Anomalous europium luminescence in LaF_3

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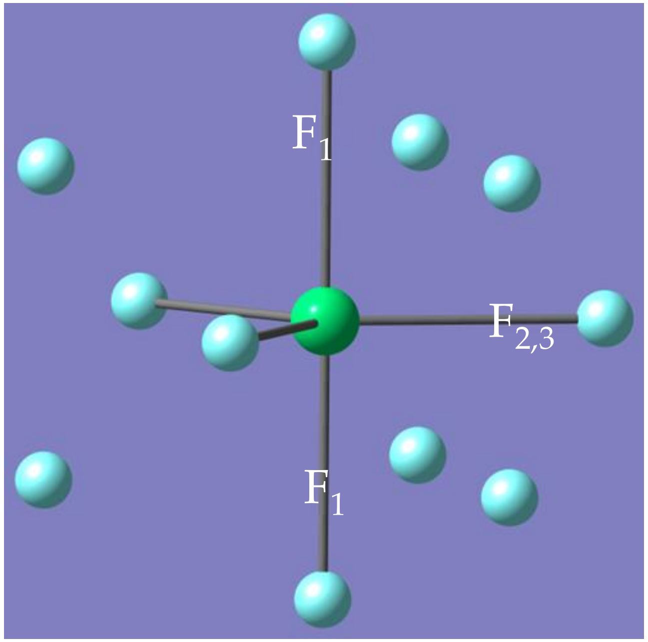
Introduction

Apart to detailed studies of LaF_3-Re^{3+} the spectroscopy of Re^{2+} in this host remains uninvestigated. Europium Eu^{2+} ions are known as very efficient luminescence impurity in dense scintillating hosts. Besides the normal 5d-4f luminescence in most materials, the Eu^{2+} shows so called anomalous luminescence with large Stokes shift near 1 eV in certain crystals . No data on absorption and luminescence of Eu^{2+} in LaF_3 were found.

The aim of this paper is investigation of dielectric and optical spectra of divalent Eu, Sm in crystal LaF_3 and clarification the nature of charge compensator as well as its influence on optical transitions.

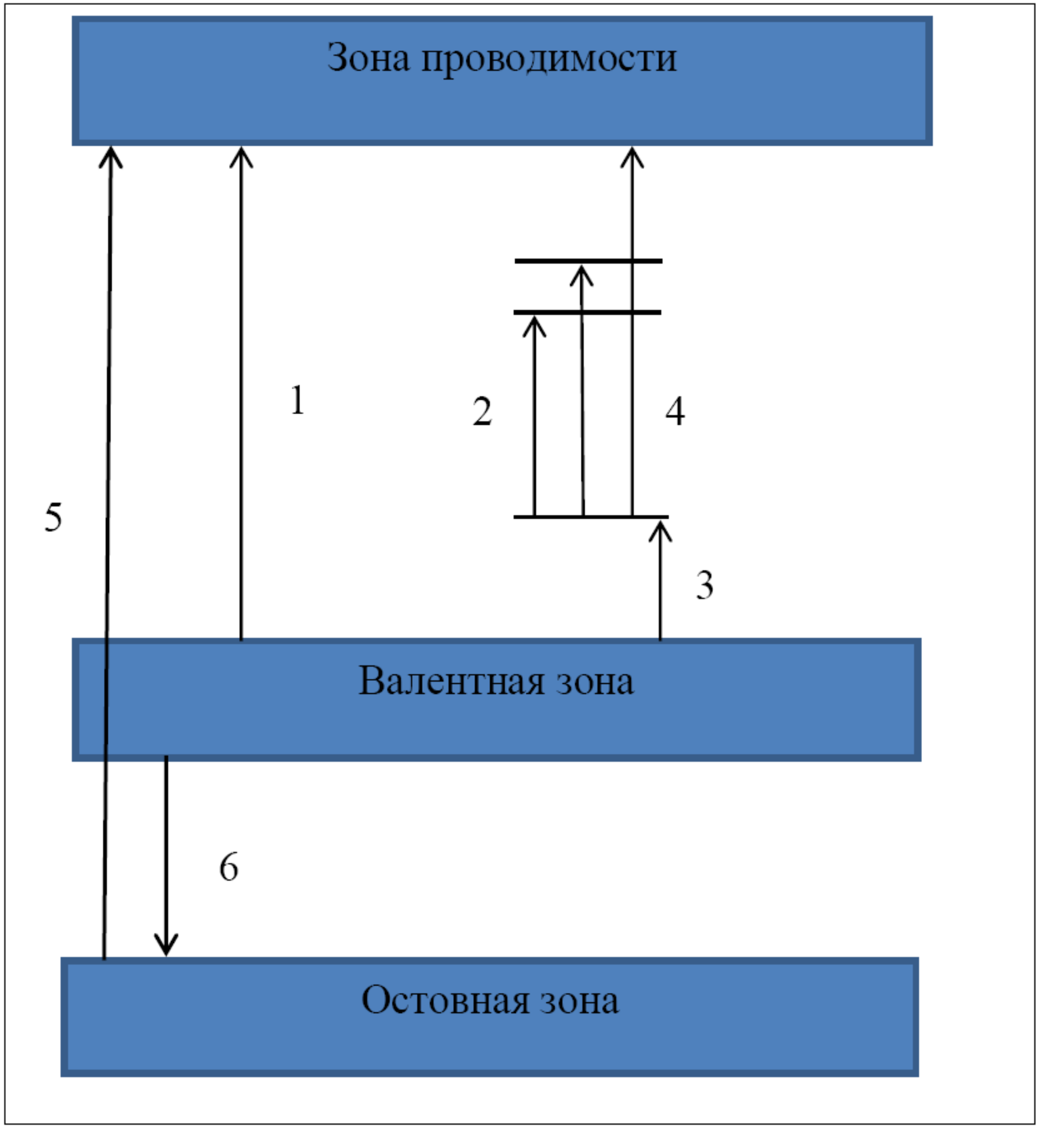


La in centre and nearest fluorines in LaF_3 lattice D_{3h} -symmetry

Типы переходов в диэлектриках

Типы переходов в диэлектриках

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)



Conductivity

A feature of LaF_3 is high electrical conductivity undoped crystals at room temperature, which amounts to about 10^{-6} $ohm^{-1}cm^{-1}$. The conductivity of lanthanum fluoride for several orders of magnitude higher conductivity of alkaline earth fluorides. Numerous studies have found that the conductivity is due to the migration of LaF_3 fluorine vacancies. When introducing divalent ion Ba, Sr, Ca the LaF_3 conductivity increases significantly, that due to the presence of anionic vacancies.

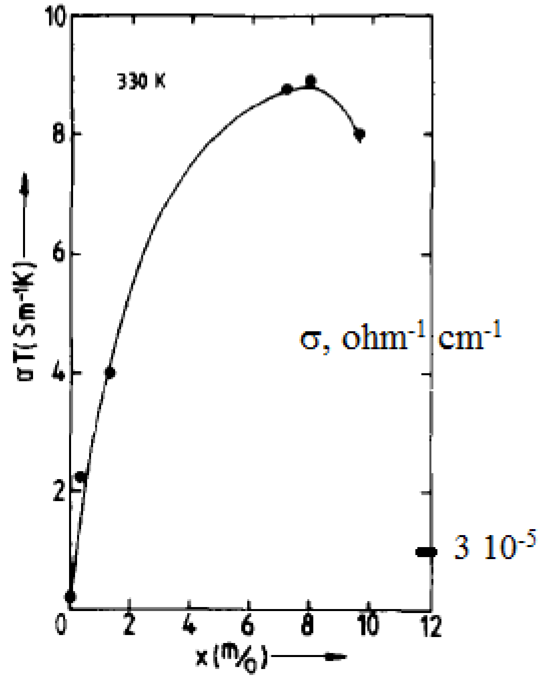
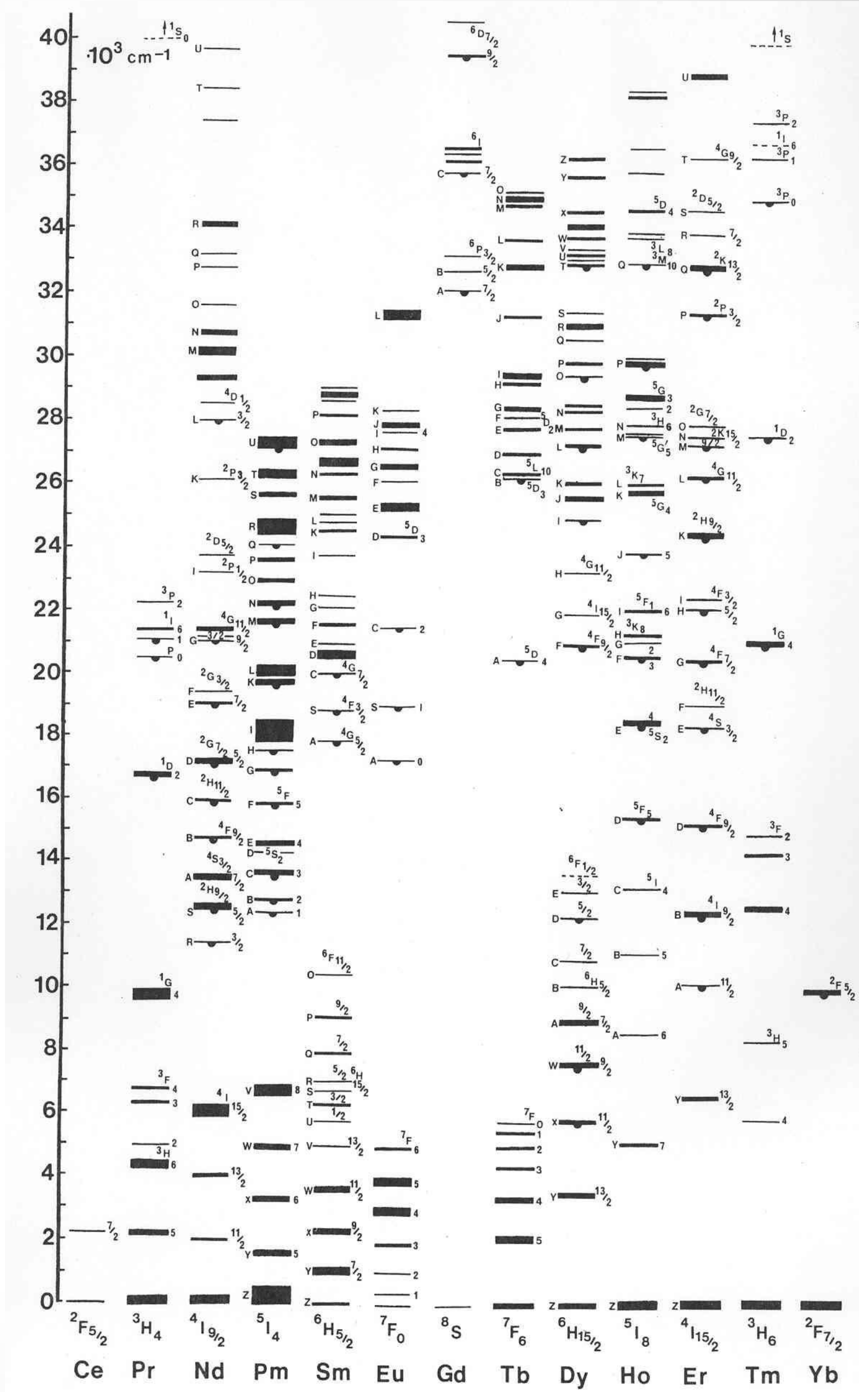


Fig. 3. The isothermal conductivity at 330 K plotted as σT versus x for the solid solutions $La_{1-x}Ba_xF_{3-x}$ ($\perp c$ axis).

A.Roos et al. Sol.St.Ionics, **13** (1984) 191-203

Уровни f-оболочки

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



Levels in band scheme

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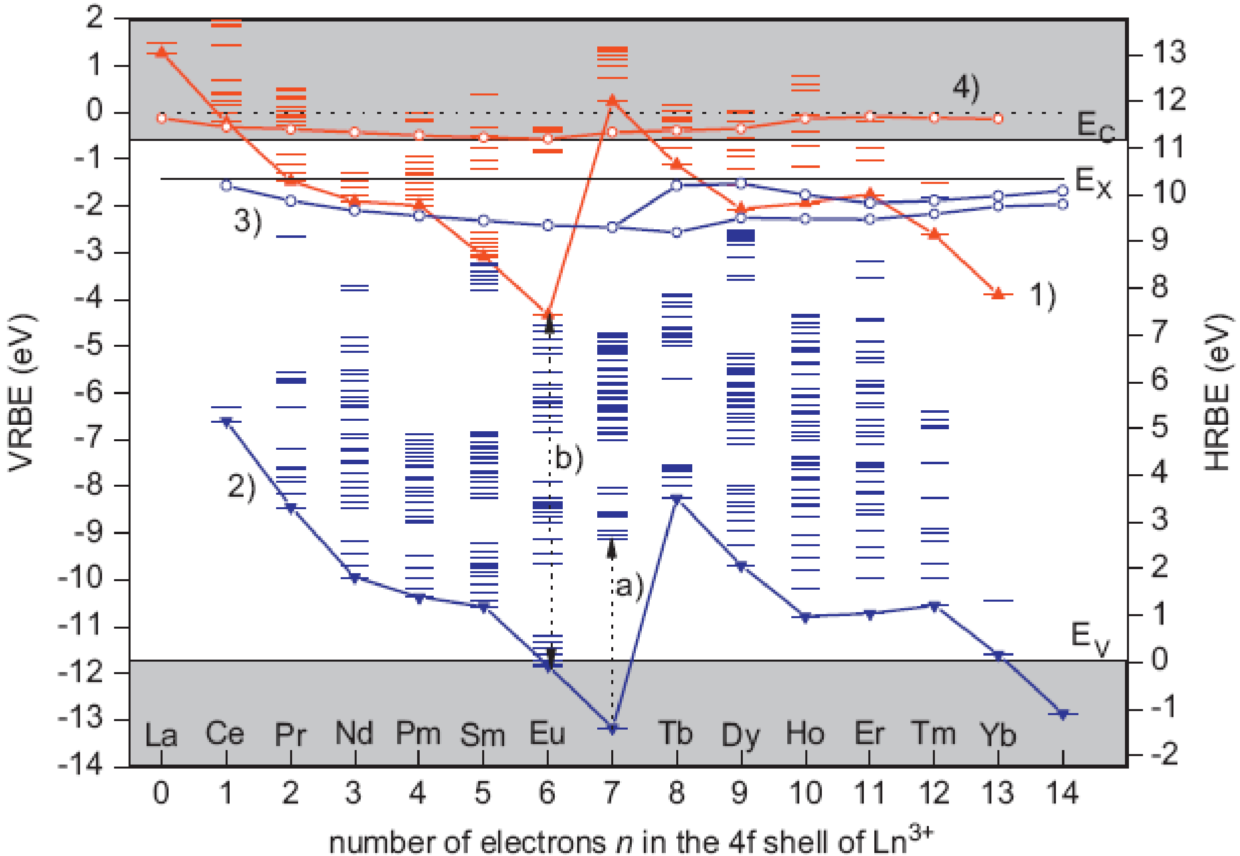

LaF_3

Sm, Eu, Tm, Yb - can be divalent
Possibility of "anomalous" luminescence for divalent lanthanides

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J. Phys.: Condens. Matter **15** (2003) 2645–2665 — PII: S0953-8984(03)59379-1

Anomalous luminescence of Eu^{2+} and Yb^{2+} in inorganic compounds

P Dorenbos

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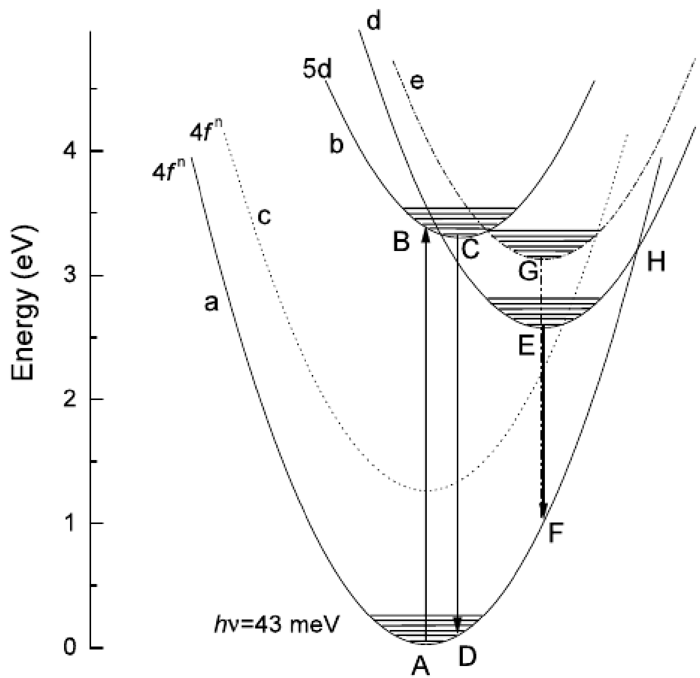

Figure 2. The configuration coordinate diagram illustrating normal df emission and anomalous emission. Energy values realistic for SrF_2 and BaF_2 were used with $h\nu = 43$ meV.

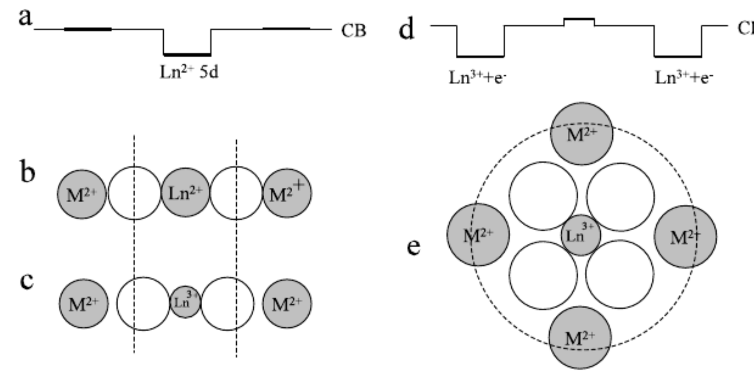

Figure 3. An illustration of the impurity-trapped exciton configuration in an MX_2 type of compound. (a) The occupied 5d energy level located just below the conduction band. (b) Ionic radii before the fd transition. (c) Ionic radii plus relaxation after autoionization. (d) Energy levels after autoionization and relaxation. (e) An electron orbiting around Ln^{3+} in the impurity-trapped exciton configuration.

Table 1. Properties of Eu^{2+}-doped compounds with (suspected) anomalous luminescenc Wavelengths are in nanometres and Stokes shifts ΔS and widths Γ are in electron volts. Unles otherwise indicated, the width is specified at room temperature. 'xx' means that broadband emissio is not observed down to ≈10 K.

Compound	λ_{abs}	λ_{em}^{df}	λ_{em}^{anom}	ΔS^{anom}	Γ_{Eu}^{anom}
BaF_2	382	403	590	1.14	0.51 (77 K)
$BaLiF_3$	333		410	0.70	0.37 (270 K)
CdF_2	407		xx		
$CsCaF_3$ (300 K)	425		510	0.49	0.60
$CsCaF_3$ (77 K)	425		610	0.88	0.48 (77 K)
$RbMgF_3$ (Rb)	340	365	405	0.59	0.40
$Ba_5(PO_4)_3F$ (6h)		432	475		
Sr_2LiSiO_4F	400		533	0.77	0.49
$Ba_2Y(BO_3)_2Cl$		538	634		0.30 (4 K)
Cs_2SO_4	378		450	0.52	0.66

Измерение спектров

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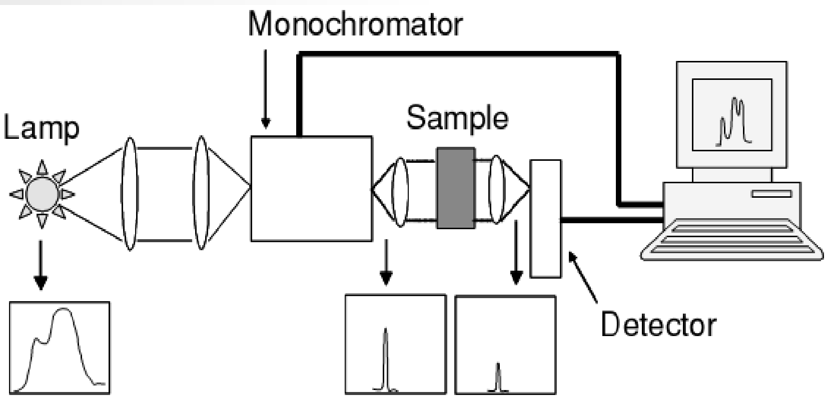
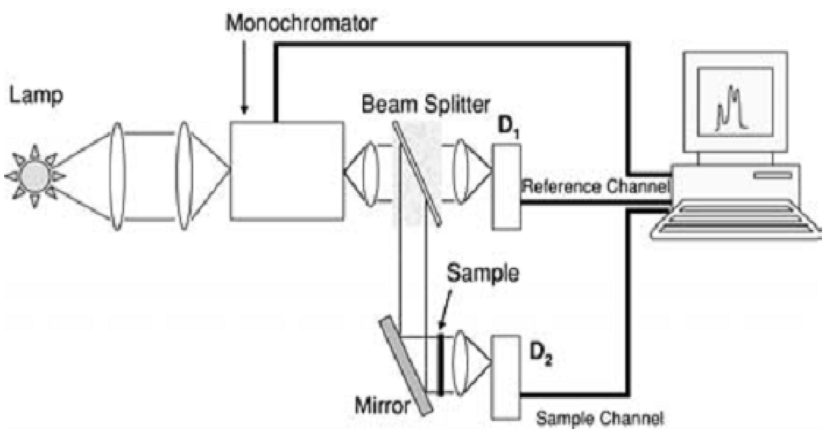
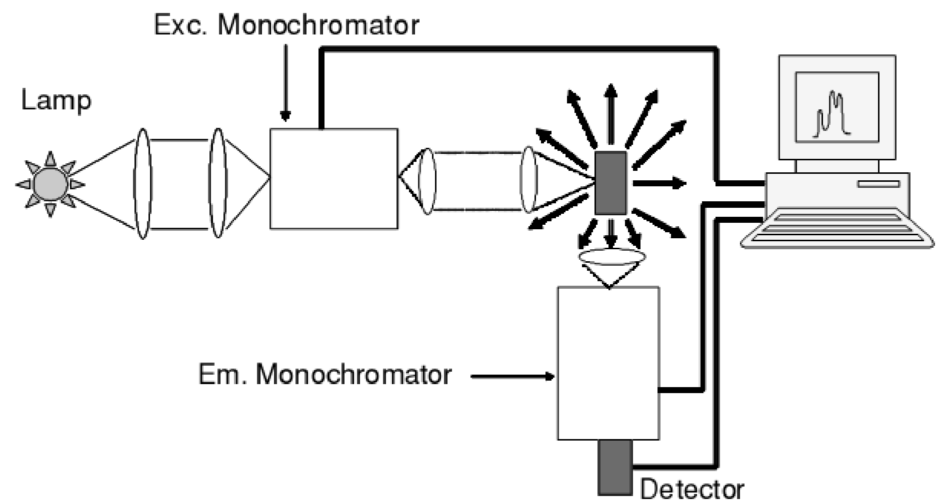


(a)





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

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

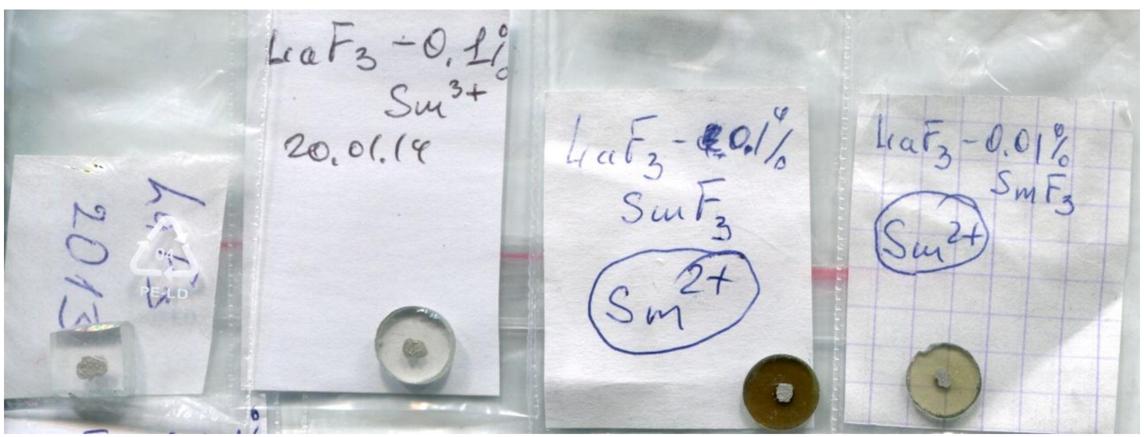
$$(I_{em}) \cong k_g \times \eta \times I_0 \times (OD)$$

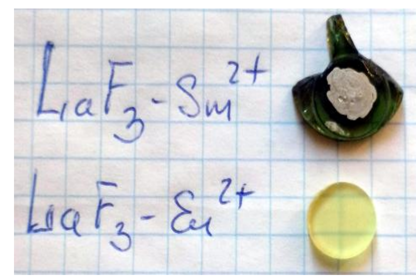
$$T = I / I_0$$

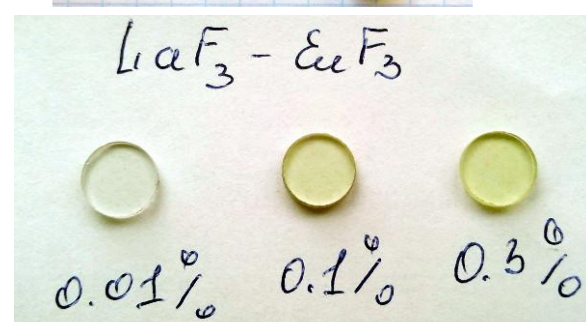
$$OD = \log(I_0 / I),$$

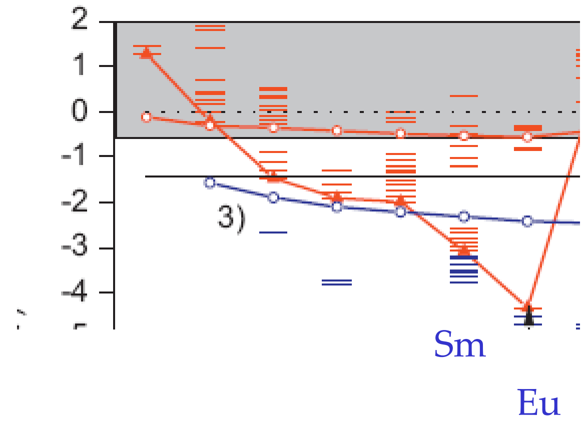
Experimental

- The crystals were grown by Stockbarger method in graphite crucible in vacuum. A few percent of CdF_2 was added into raw materials for purification from oxygen impurity during growth. Impurity REF_3 was added into LaF_3 powder in concentration of 0.01, 0.1 and 0.3 mol. % .
- They were grown crystals containing only Sm^{3+}, and crystals in which a substantial proportion of the trivalent samarium converted to divalent form. Color of crystals LaF_3-Sm^{2+} varied from light to dark green with increasing concentration samarium. Crystals LaF3-Sm^{3+} are colorless.
- The crystals are polished to optical measurements . For conductivity measurements on the polished surface applied electrodes (conductive silver adhesive " kontaktol ")

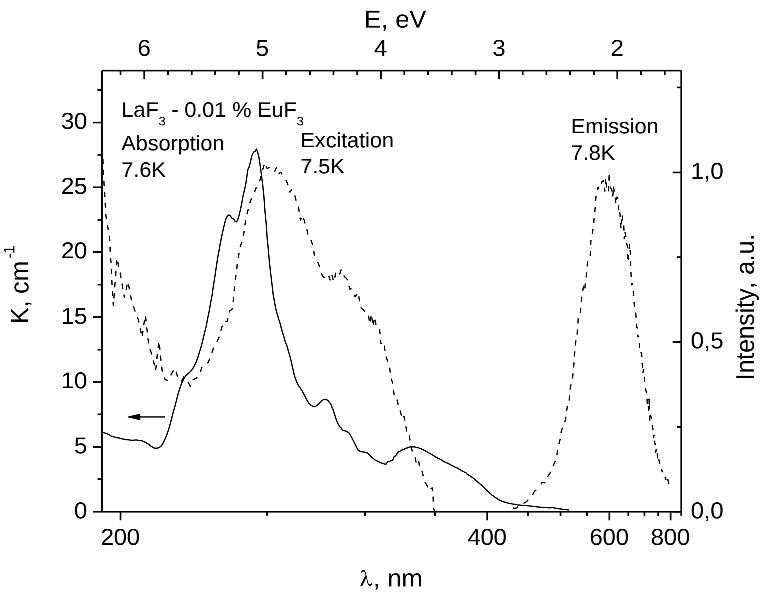








Spectra of Eu^{2+}

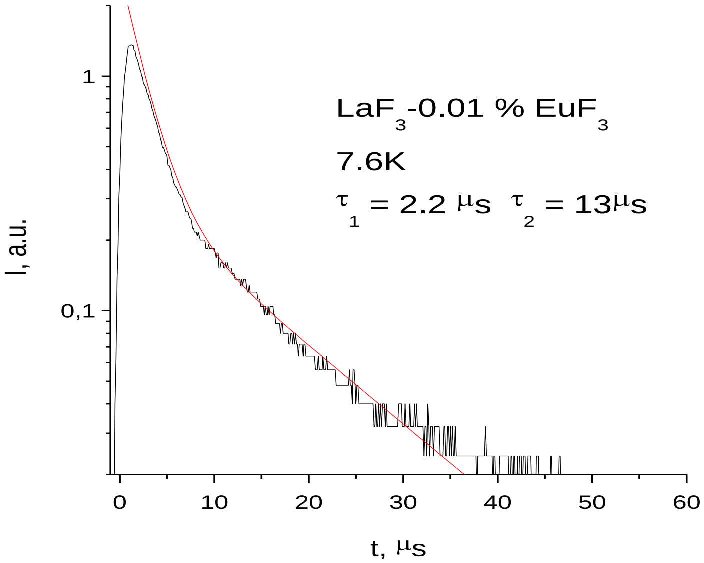


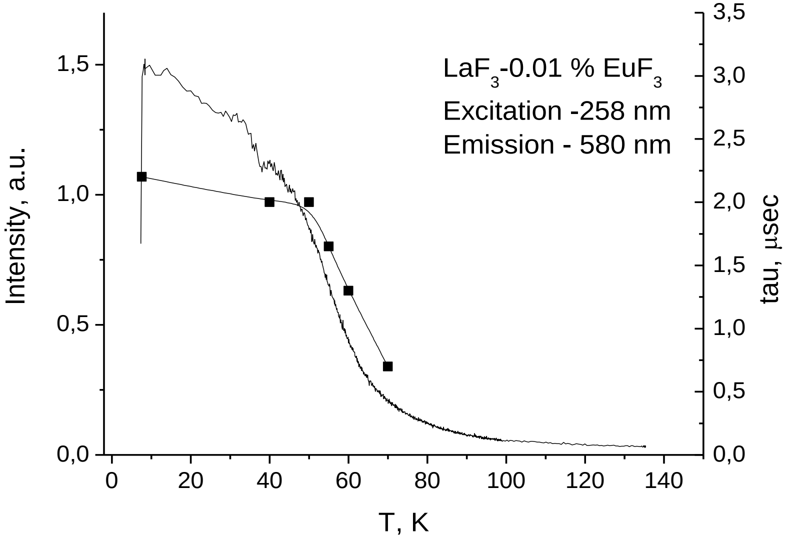
Luminescence with large Stokes shift
Excited within f-d region.

Anomalous Eu^{2+} luminescence

Absorption, emission and excitation spectra of LaF_3-0.01 % Eu^{2+}

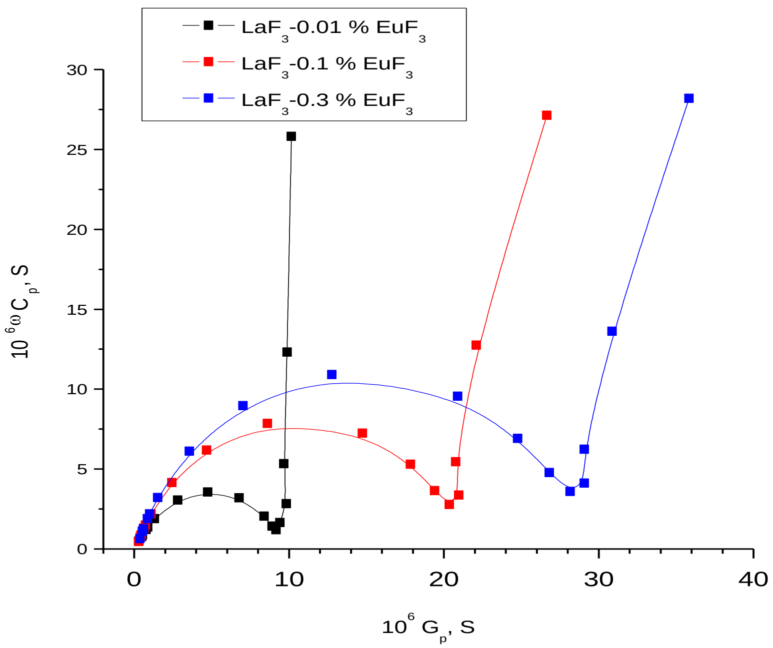
Luminescence of LaF_3-Eu^{2+}

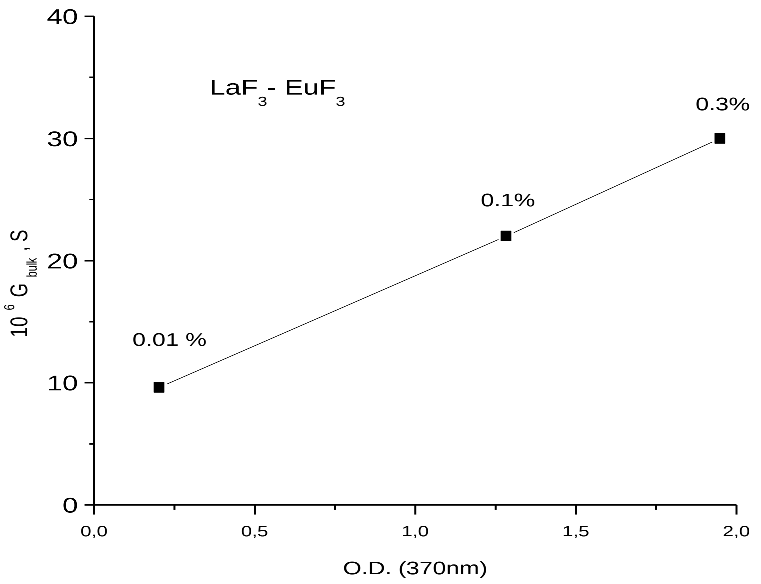




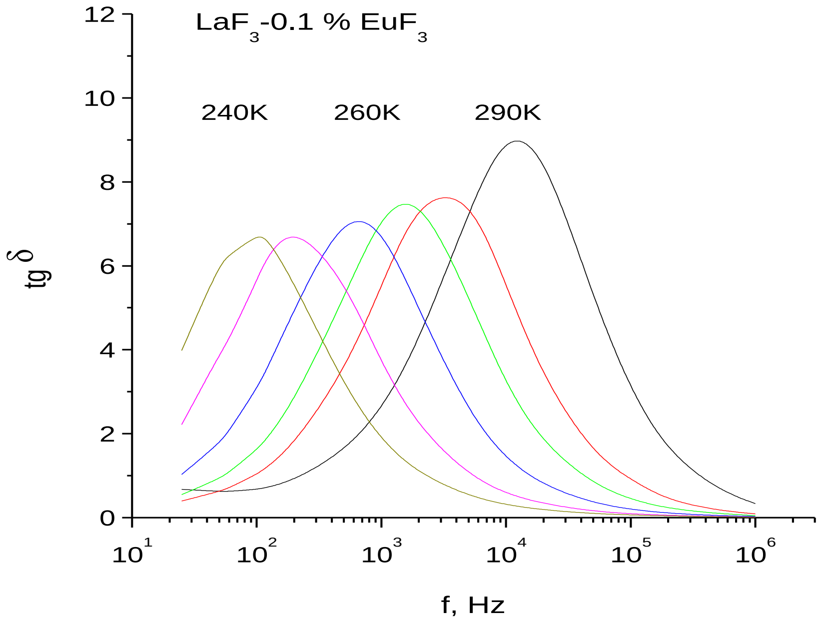
Temperature dependence of emission and decay times of LaF_3-0.01 % Eu^{2+}

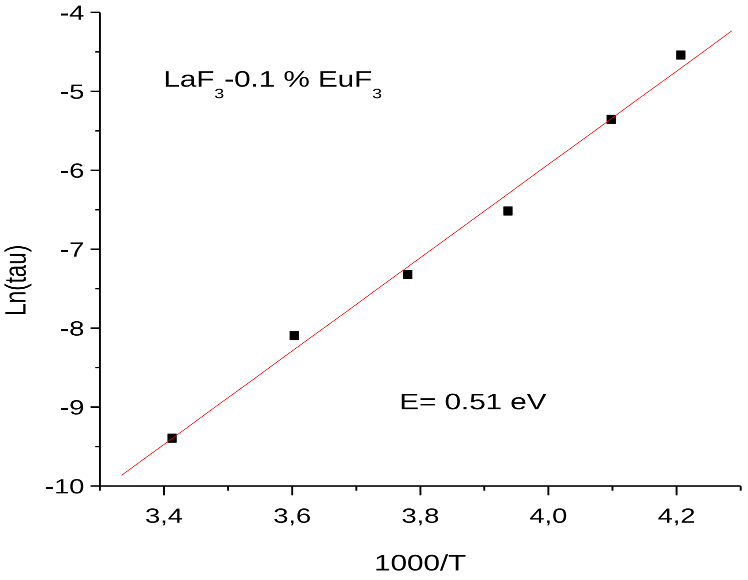
LaF_3-Eu^{2+} conductivity



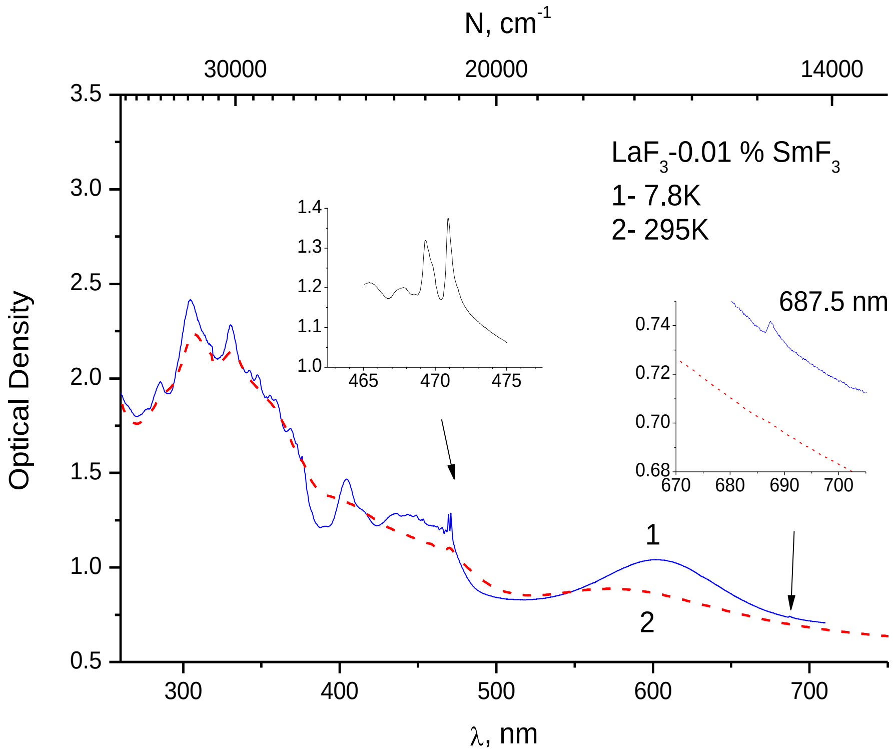


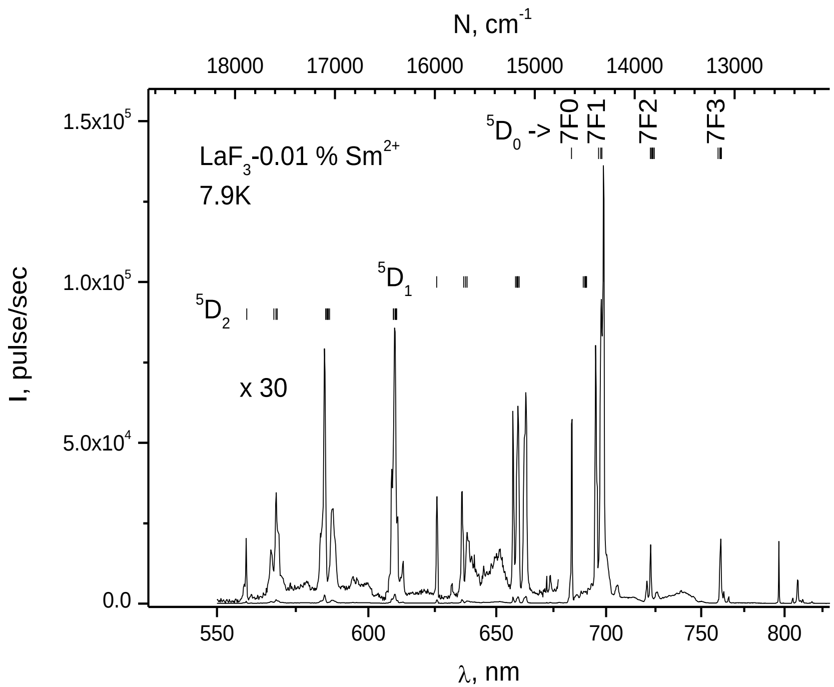
LaF_3-Eu^{2+} dielectric loss





Spectra of Sm^{2+}



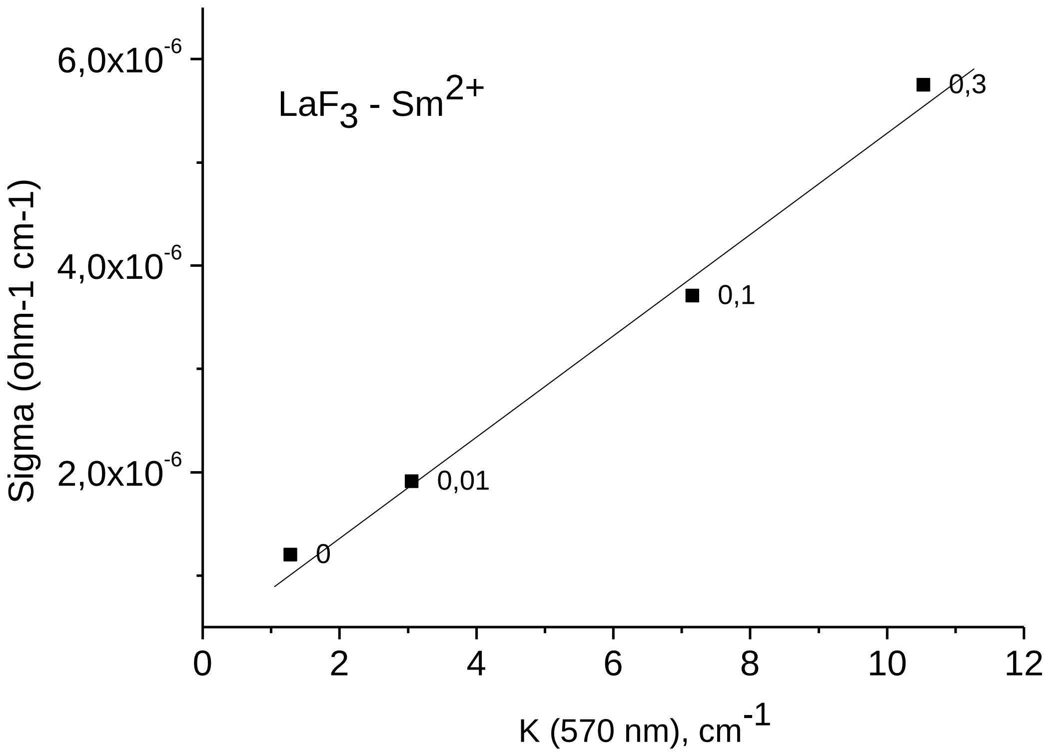


Absorption and emission spectra of Sm^{2+} in LaF_3- 0.01 % SmF_3.

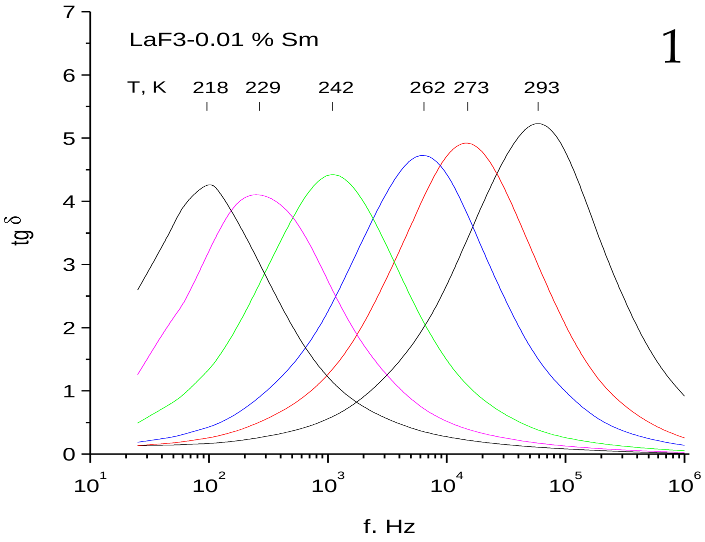
LaF_3-Sm^{2+} conductivity

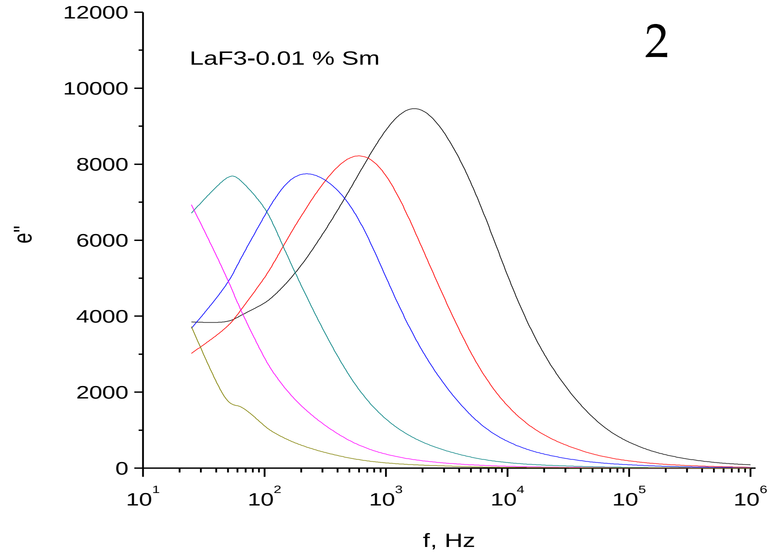
Conductivity of LaF_3-Sm^{2+} samples against of absorption coefficient of band at 570 nm at room temperature. Concentration of doped SmF_3 are shown near experimental points.

кристалл	10^6 σ ($ом^{-1}см^{-1}$)
LaF_3(L13)	0,37
LaF_3-0.1 % Sm^{3+}	1,20
LaF_3-0.3 % Sm^{2+}	5,75
LaF_3-0.1 % Sm^{2+}	3,71
LaF_3-0.01 % Sm^{2+}	1,91
LaF_3-0.1% EuF_3(Eu^{2+})	3,33



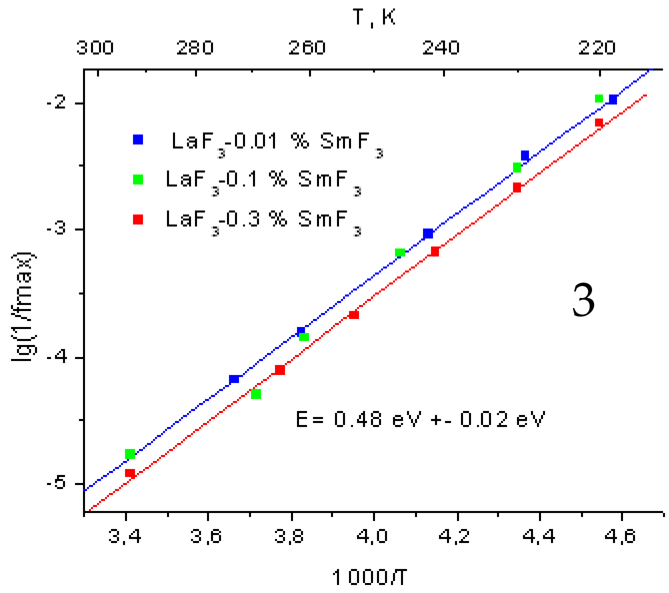
Dielectric losses LaF_3-Sm^{2+}

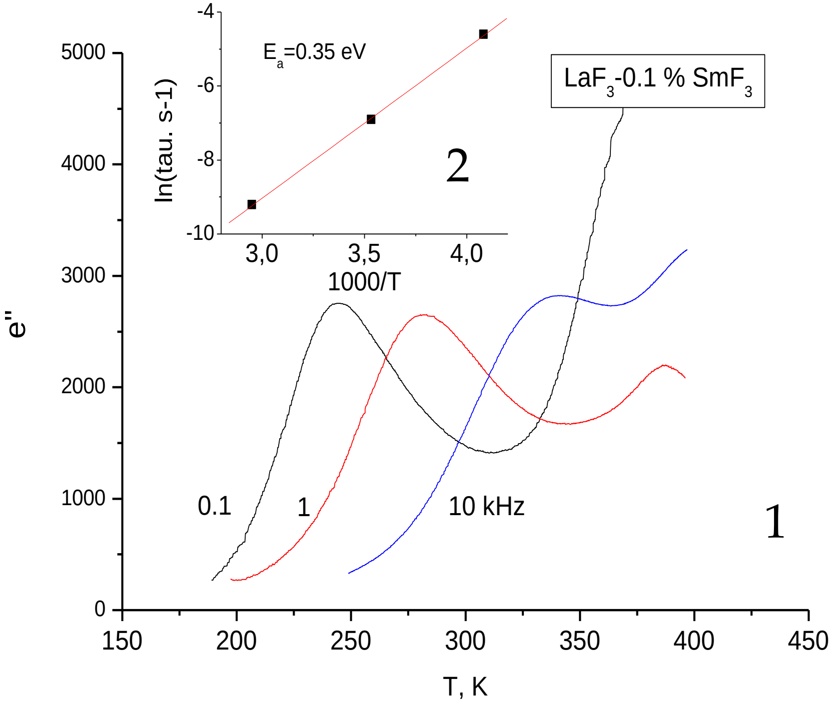




Temperature dependence of tg(δ) (1) and e'' (2) of LaF_3-Sm^{2+}

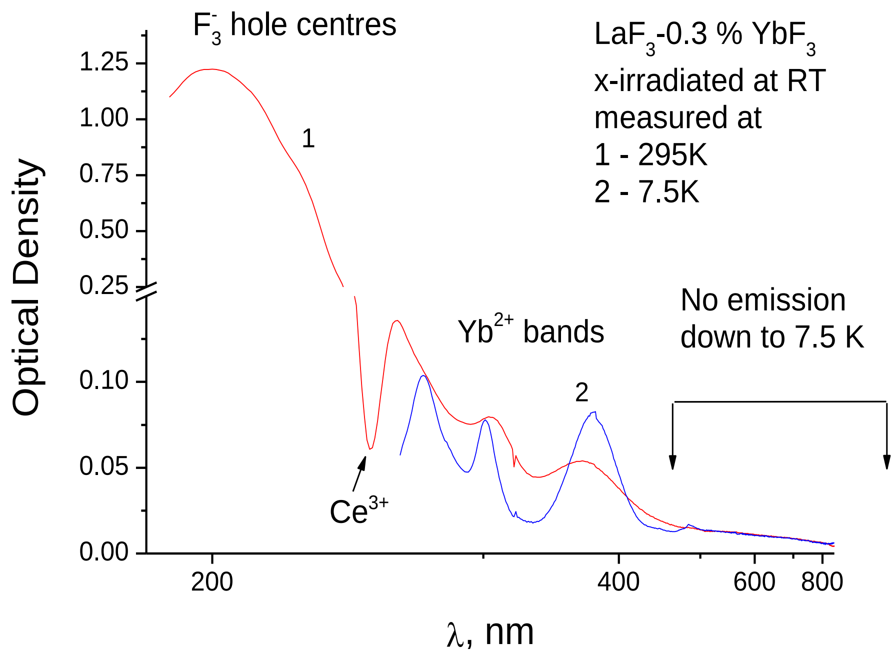
Dielectric losses LaF_3-Sm^{2+}





Temperature dependence of e''(1) and Arrenius plots (2,3) of LaF_3-Sm^{2+}

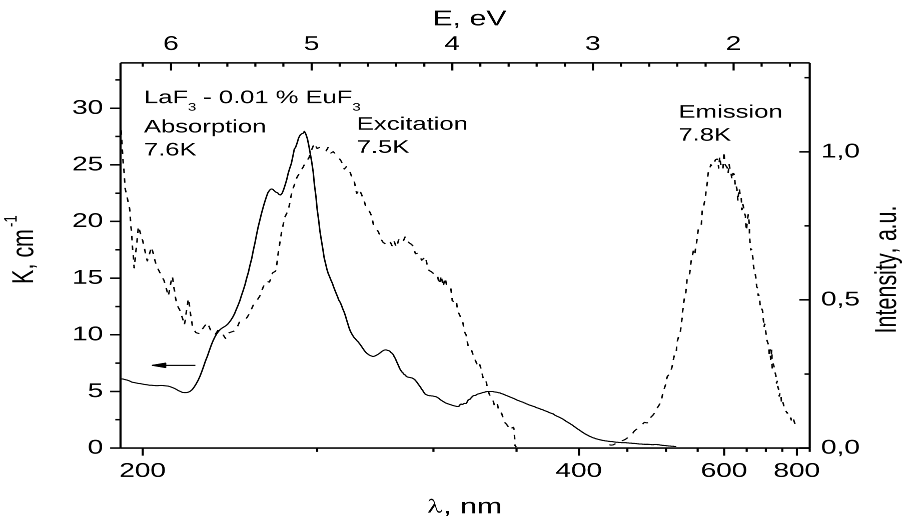
Spectra of Yb^{2+}

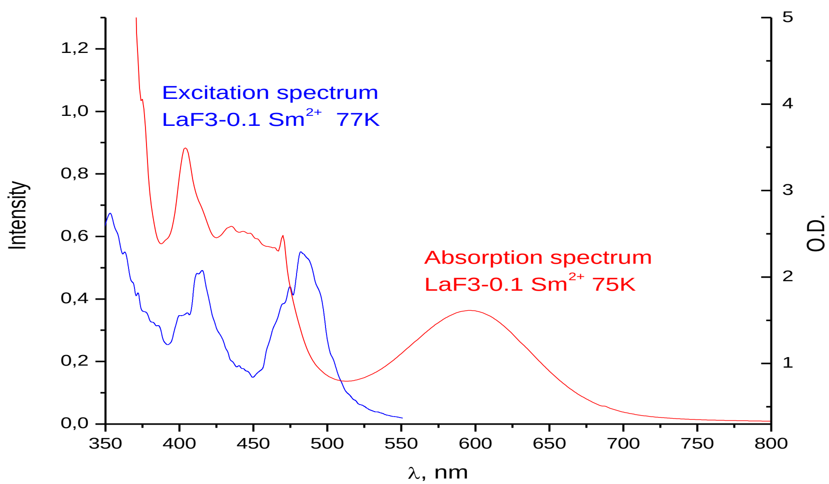


Absorption spectra of LaF_3-0.3% YbF_3
created by X-irradiation at 295K

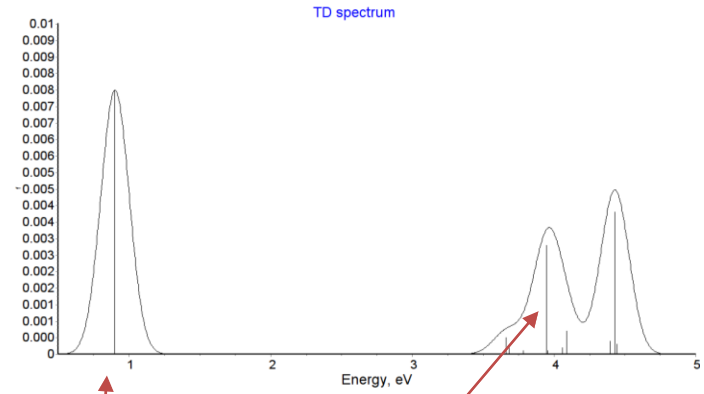
Yb^{2+} ions were obtained by X-irradiation (Pd 20mA 40kV) of LaF_3-YbF_3 crystal. Small part of Yb^{3+} was reduced to Yb^{2+} with absorption bands at 310, 370 nm. No emission of Yb^{2+} was observed.

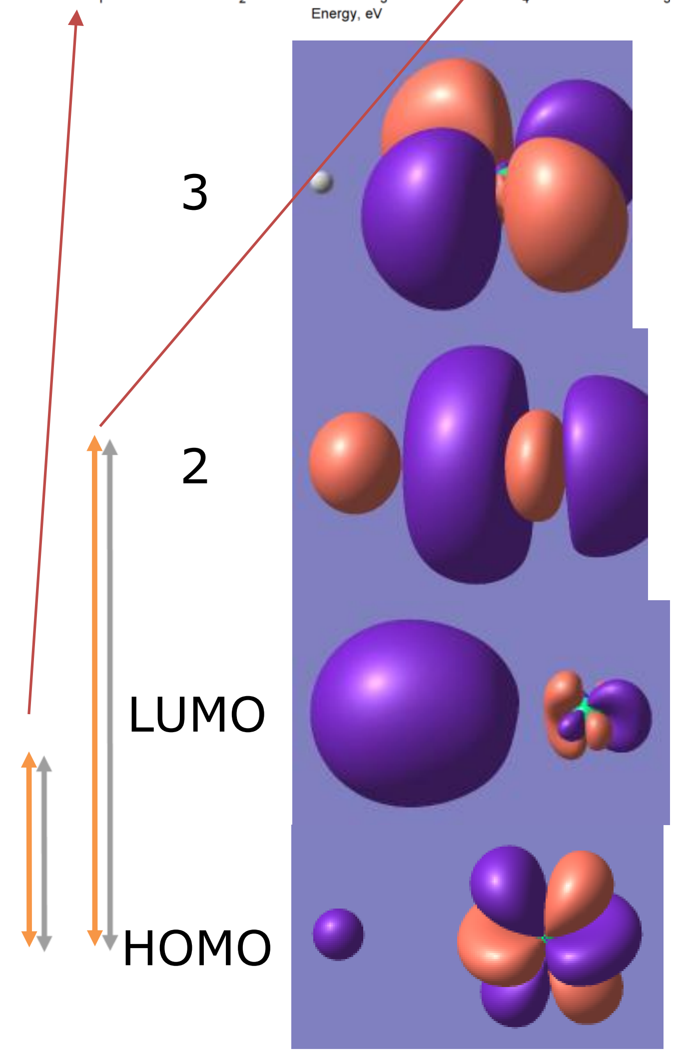
Model





Molecule
Sm^{3+} - H





Conclusion

- Finally, a set of studies allow us to establish the nature of the charge compensator of divalent rare earth Sm^{2+} and Eu^{2+} ions and explain the details of the optical and dielectric properties of these centers in the lanthanum fluoride crystals