Fast UV luminescence of Calcium Lutetium Whitlockite doped with Pr$^{3+}$

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Lanthanide-doped inorganic materials able to convert ionizing radiation (X- and γ-rays) to UV and visible emission have been intensively investigated in the past decade as possible scintillating materials and presently find numerous applications in important technological fields. Among these fields are the detection of ionising radiation and in particular medical diagnostics such as Positron Emission Tomography (PET). The fundamental requirements for the development of new time-of-flight (TOF) PET scanners based on scintillator materials are short decay times (less than 25 ns) and minimal rise time (< 0.5-1 ns). These requirements can be met with the Pr$^{3+}$ dopant ion that gives rise to fast and efficient 5d-4f electric-dipole allowed transitions located in the UV spectral region [1]. The purpose of this work was to continue our research on Pr$^{3+}$ doped double phosphates [2] and examine potentials of Ca$_9$Lu(PO$_4$)$_7$ to provide efficient Pr$^{3+}$ 5d-4f interconfigurational emission transitions upon high energy excitation. This host, belonging to the whitlockite family, has a trigonal structure of the β-Ca$_3$(PO$_4$)$_2$ type with several sites available for the Pr$^{3+}$ ion. In the present research, we performed time-resolved VUV spectroscopy study of Ca$_9$Lu(PO$_4$)$_7$ using the SUPERLUMI setup (beamline I, project no. I-20100220 EC). The sample for this research was synthesised using a high temperature solid state reaction and it was characterized by powder X-ray diffraction (XRD).

Fig. 1-a shows time-resolved and time-integrated emission spectra of Ca$_9$Lu(PO$_4$)$_7$ doped with 1% Pr$^{3+}$, obtained at 300 K upon VUV Pr$^{3+}$ intra-centre excitation. The time-integrated mode emission spectrum is dominated by a broad band with two prominent maxima at 245 and 280 nm. These emission features are well pronounced in the fast time gate (2-14 ns) and are identified as the parity-allowed interconfigurational optical transitions from the lowest excited Pr$^{3+}$ 4f$^1$5d$^1$ state to the $^3$H$_J$ and $^3$F$_J$ multiplets of the ground 4f$^2$ electronic configuration. The Stokes shift of the Pr$^{3+}$ emission, calculated as energy difference between the maxima of the lowest energy Pr$^{3+}$ 4f$^1$5d$^1$→4f$^2$ excited band and the highest energy Pr$^{3+}$ 4f$^1$5d$^1$→4f$^2$ emission band is about 3100 cm$^{-1}$. According to the model recently proposed by Srivastava et al., the Stokes shift of the Pr$^{3+}$ emission should be lower than $\approx$ 3200 cm$^{-1}$ to encourage domination of radiative 5d-4f transitions in relaxation of Pr$^{3+}$ 4f$^1$5d$^1$ excited state. This supports present assignment of the interconfigurational 5d-4f luminescence. The weak broad emission band around 440 nm that dominates within slow time gate (72-172 ns) is assigned to excitonic or defect related emission. Additionally the very weak emission peak at 609 nm occurred in the slow time gate spectrum is assigned to Pr$^{3+}$ 4f-4f intraconfigurational transition from the $^1$D$_2$ level to the ground state $^3$H$_6$.

![Emission spectra](image1)

**Figure 1:** Emission spectra recorded at T = 300K upon excitation at 200 nm (a) and at 150 nm (b) in integrated mode (1), and within fast (2) and slow (3) time gates.
Increasing the excitation energy up to 8.27 eV ($\lambda_{\text{exc}} = 150$ nm), that corresponds to the host lattice absorption, leads to significant transformation of the emission spectra (Fig. 1-b) due to appearance of a broad emission band centered at 321 nm. The band clearly dominates in the slow time gate spectrum and demonstrates a smooth Gaussian shape with halfwidth of about 1.5 eV. We tentatively assigned this spectral feature to defect emission.

The decay kinetics of the Pr$^{3+}$ 5d-4f emission under excitation into 5d levels at $\lambda_{\text{exc}} = 198$ nm can be satisfactory fitted by a single exponential function with a decay constant of 17 ns. The lifetime remains nearly the same when sample is cooled down to 8 K that suggests no thermal quenching for the 5d-4f emission within the temperature range of 8–300 K. It is important to note the Pr$^{3+}$ 5d-4f emission time profile does not reveal any significant build-up indicating that excited Pr$^{3+}$ 4f$^5$5d$^1$ state does not experience any thermally assisted depopulation.

The time-integrated excitation spectra recorded monitoring the emission bands at 258 nm (Pr$^{3+}$ 5d-4f emission) and 440 nm (intrinsic emission) are presented in Fig. 2-b. The 5d-4f emission shows a strong structured excitation feature with most pronounced maxima at about 210, 200 and 175 nm. The peaks at 210 and 200 nm are assigned to transitions to Pr$^{3+}$ 5d levels while the peak at 175 nm can be related either to population of higher energetic Pr$^{3+}$ 4f$^5$5d$^1$ component or to defect absorption and/or to the formation of defect localized excitons. Moreover, we note that the interband transitions for several double phosphates constituted of lanthanide ions is generally located in the range 130-170 nm as observed by the Schwarz et al. [3]. Below 130 nm no significant excitation features are observed indicating that the host→Pr$^{3+}$ energy transfer is not the only way to release the energy absorbed by host. A potential reason is that the host lattice excitations are predominantly captured by defects which may decay radiatively or non-radiatively. Emission of the defects, in turn, is energetically too low to feed the 5d states of Pr$^{3+}$, as there is no spectral overlap between the defect emission and the 4f-5d absorption. Nevertheless, the interplay between host absorption and Pr$^{3+}$ and defect emission appears to be complex and requires further investigations. The time-integrated excitation spectrum of the intrinsic defect emission ($\lambda_{\text{em}} = 440$ nm) shows a broad complex band in the range of 170–240 nm that probably represents a formation (excitation) of defects. Increase of emission intensity upon excitation below 90 nm may be connected with multiplication of electronic excitations. For better understanding of relaxation processes occurred under host excitation further study on undoped Ca$_9$Lu(PO$_4$)$_7$ is required.

References