Luminescent study of $Ca_{1-x}Pr_xF_{2+x}$ (x=0.35) solid solution

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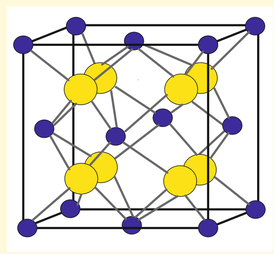
Introduction

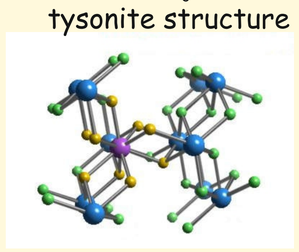
The nonstoichiometric $M_{1-x}R_xF_{2+x}$ ($M=Ca^{2+}$, Sr^{2+}, Ba^{2+}, $RE=Ln^{3+}$, $0.1\le x\le 0.5$) solid solutions are interesting from the point of host properties modification through variation of dopant concentration.

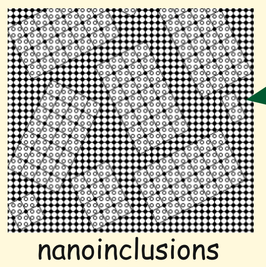
- Despite different structure types MF_2 and RF_3 form a continuous series of fluorite-structured solid solutions $M_{1-x}R_xF_{2+x}$ in a wide concentration range .
- $M_{1-x}R_xF_{2+x}$ systems are characterized by formation of rare earth clusters, which contain two or more rare earth ions, anionic vacancies and interstitial fluorine ions [1].
- The presence of defect-free regions (MF_2 matrix) in the $M_{1-x}R_xF_{2+x}$ crystals indicates that they are built by large associates of clusters (nanoinclusions with linear dimensions 10–100 Å) dispersed over the undistorted fluorite matrix.
- The associates of rare earth clusters have different dimensions and the orientations in the crystalline matrix. Adjustment of nanoinclusions in the MF_2 host do not change the initial fluorite motif of the crystal, i.e. the matrix and nanoinclusions continuously pass into one another.

CaF_2 fluorite structure

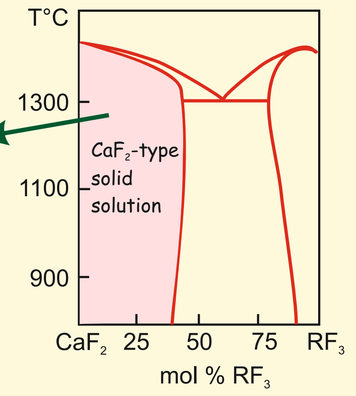


RF_3 tysonite structure





nanoinclusions in $M_{1-x}R_xF_{2+x}$ [1]



Experimental

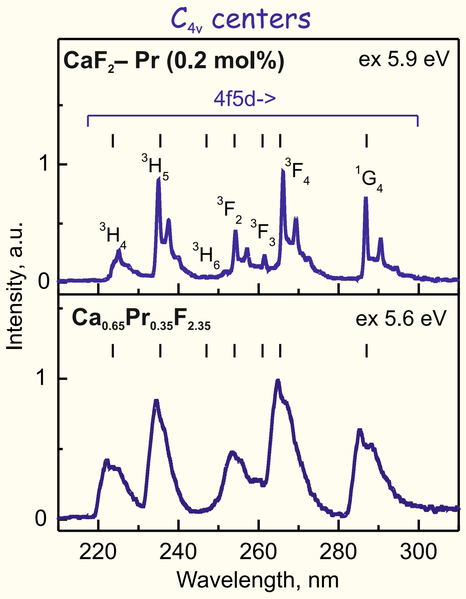
- PrF_3-doped CaF_2 crystals were grown by slow cooling down the melt inside the crucible in CF_4 atmosphere from high purity (>99.99%) powders [2].
- XRD pattern of $Ca_{0.65}Pr_{0.35}F_{2.35}$ corresponds to fluorite structure with lattice constant a=5.613 Å. No CaF_2 or PrF_3 phases were found.
- Emission and excitation spectra have been measured at 10K using the SUPERLUMI set-up operated at the DORIS storage ring of HASYLAB at DESY [3].

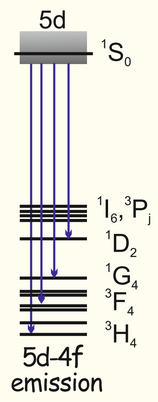
The goal: study of luminescent properties of Pr^{3+} ions in $Ca_{0.65}Pr_{0.35}F_{2.35}$ solid solution containing nanoinclusions.

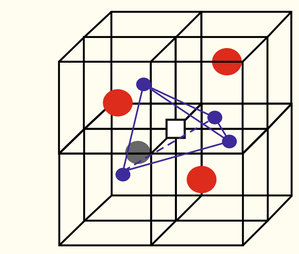
Results

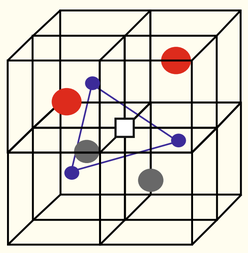
Emission of different regions in $Ca_{0.65}Pr_{0.35}F_{2.35}$

C_{4v} centers

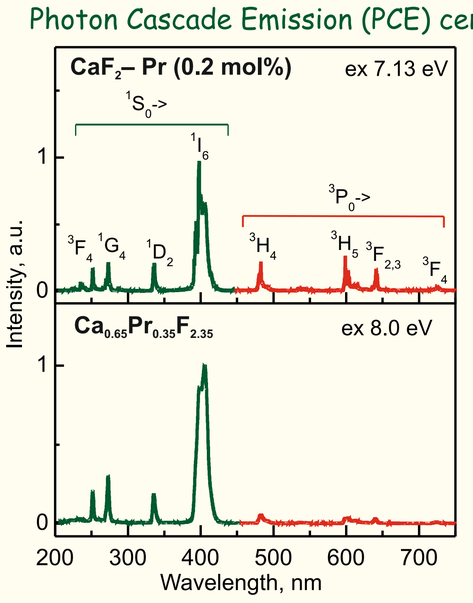


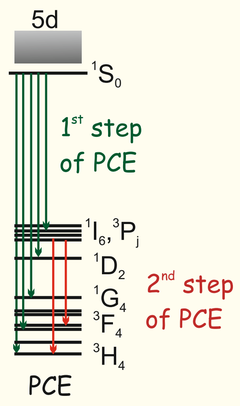






Photon Cascade Emission (PCE) centers





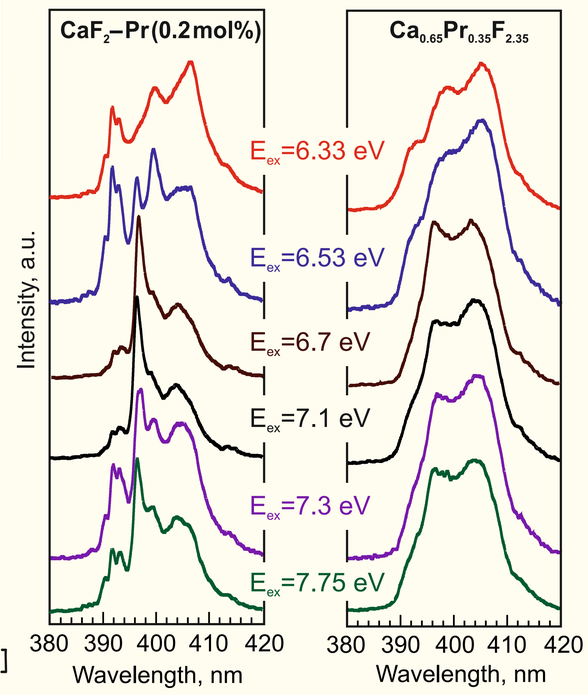
- Non-uniform distribution of C_{4v} emission centers over the crystalline matrix of $Ca_{0.65}Pr_{0.35}F_{2.35}$ whereas PCE centers are observed in all samples
- Different regions in $Ca_{0.65}Pr_{0.35}F_{2.35}$ solid solution:

Pr^{3+} depleted→emission of C_{4v} center

Pr^{3+} enriched (nanoinclusions)→emission of PCE centers

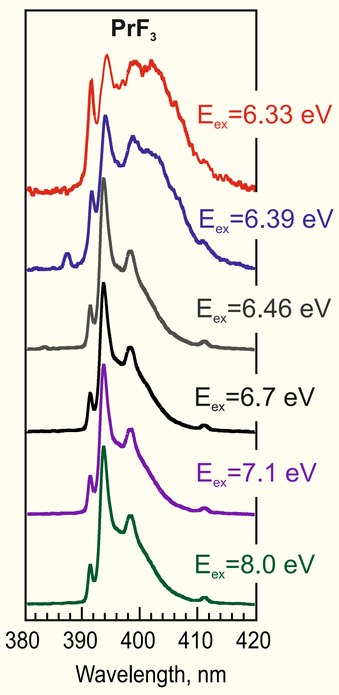
Evolution of emission spectra depending on excitation energy

PCE centers ($^1S_0 \rightarrow {}^1I_6$ transition)

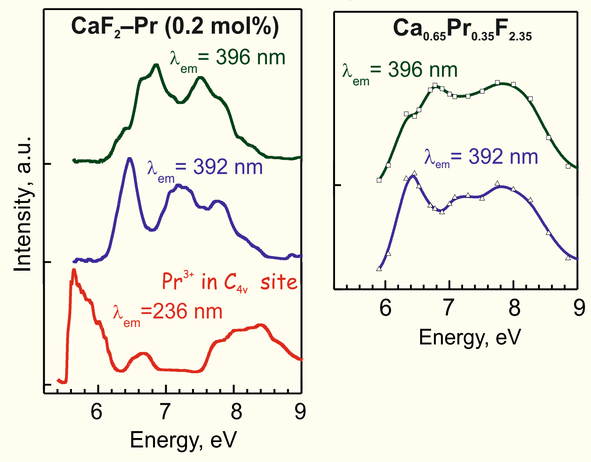


- transformation of emission spectra depending on excitation energy implies the presence of different types PCE centers
- in CaF_2-Pr (0.2 mol%) PCE centers may be assigned to isolated 1:0:3 and 1:0:4 clusters

- similar transformations of emission spectra suggest similar origin of PCE centers in CaF_2- Pr (0.2 mol%) and $Ca_{0.65}Pr_{0.35}F_{2.35}$. Different relative intensities of radiative transitions imply redistribution between types of PCE centers in CaF_2- Pr (0.2 mol%) and $Ca_{0.65}Pr_{0.35}F_{2.35}$
- Observed broadening of emission lines in $Ca_{0.65}Pr_{0.35}F_{2.35}$ (about 2 times in comparison with CaF_2- Pr (0.2 mol%) may be caused by small changes in local crystal field around Pr^{3+} ions and shifts of emission lines as a result of interaction of Pr^{3+} ions with great number of nearest F^-_i and v^+_a in nanoinclusions
- Despite some similarity in evolution of emission spectra of PrF_3 crystals luminescence observed in CaF_2- Pr (0.2 mol%) and $Ca_{0.65}Pr_{0.35}F_{2.35}$ can not be regarded as transitions in PrF_3 phase



Excitation spectra



- differences in excitation spectra confirm the suggestion about the presence of several types of PCE centers
- as expected the onset of 4f-5d transition of PCE centers are shifted to high energy side in comparison with C_{4v} centers, enabling emission from $^1S_0$ level

Conclusions

Luminescent study points to presence in $Ca_{0.65}Pr_{0.35}F_{2.3}$ states with different concentration and local symmetry of Pr^{3+} ions:

- ☐ 5d-4f luminescence of C_{4v} sites in parts of undistorted CaF_2 matrix depleted with Pr^{3+} ions.
- ☐ Photon Cascade Emission centers are supposed to be due to Pr^{3+} ions in nanoinclusions.
- ☐ The absence of C_{4v} sites in some regions suggests large dimensions of aggregates.

Acknowledgments

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