Emission and excitation spectra of Ce$^{3+}$ and Pr$^{3+}$ ions in hexafluoroelpasolite lattices

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The interconfigurational $4f^N-4f^{N-1}5d$ electronic transitions of the tri-positive lanthanide ions, Ln$^{3+}$, doped into wide band-gap crystals attract much attention because of potential applications of Ln$^{3+}$ doped materials for ultraviolet lasers, scintillators, quantum cutters and VUV or x-ray phosphors. In the hexafluoroelpasolite host Cs$_2$NaYF$_6$ the Ln$^{3+}$ ions occupy octahedral symmetry ($O_h$) sites. This results in high energy level degeneracies (of up to fourfold) and to restrictive $O_h$ symmetry selection rules for electronic transitions. The spectra of $4f^N-4f^{N-1}5d$ transitions of Ln$^{3+} = $Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$ doped into Cs$_2$NaYF$_6$ have been studied in detail earlier [1]. In the present work [2], emission and excitation spectra of Ce$^{3+}$ and Pr$^{3+}$ ions doped into Cs$_2$NaYF$_6$ crystals have been investigated using for excitation UV/VUV synchrotron radiation at the Superlumi station of HASYLAB at DESY. The crystals of Cs$_2$NaYF$_6$ doped with Ce$^{3+}$ (or Pr$^{3+}$) were synthesized by a hydrothermal technique [3].

Excitation of Cs$_2$NaYF$_6$:Ce$^{3+}$ into the major Ce$^{3+}$ 4$f$-5$d$ absorption band, using 315 or 300 nm radiation, gives the emission spectrum (Fig.1), which corresponds to electronic and vibronic structure of transitions from the lowest 5$d$ level to the 4$f$ $^2F_{5/2}$, $^2F_{7/2}$ multiplets of Ce$^{3+}$. Altogether, there are 5 unresolved electronic transitions within the band extending from 325 nm to 450 nm. In the excitation spectrum, zero phonon lines corresponding to transitions to the two 5$d$ $^2T_{2g}$ states of Ce$^{3+}$ in this matrix have been located within the major Ce$^{3+}$ 4$f$-5$d$ band at 319 and 295 nm. The 5$d$ $^2E_g$ levels of Ce$^{3+}$ have been estimated to lie within the conduction band of the host crystal. The fine structure in the excitation spectrum at the high-energy side of the major Ce$^{3+}$ 4$f$-5$d$ band was well resolved and can be interpreted by vibrational progressions corresponding to three types of totally-symmetric modes of lattice vibrations near the Ce$^{3+}$ ion. Decay measurements of Ce$^{3+}$ emission, and spectra collected using spectrally selective excitation, indicate the occupation of at least two types of sites by Ce$^{3+}$ in this host lattice. The second type of Ce$^{3+}$ centers can be associated with the occupation of the cubic Cs$^+$ site by Ce$^{3+}$, where the crystal field strength is very small. The bands in the excitation spectrum between 275-200 nm could correspond to excitation of these centers.

The measurements of emission and excitation spectra of Cs$_2$NaYF$_6$:Pr$^{3+}$ have shown that emission spectrum of Pr$^{3+}$ in this host under 4$f$-4$f/5d$ excitation (using 206, 210 or 225 nm radiation) is purely due to interconfigurational 4$f$5$d$ transitions of Pr$^{3+}$ and shows four main broad bands in the range 235-325 nm corresponding to transitions from the lowest 4$f$5$d$ level to the 4$f$ $^2F_{5/2}$, $^2H_g$, $^2H_s$, $^2H_{6s}$, $^2F_2$ and $^2F_{3,4}$ multiplets of Pr$^{3+}$ (Fig.2). In the excitation spectrum of Pr$^{3+}$ luminescence, five 4$f$-4$f/5d$ $^2T_{2g}$ transitions can be identified in the spectral range 200-230 nm. Since electronic transition from the ground 4$f$ state to the lowest 4$f$5$d$ level of Pr$^{3+}$ in Cs$_2$NaYF$_6$ is forbidden due to symmetry selection rules there exists an energy gap between emission band and the edge of excitation spectrum. The obtained spectral and decay data show that the Pr$^{3+}$ ions occupy a single site in the Cs$_2$NaYF$_6$ host lattice. The 5$d$ emission lifetimes for Ce$^{3+}$ and Pr$^{3+}$ in this host were measured to be 42 and 29±1 ns, respectively.

The Pr$^{3+}$ doped crystals which show narrow-line emission from the Pr$^{3+}$ 4$f$ $^1S_0$ level under Pr$^{3+}$ 4$f$ → 4$f/5d$ excitation are considered as possible quantum cutting materials. The present study have shown that emission of Pr$^{3+}$ in the Cs$_2$NaYF$_6$ host comprises 4$f$5$d$ → 4$f$ transitions but not 4$f$ $^1S_0$ → 4$f$ ones because the lowest 4$f$5$d$ level of Pr$^{3+}$ lies below the 4$f$ $^1S_0$ energy level, i.e. Pr$^{3+}$ doped Cs$_2$NaYF$_6$ cannot be employed as quantum cutter.
Figure 1: Low temperature emission (right) and excitation (left) spectra of Cs$_2$NaYF$_6$:Ce$^{3+}$. Narrow lines in emission spectra in the range 250-315 nm correspond to scattered excitating radiation.

Figure 2: Low temperature emission (right) and excitation (left) spectra of Cs$_2$NaYF$_6$:Pr$^{3+}$. Narrow lines in emission spectra in the range 205-225 nm correspond to scattered excitating radiation.

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References