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# on luminescent properties of $Ba_{1-x}Pr_{x}F_{2+x}$ crystals

Influence of Pr<sup>3+</sup> concentration

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#### Introduction

Despite different structure types  $MF_2$  and  $RF_3$  ( $M^{2+}=Ca$ , Sr, Ba,  $R^{3+}=Ln$ ) form a continuous series of fluorite-structured solid solutions  $M_{1-x}R_{x}F_{2+x}$  in a wide concentration range (up to x=0.5) [1, 2]. The specific feature of nonstoichiometric  $M_{1-x}R_{x}F_{2+x}$  phases is preserving of disordered high-temperature structure in cooling.

#### Phase diagram of $BaF_2$ -PrF<sub>3</sub> system [2] T°C



### Experimental

O PrF<sub>3</sub>-doped BaF<sub>2</sub> crystals were grown by Bridgmen technique in  $CF_4$  atmosphere from high purity (>99.99%) powders. These crystals are stable materials and do not decompose during cooling, storage and thermal cycling from low to high temperatures [1]

Mixed  $Ba_{1-x}Pr_{x}F_{2+x}$  crystals are interesting from the point of host properties modification through variation of PrF<sub>3</sub> concentration. According to the studies of  $BaF_2$ -Pr crystals, increasing of  $Pr^{3+}$  content results in appearance of emission from  ${}^{1}S_{0}$  level if  $PrF_{3}$  concentration reaches up to 3 mol% [3, 4]. This work is devoted to the investigation of  $BaF_2$  crystals with higher  $PrF_3$  concentration.

fluorite-type solid 1100 solution 900 50 75 PrF<sub>3</sub> BaF, 25 mol % PrF<sub>3</sub>

- **O** XRD patterns of  $Ba_{1-x}Pr_{x}F_{2+x}$  correspond to fluorite structure and do not reveal any presence of  $PrF_3$  phase.
- o Emission and excitation spectra at 10K were measured using the SUPERLUMI set-up operated at the DORIS storage ring of HASYLAB at DESY [5].
- O Luminescent and decay time parameters at 300K were recorded by FLS 920 Edinburgh Instruments spectrometer.

The goal is to study the influence of  $Pr^{3+}$  concentration on luminescent properties of  $Ba_{1-x}Pr_{x}F_{2+x}$  (2.10<sup>-4</sup>  $\leq x \leq 0.3$ ) crystals.

# Results





**Emission spectra** 











Characteristic emission of  $Pr^{3+}$  ions in  $C_{3v}$  sites was observed in crystals with low PrF<sub>3</sub> content. Increase in PrF<sub>3</sub> concentration in BaF<sub>2</sub> host results in redistribution between  $5d^14f^1 \rightarrow 4f^2$  and  $4f^2 \rightarrow 4f^2$ radiative transitions in favor of  ${}^{3}P_{0} \rightarrow 4f^{2}$  emission at 10K.

#### Discussion and conclusions

Increasing of RF<sub>3</sub> concentration in MF<sub>2</sub> host leads to aggregation of R<sup>3+</sup>-F<sup>-</sup><sub>i</sub> dipoles into dimers, trimers, and so on. The typical feature of high-concentrated M<sub>1-x</sub>R<sub>x</sub>F<sub>2+x</sub> solid solutions is the formation of defect clusters which include alkali-earth M<sup>2+</sup> and rare-earth R<sup>3+</sup> ions as well as anion vacancies u<sup>+</sup> and interstitial fluorine ions F<sup>-</sup>[1, 6, 7]. The composition and structure of clusters depend on the ratio of the ionic radii (r) of the rare-earth (R<sup>3+</sup>) and the host (M<sup>2+</sup>) cations  $r(R^{3+})/r(M^{2+})$  [7]. In Ba<sub>1-x</sub>Pr<sub>x</sub>F<sub>2+x</sub> systems [(M,Pr)<sub>6</sub>F<sub>36</sub>] clusters are typical. This type of clusters may contain up to six neighbour R<sup>3+</sup> ions.



 $. Ba_{0.7} Pr_{0.3} F_{2.3}$ λ<sub>em</sub>=270 nm 0,0 Energy, eV

Starting from  $c(PrF_3)=2 \mod \%$ , an additional excitation band at ~ 5.5-5.6 eV appears in excitation spectra both for  $5d^14f^1 \rightarrow 4f^2$  and  $^{3}P_0 \rightarrow 4f^2$ emission.

 $[(M,R)_{6}F_{36}]$  cluster [8]

Weak  ${}^{1}S_{0} \rightarrow 4f^{2}$  radiative transitions are observed only at 10K for crystals with comparatively low concentration of  $PrF_3$ . No  $^{1}S_0$ -luminescence was registered for  $BaF_2$ -Pr crystals with higher doping level. Emission spectra at 300K show only  $5d^{1}4f^{1} \rightarrow 4f^{2}$  luminescence. The absence of  ${}^{3}P_{0} \rightarrow 4f^{2}$  transitions may be caused by strong thermal quenching.

Essential shortening of decay kinetics of  $5d^{1}4f^{1} \rightarrow 4f^{2}$  emission was observed with increase in  $PrF_{3}$ concentration. One may suggest the growth of efficiency of 5d<sup>1</sup>4f<sup>1</sup> states nonradiative relaxation.

O Coordination polyhedron of Pr<sup>3+</sup> ion in [(Ba,Pr)<sub>6</sub>F<sub>36</sub>] cluster is square antiprism with D<sub>4d</sub> crystal field symmetry [8], i.e. local environment of Pr<sup>3+</sup> ions in clusters is modified in comparison with the single C<sub>3V</sub> sites. One may suppose that change in coordination polyhedron of Pr<sup>3+</sup> ions due to the clusters formation causes the shifting of the lowest excited 4f<sup>1</sup>5d<sup>1</sup> state to the low-energy region. As the result the additional excitation band at ~ 5.5-5.6 eV is observed in  $BaF_2$ -PrF<sub>3</sub> crystals with increase in PrF<sub>3</sub> concentration.

O The redistribution between  $5d^14f^1 \rightarrow 4f^2$  and  $4f^2 \rightarrow 4f^2$  radiative transitions in favor of  $^{3}P_{0} \rightarrow 4f^2$  emission at 10K may be due to the population of  $^{3}P_{0}$  level of the neighbour  $Pr^{3+}$  ions via nonradiative relaxation of  $5d^{1}4f^{1}$  according to the following mechanism:  $5d^{1}4f^{1} + {}^{3}H_{4} \rightarrow {}^{3}P_{0} + {}^{3}P_{0}$ . The similar effect was observed earlier in LiLuF<sub>4</sub>-Pr crystals [9].

Observation of the  ${}^{1}S_{0}$ -luminescence only in crystals with comparatively low PrF<sub>3</sub> content allows assigning  ${}^{1}S_{0} \rightarrow 4f^{2}$  radiative transitions to Pr<sup>3+</sup> ions in some intermediate aggregates, i.e. dimers or trimers.

#### References

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