# *СЦИНТИЛЛЯТОРЫ С УЛУЧШЕННЫМИ СВОЙСТВАМИ НА ОСНОВЕ ФТОРИДНЫХ КРИСТАЛЛОВ*

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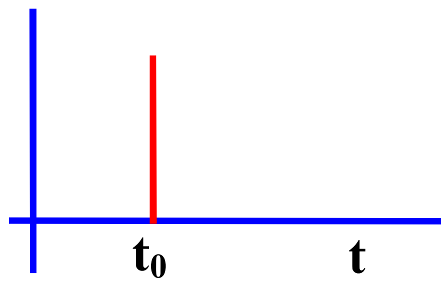
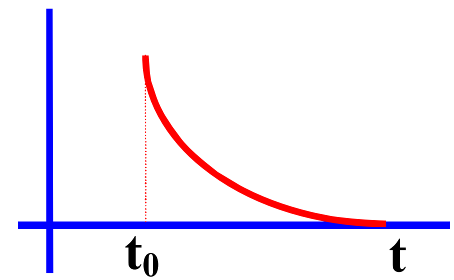
# Outline

- Введение
- Сцинтилляционые свойства фторидов
- Механизмы переноса энергии
- Перспективы
- Выводы

# 1. Что такое сцинтиллятор?

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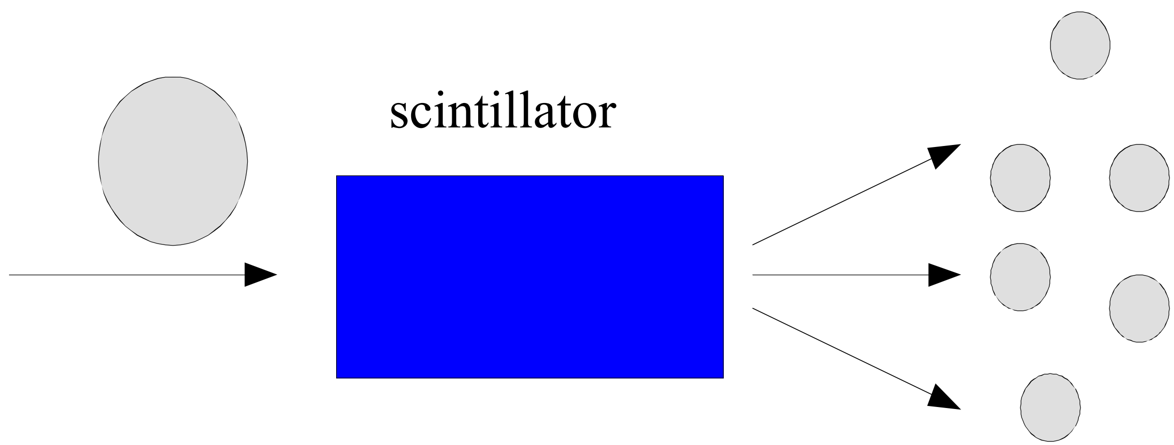
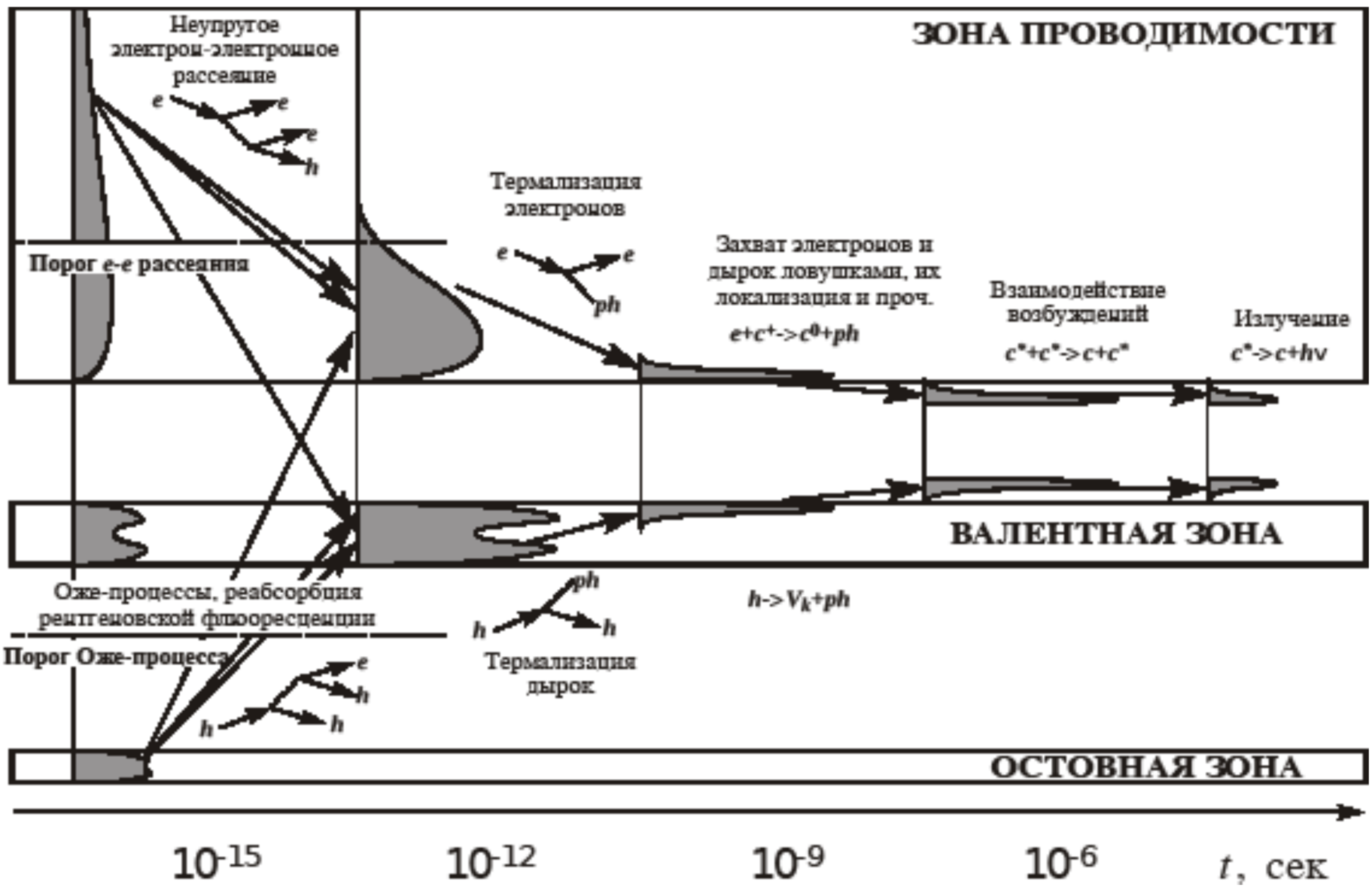
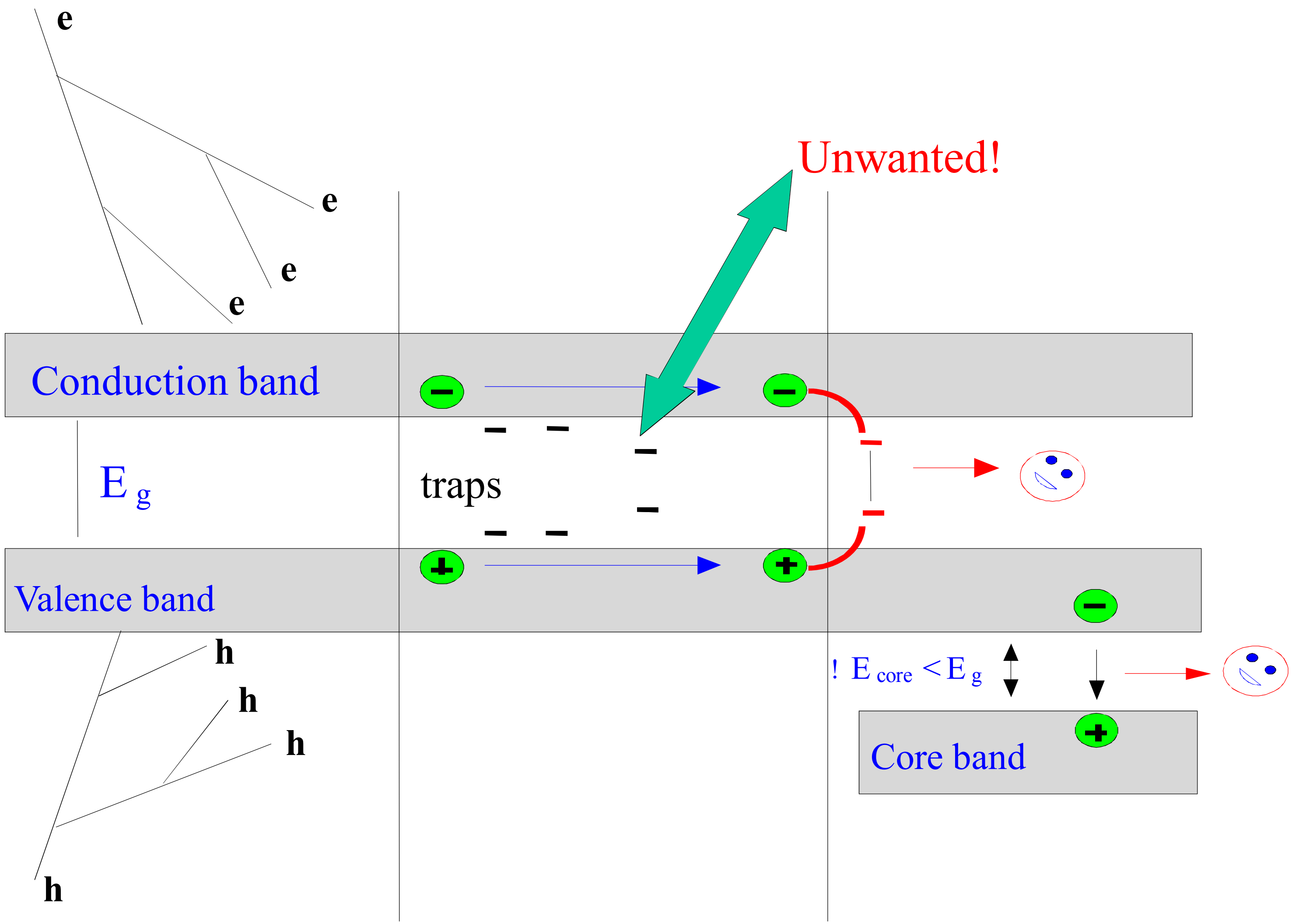



**Световой выход=Количество фотонов испущенных при поглощении частицы E=1МэВ**

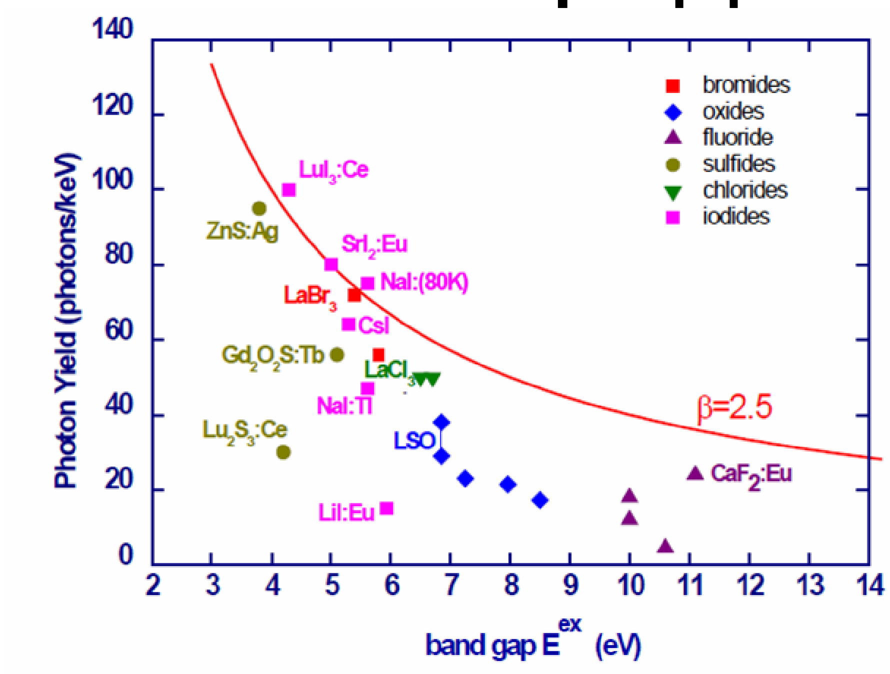
# 1. Сцинтилляционный процесс



# 1. Что такое сцинтиллятор?



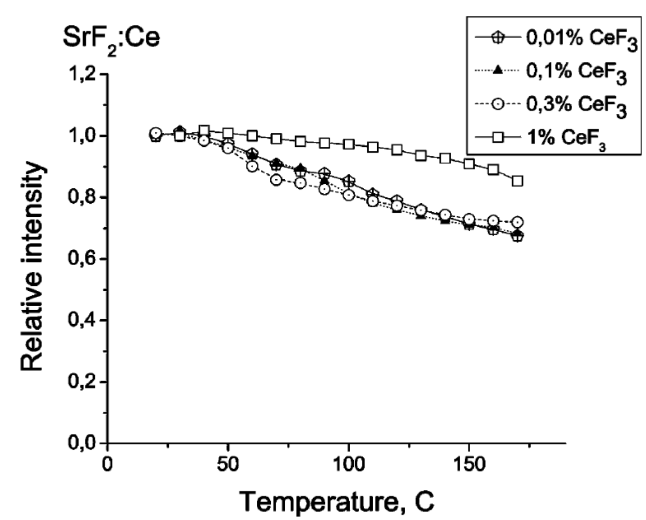
# 1. Фториды-сцинтилляторы




[P. Dorenbos, SCINT 2009]

**Pros**: 1) No hydroscopic
2) High temperature stability of LY

**Cons:** 1) Low LY (at this moment)




Light yields of fluorides:

1) CaF2-Eu – 18000-24000 ph/MeV [1]
2) BaF2 – 10000 ph/MeV [1]
3) SrF2 – 14000 ph/MeV [3] (questionable due to low purity of the sample)

SrF2 is almost not investigated! But it can be perspective scintillator for well-logging.

# 2. Сцинтилляционные свойства фторидов

COMPILATION OF INTEGRAL QUANTUM EFFICIENCIES, WAVELENGTH OF LUMINESCENCE MAXIMA, PHOTOELECTRON ($Y_{phe}$) AND ABSOLUTE PHOTO ($Y_{ph}$) YIELDS, AND FULL WIDTH AT HALF MAXIMUM (FWHM) OF TESTED SCINTILLATORS IN COMPARISON WITH LITERATURE PHOTOELECTRON YIE DATA

| Scintillator | Primary decay time [ns] | Wavelength of emission max [nm] | Integral quantum efficiency $QE_{eff}$ | Photoelectron yield $Y_{phe}$ [phe/MeV] | Reference data $Y_{phe}$ [phe/MeV] | Photon yield $Y_{ph}$ [ph/MeV] | Full width at half maximum FWHM [%] |
|---|---|---|---|---|---|---|---|
| NaI-Tl | 250 | 415 | 0.21 | 8500±600 | 8900 [17] | 38000 | 8 |
| CsI-Tl | 1000 | 540 | 0.07 | 4900±390 | 4400 [6] | 55700 | 7.1 |
| BGO | 300 | 480 | 0.13 | 1380±100 | 1200 [6] | 8200 | 15 |
| $BaF_2$ | 600 | 280 | 0.21 | 1930±120 | 2110 [5] | 9400 | 13 |
| $BaF_2$-0.15 mol.% $Pr^{3+}$ | 21 | 228; 257 | 0.20 | 1230±80 | | 6300 | 23 |
| $BaF_2$-0.15 mol.% $Pr^{3+}$ | 21 | 228; 257 | 0.20 | 1500±100 | | 7700 | 19 |
| $SrF_2$ | 1000 | 285 | 0.21 | 6010±420 | | 29200 | 10 |
| $SrF_2$ [a] | 1000 | 285 | 0.21 | 4020±280 | | 19500 | 13 |
| $SrF_2$-0.3 mol.% $Ce^{3+}$ | 130[b] | 310; 325 | 0.23 | 2100±150 | | 9300 | 13 |
| $SrF_2$-0.15 mol.% $Pr^{3+}$ | 25 | 232; 250 | 0.19 | 2200±150 | | 11800 | |
| $SrF_2$-0.3 mol.% $Pr^{3+}$ | 25 | 232; 250 | 0.19 | 1300±90 | | 7000 | 20 |
| $SrF_2$-1 mol.% $Pr^{3+}$ | 24 | 232; 250 | 0.19 | 220±20 | | 1200 | |

[a] Cleaved sample

[b] The crystal has long decays [3]

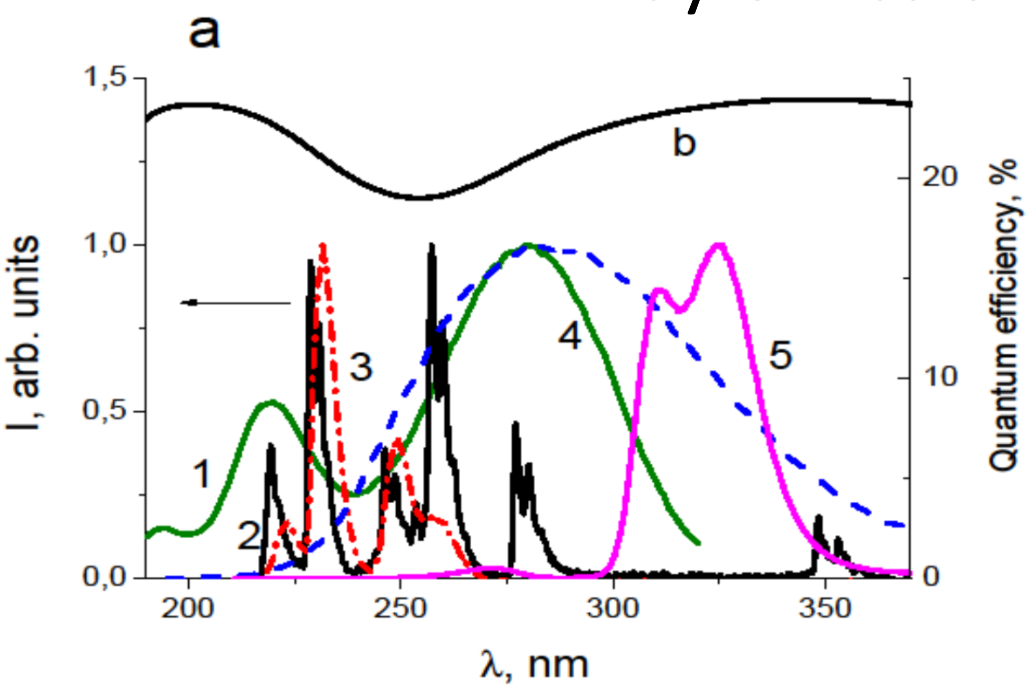
Shendrik, ArXiv.org, 2013

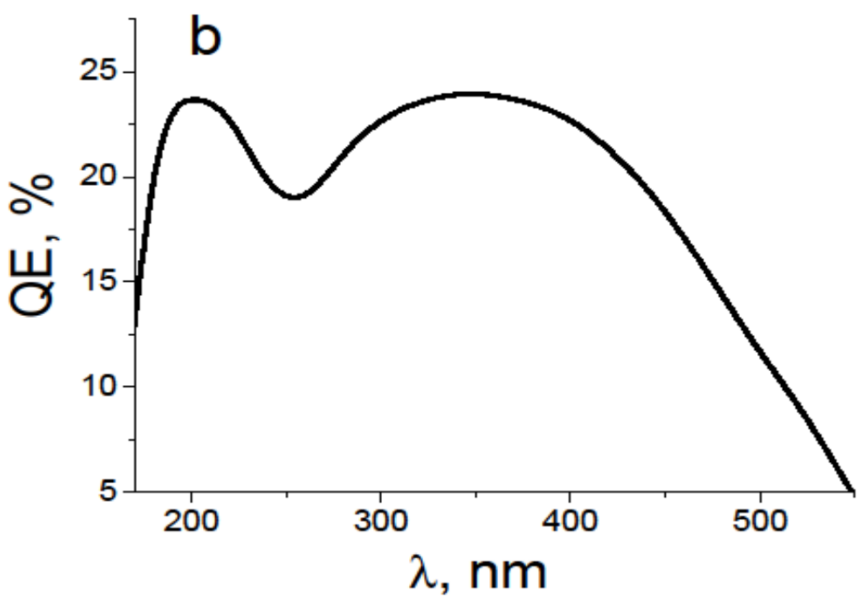
Потери в процессах передачи энергии от первичных e-h к ионам активатора!

# 3. Методы исследования

- Спектры рентгенолюминесценции (РЛ)
- Спектры поглощения облученных и необлученных кристаллов
- Спектроскопия с временным разрешением при оптическом, рентгеновском и синхротронном возбуждении
- Кривые затухания свечения
- Термолюминесценция и температурные зависимости РЛ
- Квантово-химические расчеты

# 2. X-ray emission spectra



# 2. X-ray emission spectra

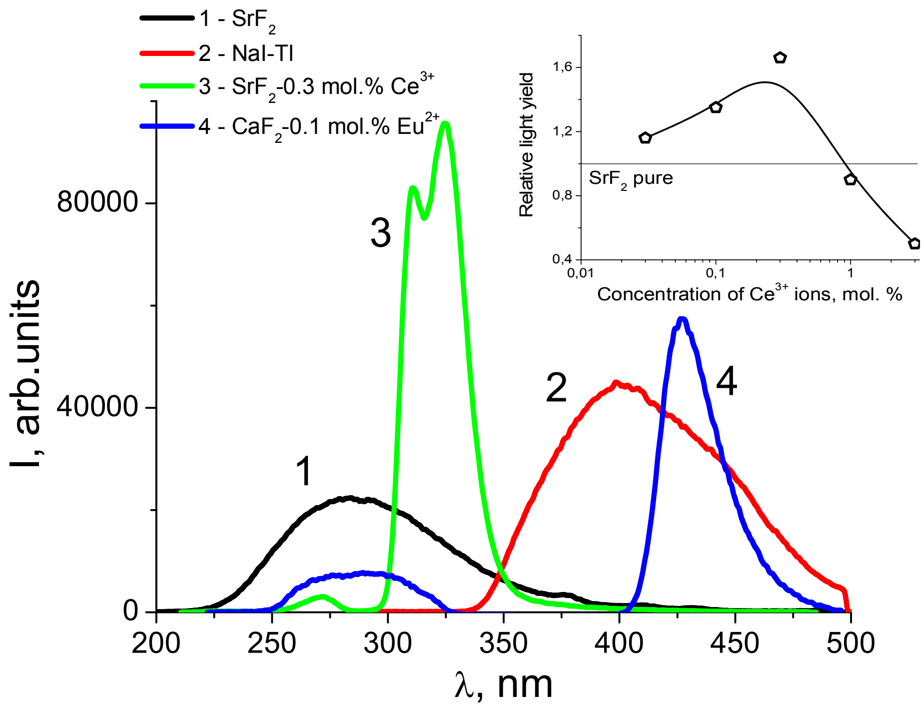


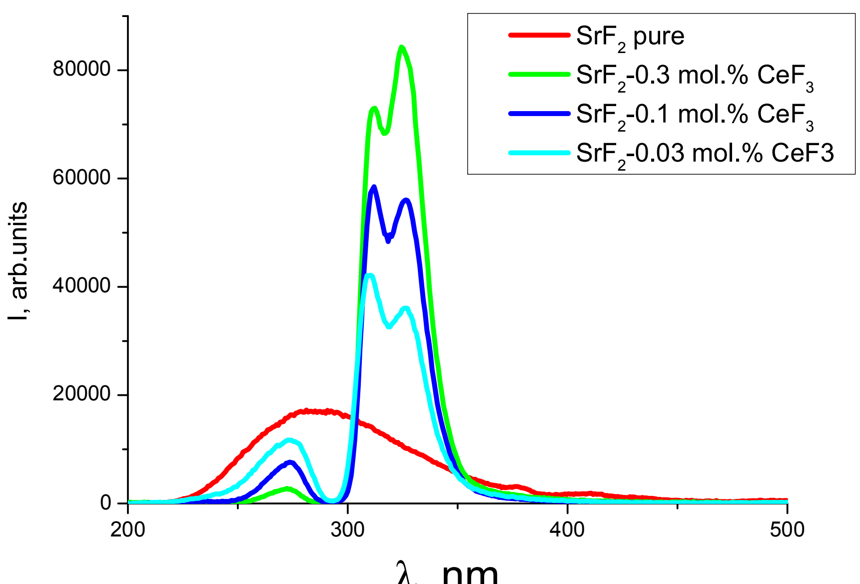

Figure shows luminescence spectra of pure SrF2 (curve 1), NaI-Tl (curve 2), SrF2-0.3 mol.% Ce3+ (curve 3), and CaF2-0.1 mol.% Eu2+ (curve 4). The spectra were not corrected for spectral sensitivity of registration channel

Light yield (LY) of x-ray luminescence is derived from integral emission intensity of the crystals.

LY(SrF2)=0.48*LY(NaI-Tl)

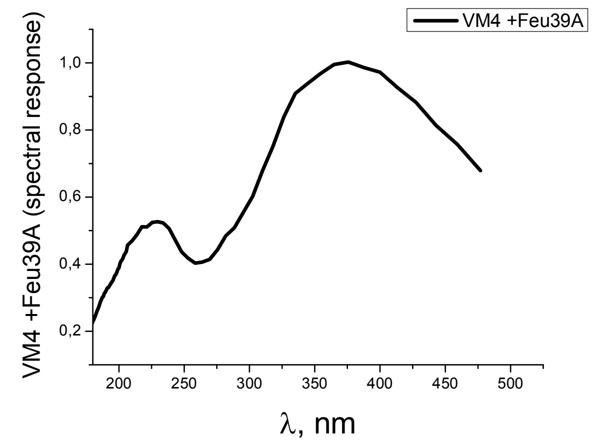
**LY(SrF2-0.3 mol.% Ce)=0.71*LY(NaI-Tl)**

LY(CaF-Eu)=0.5*LY(NaI-Tl)



# 3. Light yield measurements

| | Pulse height | X-ray emission |
|---|---|---|
| NaI-Tl (LY= 45000 ph/MeV) | 1 | 1 |
| CaF2-0.1 mol. % Eu2+ | 0.42 | 0.5 |
| SrF2 | 0.42 | 0.48 |
| SrF2-0.3 mol. % CeF3 | 0.32 | 0.79 |
| SrF2-1 mol. % CeF3 | 0.2 | 0.43 |




*) In the table LY is pointed without spectral sensitivity correction factor.

**<u>After correction:</u>**

Corrected light yield of SrF2 – $^{corr}$LY(SrF2)=2*LY(SrF2)

Corrected light yield of SrF2-Ce – corrLY(SrF2-Ce)=1.5*LY(SrF2-Ce)

# 3. Decay curves

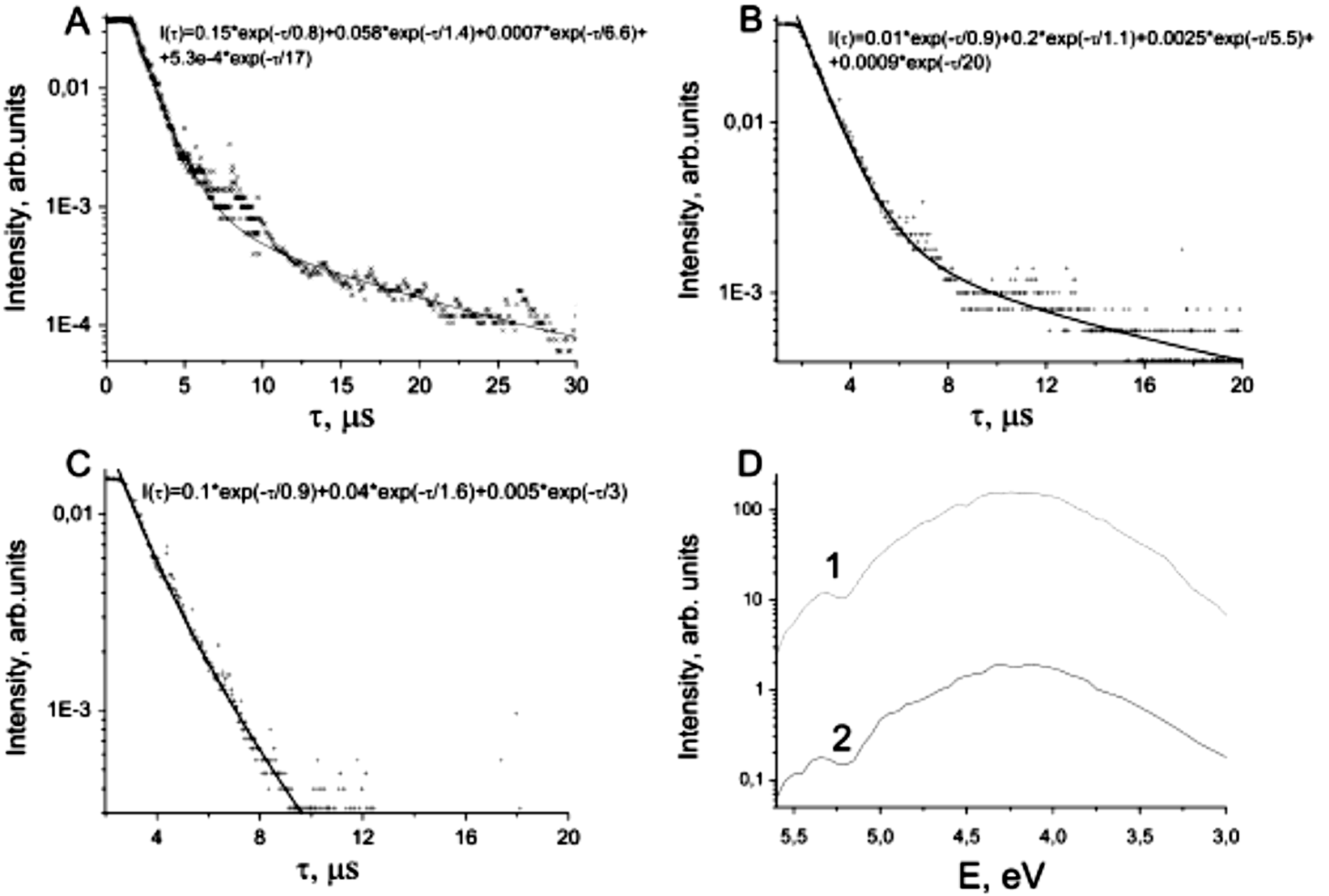
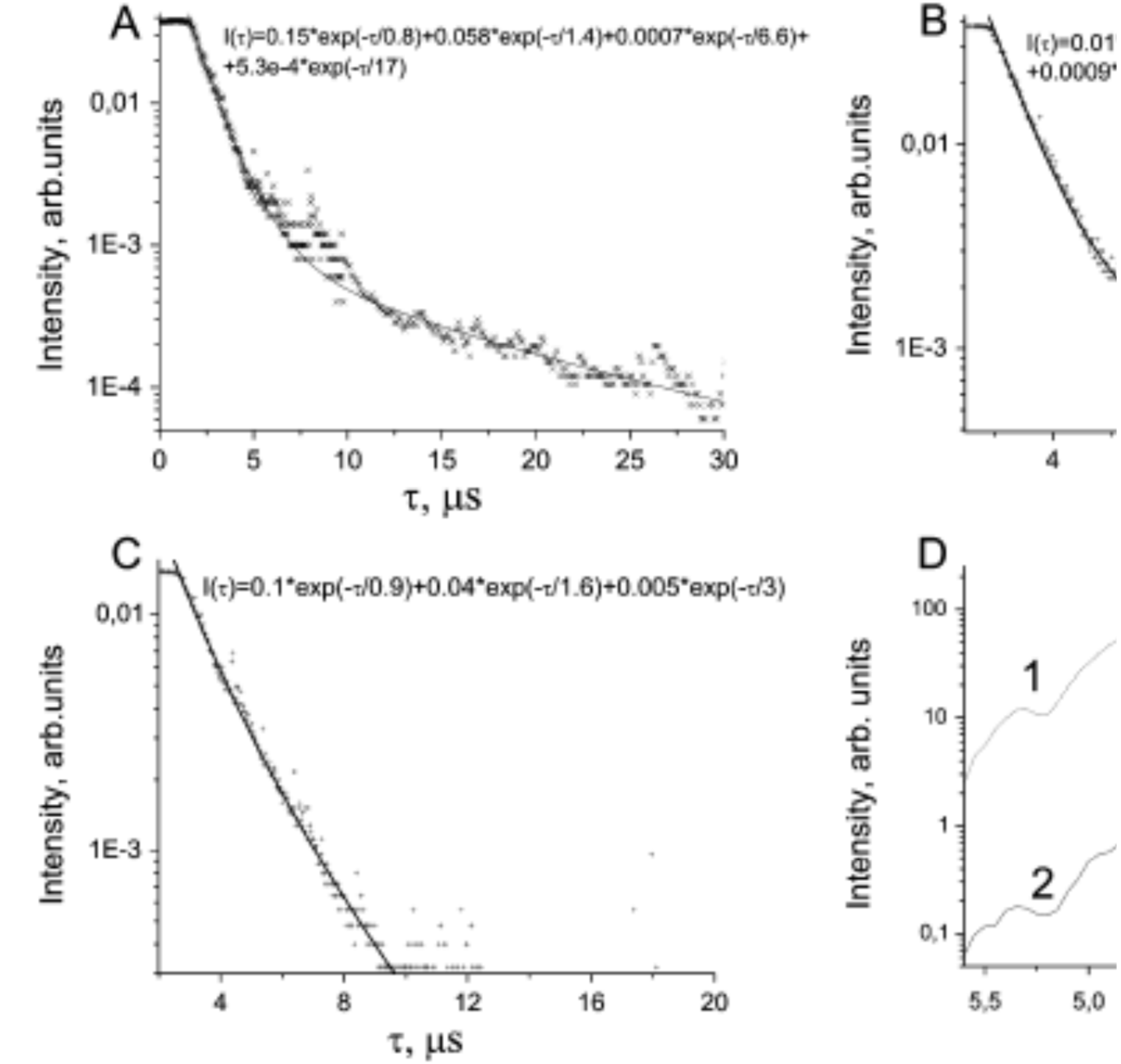



Fig. 4. 5d-4f luminescence decay curves of $SrF_2$ crystals doped with 0.015 mol.% (A), 0.15 mol.% (B) measured at around RT, and 1 mol.% (C) measured at around 300 K. All curves are approximated by sum of single exponential decays. The equations of approximation are given in labels in right parts of figures. In figure D time-resolved spectra of $SrF_2$-0.15 mol.% $Pr^{3+}$ crystal measured in 0–1 $\mu$s (1) and 6–8 $\mu$s time windows is shown.

Shendrik, IEEE TNS, 2012

# 3. Decay curves

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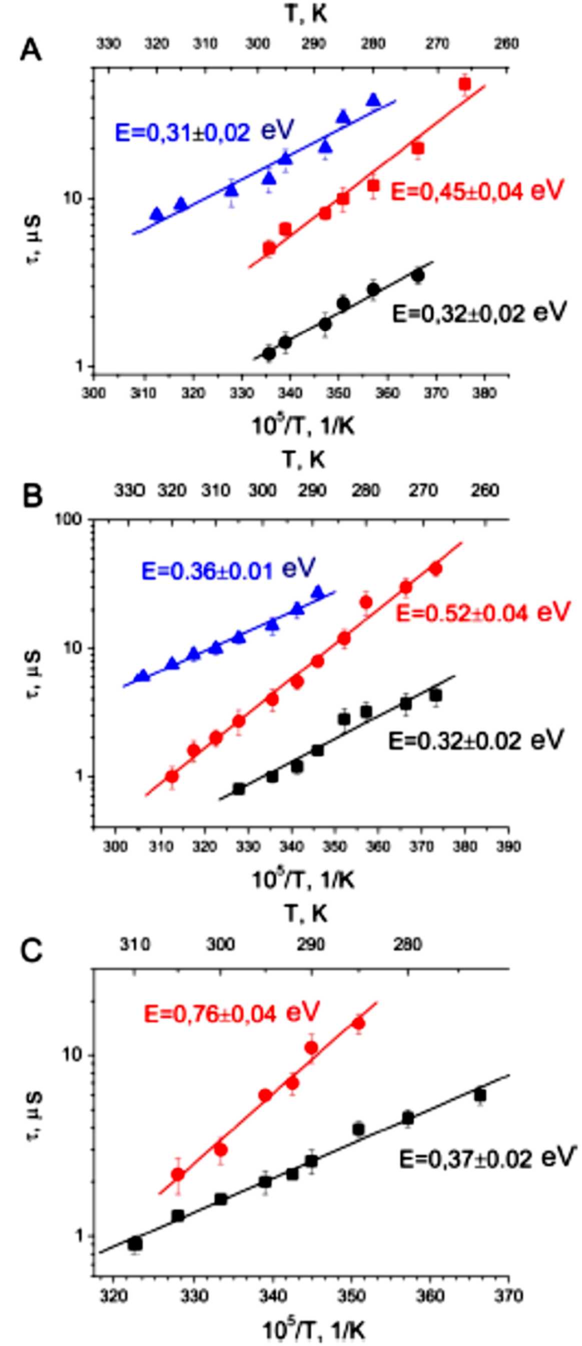
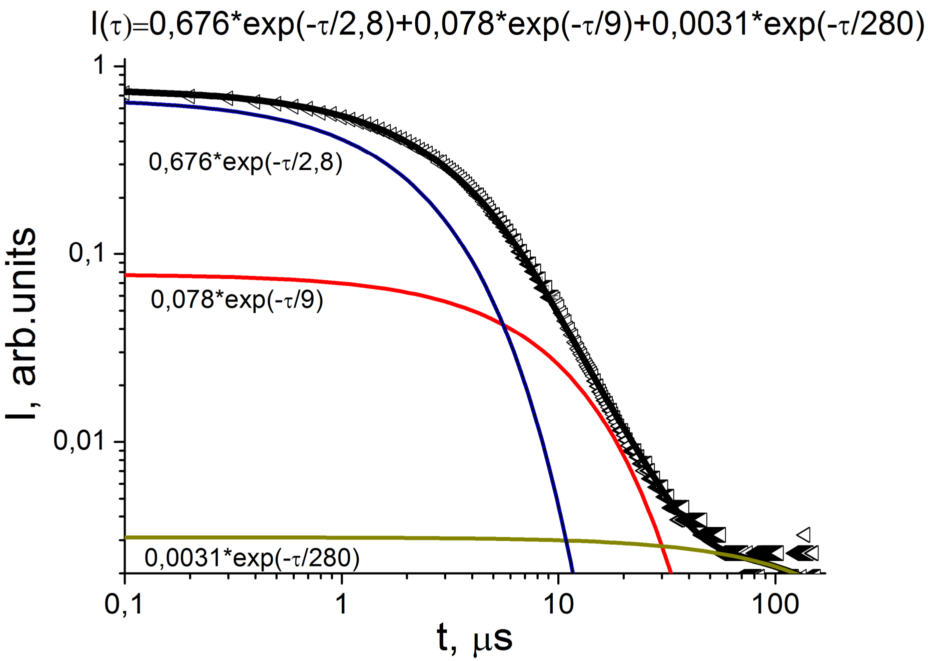



Shendrik, IEEE TNS, 2012

# 4. Scintillation decay time profile




Decay of 5d-4f luminescence under x-ray and gamma excitation can be described by several single exponential curves. The shortest component is 120 ns. An integrating resistor 2.8 KΩ was used in scintillation decay profile registration. First exponential curve with τ=2.8 μs is presented after integration.

**1) 5d-4f emission of Ce3+ ions decay:**
**Fast component: 120-130 ns (57 %)**
**Slow components: 9-280 μs (43 %)**

# Energy transfer in SrF2-Ce3+. STE.

1) STE transfer is efficient in alkali-earth fluorides doped with Ce3+
[Wojtowicz RadMeas 2003, Radzhabov NIM 2002]

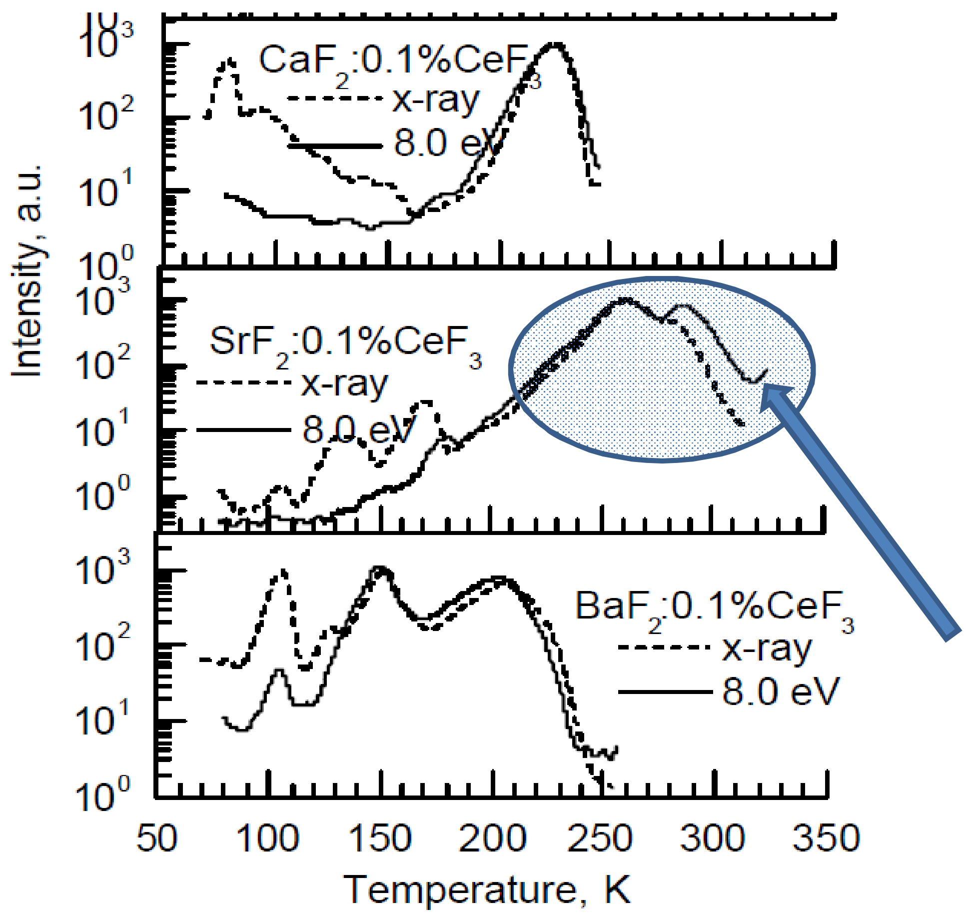
Contribution of STE energy transfer is about 50-60 %

The most energy is transferred by resonant mechanism.
Forster radius of dipole-dipole interaction calculated from overlapping STE emission and 4f-5d Ce3+ absorption:

Rc=15 Å (from $R_c^6 = \frac{B}{n^4 N_A} \int_0^\infty \frac{f_D(E)\mu_A(E)}{E^4} dE,$

Rc=13.5 Å (calculated from quenching of STE with increasing Ce3+ concentration in SrF2-Ce3+.

# Electron-hole energy transfer



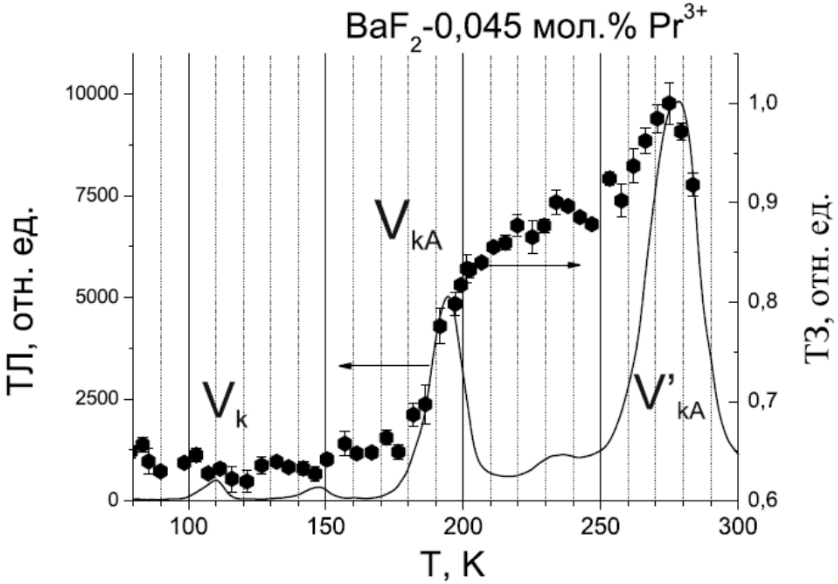

[Radzhabov, NIM 2002]

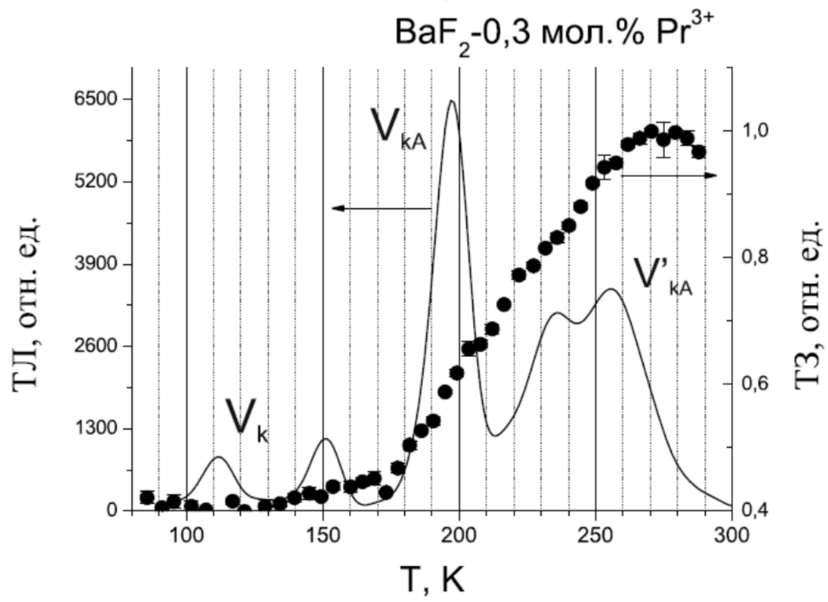
1) Fast consecutive electron-hole transfer is not efficient in fluorides doped with rare earth [Radzhabov, IEEE TNS 2012; Shendrik, IEEE TNS 2012]

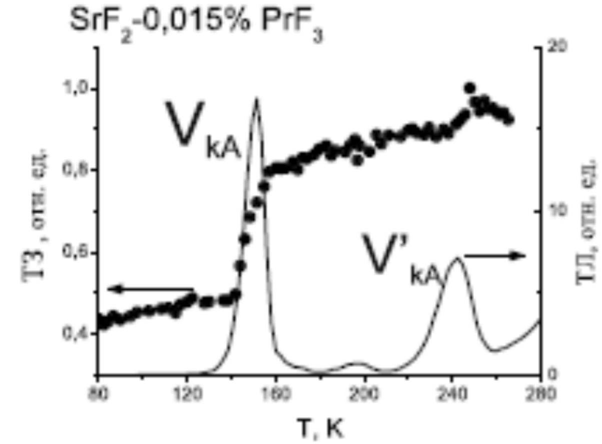
2) Delayed energy transfer. Hole or electron is captured by a trap and then transferred to emission center.

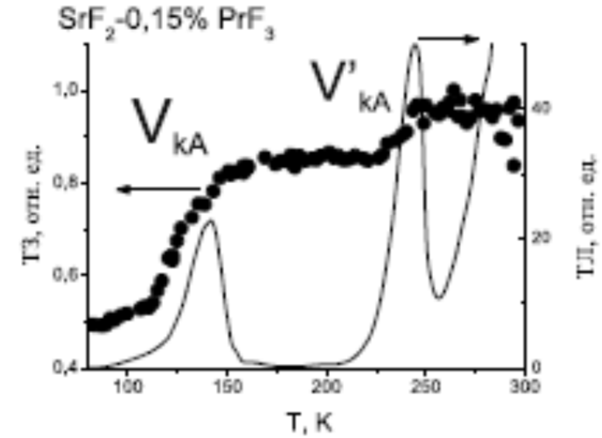
In SrF2-Ce electron can be first captured by a trap and only then transferred to Ce ion. [Radzhabov, NIM 2002]

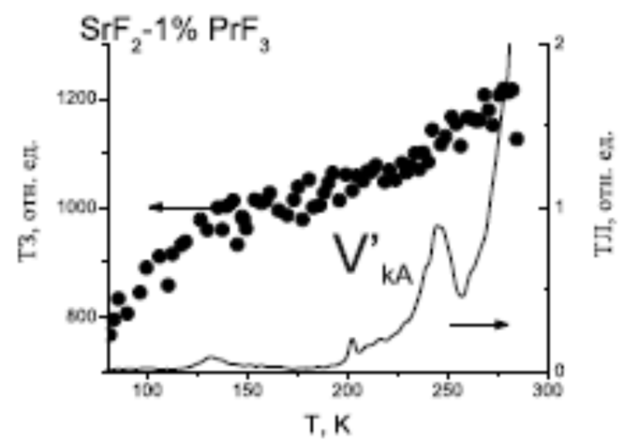
# 3. Температурные зависимости



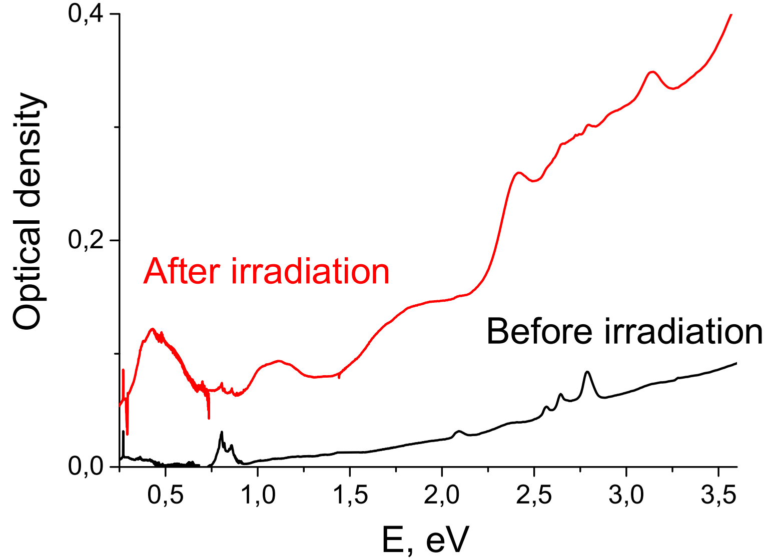



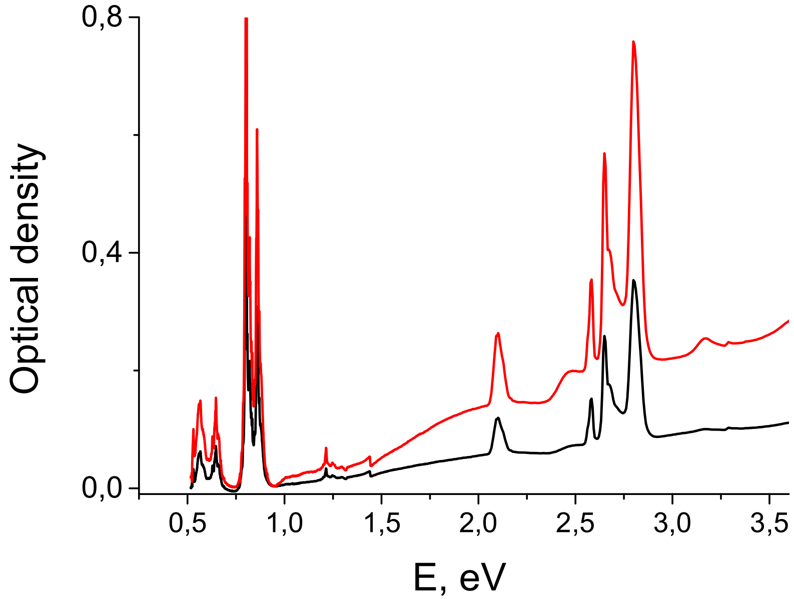



# 3. Спектры поглощения. Crystal doped with $Pr^{3+}$

Calcium fluoride



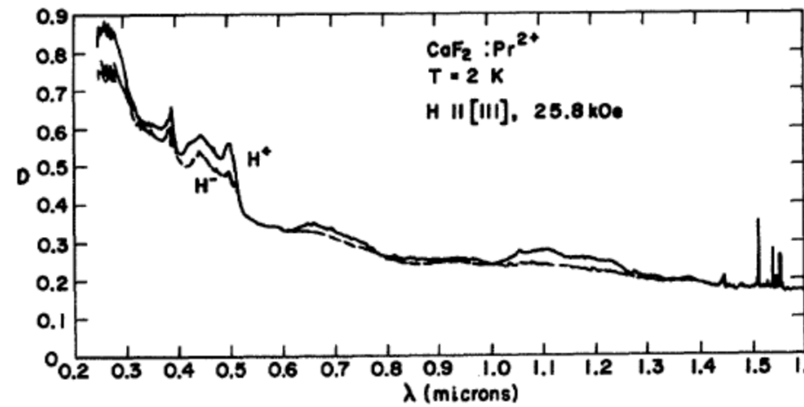




FIG. 3. MCD spectra of $CaF_2{:}Pr^{2+}$ with $H \parallel [111]$. $D$ denotes optical density, $\ln(I_0/I)$, in this and the other figures.

Data by Weaklem, PhysRevB, 1970

Observed bands can be corresponded to 4f-5d transitions in $Pr^{2+}$ ions. The lowest energy transition is related to transition of $^4I_{9/2}$ ground state to $e_g$ level of 5d state

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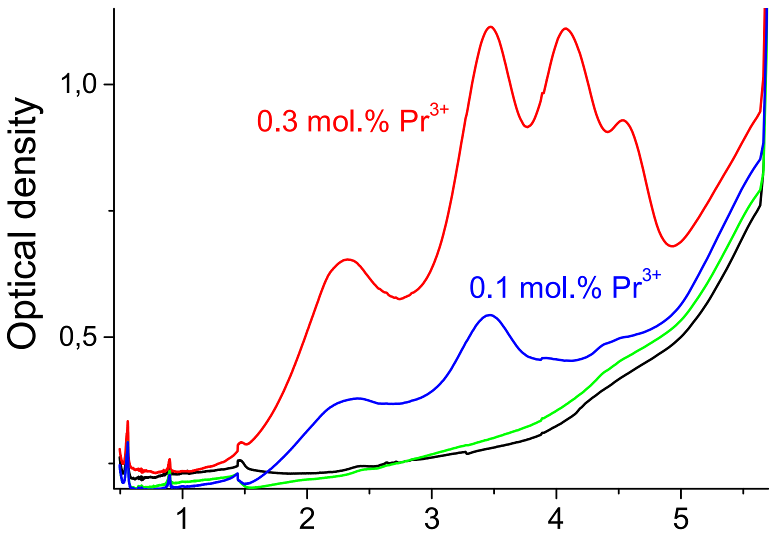
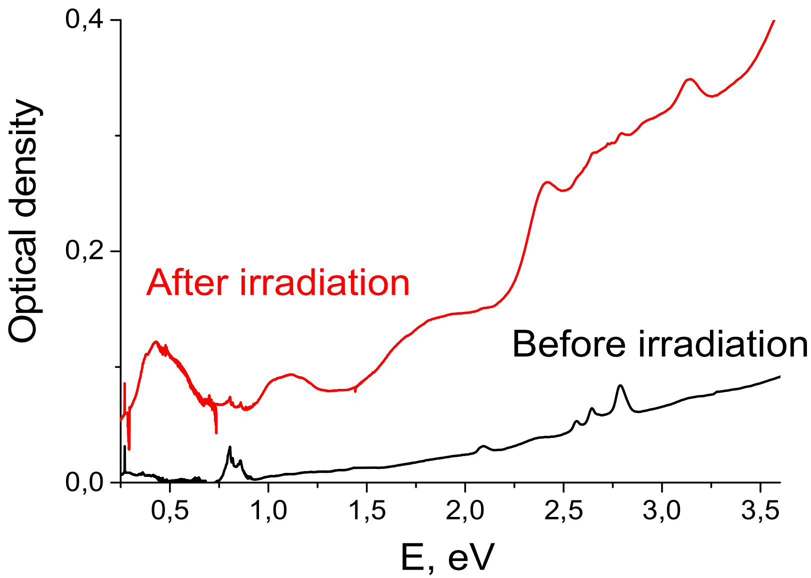
Институт геохимии им. А.П. Виноградова СО РАН Иркутск Россия

# 3. Crystal doped with $Pr^{3+}$

Barium fluoride




Calcium fluoride

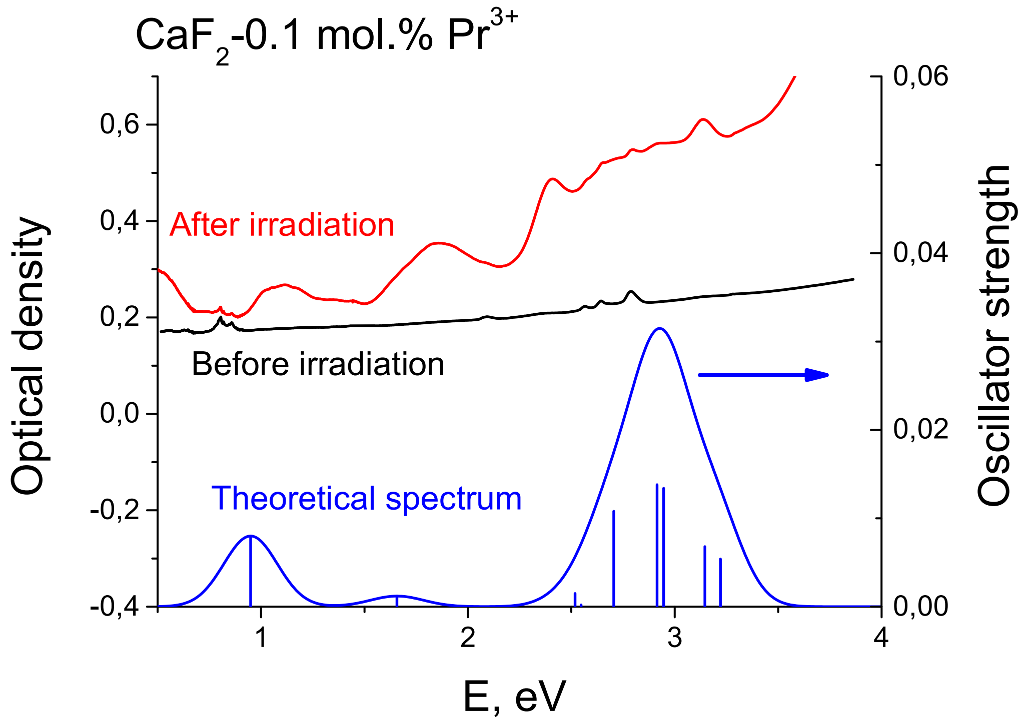



Structure of absorption spectra of irradiated $CaF_2$ and $BaF_2$ doped with $Pr^{3+}$ ions is quite similar. The spectra of $BaF_2$ are shifted to blue region. But we observe no bands at about 0.5 eV in $BaF_2$.

Optical density of absorption bands at in irradiated crystals depends on concentration.

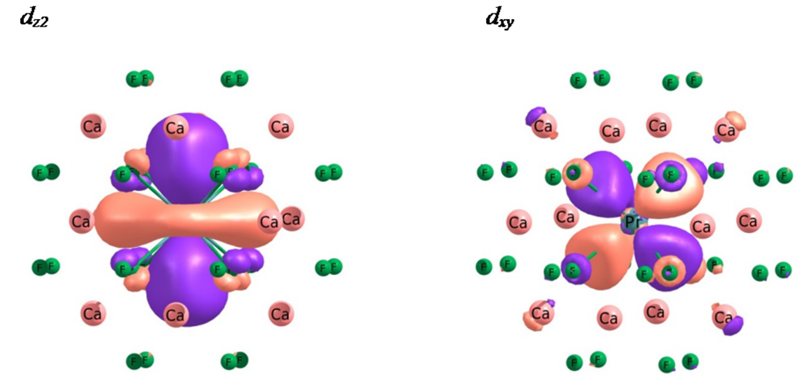
The bands at 2.3, 3.4, 4.1, 4.4 eV are corresponded to f-d transitions in $Pr^{2+}$ ions.

# Theoretical calculation. Results




Experimental and theoretical absorption spectra of $CaF_2$-$Pr^{2+}$ crystals

The band at 0.9 eV corresponds to 4f→5d ($e_g$) transition. Group of lines with energies at 2.5-3.3 eV is related to transitions from 4f to 5d ($t_{2g}$) states containing 3d and 4s orbitals of calcium ions.

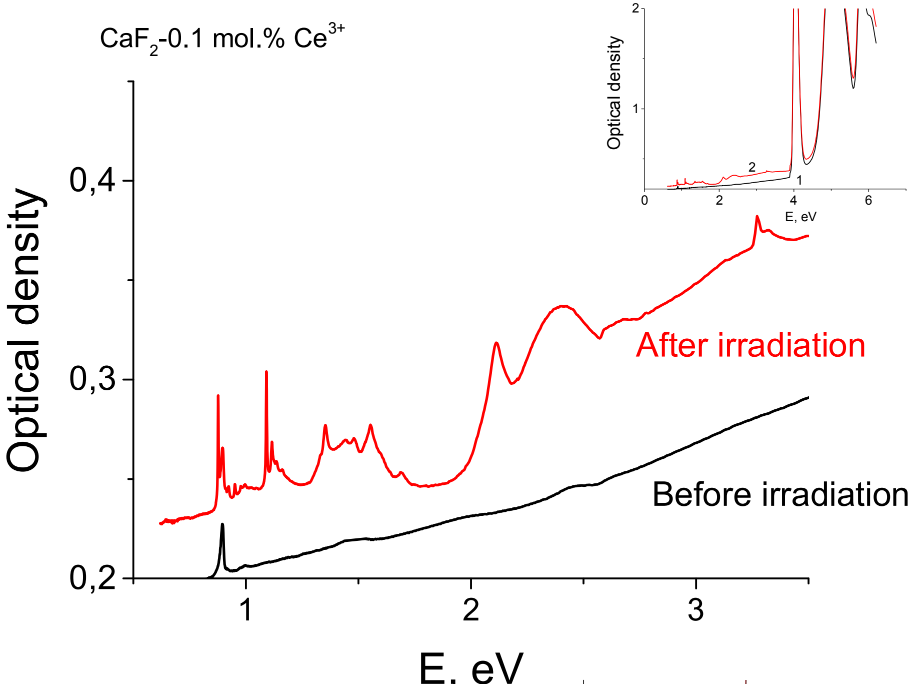


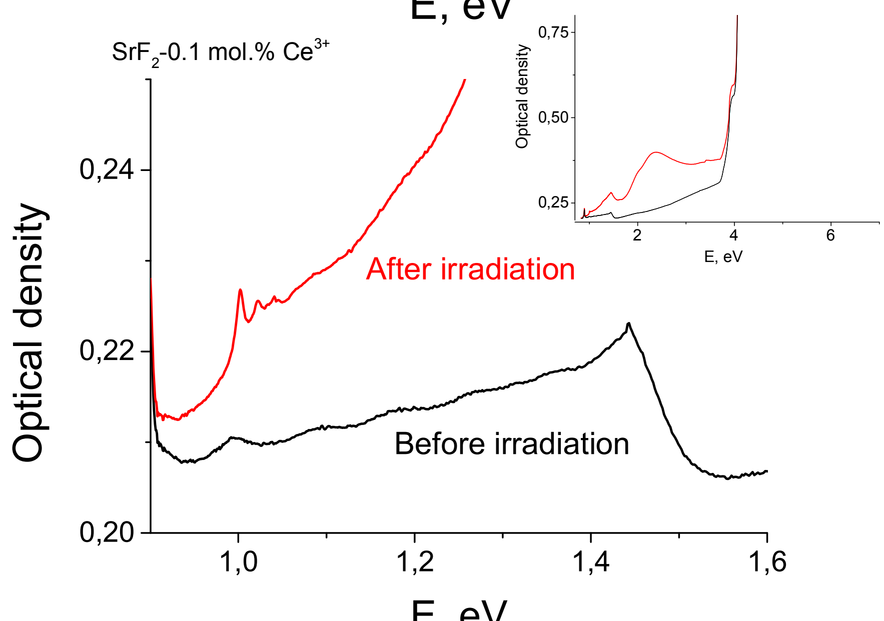

Single electron orbitals of $e_g$ (*left*) and $t_{2g}$ (*right*) energy levels of 5d state of $Pr^{2+}$ ion in $CaF_2$

| Symmetry | $O_h$ |
|---|---|
| Displacement of fluorine ion | 0.08 Å |
| Displacement of calcium ion | 0.05 Å |

Geometry calculation of $CaF_2$-$Pr^{2+}$

# 3. Crystal doped with $Ce^{3+}$




Wide bands with energies higher 1.8 eV correspond to photochromic centers [Sizova, IEEE TNS, 2012]

Sharp lines are related to 4f5d-4f transitions in $Ce^{2+}$ in $CaF_2$ [Alig]. In $SrF_2$-Ce crystals the similar structure of the bands is observed

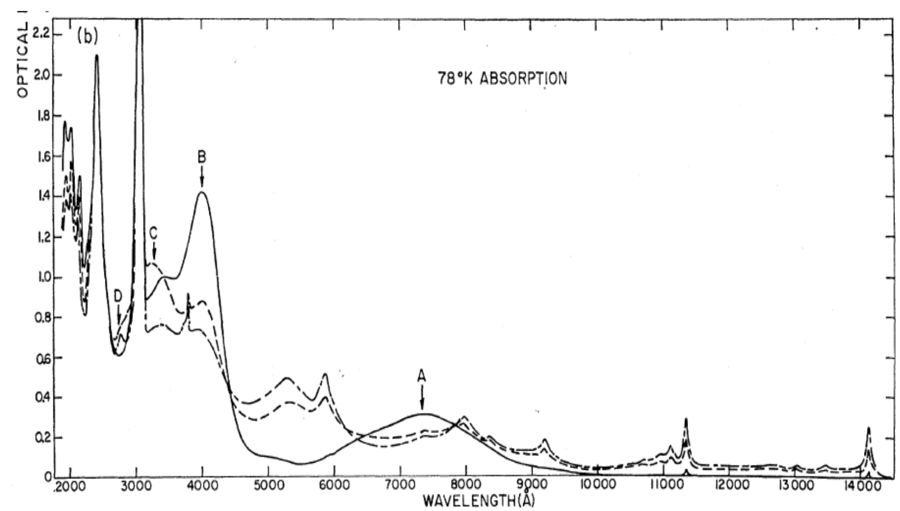



FIG. 1. Absorption spectrum of additively colored $CaF_2:Ce^{2+}$ at 78 and 300°K after different photochemical treatments.

[Alig, PhysRevB, 1969]

# Electron-hole energy transfer

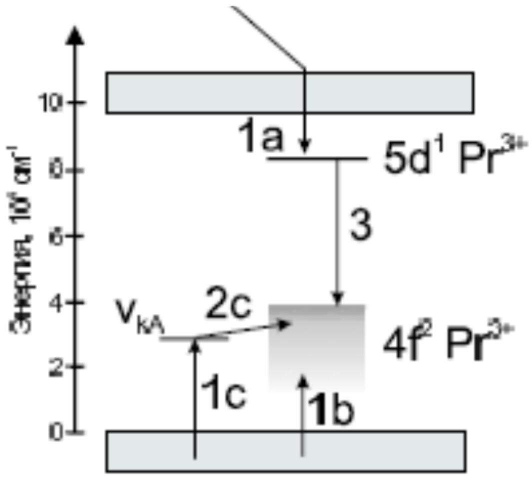



Рис. 4.13. Процессы последовательного электрон-дырочного захвата в кристалле $CaF_2$-$Pr^{3+}$. На рисунке: 1a – захват ионом $Pr^{3+}$ электрона из зоны проводимости, 1b – захват ионом $Pr^{2+}$ «горячей» дырки, 1c – автолокализация дырки в $V_{kA}$ центре, 2c – освобождение дырки из $V_{kA}$ центра и перенос ее на ион $Pr^{2+}$, 3 – люминесценция возбужденного иона $Pr^{3+*}$.

1) Fast consecutive electron-hole transfer is not efficient in fluorides doped with rare earth [Radzhabov, IEEE TNS 2012; Shendrik, IEEE TNS 2012]

2) Delayed energy transfer. Hole or electron is captured by a trap and then transferred to emission center.

In SrF2-Ce electron can be first captured by a trap and only then transferred to Ce ion. [Radzhabov, NIM 2002]

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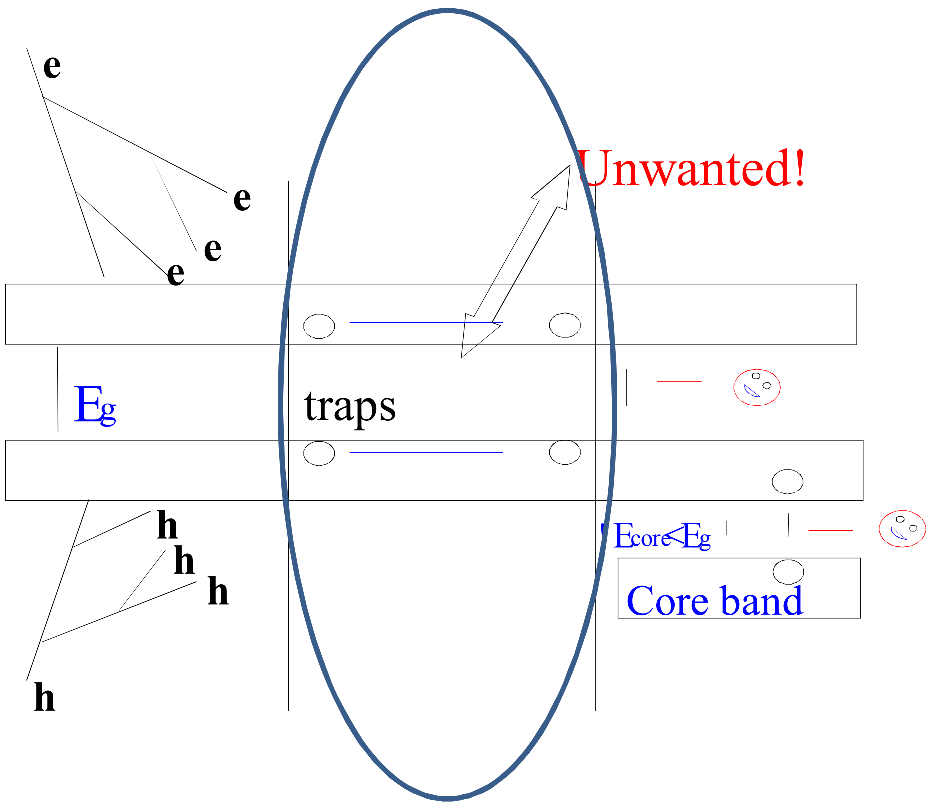


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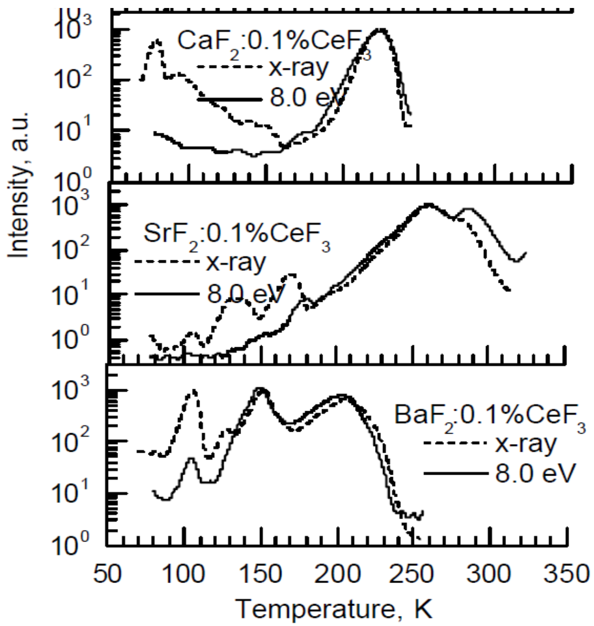
# Electron-hole energy transfer

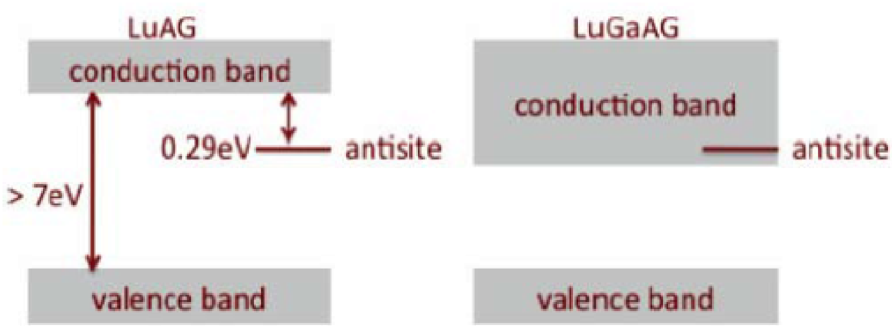



[Radzhabov2002, NIM]

Delayed energy transfer explains longtime decay components in 5d-4f emission of Ce3+ ions.

**How to diminish an influence of the delayed transfer mechanism?**

Co-doping of the SrF2-Ce crystals to decrease band gap -- “Band-gap engineering” was applied in garnets. [LuAG→LuGaAG, M.Fassoli et al, Phys. Rev.B 2010]



# Electron-hole energy transfer

**Possible co-activators of SrF2-Ce –**

1) **Ga3+, In3+**, such in LuAG. Expected effect:

+ Decrease of band-gap to 1-1.4 eV.

-- Creation of interstitial fluorine ions (charge compensation) after co-doping => using Na+ ions co-doping simultaneously

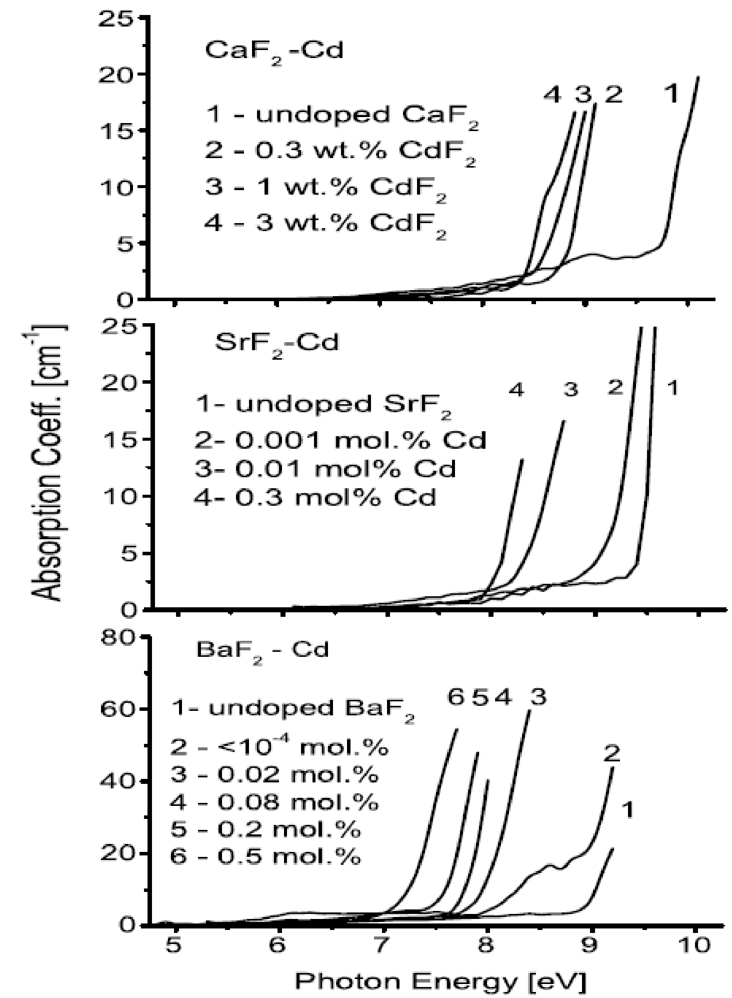
2) **Cd2+**

+ Decrease of band-gap to 1.3-1.7 эВ [Radzhabov, pss 2005].

+ No interstitial fluorine ions

-- Crystal doped with high concentration of Cd2+ is grown complicated

-- STE suppressing by Cd ions. Possible decreasing of Ce3+emission.

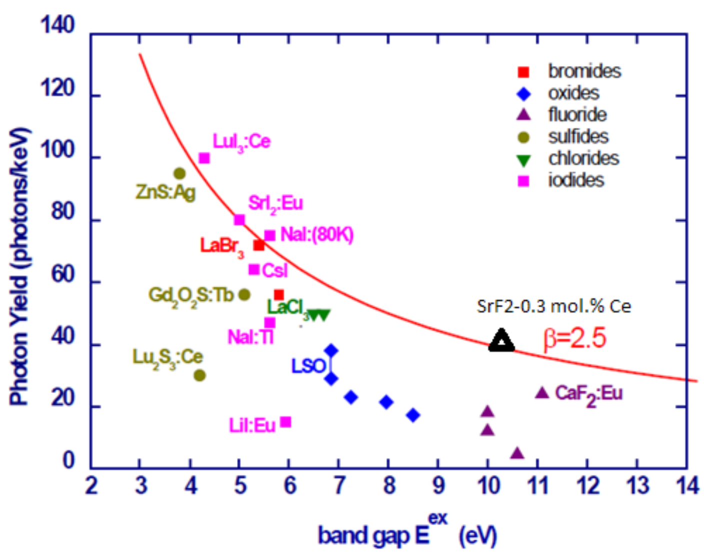


# Perspectives

Measured light yield will be increased:

- Co-doping SrF2-Ce with Ga3+, or In3+. The maximum scintillation yield will reach x-ray luminescence light output (about 50000 ph/MeV).
- To find PMT with better parameters (spectral sensitivity).

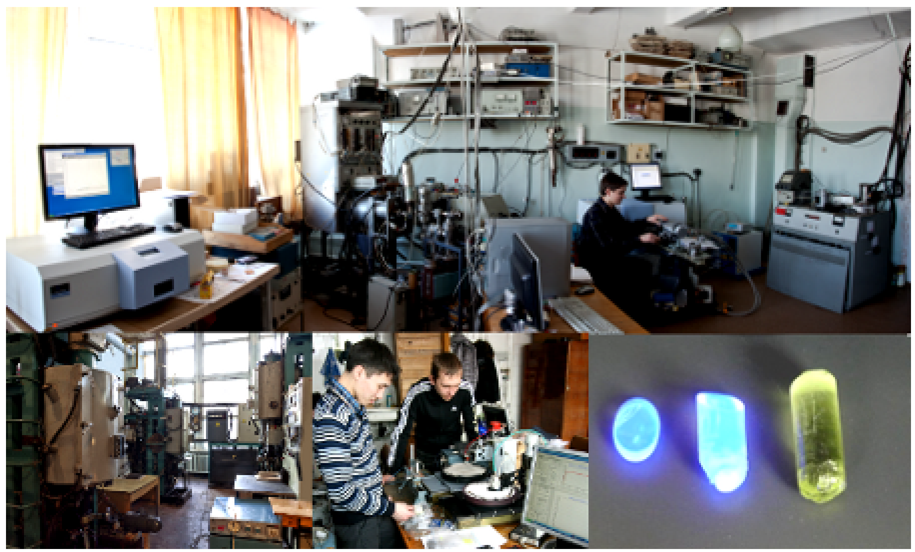
- **Future of SrF2:**
- SrF2-Ce and SrF2-Pr are new scintillators with better than NaI-Tl parameters: higher density, similar light yield, shorter decay time, and no hygroscopic.
- New scintillator for well-logging. High temperature stability of LY.



# Выводы

1) Большое влияние на сцинтилляционные свойства кристаллов оказывает то, каким способ передается энергия возбуждения от кристаллической решетки к центрам свечения
2) Комплексное изучения экспериментальными и теоретическими методами позволяет установить механизмы передачи энергии и «мешающие факторы»
3) По результатам таких исследований возможно принять меры по улучшению сцинтилляционных характеристик и дальнейшему практическому использованию данного материала.

- Спасибо за внимание!

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