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

E. Radzhabov$^{1,2}$, V. Nagirnyi$^3$, and A. Lushchik$^3$

$^1$ 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

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

Excitation spectra of BaF$_2$-Pr in vacuum ultraviolet region were investigated earlier [2]. 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 due to 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 [3]. No core-valence transitions were observed in SrF$_2$ or CaF$_2$ [3]. The present paper aims to clarify Pr$^{3+}$ emission and excitation mechanisms by a comparative spectroscopic study in the vacuum ultraviolet region of the three homologous hosts CaF$_2$, SrF$_2$, BaF$_2$ with different concentrations of the PrF$_3$ dopant.

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method. 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) [4]. 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-blind photomultiplier FEU142 attached to a vacuum grating monochromator VM4.

Excitation spectra for the 5d-4f (for the line 5d - $^3$H$_4$ ), 4f-4f (for the line $^3$P$_0$ - $^3$H$_4$ ) and exciton emissions are shown in Figure 1. 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 are very smooth above the exciton peaks in the range of interband transitions (Fig. 1).

**4f-4f excitation** The excitation spectra of the $^3$P$_0$ - $^3$H$_4$ emission line show a peak near 7 eV (not shown on Fig. 1). This band is the most intense in CaF$_2$, less pronounced in SrF$_2$ and the weakest in BaF$_2$ crystals. It belongs to the aggregate Pr centres, which possess photon cascade emission [5]. 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$_3$ [6].

**5d-4f excitation** The excitation spectra of the 5d-4f emissions show a sharp decrease at the exciton edge energies in CaF$_2$ and SrF$_2$ (Fig. 1). 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$_2$, while it was absent in CaF$_2$ and 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 (Fig. 1).

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 have compared the radioluminescence emission spectra of undoped and Pr-doped BaF$_2$ with the absorption spectrum of...
Pr$^{3+}$ ion in BaF$_2$. The absorption is the strongest at 200-220 nm where it largely overlaps with the 220 nm crossluminescence band. The intensity of the Pr emission lines grows with the increasing of Pr concentration, while the intensity at 210 nm gradually decreases partially due to the enhancement of Pr absorption. The changes in crossluminescence intensity can be better monitored at 193 nm, where the Pr absorption is relatively weak. The intensity of the 193 nm band also decreases with the rise of Pr concentration. At the level of 0.3 mol.\% of PrF$_3$ the crossluminescence is almost completely suppressed. Considering the uniform Pr distribution across the BaF$_2$ lattice one can estimate the radius of the resonant transfer from a crossluminescent centre to a Pr ion, as half the distance between Pr ions. The half Pr-Pr distance at the level of 0.3 molar \% is near 21.5 Å. Using the Förster’s approach [7], one can also estimate this radius from the overlapping of crossluminescence emission and praseodymium absorption spectra. From the above-described data we evaluate the Förster's 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 agreement.

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.

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References