

1S_0 -luminescence in $\text{Ca}_{1-x}\text{Pr}_x\text{F}_{2+x}$ crystals

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Received 22 March 2012

Luminescence properties of $\text{CaF}_2:\text{Pr}$ (0.2 mol %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals were studied at 10 K. Excitation and emission spectra show two types of the Pr^{3+} centers with the typical $^1S_0 \rightarrow 4f^2$ radiative transitions. High level of rare-earth ions aggregation in CaF_2 and peculiarities of the defect structure in $\text{Ca}_{1-x}\text{Pr}_x\text{F}_{2+x}$ solid solutions point to the formation of Pr^{3+} -based clusters. Emission from 1S_0 -level is attributed to Pr^{3+} ions included in the clusters.

Исследованы люминесцентные свойства кристаллов $\text{CaF}_2:\text{Pr}$ (0.2 мол %) и $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ при 10 К. Спектры возбуждения и люминесценции указывают на наличие двух типов центров свечения, для которых характерны $^1S_0 \rightarrow 4f^2$ излучательные переходы. Высокая эффективность агрегации редкоземельных ионов в CaF_2 и особенности дефектной структуры твердых растворов $\text{Ca}_{1-x}\text{Pr}_x\text{F}_{2+x}$ свидетельствуют об образовании Pr^{3+} -кластеров. 1S_0 -люминесценция может быть отнесена к ионам Pr^{3+} , входящим в состав кластеров.

1. Introduction

Praseodymium doped fluoride crystals are of the special interest due to the process of Photon Cascade Emission (PCE), i.e. obtaining two luminescence photons by one excitation photon [1]. Crystals of such type are already used as transformers of VUV radiation in various devices [2]. The possibility of the cascade emission in low-doped $\text{CaF}_2:\text{Pr}$ crystals was shown in [3, 4]. The efficiency of $^1S_0 \rightarrow 4f^2$ radiation transitions increases with rise in Pr^{3+} concentration up to 1 % PrF_3 . However there is no information as to evolution of emission centers and their structure in high-concentrated CaF_2 - PrF_3 crystals.

High reciprocal solubility of CaF_2 and PrF_3 enables obtaining stable $\text{Ca}_{1-x}\text{Pr}_x\text{F}_{2+x}$ solid solutions with the fluorite structure in wide concentration range [5]. In other words there is a possibility for increasing of the doping level up to 35 mol % PrF_3 in the case of $\text{Ca}_{1-x}\text{Pr}_x\text{F}_{2+x}$.

In this work the origin of 1S_0 -emission centers were studied in a wide concentration range starting from the small content in case of $\text{CaF}_2:\text{Pr}$ (0.2 mol %) crystal and up to high values of PrF_3 in fluorite type solid solutions $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$.

2. Experimental

Mixed systems $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ as well as $\text{CaF}_2:\text{Pr}$ (0.2 mol %) crystals were grown by slow cooling down the melt inside a cruci-

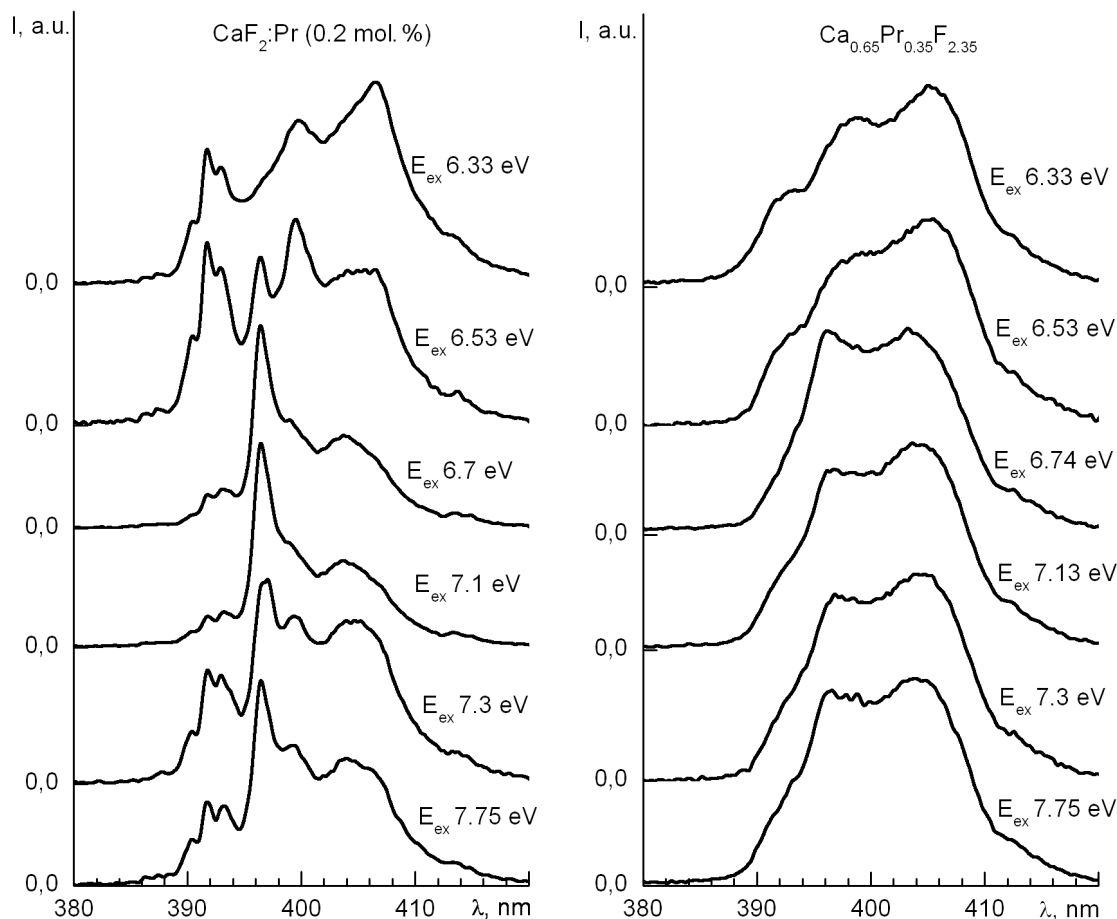


Fig. 1. Emission spectra of $\text{CaF}_2:\text{Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals in the region of $^1S_0 \rightarrow ^1I_6$ transition.

ble, similar to the growth by the Bridgman technique in CF_4 atmosphere from high purity (>99.99 %) powders [6]. According to electron probe microanalysis (EPMA) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), the chemical composition of investigated solid solution corresponds to $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ formula.

According to XRD analysis $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystal has the fluorite lattice and does not contain PrF_3 phase.

Measurements of emission and excitation spectra were performed at Deutsches Elektronen Synchrotron (DESY, Hamburg) using synchrotron radiation from DORIS III storage ring and facility of SUPERLUMI station at HASYLAB [7]. Time-integrated emission and excitation spectra were measured at 10 K using an ARC 0.3 m Czerny-Turner monochromator-spectrograph "Spectra Pro 300i" ($f/4$) equipped with CCD detector from Princeton Instruments. The spectral resolution was 3.3 and 5.5 Å for excitation and luminescence measurements,

respectively. Excitation spectra were corrected on the incident photon flux. Emission spectra were not corrected for the spectral sensitivity of the detection system.

3. Results

Luminescence spectra of $\text{CaF}_2:\text{Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals in the region of $^1S_0 \rightarrow ^1I_6$ transition (~400 nm) under synchrotron excitation in 6.0–8.0 eV energy range are shown in Fig. 1. Variation of emission spectrum caused by transitions from 1S_0 level depends on the excitation energy.

The set of three luminescence bands in the range of 390–393 nm is observed in crystal with low Pr^{3+} concentration. The relation between the intensities of these transitions remains constant at different excitation energies. Transitions with maxima at 396, 400 and 406 nm dominate in the emission spectra; their relative intensities vary with excitation energies. In $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals peaks broaden and merged.

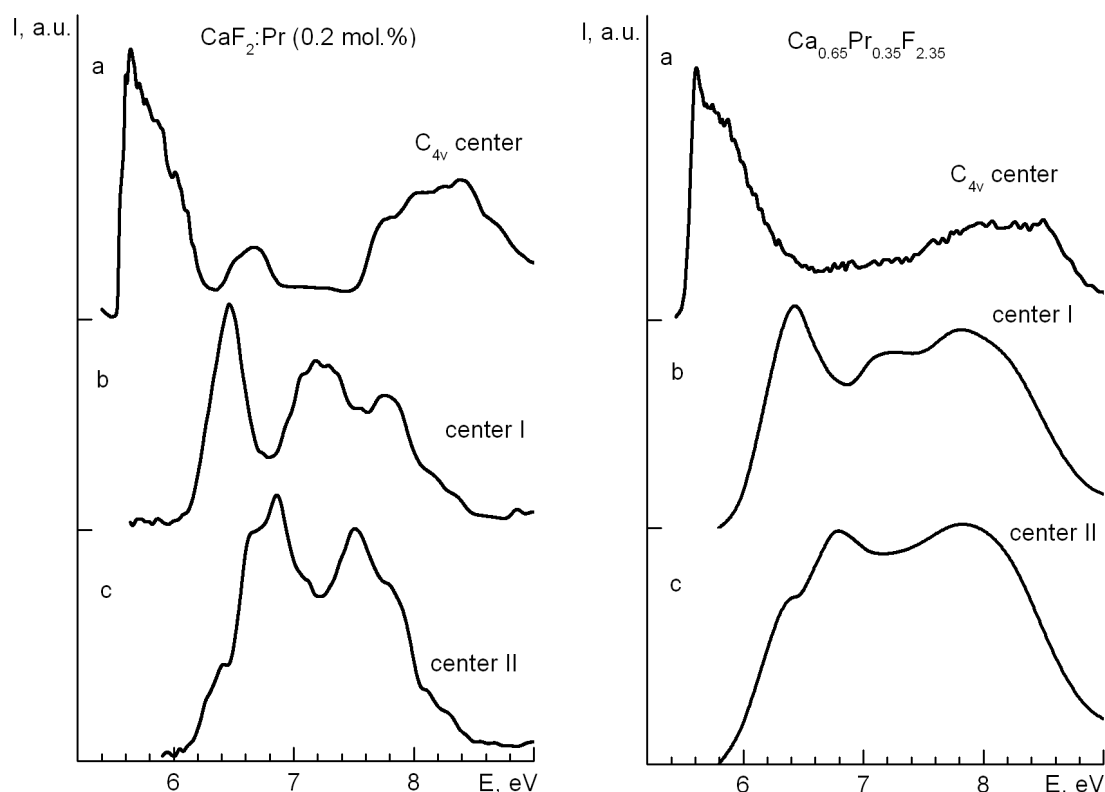


Fig. 2. Excitation spectra of $\text{CaF}_2:\text{Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals at 10 K for emission 235 nm (a), 392 nm (b) and 396 nm (c).

Excitation spectra of the observed luminescence bands are shown in Fig. 2. Excitation of 390–393 nm emission is characterized by the bands with maxima at 6.46, 7.17 and 7.8 eV. Excitation spectrum of 396 nm peak is represented by two maxima at 6.85 and 7.52 eV, and "shoulders" caused by the excitation bands for 390–393 nm. The direct $^3H_4 \rightarrow ^1S_0$ transition (~ 5.8 eV) is strongly forbidden and cannot be seen in the excitation spectra.

Results, presented in Figs. 1 and 2, point to presence of at least two types of centers with the typical $^1S_0 \rightarrow ^1I_6$ transition of Pr^{3+} in $\text{CaF}_2:\text{Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals.

Redistribution in emission intensities depending on the excitation energy implies that observed spectra are the superposition of the different transitions. As shown in Fig. 1, under excitation in the 6.7–7.8 eV energy range luminescence bands peaking at 396 and 403 nm dominate in the spectrum of CaF_2-Pr (0.2 mol. %). The change of excitation energy results in the increase of 393 and 400 nm bands and shift of low energy peak from 403 to 406 nm. Basing on this correlation, one may assign the observed radiative transitions at 390–393,

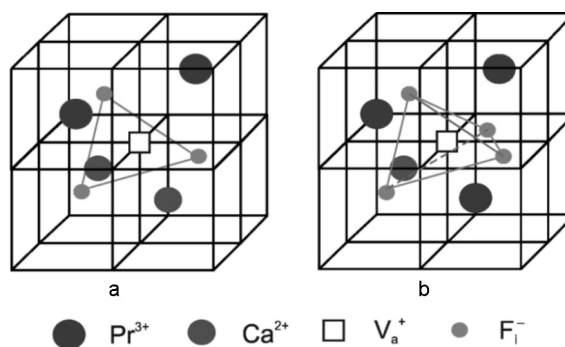


Fig. 3. Schematic views of 1:0:3 (a) and 1:0:4 (b) clusters [9].

400 and 406 nm to one type of emission centers (centers I), whereas the second type is characterized by bands with maxima at 396 and 403 nm (centers II).

Variation of emission spectrum depending on excitation energy is observed for both $\text{CaF}_2:\text{Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$. An increase in contribution of the centers II results in redistribution in transition intensities in $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ system.

Two types of emission centers are clearly evident in excitation spectra of $\text{CaF}_2:\text{Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals (see Fig. 2). Observed excitation bands at

6.46, 7.17 and 7.8 eV (centers I) and 6.9, 7.5 eV (centers II) correspond to the transitions from the ground state to components of split $4f^15d^1$ configuration of Pr³⁺ ions. For single Pr³⁺ ions in tetragonal sites maxima of excitation bands for $4f^2 \rightarrow 4f^15d^1$ transitions are at 5.6, 6.7 eV (e_g) and 8.4 eV (t_{2g}).

4. Discussion

At least two types of emission centers with typical ¹S₀-luminescence were revealed in CaF₂-Pr (0.2 mol. %) and Ca_{0.65}Pr_{0.35}F_{2.35} crystals. The observed structure of emission spectra in the region of 400 nm is caused by radiative transitions from ¹S₀ level to Stark components of ¹I₆ multiplet and their phonon replicas. For low symmetry of emission center maximal number of sub-levels of split ¹I₆ multiplet can reach 13 (2J+1). The proximity of ¹S₀ level with $4f^15d^1$ configuration permits efficient admixture of $5d$ components to ¹S₀ state. Strong intrinsic coupling of $5d$ states with lattice can also influence on the line shapes of the optical transitions emanating from ¹S₀ state, and ¹S₀-luminescence can take on the vibronic character [8].

The main condition for observation of ¹S₀-emission is the energy gap between ¹S₀ and $4f^15d^1$ states of Pr³⁺ ion [2, 4]. The energy of ¹S₀ level ($\approx 47\,000\text{ cm}^{-1}$) slightly depends on crystal host whereas the energy of $4f^15d^1$ state of Pr³⁺ ion is determined by crystal field in particular local environment. If the energy of the lowest excited $4f^15d^1$ state is higher than the energy of ¹S₀ level, i.e. $E(4f^15d^1) > E(^1S_0)$, ¹S₀ → $4f^2$ emission is observed. In case of $E(4f^15d^1) < E(^1S_0)$, the result of excitation to $4f^15d^1$ levels is the inter-configurational $4f^15d^1 \rightarrow 4f^2$ luminescence.

For low Pr-doped calcium fluoride crystals (≤ 0.01 mol. % PrF₃) Pr³⁺ single ions in tetragonal symmetry (C_{4v}) sites are the dominating emission centers. In this case $E(4f^15d^1) < E(^1S_0)$ and $4f^15d^1 \rightarrow 4f^2$ luminescence is typical [2, 4].

Appearance of ¹S₀ → $4f^2$ radiative transitions with the increase of PrF₃ content in CaF₂ crystals and their domination in the high-concentrated Ca_{0.65}Pr_{0.35}F_{2.35} solid solution indicate the formation of emission centers with local environment different from C_{4v}.

One of the typical features of fluorite-like non-stoichiometric solid solutions Ca_{1-x}R_xF_{2+x} is the formation of defect clusters, which

include anion vacancies (v_a^+) in the main position 8c (0.25, 0.25, 0.25), interstitial F_i⁻ fluorine ions, alkali-halide M²⁺ and rare-earth R³⁺ cations. Neutron diffraction studies of Ca_{0.68}La_{0.32}F_{2.32} crystals [9] revealed the fluorine interstitials located on three-fold symmetry axes in 32f (0.41, 0.41, 0.41) position. Interpretation of the obtained structural data resulted in the model of associates known as 1:0:3 and 1:0:4 clusters [9], which in general can be regarded as dimers (1:0:3) and trimers (1:0:4) of rare-earth ions. The local environment of R³⁺ ions in the clusters are irregular polyhedra with 9-(in case of 1:0:3) or 10-vertices (1:0:4).

Taking into account the proximity of La³⁺ and Pr³⁺ ionic radii (1.32 Å and 1.28 Å for c.n. 8) and similar to Ca_{0.68}La_{0.32}F_{2.32} results as to occupation of crystallographic positions in Ca_{0.9}Pr_{0.1}F_{2.1} system [10], one may suggest similar cluster structure for Ca_{0.65}Pr_{0.35}F_{2.35} and Ca_{0.68}La_{0.32}F_{2.32} crystals.

Proposed in [9] possible types of clusters structure point to the modification of local environment of Pr³⁺ ions in clusters in comparison with the C_{4v} centers. It is well known that splitting of $5d$ state depends on crystal field symmetry of the rare-earth ion [11]. One may suppose that changing in coordination polyhedron of Pr³⁺ ions due to the clusters formation causes the shifting of the lowest excited $4f^15d^1$ state to the high-energy region. The latter enables observation of radiation transitions originating from ¹S₀ level. Similar luminescent properties of CaF₂:Pr (0.2 mol. %) and Ca_{0.65}Pr_{0.35}F_{2.35} imply the structural similarity of emission centers in these crystals. In terms of the cluster model, centers I and II can be assigned as praseodymium ions in 1:0:3 and 1:0:4 clusters.

Theoretical calculations [12] indicate the stability of dimers and trimers of rare-earth ions in low-doped CaF₂ crystals. According to [13] the dimers are considered to be dominant aggregate defects. At the same time observation of three ion up-conversion in CaF₂:Pr (0.1 mol. %) crystals [14] indicates the presence of the trimers. Centers I may be 1:0:3 clusters, since concentration of the dimers is high enough even at small praseodymium content due to the high aggregation efficiency of rare-earth ions in CaF₂ crystals [13]. At the same time centers II can be assigned to 1:0:4 clusters. The aggregate origin of ¹S₀-emission centers in CaF₂:Pr was suggested earlier in [3].

Thereby $^1S_0 \rightarrow 4f^2$ luminescent transitions in $\text{CaF}_2\text{-Pr}$ (0.2 mol%) crystals can be related to isolated clusters (dimers and trimers) of Pr^{3+} ions dispersed in CaF_2 host.

For high PrF_3 concentration distances between separate clusters decrease and clusters form extended regions with different dimensions and spatial orientations in the crystalline matrix [15]. In this case Pr^{3+} ions in the clusters are strongly perturbed by the neighboring ions. Some distortion of the crystal field on different Pr^{3+} ions would occur resulting in small shifts in excitation and emission energies. Correspondent broadening of emission and excitation bands is observed experimentally in the spectra of $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals (see Figs. 1 and 2).

5. Conclusions

Luminescent properties of $\text{CaF}_2\text{:Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ crystals under excitation in 6.0–8.0 eV energy range were studied. Excitation and emission spectra show two types of Pr^{3+} centers with the typical $^1S_0 \rightarrow ^1I_6$ transition. Similar luminescent properties of $\text{CaF}_2\text{:Pr}$ (0.2 mol. %) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ implies the structural similarity of emission centers in these crystals.

Taking into account the high aggregation efficiency of rare-earth ions in CaF_2 crystals and data on the defect structure of high-concentrated solid solutions 1S_0 -emission centers are considered to be Pr^{3+} ions in 1:0:3 and 1:0:4 clusters. In the case of low-doped CaF_2 crystals isolated praseodymium-containing clusters are randomly dis-

tributed in CaF_2 matrix. In $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ system the clusters tend to form associates with different dimensions and spatial orientations in fluorite host, resulting in some differences between luminescent properties of $\text{CaF}_2\text{:Pr}$ (0.2 mol.%) and $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$.

This work is supported by 7th FP INCO.2010-6.1 grant agreement No. 266531 (project acronym SUCCESS).

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1S_0 -люмінесценція в кристалах $\text{Ca}_{1-x}\text{Pr}_x\text{F}_{2+x}$

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Досліджено люмінесцентні властивості кристалів $\text{CaF}_2\text{:Pr}$ (0.2 mol. %) та $\text{Ca}_{0.65}\text{Pr}_{0.35}\text{F}_{2.35}$ при 10 К. Спектри збудження та люмінесценції вказують на присутність двох типів центрів світіння, для яких є характерними $^1S_0 \rightarrow 4f^2$ випромінювальні переходи. Висока ефективність агрегації рідкісноземельних іонів у CaF_2 та особливості дефектної структури твердих розчинів $\text{Ca}_{1-x}\text{Pr}_x\text{F}_{2+x}$ свідчать про утворення Pr^{3+} -кластерів. 1S_0 -люмінесценція може бути віднесена до іонів Pr^{3+} , що входять до складу кластерів.