11th Europhysical Conference on Defects in Insulating Materials (EURODIM 2010) IOP Publishing
IOP Conf. Series: Materials Science and Engineering **15** (2010) 012029 doi:10.1088/1757-899X/15/1/012029

Excitation of Pr^{3+} ions in alkaline-earth fluorides

E Radzhabov[1,2] **and V Nagirnyi**[3]
[1]Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii street 1a, P.O.Box 4019, 664033 Irkutsk, Russia
[2]Irkutsk State University, Physics department, Gagarin boulevard 20, 664003 Irkutsk, Russia
[3]Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

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

Abstract. Emission and excitation spectra of CaF_2, SrF_2, BaF_2 doped by PrF_3 were measured in vacuum ultraviolet region at 11 K. Emission spectra of several 5d-4f bands of CaF_2 and BaF_2 show evident vibronic structure with apparent line separated by 400 cm^{-1} from the main zero phonon line. No such structure was observed in SrF_2-Pr. The absence of vibronic structure in SrF_2 is assumed to be caused by the closeness of a local vibronic frequency to the lattice phonon one.

Excitation spectra of 4f-4f and 5d-4f transitions are substantially different pointing on to the different excitation mechanisms of both groups of lines. The 4f-4f lines show an intense excitation peak adjacent to the exciton peak. This infers that excitons created near to Pr^{3+} ions can feed the 4f-4f transitions. The efficiency of excitation of the 4f-4f and 5d-4f emission bands is quite low in the region of band-to-band transitions. An apparent peak at 19 eV in the excitation spectrum of the BaF_2-Pr 5d-4f emission (230 nm) coincides well with that of the crossluminescence. No similar peaks were observed in CaF_2 or SrF_2 excitation spectra. We conclude that the main channel of energy transfer from the host to Pr^{3+} ions is realized resonantly through crossluminescence in BaF_2-Pr.

1. Introduction

Crystals doped by Pr^{3+} ions could be considered as perspective materials for scintillator or quantum cutting applications [1]. The mechanism of energy transfer from a host to Pr ions still remains one of the unsolved questions. The spectroscopic investigation in the vacuum ultraviolet region is one of the most powerful methods for studying the mechanisms of energy transfer.

After excitation by vacuum ultraviolet photons of Pr^{3+} ion doped into alkaline-earth fluorides two systems of lines are emitted. Ultraviolet bands observed in the region 215-370 nm belong to 5d-4f allowed interconfigurational transitions, and the sharp lines at 390-900 nm region belong to the 4f-4f parity forbidden intraconfigurational transitions. At low temperatures interconfigurational absorption, excitation and emission bands show rich fine structure due to interaction with vibrational modes [2, 3, 4].

Excitation spectra of BaF_2-Pr in vacuum ultraviolet region were investigated earlier [5]. The authors discussed the possibility of core excitation in the process of energy transfer to praseodymium in barium fluoride. The crossluminescence (or core-valence transitions) occurs from the valence band to the outmost core band where a hole was created by the absorption of a vacuum ultraviolet photon. The crossluminescence of undoped BaF_2 consists of the main band at 220 nm, overlapping strongly with the Pr^{3+} 4f-5d absorption, and a lower-intensity band at

193 nm [6]. No core-valence transitions (or crossluminescence) were observed in SrF_2 or in CaF_2 where these transitions are energetically unfavourable [6].

The main goal of this paper is the clarification of Pr^{3+} emission and excitation mechanisms by comparative spectroscopic study of the three homologous hosts CaF_2, SrF_2, BaF_2 with different concentration of PrF_3 dopants in vacuum ultraviolet region.

2. Experimental

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method. Graphite crucible contains three cylindrical cavities 10 mm in diameter and 80 mm long, which allows to grow three crystals of Ø10x50 mm in dimensions with different impurity concentrations at the same time. As the first step a large oxygen-free crystal was grown with addition of CdF_2 as an oxygen scavenger in a simple large volume crucible. Then parts of this crystal were used for growing the doped crystals.

Emission and excitation spectra as well as the emission decay kinetics of CaF_2, SrF_2 and BaF_2 doped by 0.15 mol. % of PrF_3 were studied in the region of 2-24 eV at 11 K. The measurements were conducted at the SUPERLUMI station of HASYLAB at DESY (Hamburg, Germany) [7]. Additionally some emission spectra were measured at the Institute of Geochemistry using Kr (120 nm) or Xe (147 nm) discharge lamps as excitation sources and a solar-blinde photomultiplier FEU142 attached to a vacuum grating monochromator VM4.

3. Results

The emission spectra due to the 5d-4f Pr^{3+} transitions are shown on figure (Fig.1). The observed emission lines are due to transitions from the lowest 5d-level to different 4f levels of the Pr^{3+} ion, whose energies in CaF_2 are known from [8]. Five 5d levels of Pr^{3+} ion are split by the crystal field in two groups. Usually the 5d-4f emission lines are wider than the 4f-4f lines due to the fact that the outmost d - levels interact with lattice vibration stronger than the inner f - levels. The 5d-4f emission spectrum of CaF_2-Pr is similar to those measured earlier [3]. Each emission band of CaF_2 and BaF_2 shows a prominent zero phonon line and another strong line of smaller intensity separated by near 400 cm^{-1}. From additional measurements of lower doped crystals the fine structure of 5d-4f emission spectra was evidently observed at 78K in BaF_2-0.01 % PrF_3, the structure is less evident in CaF_2-0.01 % PrF_3 and fully absent in SrF_2-0.01 % PrF_3.

The shape of emission spectra are compared in one plot by shifting the spectra by 44300, 45300, 45500 cm^{-1} for CaF_2, SrF_2, BaF_2, respectively (Fig.2). The spectra of CaF_2 and BaF_2 are similar, while the separation between the sharp lines is slightly smaller in BaF_2. The spectrum of SrF_2 is structureless.

Excitation spectra for the 5d-4f (for the line 5d - $^3H_4$), 4f-4f (for the line $^3P_0$ - $^3H_4$) and exciton emissions are shown in Figure 3. The excitation curves of the 5d-4f and 4f-4f emission are different in the region of direct 5d-4f excitation 5.5-9 eV. Prominent excitation bands were observed below the exciton peaks only. Both spectra are of low intensity and very smooth above the exciton peaks in the range of interband transition (see Fig.3).

4f-4f excitation The excitation spectra of the $^3P_0$ - $^3H_4$ emission line show the peaks near 7 eV (see Fig.3). This band is most intense in CaF_2 less pronounced in SrF_2 and the weakest in BaF_2 crystals. It belongs to the aggregate Pr defects, which possess photon cascade emission [9]. All three crystals show intensive excitation bands right below the exciton peak. Similarly situated wide peaks were observed earlier for the 4f-4f emission of several rare- earth ions in LaF_3 [10].

5d-4f excitation The excitation spectra of the 5d-4f emissions in CaF_2 and SrF_2 show a sharp decrease at the exciton edge energies (see Fig.3). The decrease is less evident in BaF_2. The spectra are of low intensity and almost structureless in the region of the interband transitions. The prominent excitation peak near 19.5 eV was observed for BaF_2, it was absent in CaF_2 and

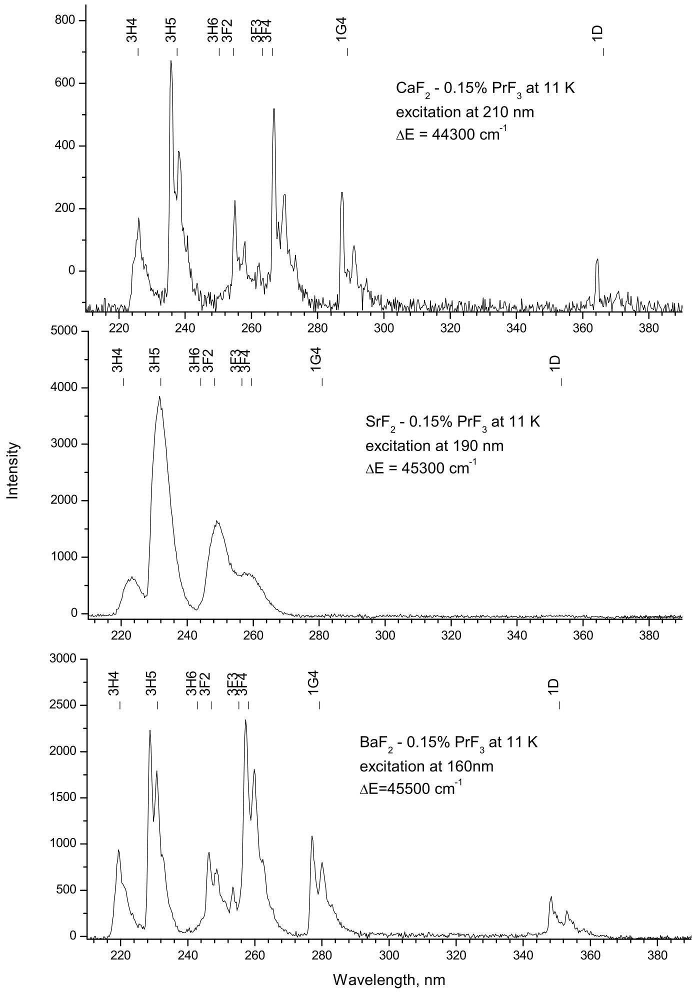

Figure 1. Emission spectra of Pr^{3+} 5d-4f transitions in CaF_2, SrF_2, BaF_2 crystals doped by 0.15 molar % of PrF_3. Positions of each line due to the transitions from the lowest 5d levels to individual 4f levels are shown at the top of each plot.

SrF_2 crystals. The excitation efficiency at 19.5 eV is only twice as low as that in the region of a direct 4f-5d excitation (see Fig.3).

To verify the possibility of energy transfer from the host to a praseodymium ion due to the absorption of a crossluminescence photon by 5d-4f states we compare the emission spectra of undoped and Pr-doped BaF_2 with the absorption spectrum of Pr^{3+} ion in BaF_2 (Fig.4). The absorption is the highest at 200-220 nm where it largely overlaps with 220 nm crossluminescent bands (see Fig.4). With increasing Pr concentration the intensity of the Pr emission lines grows, while the intensity at 210 nm, which is mostly due to the crossluminescence, is continuously decreased partially due to the increasing Pr absorption. The changes in crossluminescence intensity could be monitored via the intensity of the 193 nm band, where the Pr absorption is relatively low. The intensity of the 193 nm band also decreases with increasing Pr concentration (see Fig.4).

4. Discussion

It should be noted that fine structure of spectra was not observed in SrF_2-0.15 % PrF_3 crystal (see Fig.1). Usually many physical properties changes continuously in the row CaF_2-SrF_2-BaF_2 [11]. Therefore the observed dependence is very unusual. The transitions from the 5d to 4f state

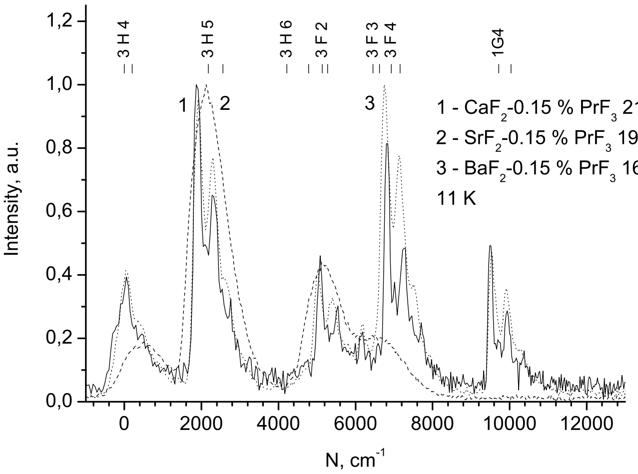

Figure 2. Comparison of the shapes of the emission spectra of Pr^{3+} 5d-4f transitions in CaF_2, SrF_2, BaF_2. The spectra are normalized for the $^3H_5$ line intensities, while the origin of the wave number scale is placed at the $^3H_4$ line.

are often assisted by lattice phonons. As a result the optical emission or absorption spectrum contains phonon wing. The emission or absorption spectra of Ce^{3+} in SrF_2 consist of a zero-phonon line and a broad phonon wing shifted from line by 400 cm^{-1} [12]. The frequencies of a longitudinal optic phonon obtained from optical data at 5 K are 484, 397 and 346 $^{-1}$ for CaF_2, SrF_2, BaF_2 respectively [11]. Typical distances between the vibronic lines in absorption spectra were 450, 430, 400 cm^{-1} for the 0.005 % PrF_3 doped CaF_2, SrF_2, BaF_2 crystals respectively [4]. The spectrum of several individual Pr emission lines caused by transitions from the 5d to $^3H_4$, $^3F_2$, $^3F_3$, ^1G states in BaF_2 and CaF_2 is shown in Fig.2. Besides the zero-phonon lines the intensive vibrational lines separated by 430 and 390 cm-1 were observed in CaF_2 and BaF_2, respectively. For CaF_2 similar 5d-4f emission spectra of Pr ion were measured with higher resolution earlier [3]. Obviously these phonon lines are due to a local vibration in the complex PrF_8 (see also [4]). The frequencies of these local vibrations are higher than the lattice phonon frequencies in BaF_2, lower then those in CaF_2 and should be almost equal to the phonon frequencies in SrF_2. Therefore the longitudinal optic phonons possessing the energy equal to that of the local vibrations of PrF_8 should wide the Pr emission lines in SrF_2 (see Fig.2). In CaF_2 or BaF_2, the frequencies of lattice phonons and PrF_8 local vibrations are sufficiently different and therefore the structure of emission spectra can be observed.

Excitation spectra of the intraconfigurational 4f-4f transitions of trivalent Nd, Er, Tm, Pr ions doped into several trifluorides were measured in an early paper [10]. Excitation bands on the low-energy wing of exciton bands were observed in all cases. Evidently the excitonic mechanism of the energy transfer to the f-shell has a common character. One can assume that the energy of self-trapped exciton (near 4.5 eV in fluorides) is transfered to the appropriated excited f-levels of rare-earth ions. The exciton energy is not sufficient for the excitation of 4f-5d transitions for all the rare-earth ions except Ce^{3+}.

Excitation spectrum for the 255 nm Pr^{3+} emission (transition 5d-^3F_j) was measured for BaF_2-0.3 % PrF_3 earlier [5]. The integrated intensity and the fast component of the 5d luminescence show a rather smooth increase in intensity above 18 eV, that is in the region of excitation of the 5p Ba core states. Authors assume that the energy of the core cation excitations to be transfered to Pr luminescence centres in BaF_2 [5]. Our measurements show an evident Pr 5d-4f excitation peak which well coincides with the crossluminescence excitation peak in undoped BaF_2 crystals. The decrease in the crossluminescence intensity accompanying the increase of Pr concentration is clearly seen from comparison of the emission intensity at the wavelength 193 nm, where the

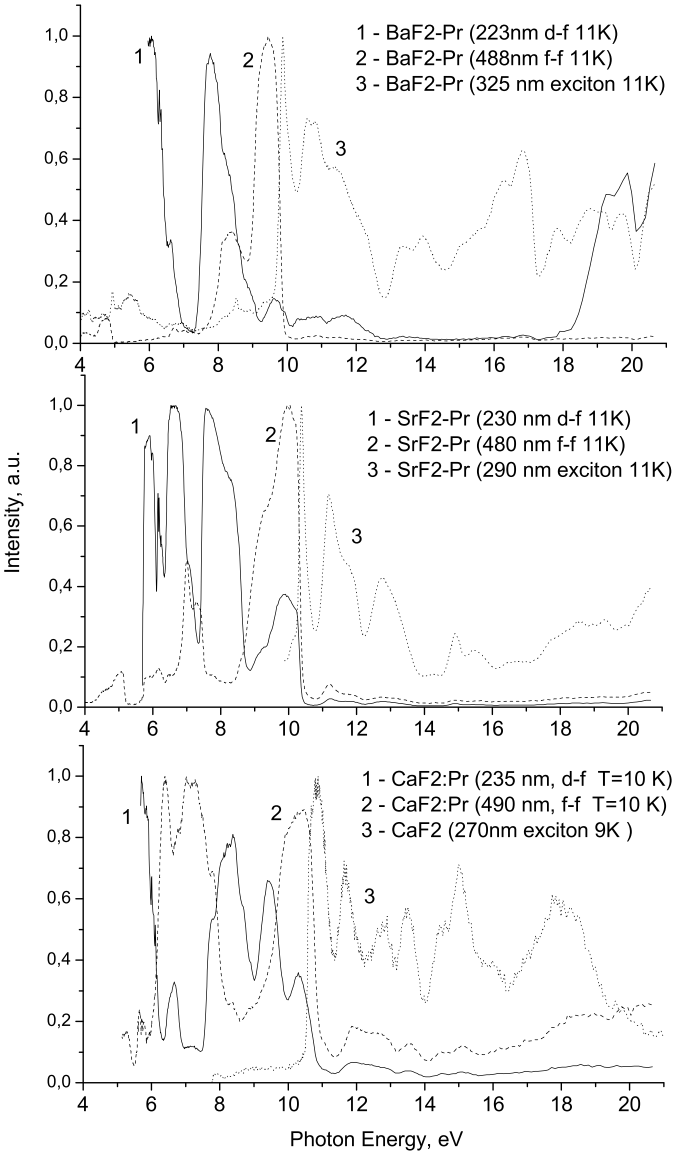

Figure 3. Excitation spectra of Pr 5d-4f and 4f-4f emission bands as well as exciton emission of CaF_2, SrF_2, BaF_2 crystals doped by 0.15 molar % of PrF_3.

Pr absorption is low (see Fig.4). At the level of 0.3 molar % of PrF_3 the crossluminescence is almost completely suppressed. Considering the uniform Pr distribution across the BaF_2 lattice one could estimate the radius of the resonant transfer from a crossluminescent centre to a Pr ion, at which the crossluminescence becomes fully suppressed, as half the distance between Pr ions. The half Pr-Pr distance at the level of 0.3 molar % is near 21.5 Å.

One could estimate this radius also from emission and absorption spectra overlapping. The radius R_c of dipole-dipole energy transfer defined as the distance at which the probability of donor (crossluminescent centre in our case) radiative transitions is equal to the probability of transfer to acceptor (Pr ion), is given by [13]:

$$R_c^6 = \frac{B}{n^4 N_A} \int_0^\infty \frac{f_D(E)\mu_A(E)}{E^4} dE$$

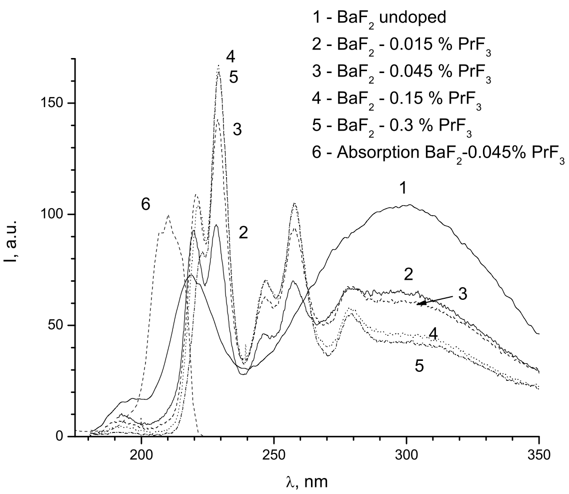

Figure 4. Emission spectra of undoped BaF_2 (curve 1) and BaF_2-PrF_3 (curves 2-5) measured under x-ray excitation at room temperature. Absorption spectrum of BaF_2-0.045 % PrF_3 in arbitrary units is added for comparison (curve 6).

Here n is the refractive index of crystal, the subscript A denotes the acceptor centre and D denotes the donor centre. The term N_A is concentration of acceptor centres (in cm^{-3}) and μ_A (E) is their absorption coefficient (in cm^{-1}). The $f_D(E)$ is the emission spectrum of the donor centres, normalised in such a way that $\int\limits_0^\infty f_D(E)dE = 1$. Constant $B = \frac{3\hbar^4 c^4}{4\pi} = 3.7 * 10^{-20}(eV^4 * cm^4)$. From the experimental data we evaluate the radius R_c as 18.3 Å. Thus, both values obtained for the distance of energy transfer from the host to the Pr^{3+} ion via the crossluminescence are in good agrement.

We can summarize the results supporting the energy transfer to the Pr^{3+} ions by crossluminescence in BaF_2-Pr as follows:

- sufficient overlap between the crossluminecence and Pr absorption,
- continuous decrease of crossluminescence intensity (at 193 nm) with Pr concentration increasing,
- appearance of the crossluminescence excitation peak near 19 eV in the Pr 5d-4f excitation spectrum.

5. Conclusion

The above-described experimental results prove that the Pr^{3+} 5d-4f emission is efficiently excited via the resonant energy transfer from crossluminescence centres in BaF_2. The excitation mechanism in CaF_2 and SrF_2 should be investigated additionally.

6. Acknowledgments

The authors gratefully acknowledge V. Kozlovskii for growing the crystals investigated in this work. Financial support by the Estonian Science Foundation (grant 7825) and the European CommunityResearch Infrastructure Action under the FP6 Structuring the European Research Area Programme (through the Integrated Infrastructure Initiative Integrating Activity on Synchrotron and Free Electron Laser Science) is gratefully acknowledged.

References

[1] Melcher C L 2005 *Nucl. Instrum. Meth.* A **537** 6
[2] Makhov V N, Khaidukov N M, Lo D, Kirm M and Zimmerer G 2003 *J. Lumin.* **102-103** 638
[3] Oskam K D, Houtepen A J and Meijerink A 2002 *J. Lumin.* **97** 107

[4] Loh E, Blazey K W, Nosenzo L and Reguzzoni E 1979 *J. Phys. C: Solid State Phys.* **12** 3879
[5] Rodnyi P A, Stryganyuk G B, van Eijk C W E et.al. 2005 *Phys. Rev.* B **72** 195112
[6] Rodnyi P A 1992 *Sov. Phys. Solid State* **34** 1053
[7] Kirm M, Lushchik A, Lushchik C, Nepomnyashikh A I and Savikhin F 2001 *Rad. Measurements* **33** 515
[8] Hargreaves W A 1972 *Phys. Rev. B* **6** 3417
[9] Radzhabov E 2009 *J. Lumin.* **129** 1581
[10] Yang K H, DeLuca J A 1978 *Phys. Rev.* B **17** 4246
[11] Crystal with fluorite structure, ed by Hayes W Clarendon Press, Oxford, 1974
[12] Radzhabov E and Kurobori T 2004 *J. Phys.: Cond. Matter* **16** 1871
[13] Visser R, Dorenbos P, van Eijk C W E, Meijerink A, Blasse G and den Hartog H W 1993 *J.Phys. Cond. Matter* **5** 1659