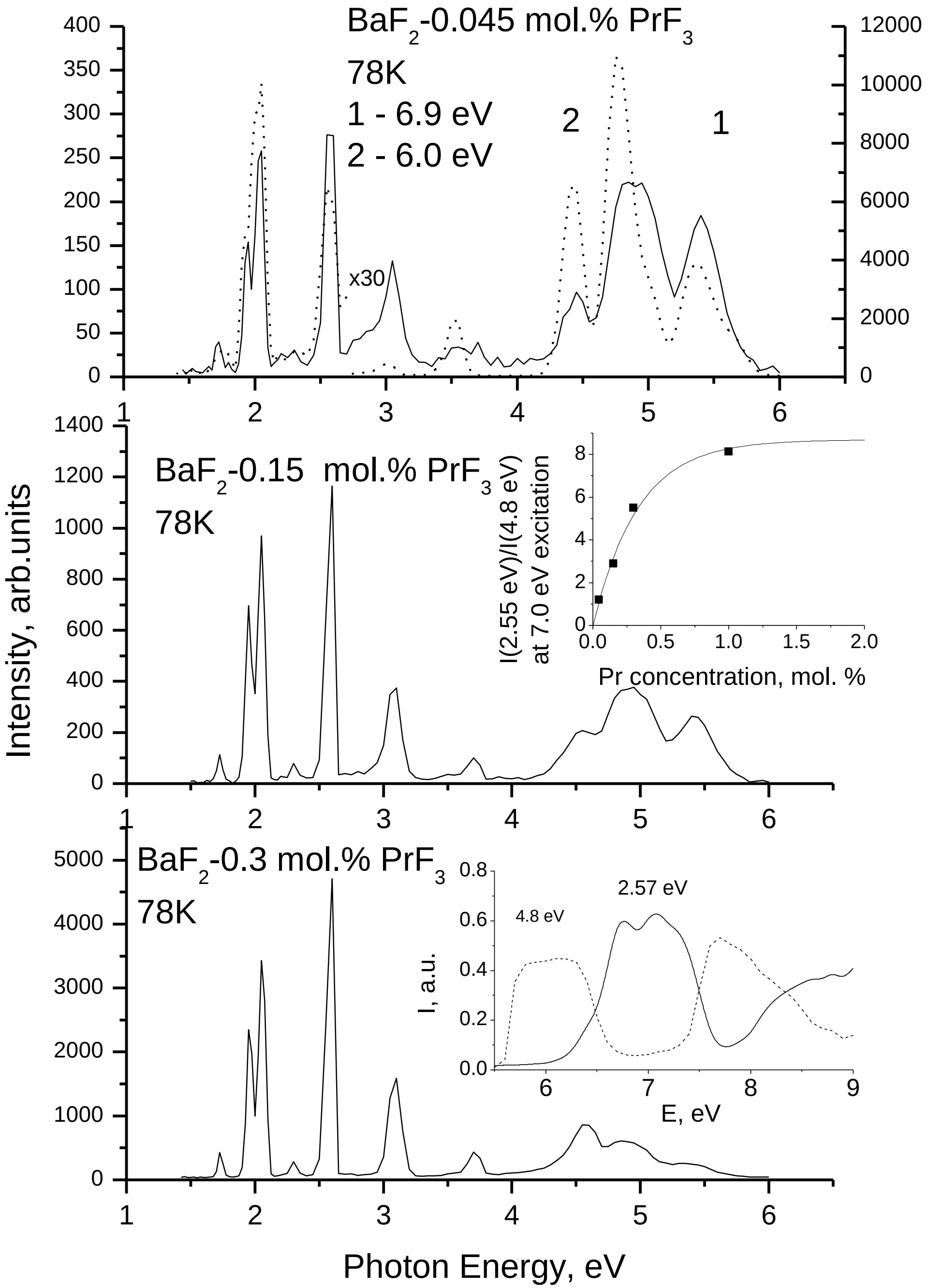
Singlet $^1S_0$, $^1D_2$, $^1G_4$, $^1I_6$

Triplet $^3P_{0,1,2}$ $^3F_{2,3,4}$ $^3H_{4,5,6}$

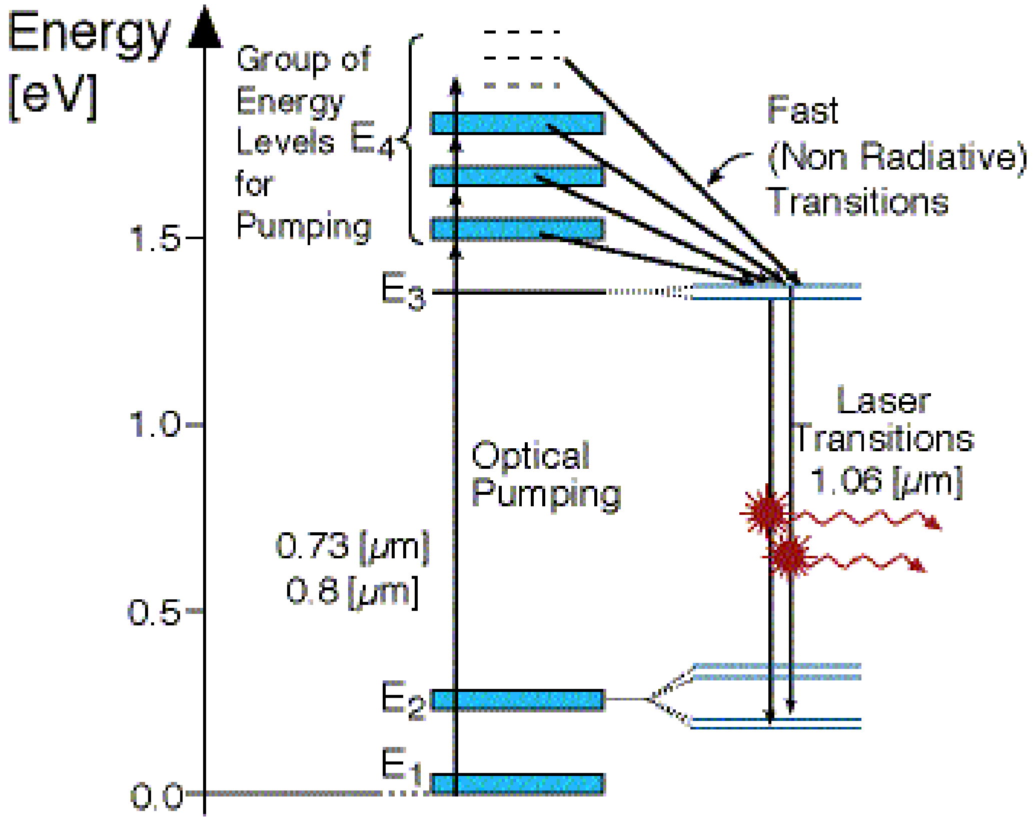
Energy-level scheme of Pr^{3+} in YF_3. The transition branching ratios for the main transitions of the cascade are also given (from S.Kusk, et.al. PHYSICAL REVIEW B 71, 165112 (2005))

Emission
BaF_2

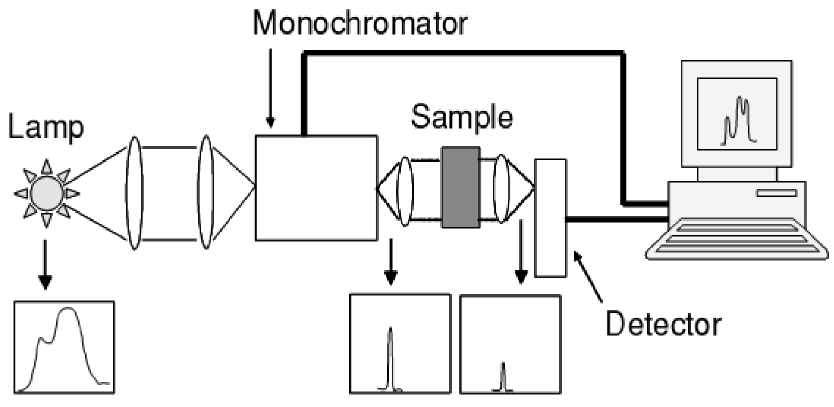
Emission spectra of BaF_2 crystal doped by PrF_3 at 78 K. Samples were excited at 6.9 eV (full curves) or at 6.0 eV (dotted curve). Middle right inset – Pr concentration dependence of intensities I(2.5 eV)/I(4.8 eV) ratio at 6.9 eV excitation at 78 K. Bottom right inset - excitation spectra of BaF_2-0.3 mol.\% PrF_3 for emission bands at 2.57 and 4.8 eV at temperature 78 K. No measurable emission was observed inBaF_2-0.015 % PrF_3 under 7.0 eV excitation at 90 K.



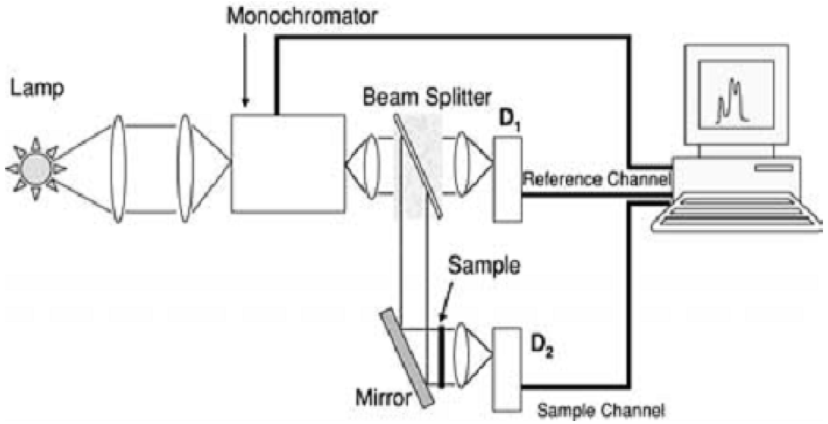
Свечение Nd3+. Nd-YAG лазеры



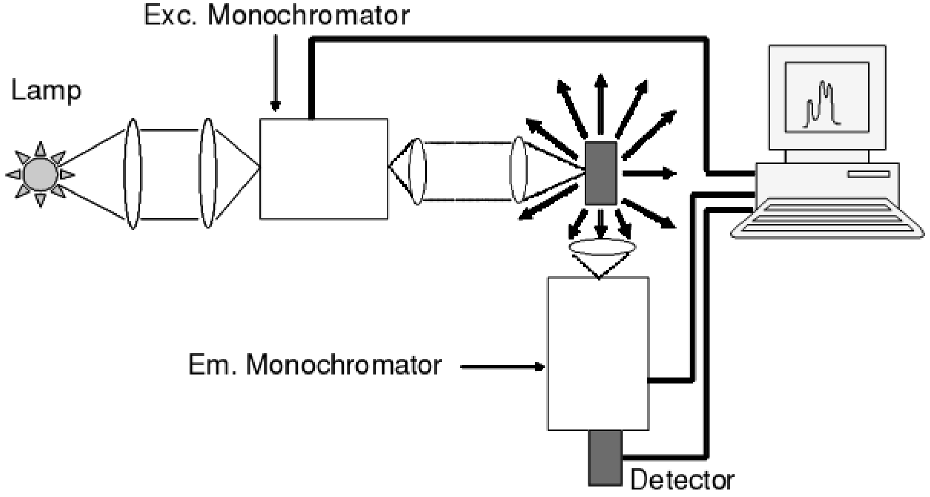
Измерение спектров



(a)



$$T = I/I_0 \qquad OD = \log(I_0/I),$$

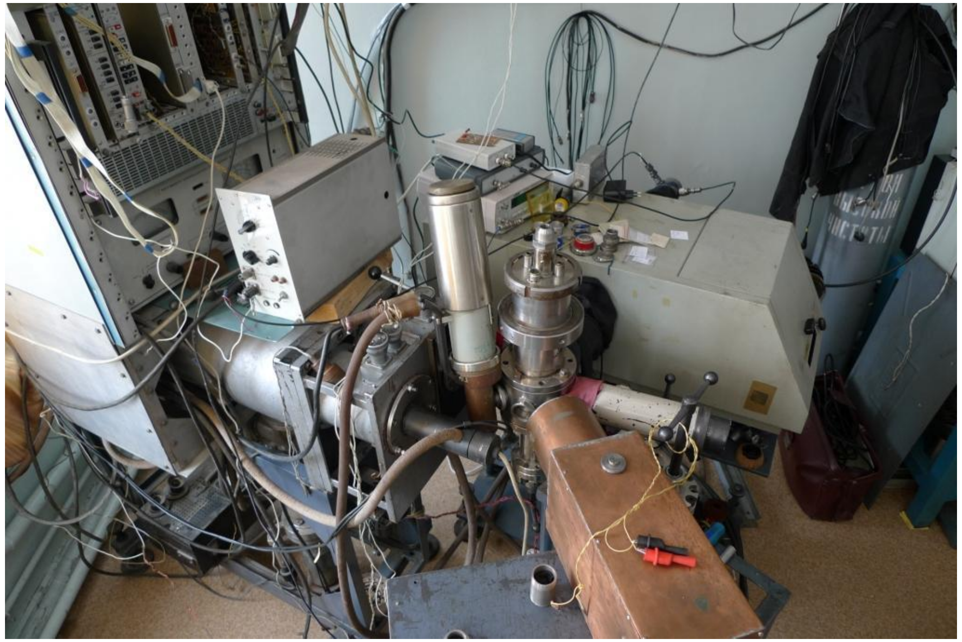


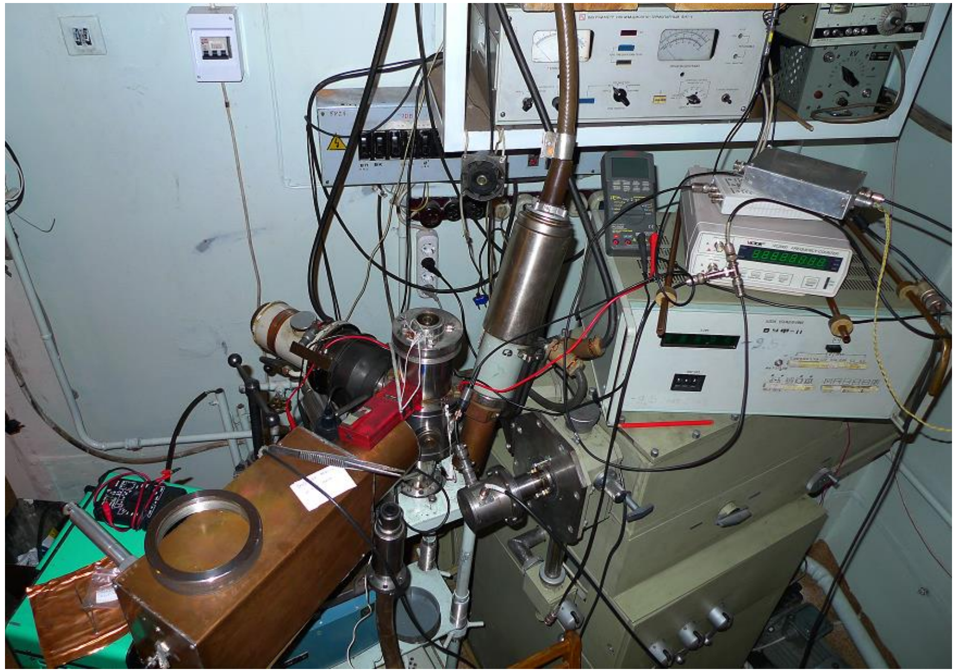
$$I_{\mathrm{em}} = \eta(I_0 - I)$$

$$(I_{\mathrm{em}}) = k_g \times \eta \times I_0(1 - 10^{-(OD)})$$

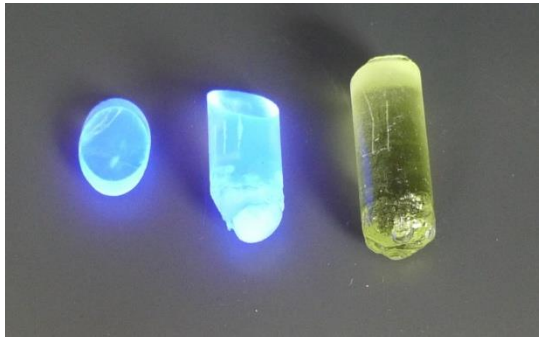
$$(I_{\mathrm{em}}) \cong k_g \times \eta \times I_0 \times (OD)$$

Спектрометры вакуумного ультрафиолета



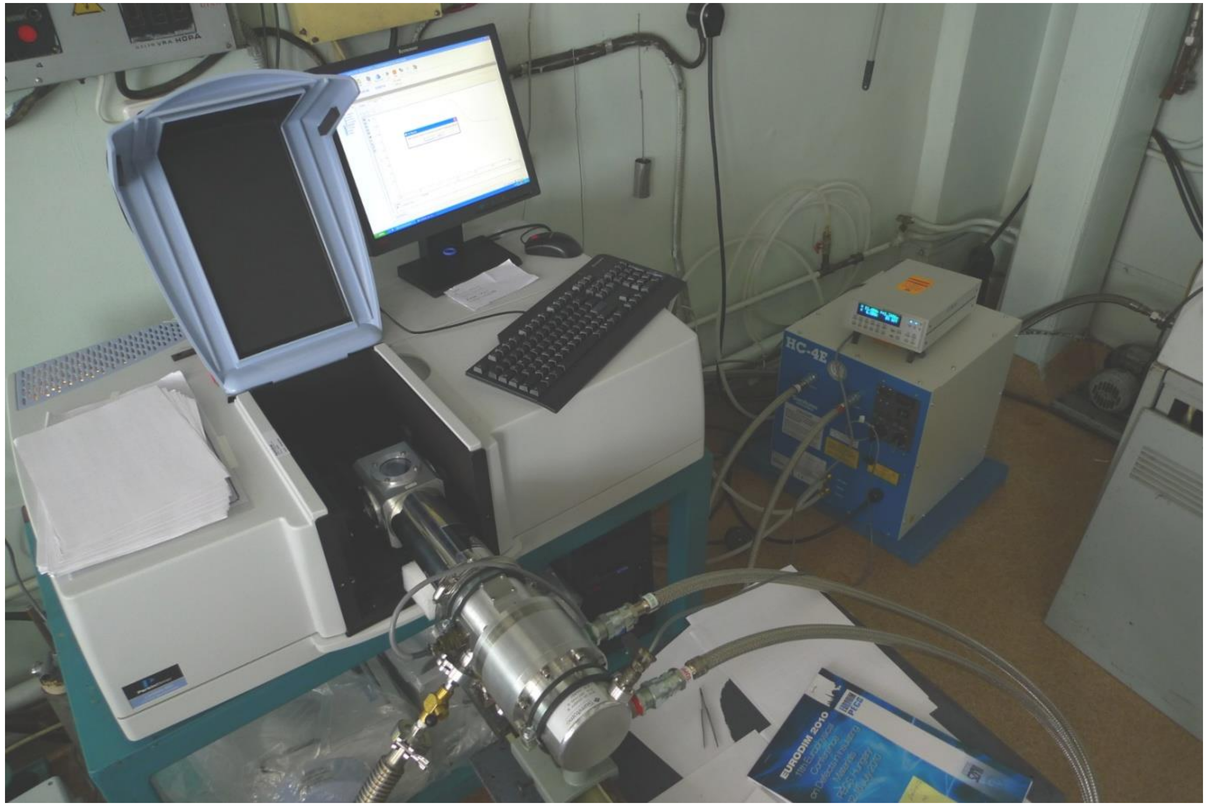


CaF_2 -0.1 моль.% EuF_3



CaF_2 -1 моль.% PrF_3

Спектрофотометр L950,
спектрометр LS55




Спектры поглощения

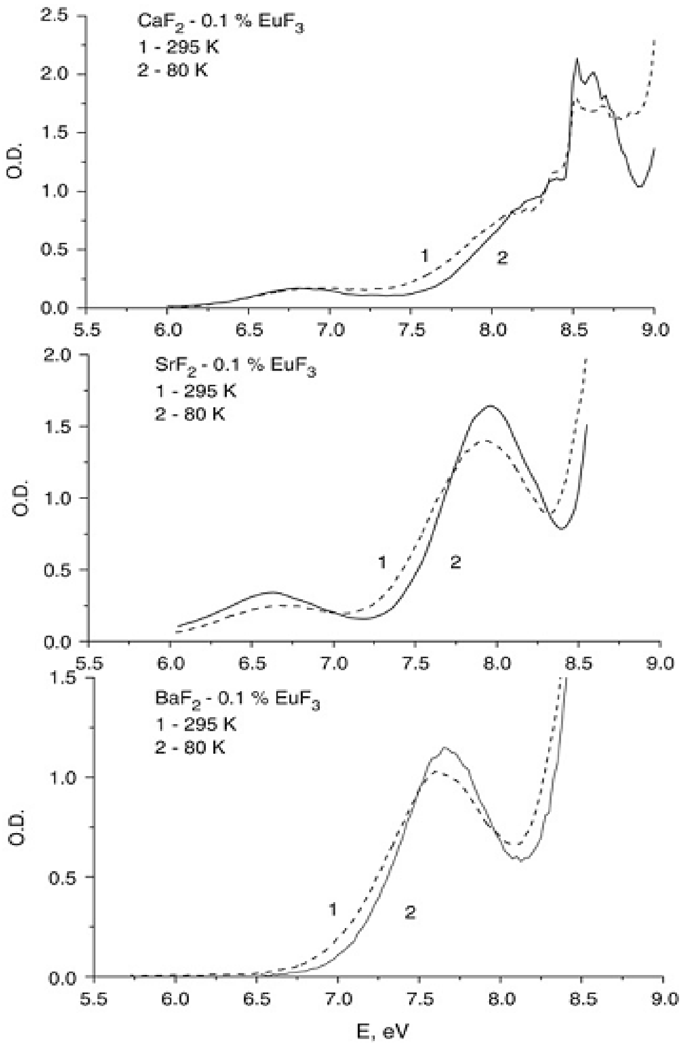


Fig. 1. Absorption spectra of CaF$_2$, SrF$_2$ and BaF$_2$ crystal doped by EuF$_3$.

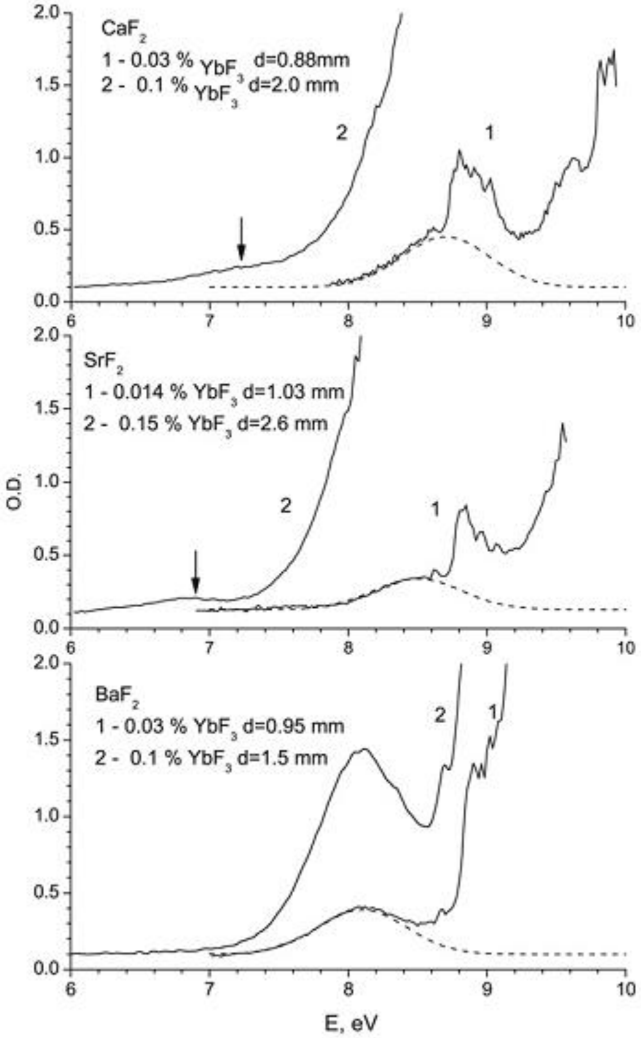


Fig. 2. Absorption spectra of CaF$_2$, SrF$_2$ and BaF$_2$ crystal doped by YbF$_3$ at room temperature. Dashed curves show the fitted CT$_1$ absorption bands.

Спектры возбуждения, свечения

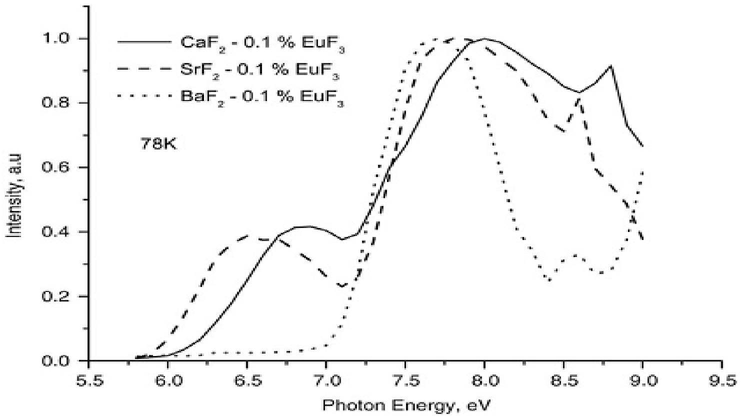


Fig. 3. Excitation spectra of CaF_2 crystal doped by 0.1 mol.% EuF_3. Emission of Eu ions was monitored at 2.1 eV ± 0.1 eV at 78 K.

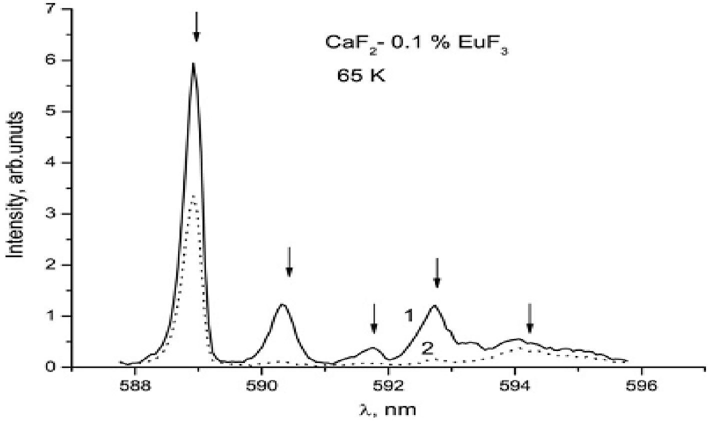


Fig. 4. Emission spectra of CaF_2 crystal doped by 0.1 mol.% EuF_3 in the region of $^5D_0$–$^7F_1$ transitions at 78 K with vacuum ultraviolet excitation. Crystal was excited by unfiltered light from DDS30 lamp which was directly connected with MgF_2 window of cryostat (curve 1) (excitation mainly into CT_1 band), and separated from window by 5 mm air space (curve 2) (excitation into CT_2 band).

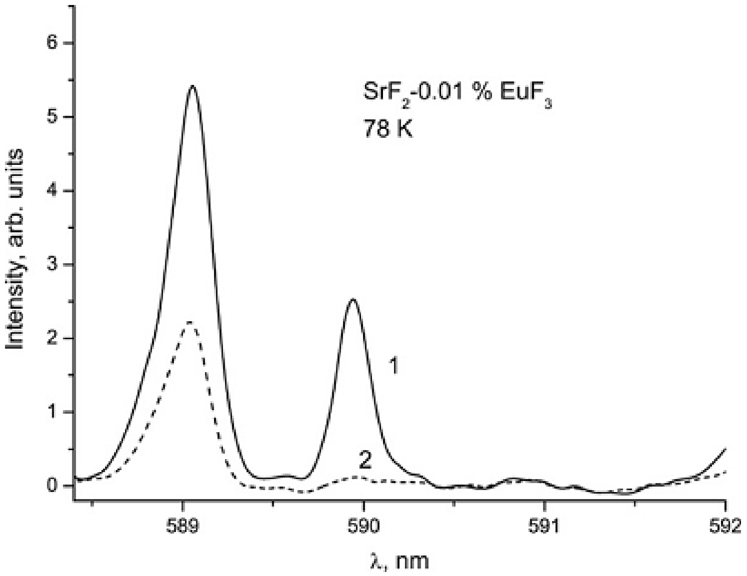
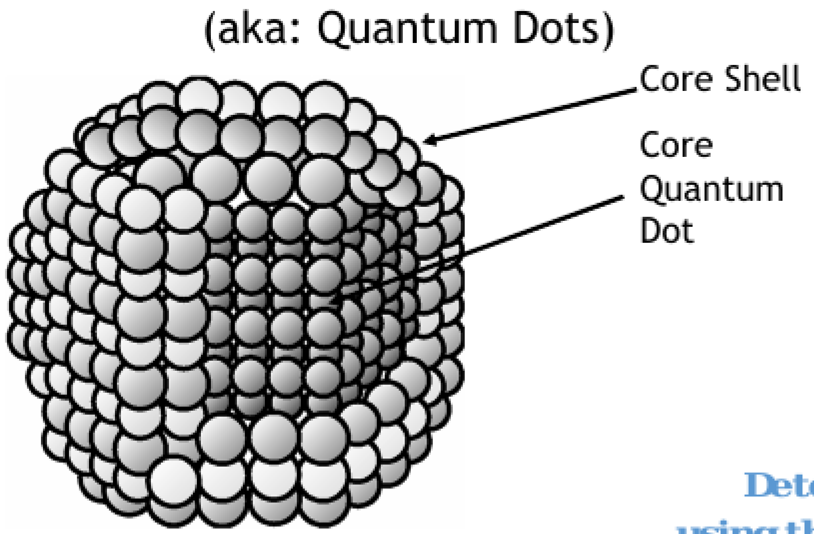


Fig. 5. Emission spectra of SrF_2 crystal doped by 0.01 mol.% EuF_3 in the region of $^5D_0$–$^7F_1$ transitions at 78 K with vacuum ultraviolet excitation into 7.8 or 6.7 eV absorption bands. Crystal was excited by unfiltered light from DDS30 lamp which was directly connected with MgF_2 window of cryostat (curve 1), and separated from window by 5 mm air space (curve 2). Position of C_{4v}, O_h lines were taken from paper [7,8].

Квантово-размерные системы. Quantum confinement

Частица в квантовой яме



Red: bigger dots!
Blue: smaller dots!

Determining QD energy using the Uncertainty Principle

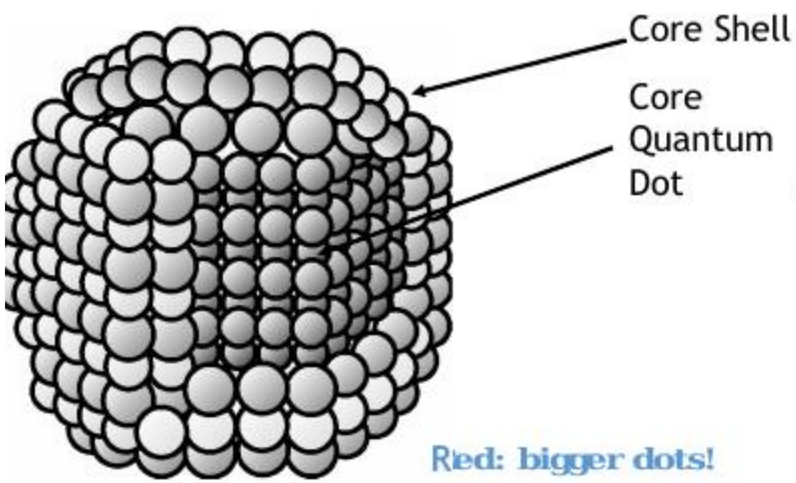
$$< \Delta x^2 > \sim R^2$$

$$< \Delta p^2 > \sim \left(\frac{\hbar^2}{2R}\right)^2$$

$$< E > = \frac{< \Delta p^2 >}{2m} \sim \frac{1}{R^2}$$

Квантово-размерные системы. Quantum confinement

(aka: Quantum Dots)



Red: bigger dots!

Blue: smaller dots!

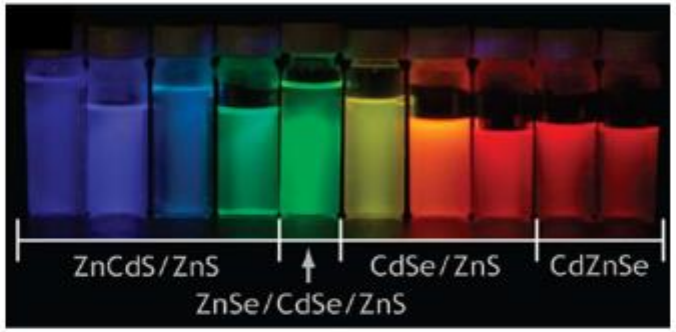
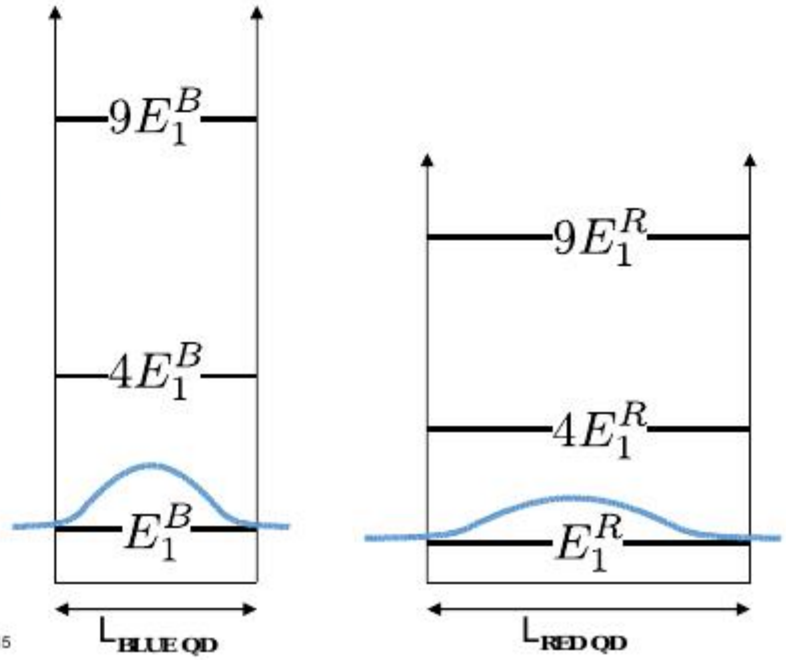


Photo by J. Halpert, Courtesy of M. Bawendi Group, EECS, MIT.

Частица в квантовой яме

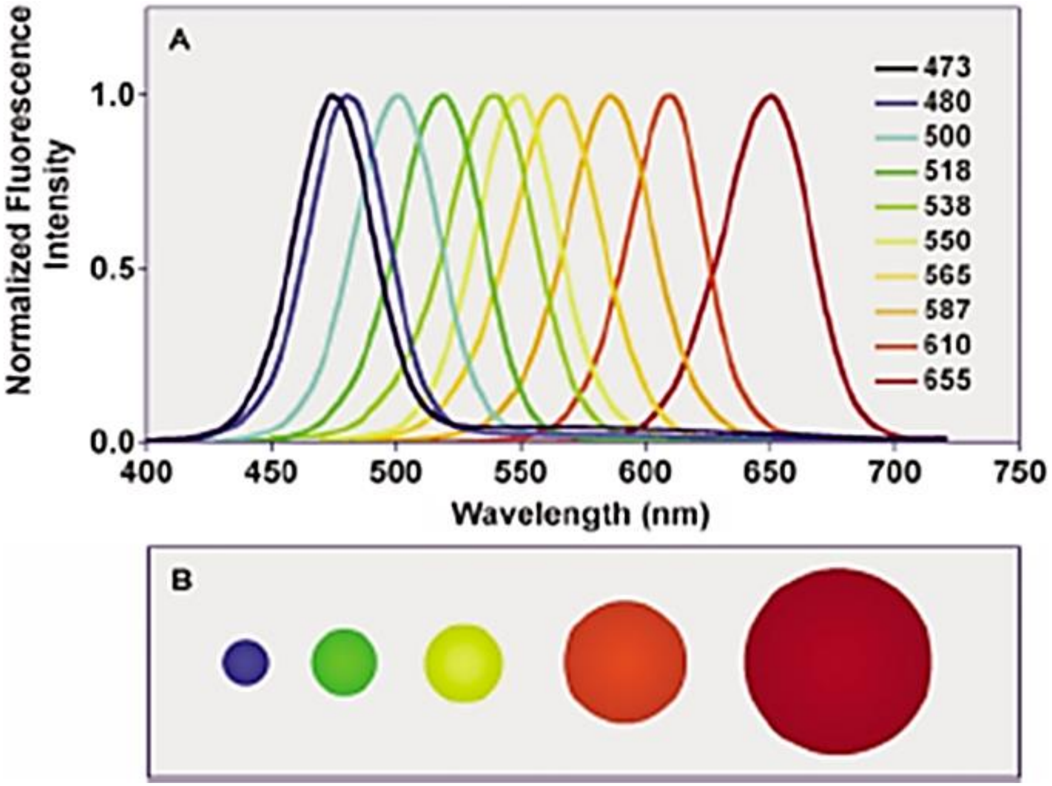
Determining QD energy using the Schrödinger Equation

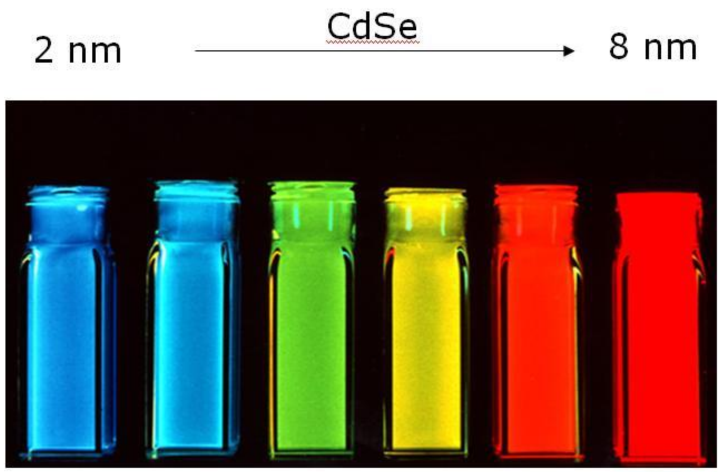
$$E_1 = n^2 E_1 \quad E_1 = \frac{\hbar^2 k_1^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}$$

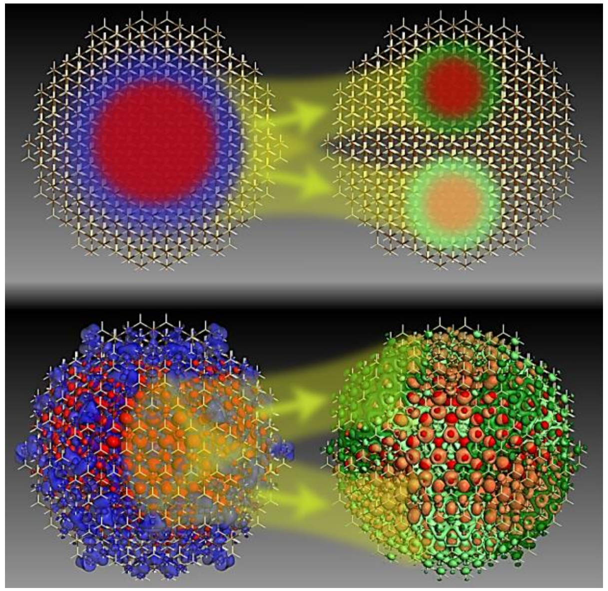


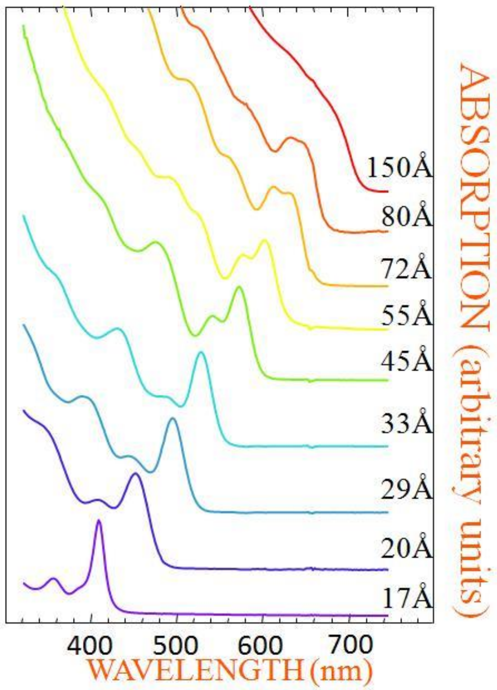
Квантово-размерные системы. Квантовые точки

Quantum Confinement



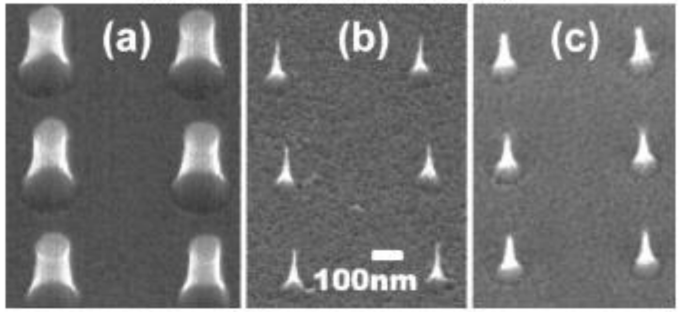


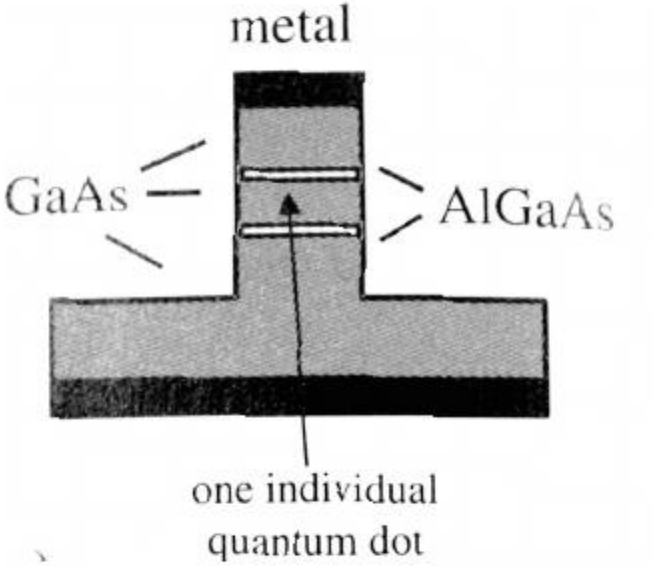




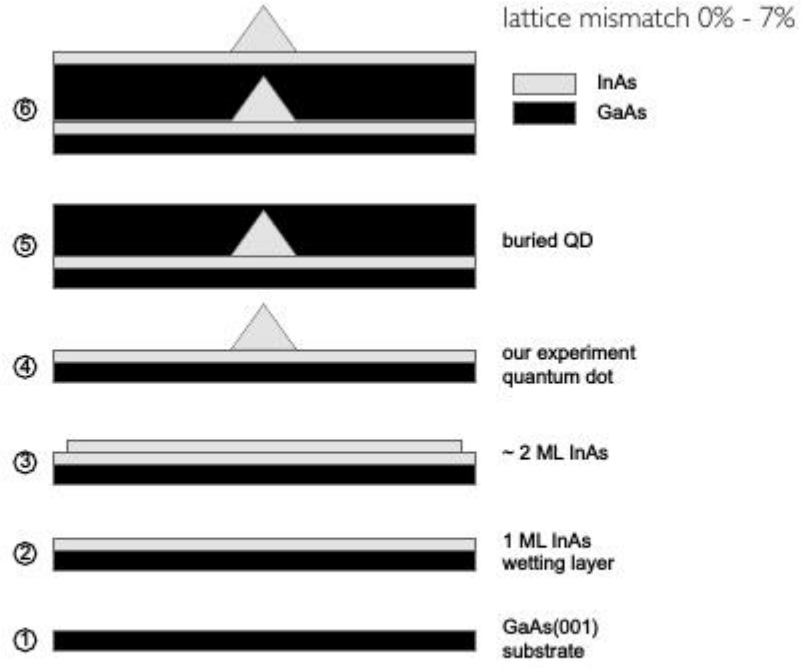
Квантово-размерные системы.

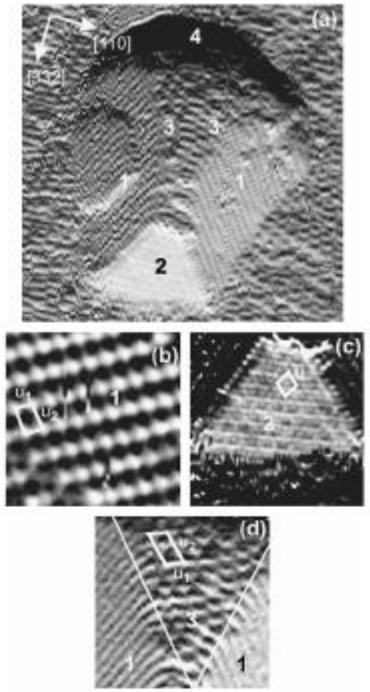
Valenta et al. Appl. Phys. Lett. 80, 1070 (2002).





Квантово-размерные системы.

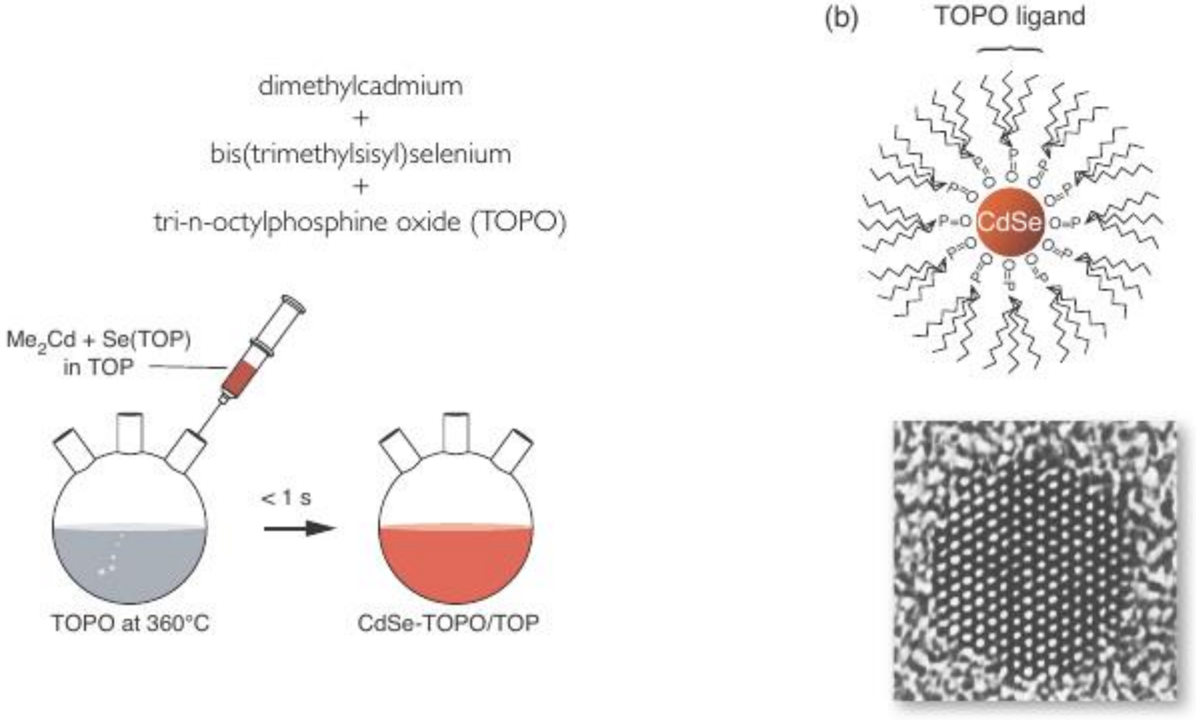




K. Jacobi, Prog. Surf. Science 71, 185 (2003).

Квантово-размерные системы.

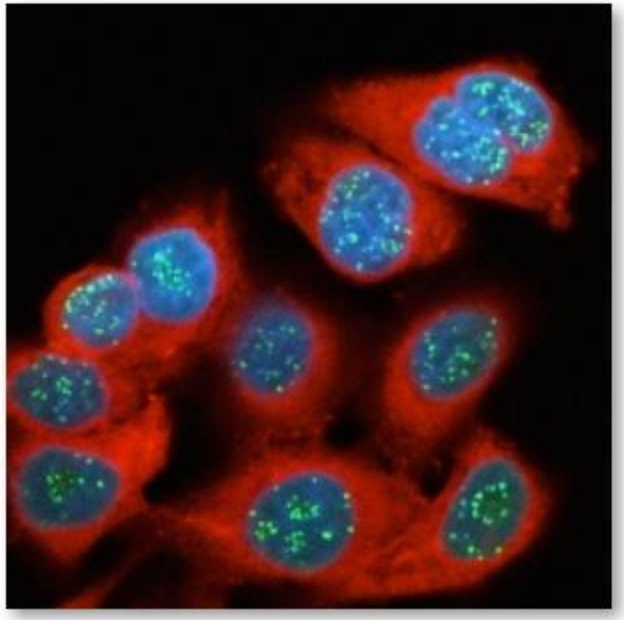
CdSe quantum dots



Квантово-размерные системы. Применение

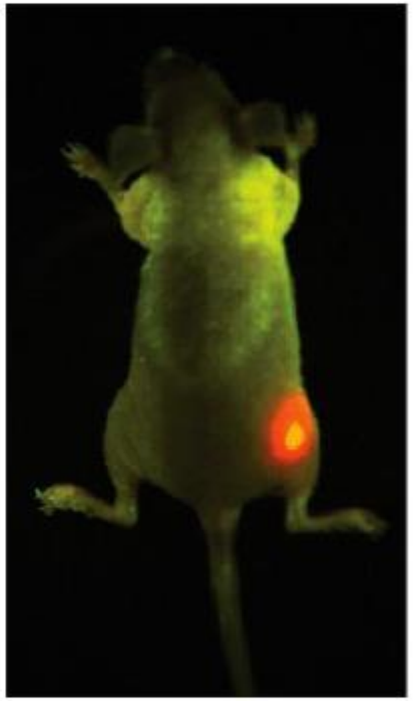
fluorescent markers

multi-color staining of different organelles in living cells



narrow emission spectra allow multicolor experiments

in-vivo observation of tumors

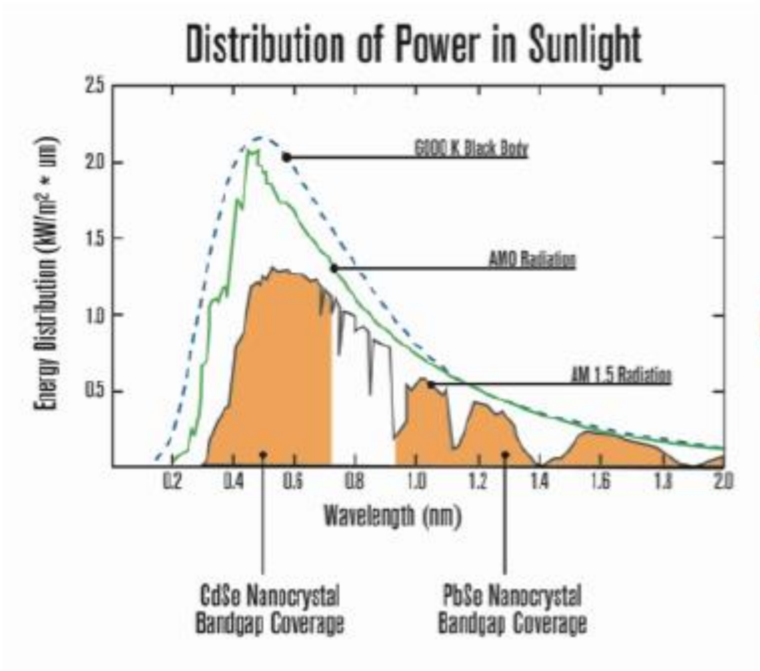


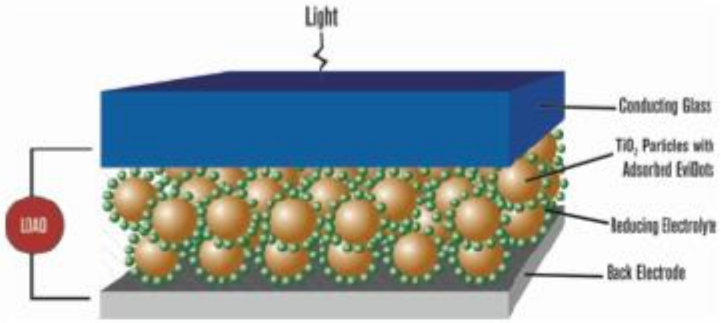
Bull's-eye. Red quantum dots injected into a live mouse mark the location of a tumor.

tuning to tissue extinction minimum

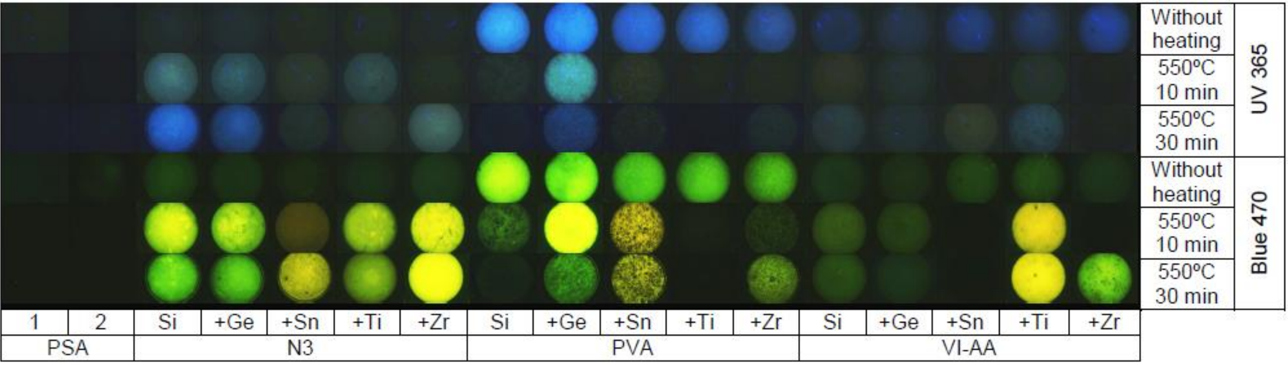
Квантово-размерные системы. Применение

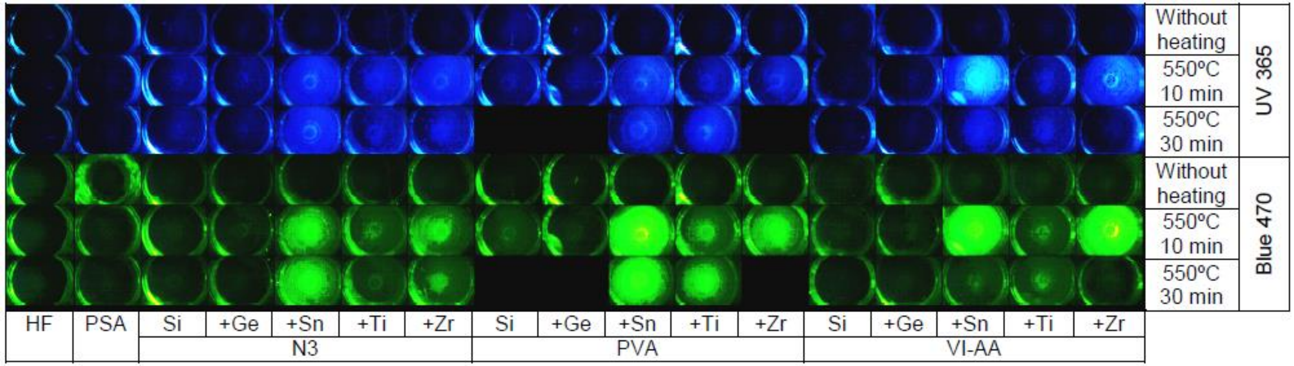
due to quantum size effect cover large spectral range
large absorption cross section

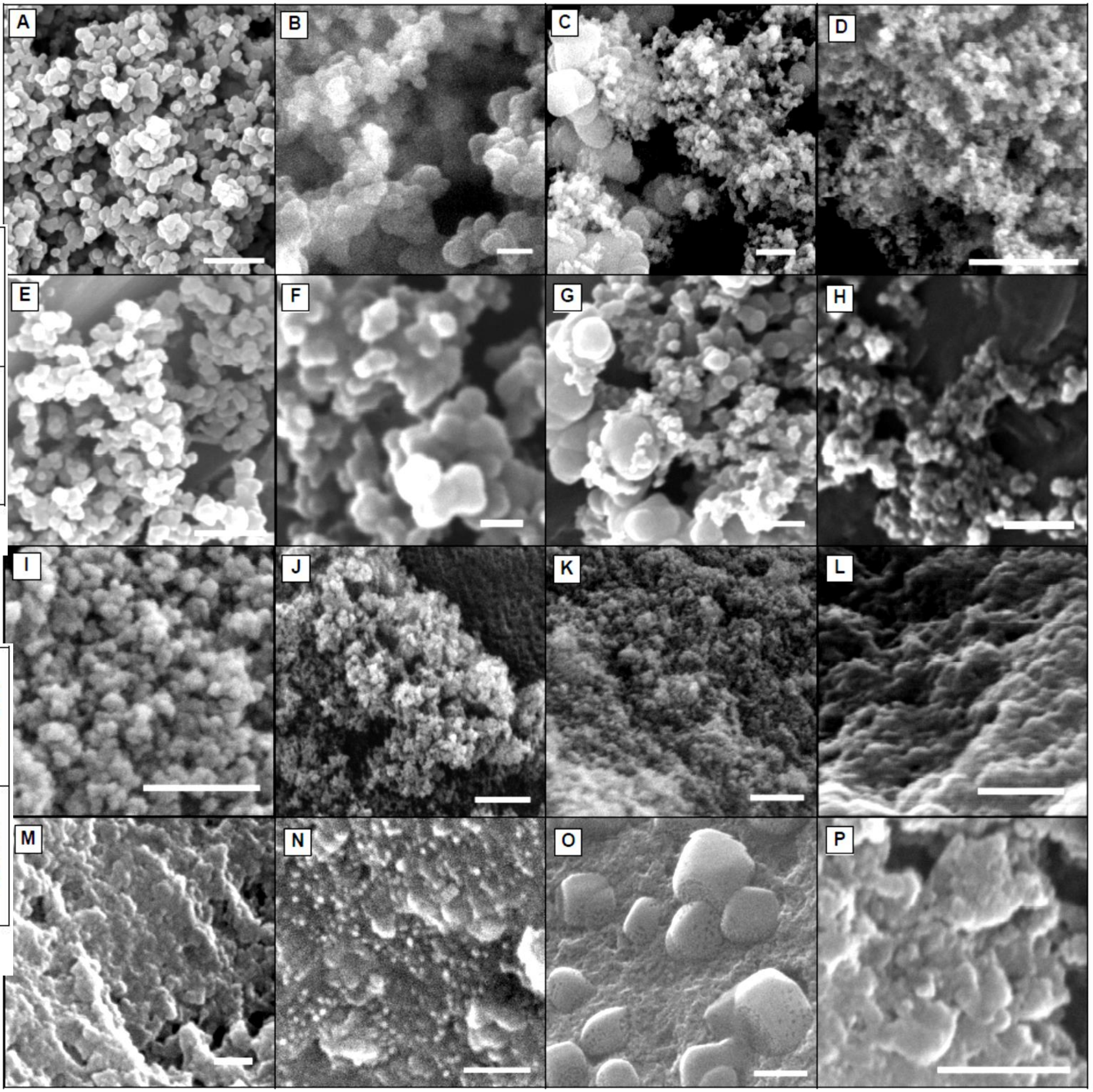




Квантово-размерные системы. Наночастицы кварца







Квантово-размерные системы. Наночастицы кварца

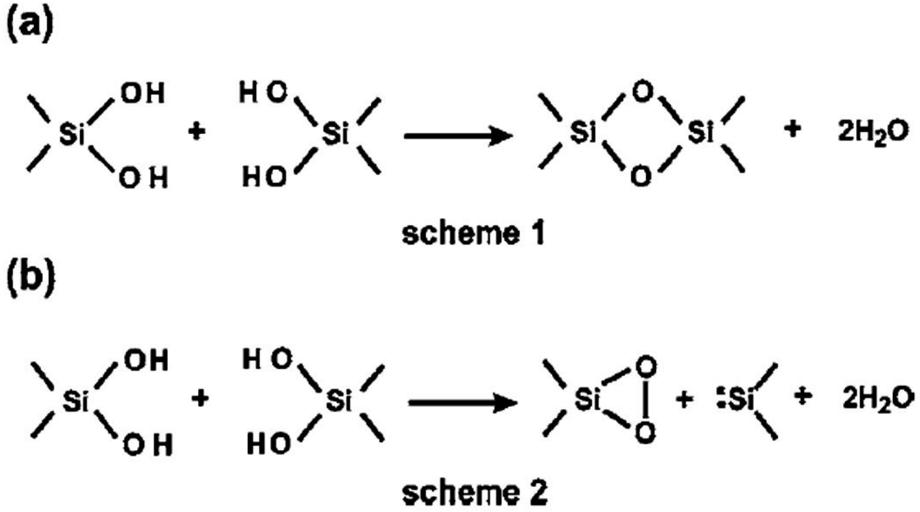
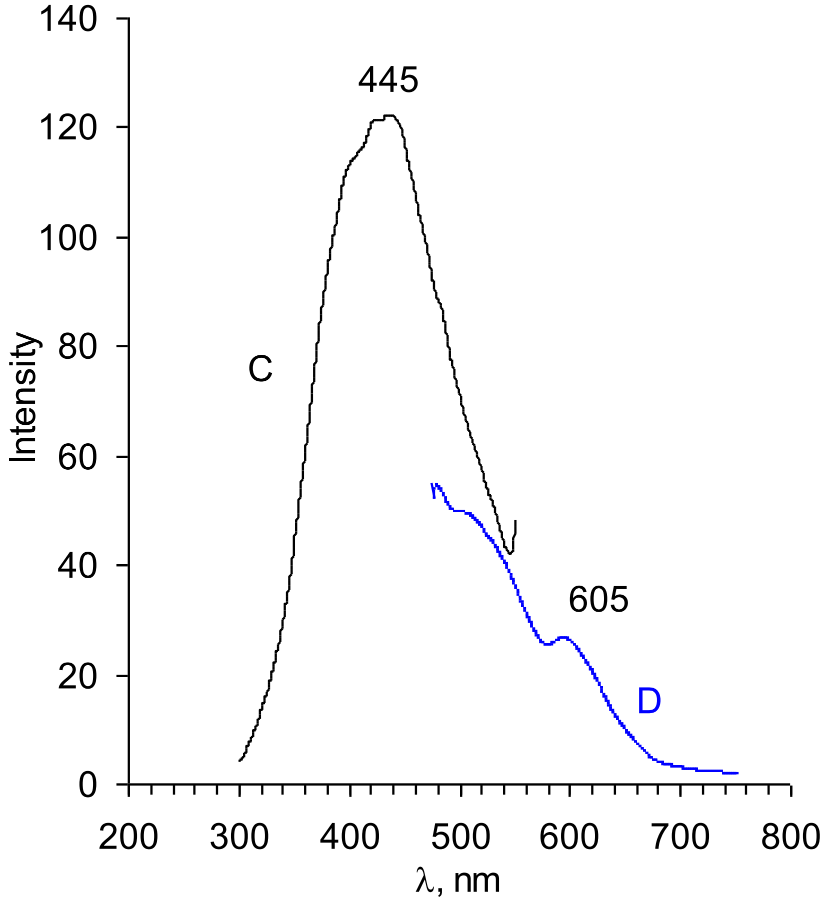
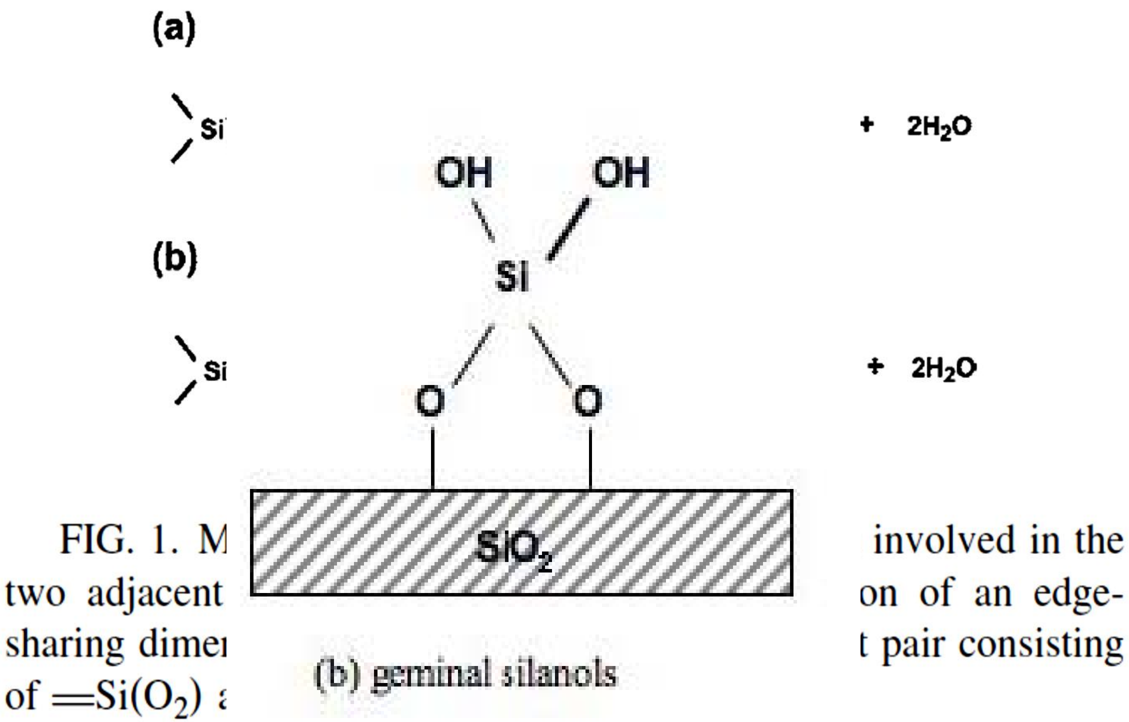


FIG. 1. Models of the dehydroxylation reaction involved in the two adjacent geminal silanol groups: (a) formation of an edge-sharing dimer (scheme 1), (b) formation of a defect pair consisting of $=\mathrm{Si(O_2)}$ and $=\mathrm{Si:}$ (scheme 2).

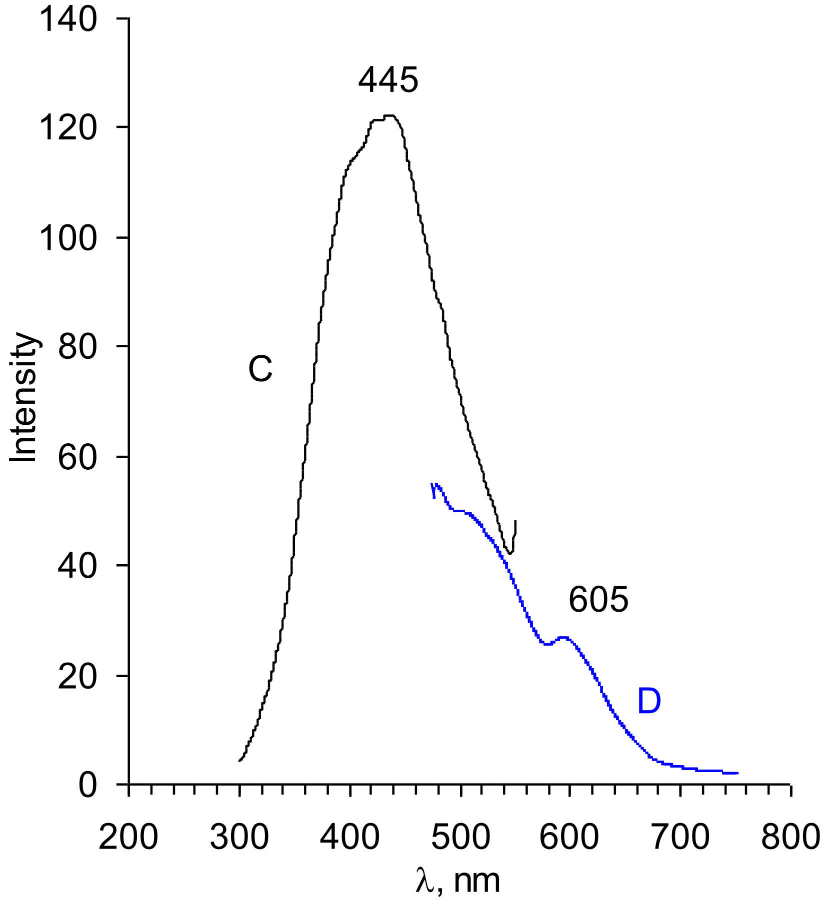


Квантово-размерные системы. Наночастицы кварца

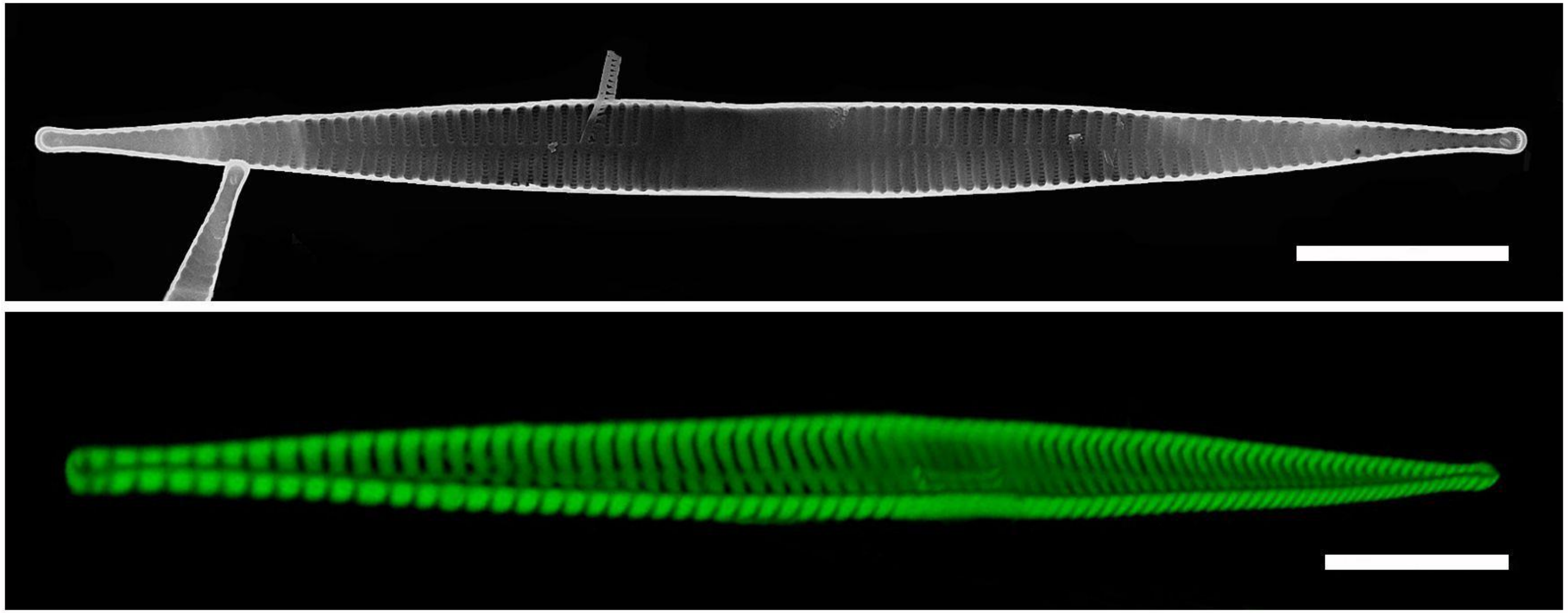


(b) geminal silanols

FIG. 1. M involved in the
two adjacent on of an edge-
sharing dimer t pair consisting
of $=\mathrm{Si(O_2)}$ a



Квантово-размерные системы. Применение



СЭМ и флуоресцентное изображение (конфокальный микроскоп) кремнистой створки S. acus, культивированной с добавлением 1 мкМ NBD-N2H. Масштаб - 10 мкм.