Sharp line and broad band UV emissions from Pr-activated YAG

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Fast and efficient broad band UV emissions from wide bandgap materials activated by rare-earth ions open new possibilities in the field of tunable UV solid state laser materials and detectors of ionizing radiation. Of the two trivalent rare-earth ions that are considered as activators for such applications, Ce and Pr, the latter is clearly the less studied one. In 1999 at Superlumi station of Hasylab we started a program of studies on various materials activated with Pr. In this note we report initial results that we obtained for $Y_3Al_5O_{12}$:Pr (YAG:Pr).

The emission from any Pr-activated material is fully characterized by relative positions of the two levels; the $^1S_0$ level of the Pr^{3+} $4f^2$ configuration and the lowest level of the Pr^{3+} *4f5d* configuration [1]. The broad band UV *d-f* emission can only occur in those materials in which the $^1S_0$ level lies *above* the lowest *d*-level. On the contrary, no UV *d-f* emission is expected of materials in which the $^1S_0$ level lies *below* the lowest *d*-level. The only emission that is expected under VUV excitation involves transitions starting at $^1S_0$ and terminating at various levels of the $^1I_6$, $^1D_2$ and $^1G_4$ multiplets, as well as cascade downward transitions from these or other close lying multiplets such as ^3P_J.

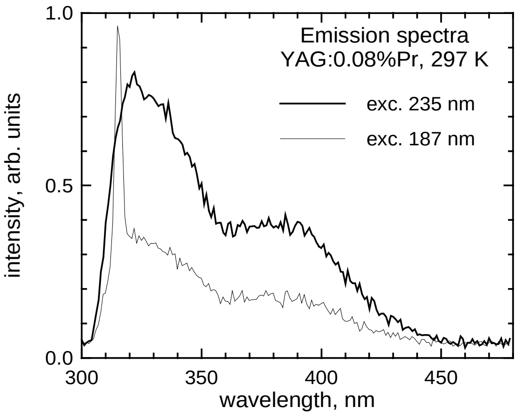

Figure 1: Uncorrected luminescence spectra (resolution 1.6 nm) of Pr-activated YAG at room temperature. The emission spectra were measured with the excitation wavelength set at 187 nm (thin solid line) and 235 nm (thick solid line).

It seems fairly well established that oxide host materials, with their strong crystal field and, consequently, the lowest *d*-level well below the $^1S_0$ level, belong to the first class of Pr-activated materials [1,2]. This is particularly true of YAG in which *d*-levels of many of the rare-earth ions including Pr occur at exceptionally low energies [2]. Accordingly we are not aware of a single paper reporting any sharp line emission in YAG:Pr that might originate at the $^1S_0$ level of the Pr^{3+} ion. On the contrary, there are reports (see e.g. [3]) that despite conscious efforts no $^1S_0$ related transitions were observed for energies up to 50,000 cm^{-1}.

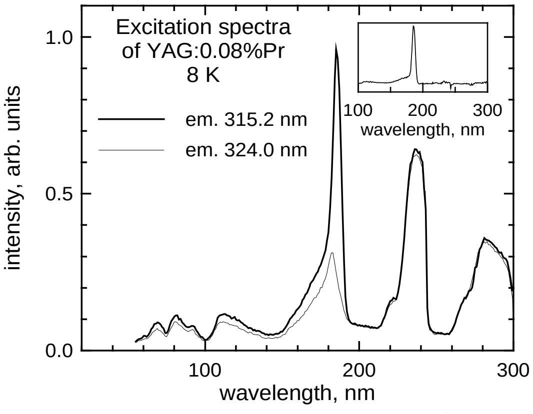

Figure 2: Uncorrected excitation spectra (resolution 1 nm) of sharp line (thick solid line) and broad band (thin solid line) emissions of YAG:Pr. The emission wavelengths were set at 315.2 and 324 nm, respectively. The insert shows the difference of the two curves.

Nevertheless, as shown in Fig. 1, we observe that under VUV excitation of 187 nm or less, the emission spectrum of YAG:Pr, in addition to expected and well known *d-f* bands peaking at about 325 and 385 nm, clearly shows a relatively sharp line at about 315.2 nm. This line disappears for excitation wavelengths above 190 nm.

In Fig. 2 we show excitation spectra of emissions presented in Fig. 1 for two emission wavelengths of 315.2 nm (at the peak of the sharp line emission) and at 324 nm (at the peak of the stronger *d-f* emission band). The spectra have not been corrected and, therefore, the structure in the VUV reflects spectral variations of the synchrotron flux introduced by the grating of the primary monochromator. The spectra overlap at the longer wavelength range corresponding to Pr^{3+} *f-d* absorption bands (at 237 and 282 nm) but differ strongly at the shorter wavelength range below 190 nm. Since the contribution of the *d-f* emission at 315.2 and 324 nm is more or less the same, the difference of the two excitation spectra, shown in the insert, presumably represents the excitation spectrum of the sharp line emission at 315.2 nm. The spectrum shows a sharp peak at 186 nm.

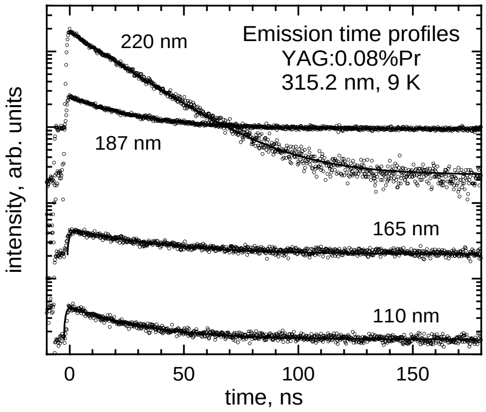

Figure 3: Emission time profiles of YAG:0.08%Pr under VUV and UV excitations by synchrotron pulses at 9 K. The consecutive curves have been shifted vertically. Experimental points are shown by open circles. Solid lines depict one- or two-exponential fits with an additional fitting constant to correct for the background and longer decay time components. The excitation wavelengths are indicated in the figure.

Finally in Fig. 3 we show the emission time profiles obtained under various wavelength excitations by synchrotron pulses. Note that under the 220 nm excitation into one of the Pr^{3+} *f-d* absorption bands the profile shows a single exponential decay of 21.9 ns, the radiative lifetime of the excited *d*-level [2]. The fast *d*-level lifetime component is also present in the VUV excited profiles but clearly these profiles are dominated by a much slower component that is responsible for a high background. We conclude that the decay time of the sharp line emission at 315.2 nm must be much longer than the radiative lifetime of Pr^{3+} *d*-level. We have also measured time profiles under UV and VUV excitations for various temperatures. In particular the room temperature value of the *d-f* emission decay time measured by us under 220 nm excitation, at about 7 ns, differs from the values reported so far (at 14.6 ns) [4]. The VUV excitations, however, produce profiles that have longer decay times of about 12 ns. These results will be fully reported later.

There are two interpretations of the origin of the relatively slow, sharp line emission at 315.2 nm that we would like to consider. We may assume that this emission is due to some inadvertent impurity; the most likely candidate being the Gd^{3+} ion with its well known sharp line emission at around 310 nm. The final state, reached by the 186 nm excitation could be due to any of the high lying ^6F and/or ^6G terms. Following relaxation to the lowest level of the ^6P term, there would be a luminescence transition terminating at the ground state of the Gd^{3+} ion, $^8S_{7/2}$, at about 315 nm. The weak point of this interpretation is that at least some of the levels due to terms such as ^6D and/or ^6I should be detectable in the excitation spectrum of the 315.2 nm emission. Clearly, there is no indication of such levels in the spectra shown in Fig. 2.

The second, we believe more likely interpretation of the 315.2 nm sharp line luminescence, is that it is due to a transition between the $^1S_0$ and $^1I_6$ levels of the Pr ion. This would place the $^1S_0$ level at 53,800 cm^{-1}, much higher that the experimental values reported so far for Pr in fluorides (at 46,500 cm^{-1}, Ref. [1]). Nevertheless we note that the $^1S_0$ energy calculated by Hargreaves for Pr in CaF_2 is 54,177 cm^{-1} [5]. If we assume that the $^1S_0$ level is indeed positioned at 53,800 cm^{-1} than, first of all, there is an 11,600 cm^{-1} energy gap to the next-lower *d*-level at 237 nm (42,200 cm^{-1}). This is enough to slow down a non-radiative depopulation of the $^1S_0$ level. Next we observe that the final state of the 315.2 nm emission transition ($^1I_6$) would be at 22,000 cm^{-1}, reasonably close to the value of 21,470 cm^{-1} established experimentally by Hargreaves [5].

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