Luminescent and radiation-induced properties of $M_{1-x}Pr_xF_{2+x}$ (M^{2+}=Ca, Sr, Ba, x=0.35) solid solutions

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ISMA

New potential applications of fluorides

SUCCESS

✓ **Homogeneous Hadron Calorimeter Detector (HHCAL)**

The problem: dual readout of Cherenkov and scintillation light to achieve good resolution for hadrons and jets

Requirements to Materials:

High density (>7g/cm^3) and Z_{eff}

wide E_g (good UV transmittance: UV cut-off < 350 nm)

Some scintillation light, *not necessary* bright and fast

Candidates: PbF_2, …?

✓ **Dark matter search**

The problem: detecting Weakly Interacting Massive Particles (WIMP)

Requirements to Materials:

Discrimination the weak and rare signal over the background caused by natural radioactivity

High interaction rates with WIMPs

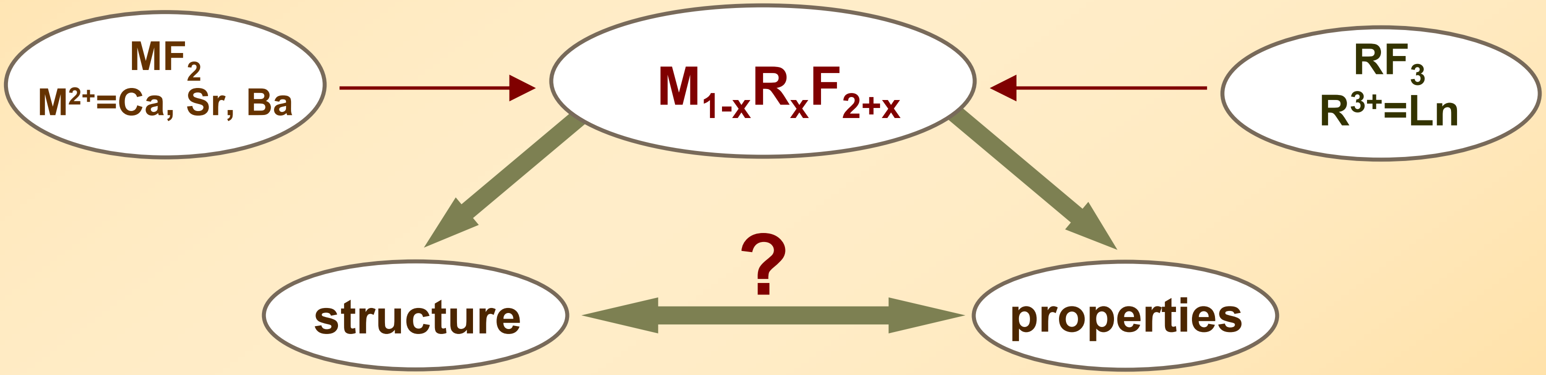
Sufficient light yield at low temperature

Candidates: LiF, CaF_2:Eu, …?

Motivation

From the engineering point of view some attempts can be made to modify **luminescent properties** of fluorides via modification of **crystalline host**

In this case **mixed $M_{1-x}R_xF_{2+x}$ crystals** are of interest as model objects, since **R^{3+}** ions become the **part** of **matrix** cations

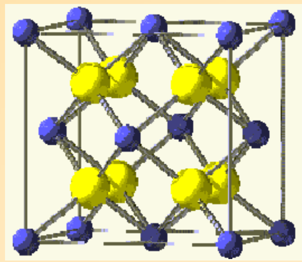


The main question:

How the modification of the crystal structure will influence on luminescent and radiation induced properties of the obtained mixed crystals?

$M_{1-x}R_xF_{2+x}$ (M^{2+}=Ca, Sr, Ba, R^{3+}=Ln) – myxed crystals

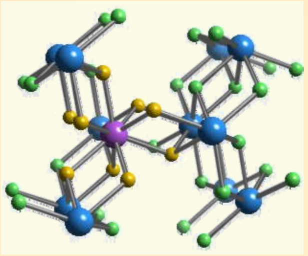
MF_2 (M^{2+}=Ca, Sr, Ba)



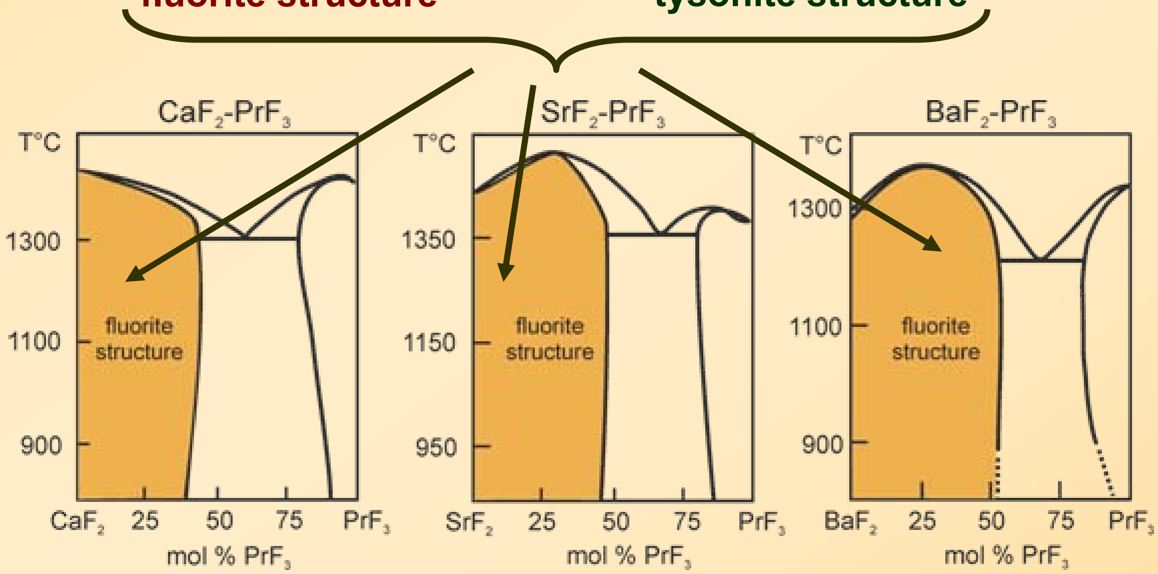
fluorite structure

+

RF_3 (R^{3+}=La–Nd)



tysonite structure



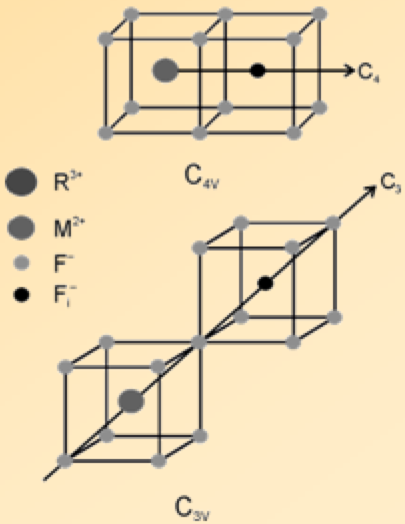
- ✓ high reciprocal solubility of MF_2 and RF_3 despite different structure types
- ✓ wide concentration range ($x \leq 0.5$) of fluorite-type $M_{1-x}R_xF_{2+x}$ solid solutions

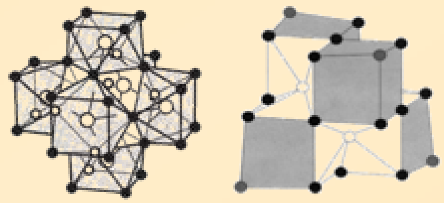
Formation of $M_{1-x}R_xF_{2+x}$ solid solutions

RF_3 concentration increase in the solid solution

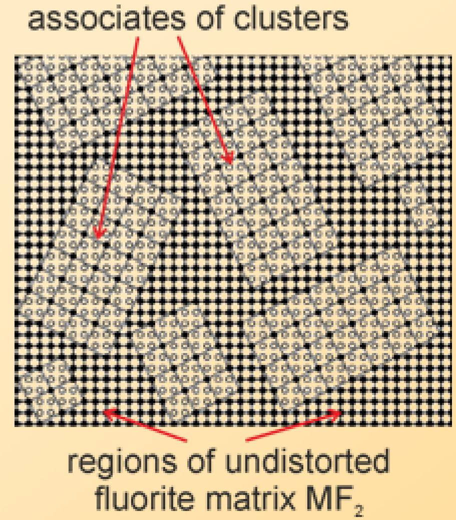
C ≤ 0.01 mol% → C~20-50 mol%

R^{3+}-F_i^- dipoles → $(R^{3+}$-$F_i^-)_n$ aggregates → Defect clusters → $M_{1-x}R_xF_{2+x}$





concentrate R^{3+}, F_i^- and v_a^+

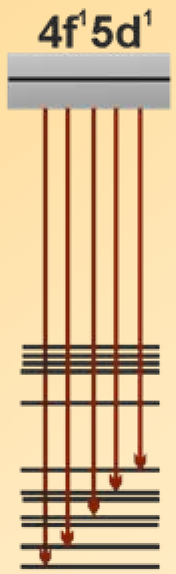


B.P. Sobolev, 2003

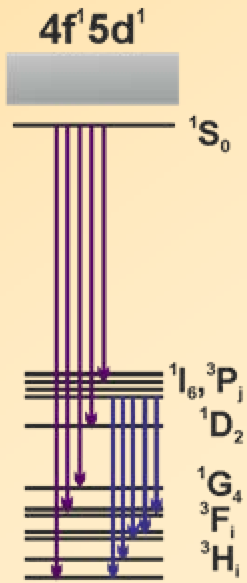
Modification of crystal structure via increasing of R^{3+} concentration

$M_{1-x}Pr_xF_{2+x}$ –why Praseodymium?

Pr^{3+}



$4f^15d^1 \rightarrow 4f^2$



Photon Cascade Emission (PCE)

coord. numb. ≤8

coord. numb. ≥9

P. Rodnyi, 2002; Makhov, 2003

MF_2:Pr,
KYF_4:Pr
$LiKYF_5$:Pr

PrF_3
YF_3:Pr
$KMgF_3$:Pr
$SrYF_5$:Pr

Pr^{3+} is suitable as "probe" ion due to the strong dependence of luminescent properties on local environment

"Background": appearance of PCE centers in MF_2-Pr with increase in Pr^{3+} concentration
[E.A.Radzhabov, 2009; P. A. Rodnyi 2005]

Outline

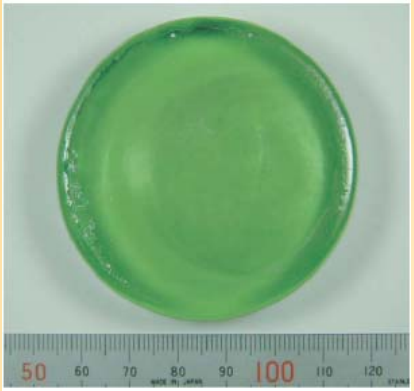
✓Characterization of $M_{1-x}Pr_xF_{2+x}$ crystals

✓Different types of emission centers in $M_{1-x}Pr_xF_{2+x}$ solid solutions and their possible origin

✓Radiation damage

✓Conclusions

Crystal characterization and experimental details



$Ca_{0.65}Pr_{0.35}F_{2.35}$ crystal

$M_{1-x}Pr_xF_{2+x}$ crystals:

- ✓ grown by Bridgeman technique in CF_4 atmosphere (Institute for Materials Science, Tsukuba, Japan)
- ✓ free from oxygen-containing impurities
- ✓ have the fluorite structure (*Fm3m)*
- ✓ no presence of PrF_3 phase

Crystal	Lattice constant, Ǻ	Structure type
CaF_2	5.463	fluorite *Fm3m*
$Ca_{0.65}Pr_{0.35}F_{2.35}$	5.613	
SrF_2	5.799	
$Sr_{0.65}Pr_{0.35}F_{2.35}$	5.815	
BaF_2	6.200	
$Ba_{0.65}Pr_{0.35}F_{2.35}$	6.037	

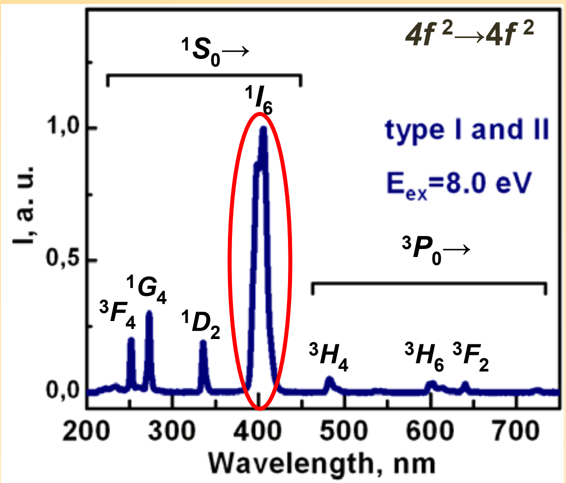
Techiques

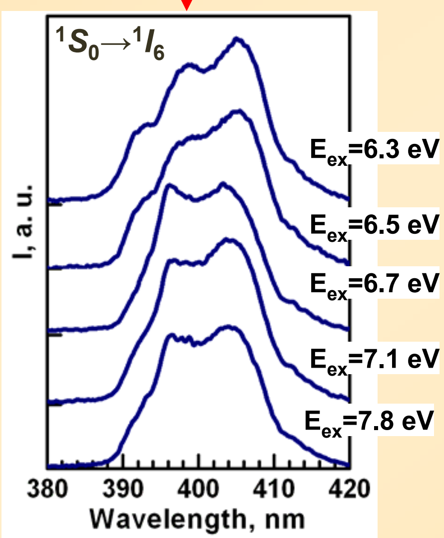
- ✓ luminescent spectroscopy under SR excitation (SUPERLUMI, DESY, Hamburg)
- ✓ absorption
- ✓ thermostimulated luminescence (TSL)

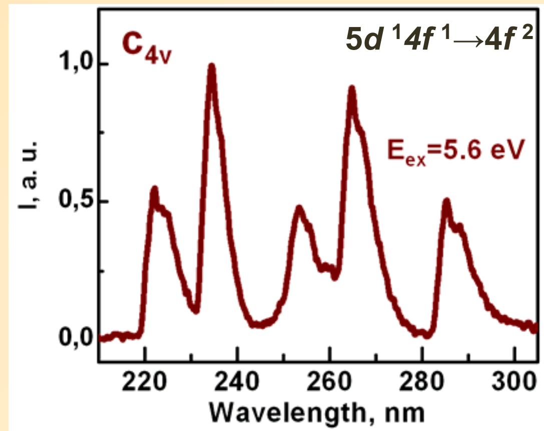
Emission centers in $Ca_{1-x}Pr_xF_{2+x}$ (x=0.35)

Emission

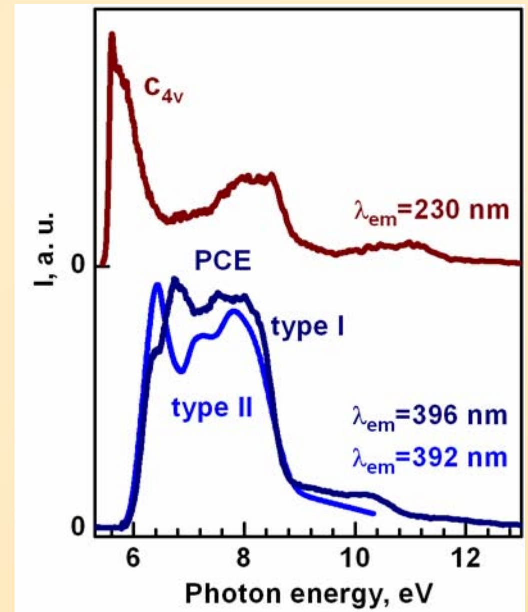
Photon Cascade Emission (PCE)







Excitation



Different emission centers

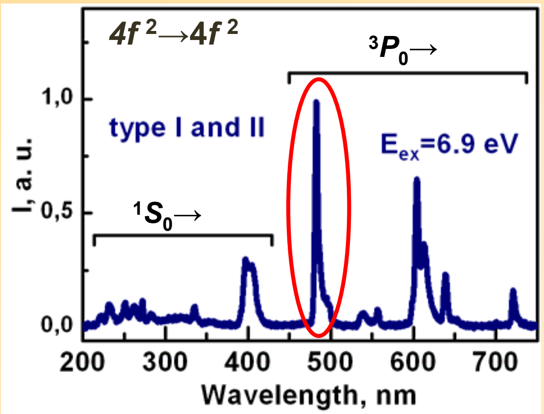
✓PCE centers (two types) – dominant

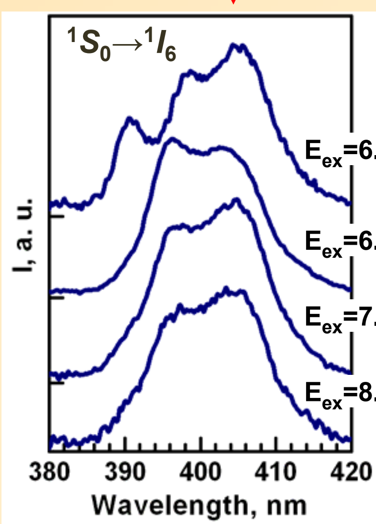
✓$5d\,^14f\,^1 \rightarrow 4f\,^2$ is typical for single Pr^{3+} ions in C_{4V} symmetry sites

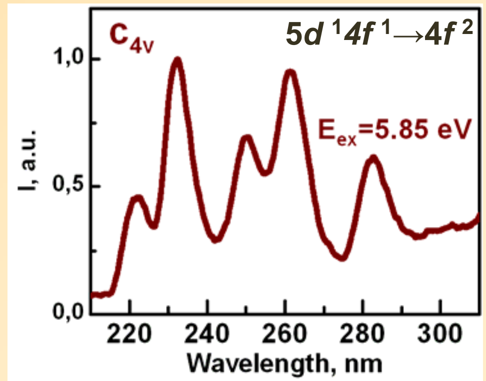
Emission centers in $Sr_{1-x}Pr_xF_{2+x}$ (x=0.35)

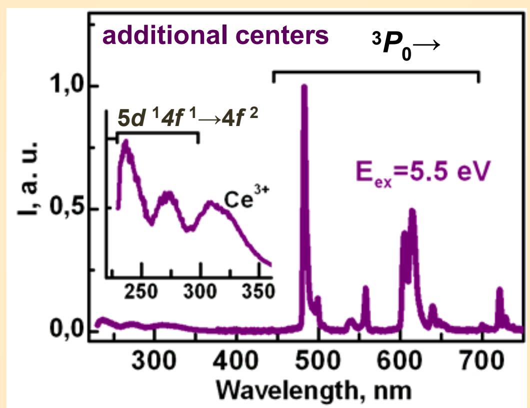
Emission

Photon Cascade Emission (PCE)

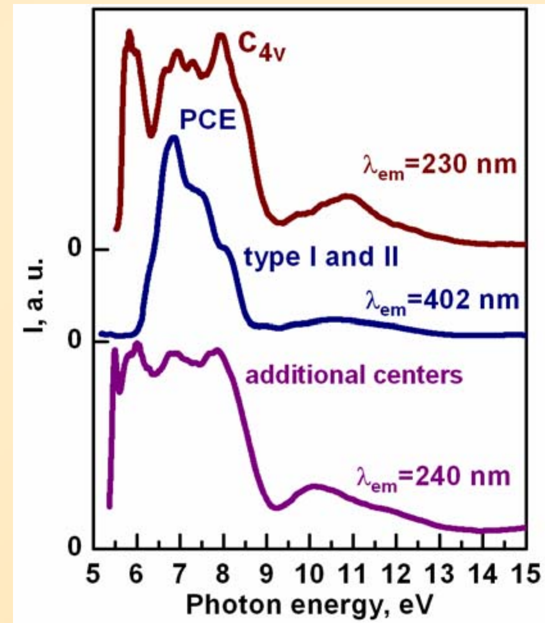








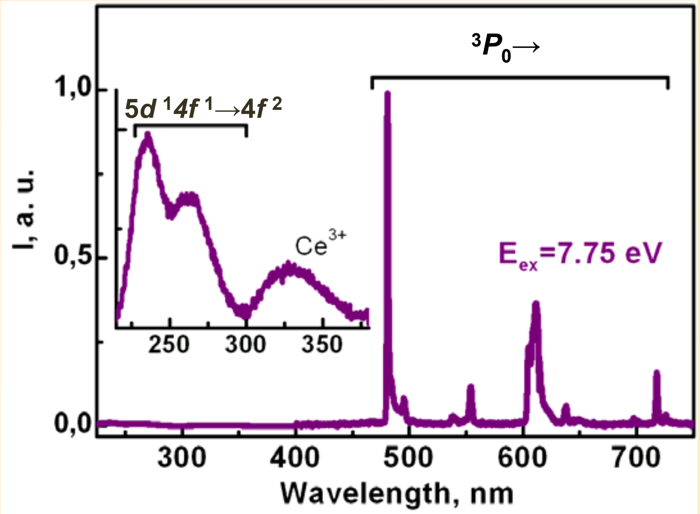
Excitation



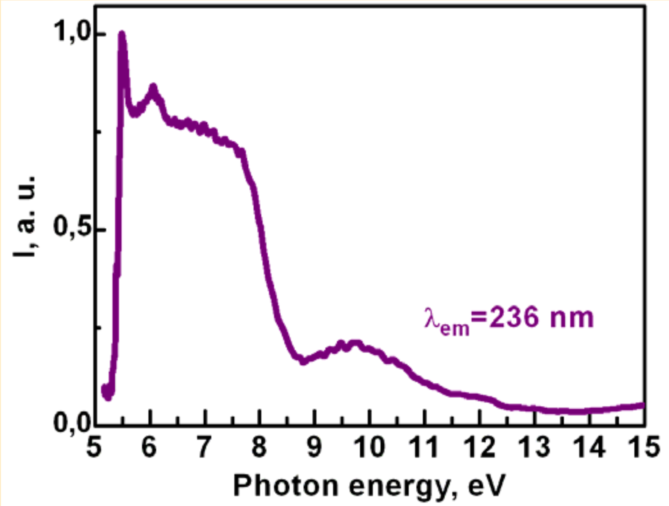
- ✓ single Pr^{3+} ions in C_{4V} sites
- ✓ two types of PCE centers
- ✓ additional type of centers (absent in $Ca_{0.65}Pr_{0.35}F_{2.35}$)

Emission centers in $Ba_{1-x}Pr_xF_{2+x}$ (x=0.35)

Emission



Excitation



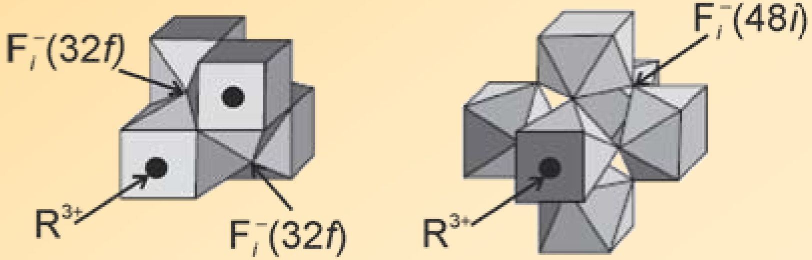
- ✓only one type of emission center
- ✓ luminescent properties of observed centers in $Ba_{0.65}Pr_{0.35}F_{2.35}$ and additional centers in $Sr_{0.65}Pr_{0.35}F_{2.35}$ are similar
- ✓low efficiency of $5d\,^14f\,^1\rightarrow4f\,^2$ emission alongside with intense transitions from $^3P_0$ level may be due to cross-relaxation between adjacent Pr^{3+} ions via the following scheme : $5d\,^14f\,^1 + ^3H_4\rightarrow{}^3P_0+^3P_0$

Possible origin of emission centers in $M_{1-x}Pr_xF_{2+x}$

Crystal	$(Pr^{3+}$,free)	Possible origin of center					
		clusters					
		1:0:3		1:0:4		8:12:0	
	E_{fd}, eV	E_{fd}, eV	D, eV	E_{fd}, eV	D, eV	E_{fd}, eV	D, eV
$Ca_{0.65}Pr_{0.35}F_{2.35}$	7.58	6.46	1.12	6.90	0.68	–	
$Sr_{0.65}Pr_{0.35}F_{2.35}$		6.40	1.18	6.85	0.73	5.46	2.12
$Ba_{0.65}Pr_{0.35}F_{2.35}$		–		–		5.49	2.08

$r(R^{3+})/r(M^{2+})$~1.02-1.08
Clusters
1:0:4 (1:0:3)

$r(R^{3+})/r(M^{2+})$~0.7-0.8
Cluster
8:12:0



up to 3 R^{3+} ions

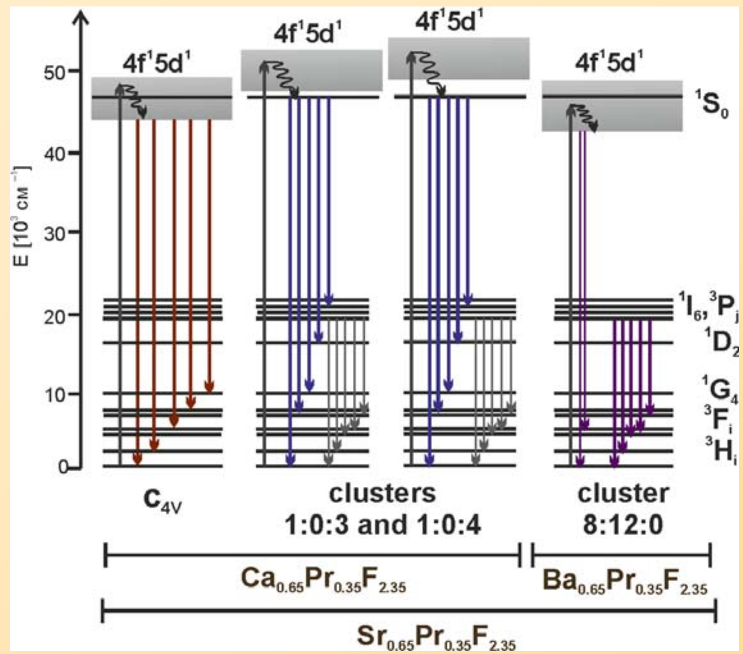
R^{3+} coord. numb. =10(9)
irregular 10(9)-vertices polyhedron

up to 6 R^{3+} ions

R^{3+} coord. numb. =8
distorted square antiprism

B.P. Sobolev, 2003; J.P. Laval, 1989l

D("redshift")=$E_{fd}(R^{3+}$, free) – $E_{fd}(R^{3+}$, A)
[P. Dorenbos, 2003]

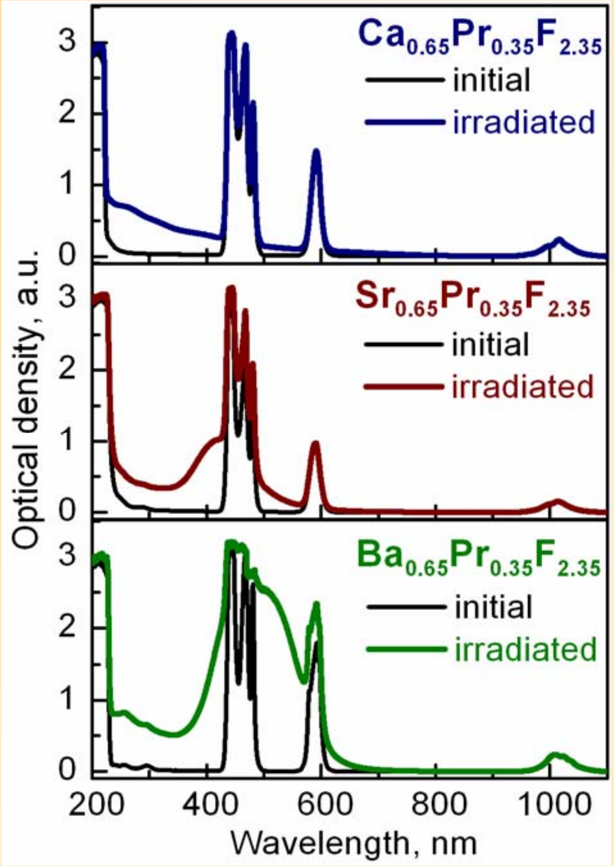


Crystal	$r(Pr^{3+})$, Å	$r(M^{2+})$, Å	$r(Pr^{3+}) / r(M^{2+})$
$Ca_{0.65}Pr_{0.35}F_{2.35}$	1.06	0.99	1.07
$Sr_{0.65}Pr_{0.35}F_{2.35}$		1.12	0.95
$Ba_{0.65}Pr_{0.35}F_{2.35}$		1.34	0.79

Radiation coloration of $M_{1-x}Pr_xF_{2+x}$ (M^{2+}=Ca, Sr, Ba, x=0.35)

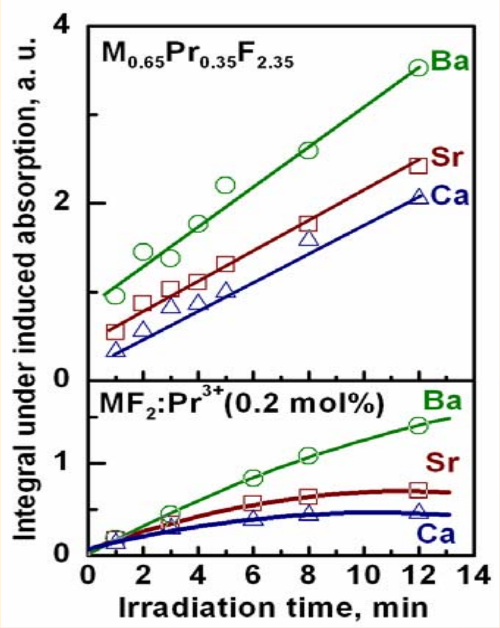
X-irradiation, 300 K

Absorption spectra, D=80 Gy



✓ **Absorption bands typical for Pr^{2+} ions are absent**

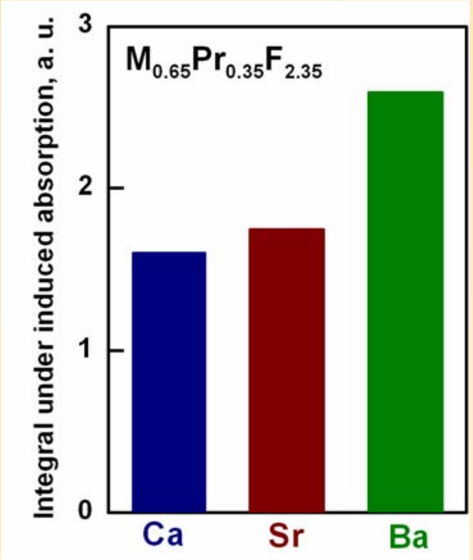
Induced absorption vs. irradiation time

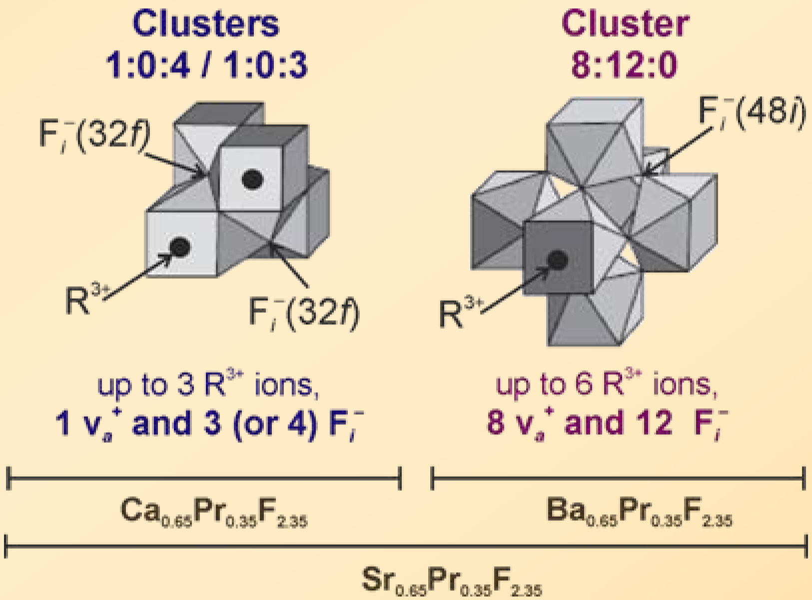


✓ **Contrary to $MF_2:Pr^{3+}$ induced absorption of mixed crystals shows linear dependence on irradiation time without saturation region → color centers formation in $M_{0.65}Pr_{0.35}F_{2.35}$ due to pre-irradiation defects**

Coloration efficiency of $M_{1-x}Pr_xF_{2+x}$ (M^{2+}=Ca, Sr, Ba, x=0.35)

Coloration efficiency, D=80 Gy





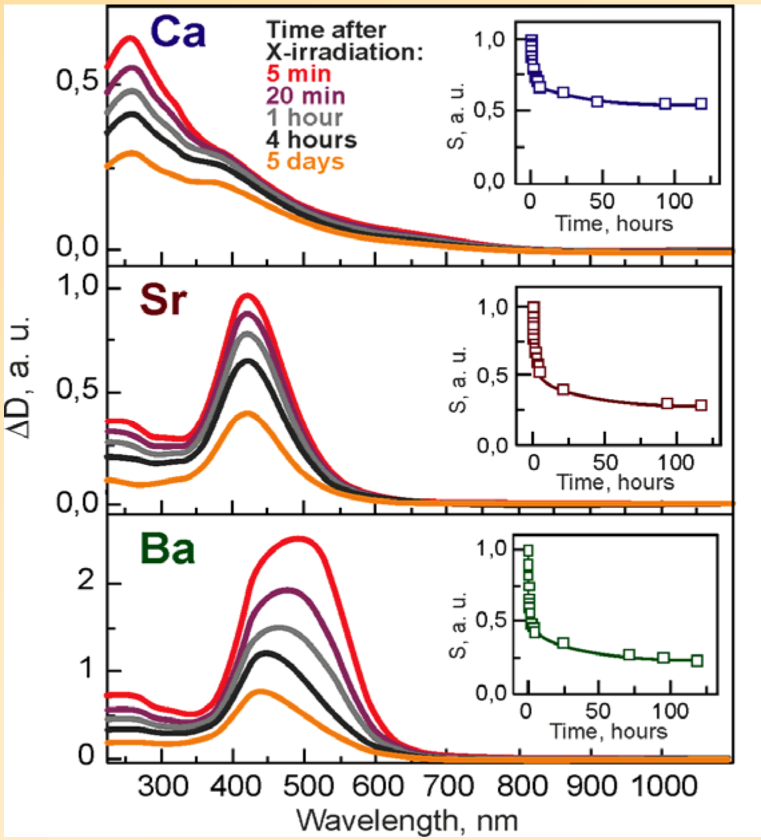
✓ the number of anion sublattice defects (V_a^+ and F_i^-) is higher for 8:0:12 clusters than for 1:0:3/1:0:4 ones

Increase in coloration efficiency in the row Ca→Sr→Ba is in agreement with cluster formation model

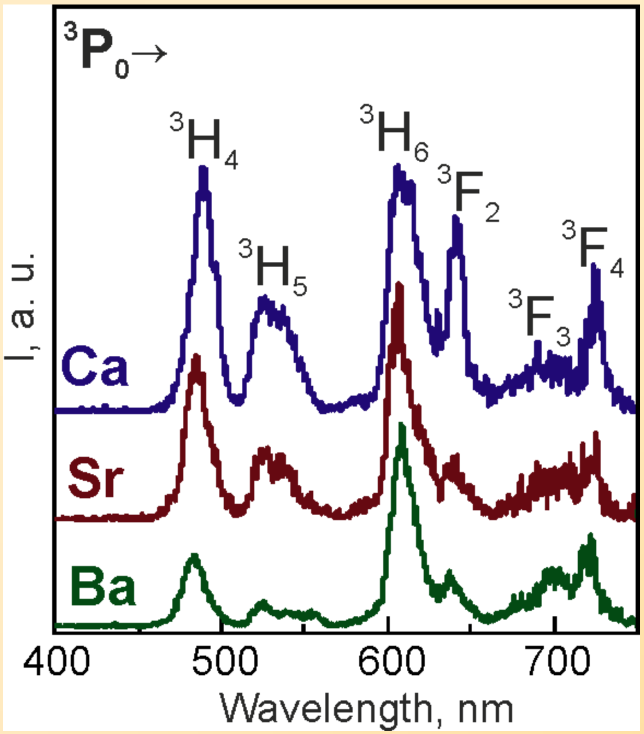
Color centers destruction

X-irradiation, 300 K, D=80 Gy

Induced absorption



Afterglow



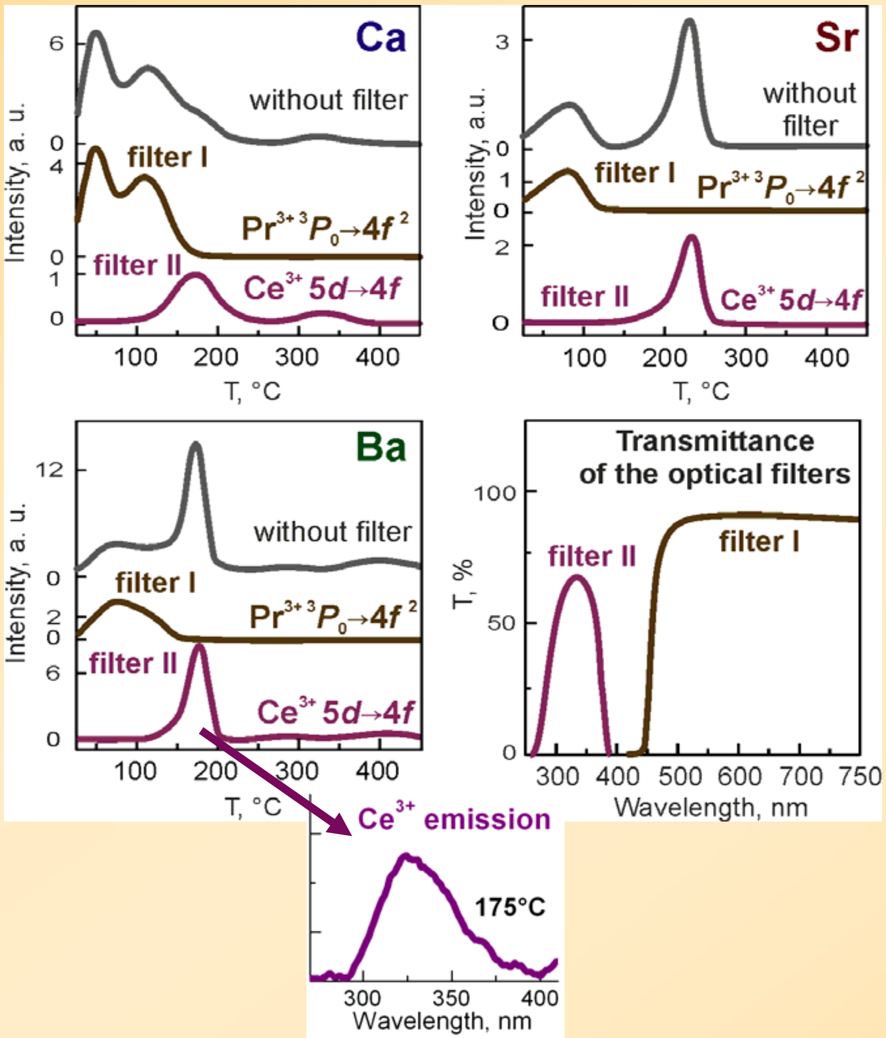
✓Color centers destruction shows two stages → the presence of defects with different thermal stability

✓the first stage of color centers destruction is accompanied by the afterglow corresponded $^3P_0\rightarrow 4f^2$ radiative transitions in Pr^{3+}

Thermostimulated luminescence

X-irradiation, 300 K, D=200 Gy

TL glow curves



✓ $5d^1 4f^1 \rightarrow 4f^2$ and $^1S_0 \rightarrow 4f^2$ radiative transitions of Pr^{3+} are not observed in TSL

✓ low temperature TL peaks (50-120°C) correspond to $^3P_0 \rightarrow 4f^2$ transitions in Pr^{3+}

✓ weak intensity of low temperature TL peaks:
* thermal quenching of emission from $^3P_0$ level
* cross-relaxation between adjacent Pr^{3+} ions

✓ high temperature peaks (170-240°C) are due to $5d \rightarrow 4f$ emission of impurity Ce^{3+} ions

✓ the energy of recombination of thermally released charge carriers may be non-radiatively transferred to the nearest Pr^{3+} ion, populating the low-lying $^3P_0$-level and giving rise to correspondent emission

Conclusions

In general

✓**Crystals of the $M_{1-x}R_xF_{2+x}$ solid solutions grown from melt are stable materials (no signs of decomposition during storage and thermal cycling).**

✓**Mixed crystals open the potential possibility for modification of fluoride material properties via the selection of a proper composition.**

In particular

- ✓ **Various emission centers observed in $M_{1-x}Pr_xF_{2+x}$ (M^{2+}=Ca, Sr, Ba, x=0.35) solid solutions may be assigned to Pr^{3+} ions in different cluster types.**
- ✓ **Modification of the crystal structure due to the process of clustering leads to changing in the local environment of Pr^{3+} ions, and as the result to shifting of the lowest excited 5*d* level.**
- ✓ **Efficiency of color centers formation for $M_{1-x}Pr_xF_{2+x}$ (M^{2+}=Ca, Sr, Ba, x=0.35) crystals is higher than for MF_2:Pr due to high concentration of pre-irradiation defects. The growth of coloration efficiency in the row Ca→Sr→Ba is due to the presence of the different cluster types in these systems.**

Thank you for attention!