

VUV – excited luminescence of YAP:Pr

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Potential applications of wide bandgap materials activated with rare earth ions in opto- and microelectronics belong to such diverse areas as lighting and display phosphors, radiation detectors, light emitting diodes and solid state lasers. The Pr^{3+} ion with its fast and efficient UV $d-f$ emission and rich $f-f$ energy structure clearly is one of the prime subjects of such a research.. In this note we report results of studies of VUV excited luminescence on YAP crystals activated with Pr^{3+} . Excitation and luminescence spectra of Pr^{3+} $d-f$ and $f-f$ emissions and luminescence time profiles under pulsed synchrotron excitation (at Superlumi station of HasyLab) are presented and analysed in order to identify and characterize various host-to-ion energy transfer channels.

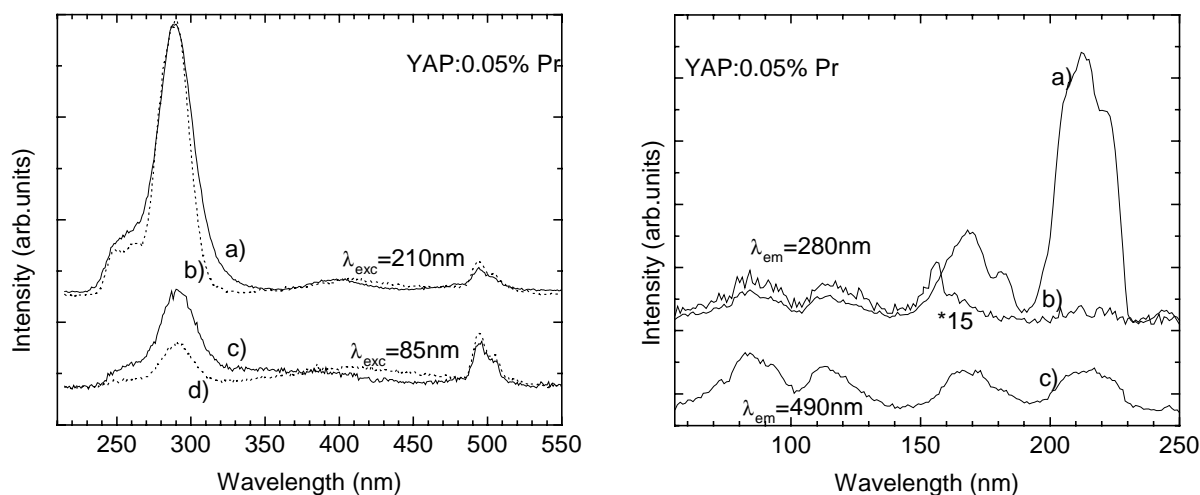


Figure 1: Luminescence spectra. under 210 nm (a - RT, b – 10 K) and 85 nm (c – RT, d – 8 K) excitations.

Figure 2: Excitation spectra of the $f-d$ emission at 280 nm. (a- “integrated“, b-“time gated“, see text) and $f-f$ emission at 490 nm (c) measured at 10 K

In Fig. 1 we present “time integrated” (the signal accumulated between the consecutive synchrotron pulses 192 ns apart) luminescence spectra under excitation into $f-d$ absorption bands of Pr^{3+} in YAP (a, b) and under VUV excitation (c, d). Spectra a) and c) were measured at 297 K while b) and d) at 8/10 K. With the sole exception of the 8 K spectrum the Pr^{3+} $d-f$ emission bands clearly dominate over the $f-f$ emission lines at about 490 nm ($^3\text{P}_j \rightarrow ^3\text{H}_j$ transitions [1]). The ratio of $d-f$ and $f-f$ emission intensities depends on the excitation wavelength, namely the VUV excitation is more efficiently promoting the Pr^{3+} $f-f$ emission at 490 nm. Also at higher temperature the relative contribution of the $d-f$ emission increases. The VUV excitation is also responsible for an additional wide emission band localized at the wavelengths between 300 and 500 nm (“host” emissions). The shape of this band varies with temperature suggesting that in fact it may well comprise two or more bands. Although the origin of these emissions is not clear it is quite likely to be due to radiative decay of an exciton trapped at some kind of a defect or impurity.

In Fig. 2 we present “integrated” (a) and “time-gated” (b and c, the signal accumulated in a 30 ns time gate set 150 ns behind the synchrotron pulse) excitation spectra of the Pr^{3+} emissions. The spectra are uncorrected and the “structure” in the VUV below 140 nm does not reflect any true physical processes but is due to spectral characteristics of the primary monochromator (the Al grating). The “integrated” excitation spectrum of the Pr^{3+} $d-f$ emission (a) is dominated by the two broad bands peaking at 185 and 214 nm which are typical

of the $f-d$ transitions of Pr^{3+} ($^3\text{H}_4 \rightarrow 4f5d$ transitions [2,3]). The “time gated” spectrum (b) reveals the prominent and well resolved so-called “host” peak at about 160 nm and a “structure” at VUV below 140 nm. These features have previously been associated with the occurrence of energy transfer mechanisms that enable the material to scintillate efficiently. The presence of such bands in “time gated” spectrum suggests the slower rate of the host-to ion energy transfer responsible for the slow components in the emission time profiles.

The $4f^2$ electron configuration of Pr^{3+} exhibits a rich energy level structure that supports numerous $f-f$ transitions. Interestingly, the Pr^{3+} 490 nm $f-f$ emission can be efficiently excited by wavelengths that belong to $f-d$ bands, a “host” peak and the VUV part same as in the case of the $d-f$ emission (c). The mere presence of $f-d$ bands proves that the $^3\text{P}_j$ level is fed by the energy transfer from the Pr^{3+} $4f5d$ levels.

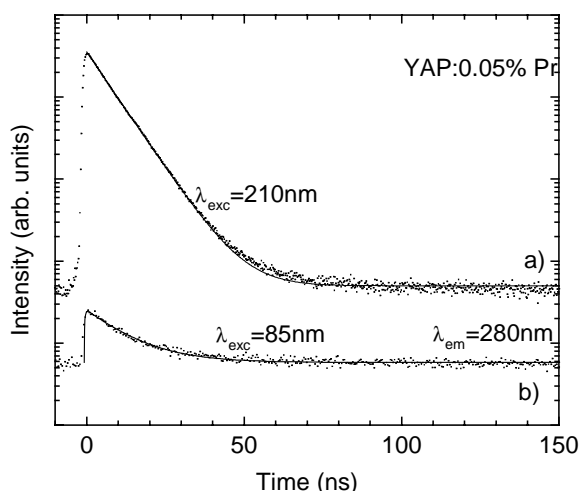


Figure 3: Emission time profiles:

a) 10 K, $\lambda_{\text{exc}} = 210$ nm, $\lambda_{\text{em}} = 280$ nm,
 $I(t) = 1.16\exp(-t/7.6) + 0.002$;
b) 10 K, $\lambda_{\text{exc}} = 85$ nm, $\lambda_{\text{em}} = 280$ nm,
 $I(t) = 0.02\exp(-t/12.4) - 0.02\exp(t/0.3) + 0.006$

Finally, in Fig. 3 we show the emission time profiles. Trace (a) represents the time profile of the Pr^{3+} $d-f$ emission at 10 K under direct excitation into one of the $f-d$ absorption bands. Thin solid line represents the exponential fit to experimental points yielding the decay time constant of ~ 7.6 ns (probably very close to the radiative lifetime). Time profiles of the $d-f$ emission under VUV excitation were measured at various temperatures in order to study the host-to-activator ion energy transfer. Decay time constants of

these profiles are longer reaching 10 to 12.5 ns. We also observe longer rise times and higher backgrounds indicative of much slower components. A representative profile is depicted by a trace (b). More experimental data and a detailed quantitative analyses of these results will be presented elsewhere.

The effect of conversion of a single γ or X-ray photon in a scintillator material is well reproduced by excitation of the material by a large number of VUV photons since both lead to a large number of free electrons and holes. In a number of Ce-activated modern scintillator materials it has been firmly established that the recombination of charge carriers via the Ce^{3+} ions provides the dominant mechanism of scintillation light production. In this note we demonstrated a number of arguments that also Pr activation in YAP leads to effects that are readily explained in a frame of the same model. These arguments include a high VUV sensitivity, a presence of the “host” peak in the excitation spectra, longer and temperature dependent decay and rise times, and higher background in time profiles. The charge carrier recombination via Pr^{3+} is more complex than in the case of Ce-activation because the higher lying levels that are due to both $4f5d$ and $4f^2$ configurations can actively participate in the process. We observe that the VUV-excitation leads not only to the Pr^{3+} $d-f$ emission but the excess Pr^{3+} $f-f$ emission is observed as well. This can only be understood by assuming that in addition to a nonradiative or radiative $4f5d \rightarrow 4f^2$ energy transfer that precedes the $f-f$ emission following the excitation into one of the $f-d$ absorption bands, there also must be a direct mechanism of an e-h pair recombination via $4f^2$ Pr^{3+} levels that feeds these levels.

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