Journal of Luminescence 129 (2009) 1581–1585

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Photon cascade emission of Pr^{3+} ion in alkaline-earth fluorides

E. Radzhabov

Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii Street 1a, P.O. Box 4019, 664033 Irkutsk, Russia

ARTICLE INFO

Available online 8 May 2009

Keywords:
Cascade emission
Pr^{3+}
Alkaline-earth fluorides
Vacuum ultraviolet
Excitation
Absorption

ABSTRACT

Absorption, emission, excitation spectra of CaF_2, SrF_2, BaF_2 crystals doped by PrF_3 in concentration ranging from 0.005% to few molar % were studied in 1.4–10 eV spectral region. Specific type of Pr centres possessing photon cascade emission (PCE active) was observed in all crystals. Concentration of centres monitored by excitation and emission spectra grows superlinearly with increasing of Pr concentration in SrF_2 and BaF_2 crystals. A new additional absorption band at 7.0 eV which coincided with excitation band of PCE-active centres was observed in CaF_2-Pr crystals. The absorption coefficient of this band grows twice that coefficient of 5.7 eV band of single Pr centres.

1. Introduction

Photon cascade emission (PCE) is phenomenon when more than one emission photons are created by each excited photon. Cascade emission phenomenon becomes important to replace the mercury by xenon in luminescent discharge lamps [1]. Despite the tendency of an ion to have the greatest transition probability to the lowest-lying states, thereby preventing efficient PCE, for the Pr^{3+} ion excited to its high-lying $^1S_0$ state, spin selection rules favour transitions to its singlet states, especially the $^1I_6$ state [1]. As a result the emission band near 400 nm (3.1 eV) is observed. Then the electron non-radiatively decays to closely lying $^3P_0$ level. At the second step of photon cascade the radiative transitions from $^3P_0$ level to several lower lying levels are observed.

Pr^{3+} ion shows photon cascade emission in many crystal lattices [2]. Alkaline-earth fluorides were not considered as hosts, where Pr^{3+} photon cascade emission should be observed, because lowest 4f–5d levels lie at lower energy than that of $4f^2$ ($^1S_0$) level [3,4]. Nevertheless the photon cascade emission was observed in $CaF_2-0.05\%$ PrF_3 [5] and in highly doped $BaF_2-3\%$ PrF_3 crystals [6]. It was assumed that cascade emission is possible only for some single Pr centres [5] or for large Pr_6F_{37} aggregates [6]. Many types of Pr-related centres were observed in CaF_2 crystals using laser excitation and high resolution emission measurements [7]. Three of them were assigned to single ion centres (C_{4v}, O_h, and the so-called L site) while others were assigned to clusters of Pr ions [7].

For generality we may divide all Pr centres into two groups. Centres from first group have 5d states below the $^1S_0$ (4f) level and the 5d–4f luminescence is predominates in emission spectra. Centres of second group have $^1S_0$ (4f) level at lower energy than that of 5d levels and the cascade emission is predominate in spectra. We will call these centres as PCE-active centres.

The origin of PCE-active centres in Pr^{3+}-doped CaF_2, SrF_2, BaF_2 was studied in this paper.

2. Experimental

Crystals of CaF_2, SrF_2, BaF_2 were grown in vacuum in graphite crucible by Stockbarger method. As the first step large oxygen-free crystal was grown with the addition of CdF_2 an oxygen scavenger in a simple large volume crucible. Then parts of this crystal were used to the growth of impurity-doped crystals. Crystals of CaF_2, SrF_2, BaF_2 doped by PrF_3 with concentrations ranging from 0.005 to 10 mol % were studied. Samples with PrF_3 concentration less than 0.3–0.5 mol % were cleaved from crystal rod, otherwise samples were sawed and were polished from both sides.

The excitation spectra in 4–12 eV region were measured with grating vacuum monochromator VMR2. The hydrogen VMF25 lamp with MgF_2 window was used as vacuum ultraviolet source. Emission spectra were measured with grating monochromator MDR2 at 1.5–3 eV with 600 lines/mm grating and at 3–6 eV region with 1200 lines/mm grating at temperatures 10–300 K. Emission spectra were not corrected for the spectral sensitivity of monochromator and photomultiplier.

3. Results

3.1. Emission, excitation

BaF_2: Two main types of Pr centres may be distinguished from excitation and emission spectra. The centres having efficient photon cascade emission, starting from lowest $^1S_0$ level, have

---

E-mail address: eradzh@igc.irk.ru

0022-2313/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2009.04.071

broad excitation band near 7 eV (see Fig. 1). Photon cascade emission was observed at Pr concentration 0.045 mol%, and moreover the admixture of 5d–4f emission bands at 4–6 eV from Pr centres of another group is also observed (see Fig. 1, top and middle plots). With increasing Pr concentration the 5d–4f emission at 7 eV excitation becomes weaker (see Fig. 1). One could consider the ratio of intensities of 2.57 and 4.8 eV emission bands as ratio of concentration of both centres (see Fig. 1, middle right inset). The relative concentration of cascade emission centres grows logarithmically with increasing of Pr concentration, becoming saturated near 1 mol% of PrF_3.

No photon cascade emission was observed at room temperature in BaF_2–Pr crystals, having Pr concentration up to 10 mol%. Evidently the lowest 5d level of PCE-active centres is very near to $^1S_0$ level and at room temperatures there is effective phonon-assisted transfer electron from $^1S_0$ level to 5d level.

SrF_2: Emission spectra of $SrF_2-0.015$ mol% PrF_3 with 6.9 and 6.0 eV excitation are almost identical (Fig. 2). Emission line at 3.1 eV is very weak under 6.9 eV excitation (see Fig. 2); it means that the concentration of PCE-active centres is very small in this sample. As in the case of BaF_2–Pr the presence of lines near 2 and 2.57 eV under 6 eV excitation points out that the photon cascade emission started from 5d level (see Fig. 2). The intensity of cascade lines is sufficiently higher than for BaF_2-Pr (compare Figs. 1 and 2, top plots).

With increasing concentration of PrF_3 the relative intensity of 3.1–4.8 eV emission bands grows logarithmically (see Fig. 2). Excitation spectra show broad bands near 7 eV. No direct $^6H_4-^1S_0$ zero-phonon excitation line on low energy wing of excitation band was observed even at 10 K.

Emission of PCE-active centres was observed at room temperature also. The intensity of first step emission line at 3.1 eV slightly reduces at room temperature (0.75 of initial intensity), while the emission lines near 2.5, 2.0 eV of second cascade emission step reduces about six times.

CaF_2: Contrary to BaF_2 and SrF_2 the emission band at 3.1 eV in CaF_2 was observed in crystal with lowest concentration of PrF_3 0.005 mol% (Fig. 3). It means that PCE-active centres are already present in very low-doped CaF_2 crystal. The emission spectra excited by 6.9 eV very slightly changed with increasing Pr concentration up to 1 mol% (see Fig. 3).

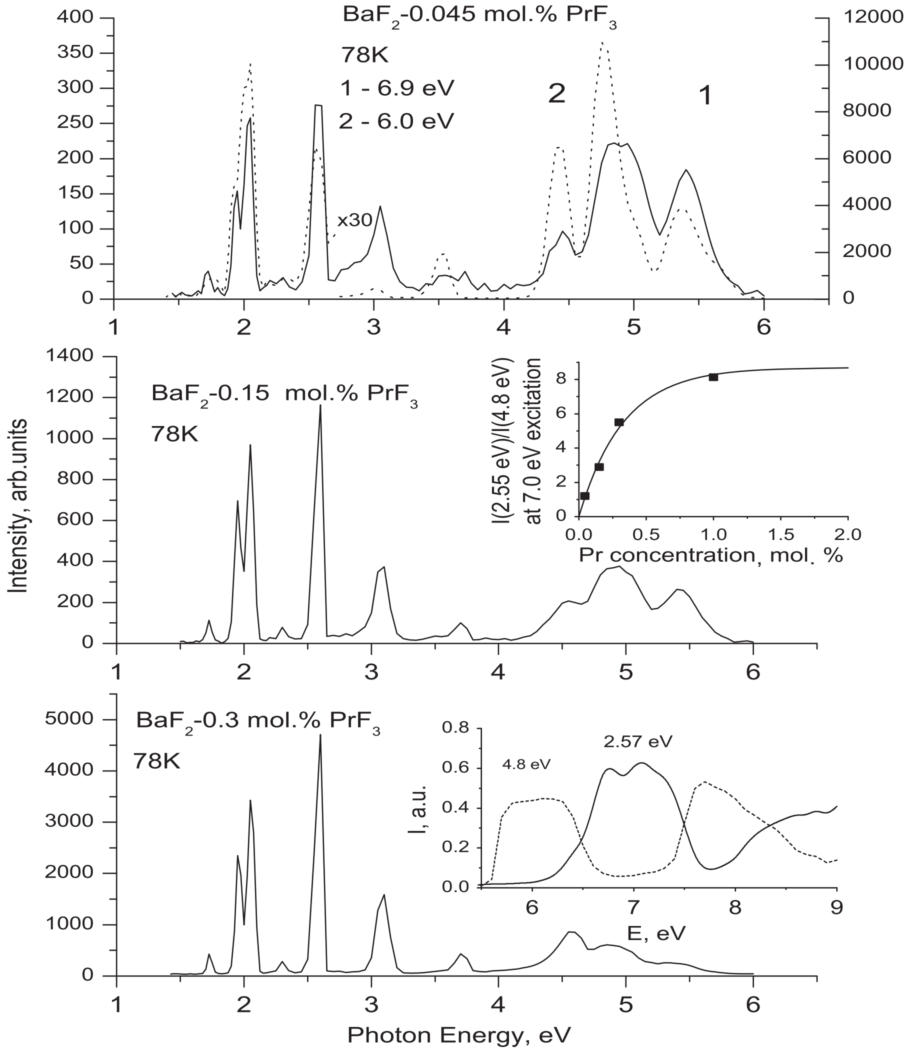

Fig. 1. Emission spectra of BaF_2 crystal doped by PrF_3 at 78 K. Samples were excited at 6.9 eV (full curves) or at 6.0 eV (dotted curve). Middle right inset—Pr concentration dependence of intensities $I(2.5\ \mathrm{eV})/I(4.8\ \mathrm{eV})$ ratio at 6.9 eV excitation at 78 K. Bottom right inset—excitation spectra of $BaF_2-0.3$ mol% PrF_3 for emission bands at 2.57 and 4.8 eV at temperature 78 K. No measurable emission was observed in $BaF_2-0.015$% PrF_3 under 7.0 eV excitation at 90 K.

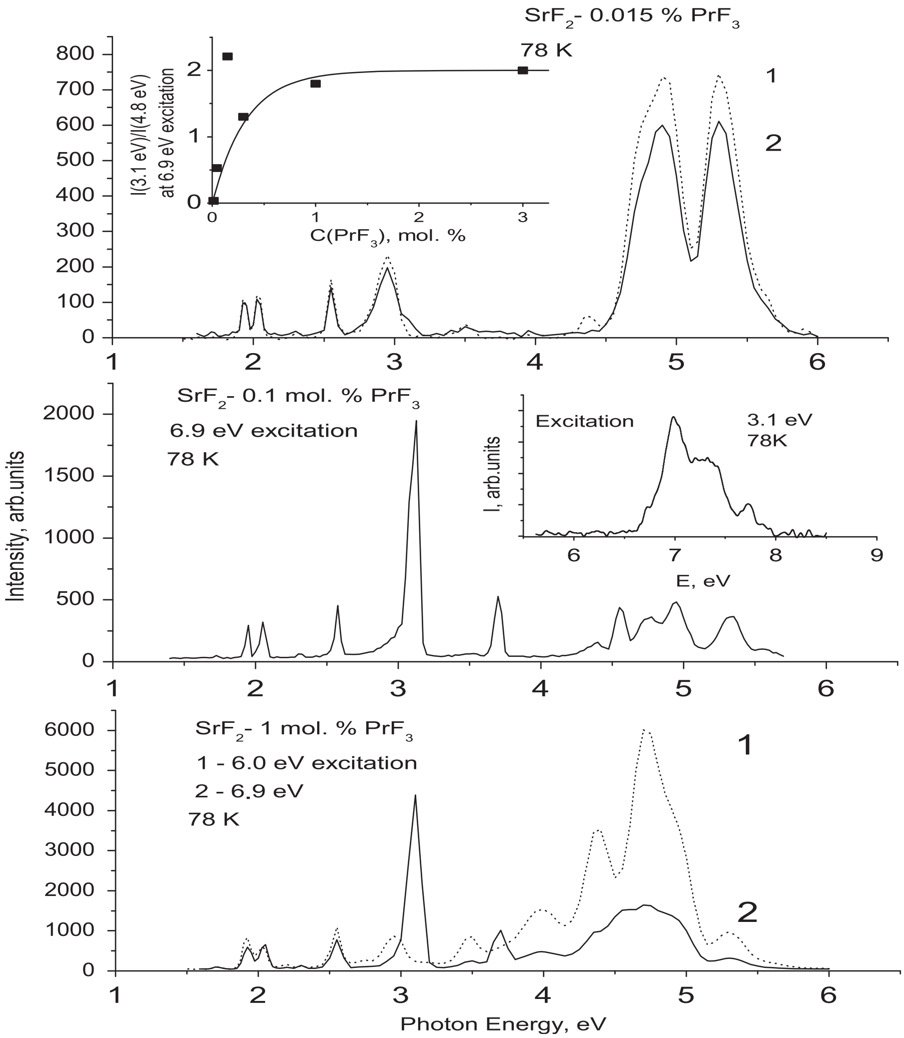

Fig. 2. Emission spectra of SrF_2 crystal doped by PrF_3 at 78 K. Samples were excited at 6.9 eV (full curves) or at 6.0 eV (dotted curve). Top left inset—Pr concentration dependence of intensities $I(3.1\,eV)/I(4.8\,eV)$ ratio at 6.9 eV excitation at 78 K.

3.2. Absorption

Absorption spectra of Pr-doped alkaline-earth fluorides show three absorption bands in CaF_2, SrF_2 and two absorption bands in BaF_2 crystal (Figs. 4 and 5).

Five d orbitals are split on two groups (e_g and t_{2g}) in cubic crystal fields. This case is very clearly observed in BaF_2-Pr crystals showing two bands at 5.9, 7.9 eV (see Fig. 5) (see also Ref. [4]). Similar 2 eV splitting of 5d orbitals was observed in Ce-doped alkaline-earth fluorides [4]. However, in CaF_2 and SrF_2 crystals we observed additional strong absorption band at 6.7 eV between 5.9, 7.9 eV bands. Similar to this the third absorption band between main 5d bands was observed in Ce-doped CaF_2 and SrF_2 and was not observed in BaF_2 crystals [4]. Later this additional band was assigned to splitting of Ce 5d e_g levels by charge compensating interstitial fluorine in nearest neighbour position [8]. Nearest neighbouring compensator of trivalent rare-earth ion is predominant in CaF_2, SrF_2 crystals [9,10], but absent in BaF_2 crystal, where compensator occupied next nearest neighbour position [11]. Therefore we may conclude that the absorption bands at 6.9 eV in Pr-doped CaF_2, SrF_2 crystals are due to perturbation of Pr^{3+} ion by nearest neighbour interstitial fluorine.

Comparing absorption spectra of CaF_2-Pr one can notice that the absorption around 7 eV grows larger than Pr absorption bands at 5.7, 6.7, and 7.7 eV (see Fig. 4). Absorption spectra of Pr-doped CaF_2 crystals show superlinear growth of absorption band with maximum near 7.0 eV with increasing of Pr concentration (see Fig. 4, top right inset) while no measurable similar absorption bands were observed in SrF_2 or BaF_2 crystals (see Fig. 5). The slope of experimental line in logarithmic coordinates of absorption coefficient of 7.0 eV band against that of band at 5.7 eV is equal to 2 (see Fig. 4, top left inset).

4. Discussion and conclusion

From the observed emission spectra one can find that the ratio of integral intensity of second cascade lines (emission from $^3P_0$ level) to the intensity of first cascade lines (emission from $^1S_0$ level) drastically decreased in a row $BaF_2-SrF_2-CaF_2$ (see Figs. 1–3). The integrated intensities in 1 mol% PrF_3-doped BaF_2, SrF_2, CaF_2 is related to each other as 36:2.4:1. It means that in SrF_2 and especially in CaF_2 crystal there is some process which efficiently quench the emission from $^3P_0$ level. At least two mechanisms are possible. One mechanism is cross-resonance energy transfer from excited Pr ion of PCE-active centre to nearest Pr ion in ground state. The probability of cross-resonance transfer depends on the distance as R^{-6} [1]. Another mechanism is that the multi-phonon and other non-radiative processes drastically grow with

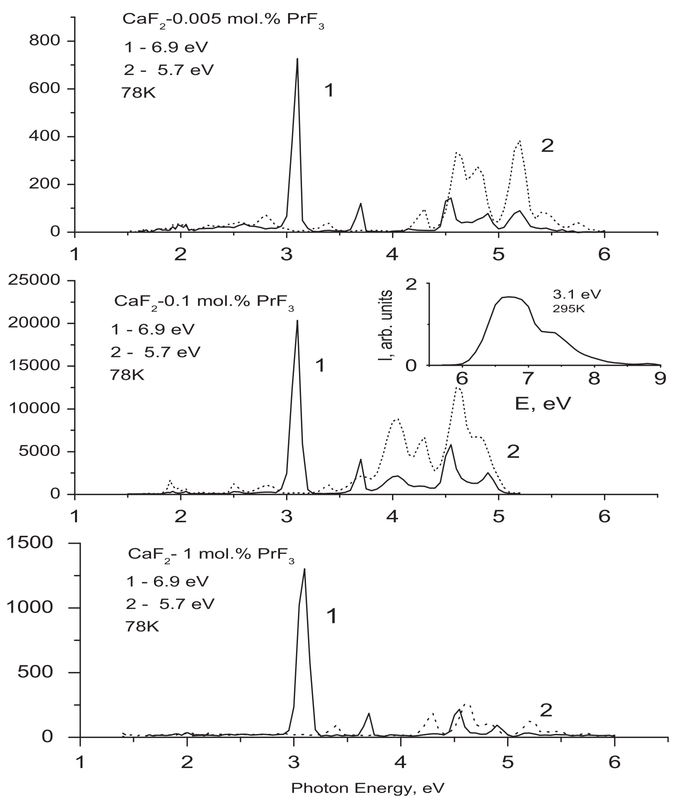

Fig. 3. Emission spectra of CaF_2 crystal doped by PrF_3. Samples were excited at 6.9 eV (full curves) or at 6.0 eV (dotted curve). Middle right inset—excitation spectrum of $CaF_2-0.1$ mol% PrF_3 of emission at 3.1 eV at 295 K.

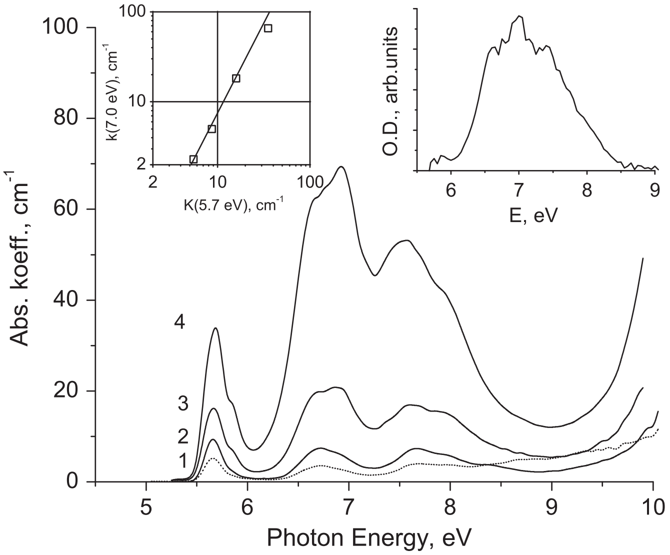

Fig. 4. Absorption spectra of CaF_2 crystal doped by PrF_3 at room temperature. Concentration of PrF_3: 1–0.005, 2–0.01, 3–0.03, 4–0.1 mol%. Top left—absorption coefficient at 7.0 eV against that at 5.7 eV. Top right—difference of absorption spectra of 0.03 mol% sample to that of 0.1 mol% sample. Both spectra were normalized to equal absorption band at 5.7 eV.

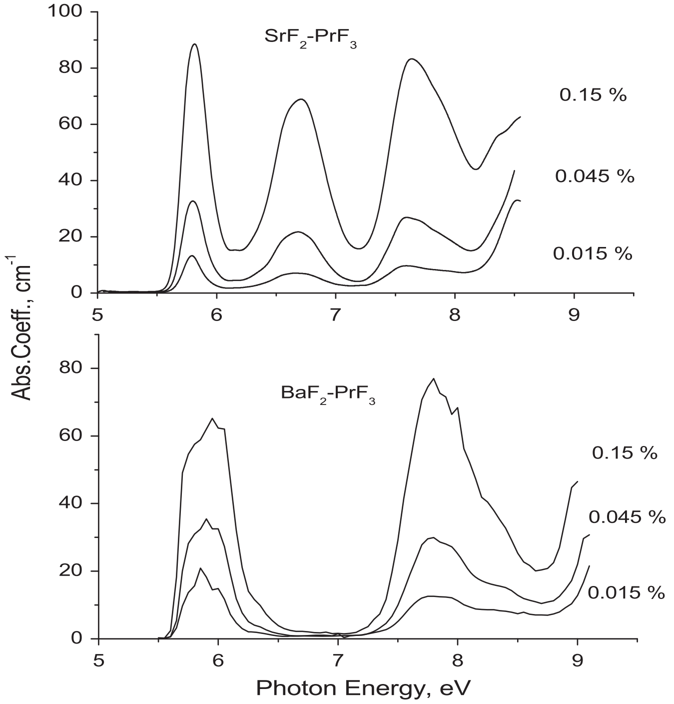

Fig. 5. Absorption spectra of SrF_2, BaF_2 crystal doped by PrF_3 at room temperature.

increasing of phonon frequency, which grows in the row from BaF_2 to CaF_2.

Superlinear growth of emission of PCE-active centres with increasing of Pr concentration in SrF_2 and BaF_2 undoubtedly proved that these centres are aggregates of initial $Pr^{3+}-F_i^-$ centres. However, in CaF_2 even at 0.005 mol% of PrF_3 the PCE-active centres are predominant at 7.0 eV excitation. At first glance there is some contradictory between CaF_2 and BaF_2, SrF_2. However, it is known that the aggregation effectiveness is higher in CaF_2 than that in SrF_2 [12]. Audio-frequency capacitance and conductance measurements were shown that defects R_{IV} (dimers) and R_{III} (higher aggregates) are observable at lower concentrations in calcium fluoride than in strontium fluoride [12]. This implies that both R_{III} and R_{IV} aggregates become less stable as the size of the host cation increases. The maximum in the dipole concentration as a function of dopant concentration reaches a maximum at a higher dopant concentration in strontium fluoride than in calcium fluoride for simple point defects [12]. Therefore it is not astonishing that the PCE-active aggregate centres are observed at lower concentrations in CaF_2 than in SrF_2, BaF_2.

The absorption spectra of CaF_2-PrF_3 show superlinear growth of absorption band at 7.0 eV against the known Pr-absorption bands (see Fig. 4) This absorption band is well coincided with excitation spectrum of PCE-active centres. Therefore one can assume that the 7.0 eV absorption band belongs to PCE-active centres. No such absorption was observed in SrF_2 and BaF_2 crystals. These results are also in line with relatively high effectiveness Pr aggregation in CaF_2 and much lower aggregation effectiveness in BaF_2 and SrF_2 crystals. The dependence of absorption at 7.0 eV against that at 5.7 eV is well described by parabola curve (see Fig. 4). In the term of aggregation process it means that one aggregate (dimer) is built from two single centres.

The influence of crystal structure on splitting of 5d levels of Pr^{3+} ion was thoroughly discussed in paper [3]. Two main consequences of Pr^{3+} introduction into cation site are observed. At first the average energy of the five 5d states is decreased relative to the value for the free ion (the so-called centroid shift). At second the crystal field of alkaline-earth fluorides splits the 5d levels of Pr by 2 eV, mainly due to different repulsion of 5d orbitals from eight negatively charged surrounded fluorines. Two 5d orbitals (d_{z^2} and $d_{x^2-y^2}$) having less repulsion are situated at lower energy than other three orbitals (d_{xy}, d_{xz}, d_{yz}). As a result the $^1S_0$

level was found at higher energy than e_g 5d level [4], and 5d–4f emission is only observed for single Pr defects.

From qualitative consideration the presence of six interstitial negative fluorines around Pr^{3+} ion should considerably reduce the splitting of 5d orbitals. Indeed, in this case the d_{z^2} and $d_{x^2-y^2}$ orbitals will have strong repulsion from negative interstitials and therefore their energy should increase.

I conclude that Pr centres, which possesses the photon cascade emission in CaF_2, SrF_2, BaF_2 crystals, are aggregates of $Pr^{3+}-F_i^-$ initial centres.

Acknowledgements

The author is grateful to V. Ivashechkin and V. Kozlovskii for the growth of studied crystals. This work was partially supported by Grant 07-02-01057 from Russian Foundation for Basic Research (RFBR).

References

[1] R.S. Meltzer, Quantum-cutting phosphors, in: W.M. Yen, S. Shionoya, H. Yamamoto (Eds.), Phosphor Handbook, second ed., CRC Press Taylor & Francis Group, 2006, pp. 507–529 (p. 3, Chapter 5).
[2] S. Kuck, I. Sokolska, M. Henke, T. Scheffler, E. Osiac, Phys. Rev. B 71 (2005) 165112.
[3] E. Van der Kolk, P. Dorenbos, A.P. Vink, R.C. Perego, C.W.E. van Eijk, A.R. Lakshmanan, Phys. Rev. B 64 (2001) 195129.
[4] E. Loh, Phys. Rev. 154 (1967) 270;
E. Loh, Phys. Rev. 175 (1968) 533;
E. Loh, Phys. Rev. 158 (1967) 273;
E. Loh, Phys. Rev. 140 (1968) 1463.
[5] K.D. Oskam, A.J. Houtepen, A. Meijerink, J. Lumin. 97 (2002) 107.
[6] P.A. Rodnyi, G.B. Stryganyuk, C.W.E. van Eijk, A.S. Voloshinovskii, Phys. Rev. B. 72 (2005) 195112.
[7] B.M. Tissue, J.C. Wright, Phys. Rev. B. 36 (1987) 9781.
[8] E. Radzhabov, T. Kurobori, J. Phys. Cond. Mat. 16 (2004) 1871.
[9] J. Corish, C.R.A. Catlow, P.W.M. Jacobs, S.H. Ong, Phys. Rev. B. 25 (1982) 6425.
[10] C.D. Cleven, S.H. Lee, J.C. Wright, Phys. Rev. B. 44 (1991) 23.
[11] J.P.R. Wells, G.D. Jones, R.J. Reeves, Phys. Rev. B. 60 (1999) 851.
[12] C.G. Andeen, J.J. Fontanella, M.C. Wintersgill, P.J. Welcher, R.J. Kimble, G.E. Matthews, J. Phys. C Solid-St. Phys. 14 (1981) 3557.