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Radio- and VUV – excited luminescence of YAP:Ce, YAP:Pr
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ABSTRACT

In this Communication we report initial results of studies on X-ray and VUV excited luminescence of YAP and YAG crystals activated with Pr3+ and Ce3+. Excitation and luminescence spectra of Pr3+ and Ce3+ d-f and Pr3+ f-f emissions and luminescence time profiles under pulsed synchrotron excitation are presented and analysed in order to identify and characterize various host-to-ion energy transfer channels. The results support the notion that direct and trap mediated capture and recombination of holes and electrons via Pr3+ or Ce3+ ions provide the dominant mechanism of radioluminescence production in both YAP and YAG crystals.

Keywords: YAG:Pr, YAP:Pr, YAP :Ce, radioluminescence, energy transfer, recombination, VUV spectroscopy

1. INTRODUCTION

Potential applications in opto- and microelectronics of systems consisting of wide bandgap materials activated with rare earth (RE) ions belong to such diverse areas as lighting and display phosphors, radiation detectors, light emitting diodes and solid state lasers. Some of these systems show fast and efficient UV d-f emission and/or a rich 4f energy structure that sustains various co-operative interactions leading to efficient up- and down-conversion. In particular two ions, Pr3+ and Ce3+, in a number of solid state hosts, became prime objects of research in the field of ionizing radiation detector and solid state laser materials.

Two host materials, YAG and YAP, have a long history of successful applications in the field of solid state laser materials (YAG:Nd12 and YAP:Nd13). Laser properties of Pr3+ activated YAG and YAP crystals have also been studied and laser action was achieved in both of these materials. Scintillation properties of YAG and YAP activated with Ce3+ and Pr3+ have been studied for some time. In particular YAP:Ce is a well established commercial scintillator material that has found many applications7 such as a small animal PET camera, a prototype gamma camera based on a position sensitive photomultiplier tube (high resolution single photon emission computed tomography or HIRESPECT,9 dosimeters, scintimammography cameras,10 and pulse shape discrimination for Astro-E Hard X-ray Detector. Nevertheless the peculiar scintillation properties of YAP:Ce, such as the longer than radiative scintillation decay time constant and large variations of the scintillation light yield with temperature, have only recently been explained in the frame of the model involving charge carrier capture and recombination mediated by traps.11

The synchrotron radiation has been extensively used in research aimed at scintillation mechanisms in RE-activated solid state materials. In particular energy transfer processes that occur in such materials can be conveniently studied by selecting a proper wavelength of the exciting synchrotron radiation. In this Communication we report results of studies on X-ray and synchrotron radiation excited luminescence of YAG and YAP crystals activated with Pr3+ and Ce3+.

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2. MATERIALS AND EXPERIMENTS

All samples used in this study were cut from the boules grown by the Czochralski method at Institute of Electronic Materials Technology in Warsaw, Poland. X-ray excited luminescence spectra were measured at Institute of Physics of N. Copernicus University in Torun, Poland. The X-ray tube with the copper anode operated at 35kV was used as an excitation source. The luminescence spectra, luminescence excitation spectra and emission time profiles under pulsed synchrotron excitation in the wavelength range of 50-300 nm were measured using experimental facilities of Superlumi station at Hasylab in Hamburg, Germany.1

3. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1 we present radioluminescence spectra of YAP:Ce (a), YAG:Pr (b), and YAP:Pr (c) measured at room temperature. The spectra are dominated by the well known broad bands at 365nm (a), 325nm, 380nm (b), and 240nm and 280nm (c) due to d-f transitions at Ce³⁺ (a) and Pr³⁺ (b, c) ions. As observed before the positions of d-f emission bands depend not only on the activating ion but also on the host material. In particular a much stronger crystal field in YAG is responsible for a red shift of the Pr³⁺-emission in this material. An additional unexpected feature of the YAG:Pr³⁺ radioluminescence spectrum is an intense sharp line peaking at around 315nm. Although this line has not been observed before it is easy to miss in the low resolution measurement. The origin of this line is not yet clear; the two possible interpretations that have been advanced include a transition between the ¹S₀ and ¹P₀ levels of the Pr³⁺ ion and an uncontrolled impurity emission (the most likely candidate being the Gd³⁺ ion).14 Other sharper longer wavelength lines (at about 490 nm, traces b and c in Fig. 1) are due to f-f transitions originating at the ³P₁ and terminating at the ³H₁ levels of the Pr³⁺ ion.15 In addition to d-f emission bands there are also much weaker bands at about 260-300nm. These bands represent so-called “host” emissions that are prominent in undoped YAG and YAP crystals16 but are strongly reduced by Ce³⁺ and Pr³⁺ doping. Note that although the “host”-to-Pr³⁺ centers radiative and nonradiative energy transfers are unlikely in YAP:Pr (Pr³⁺ absorption bands and “host” emission bands do not overlap) the radioluminescence intensity is comparable in YAP:Pr and YAP:Ce. This is consistent with recombination as the dominant mechanism of scintillation and radioluminescence light production as proposed in the case of Ce doped materials.11,16,17

Fig. 1. Radioluminescence spectra of: a) YAP:Ce (0.05%), b) YAG:Pr (0.08%) and c) YAP:Pr (0.05%). The temperature was 300 K (RT). The origin of the sharp emission line at about 315 nm in YAG:Pr is not clear (see text).

Fig. 2. Luminescence excitation spectra of YAP :Ce (a), YAP:Pr (b-b') YAG:Pr (c-c'). The emission wavelengths and temperatures: a) 369 nm, RT; b) 280 nm, RT; b') 490 nm, RT; b'') 490 nm, 10 K; c) 324 nm, RT; c') 490 nm, RT; c'') 490 nm, 10 K. Note the much higher VUV sensitivity of the Ce-doped YAP.
While radioluminescence spectra usually reflect the dominant mode of radiative decay of relevant electronic excitations of the material, photoluminescence spectra oftentimes show a strong dependence upon the wavelength of the excitation light and temperature, indicating the existence of thermally activated and competing energy transfer channels to various emitting centers. In Fig. 2 we present Ce$^{3+}$ d-f and Pr$^{3+}$ d-f and f-f emission excitation spectra measured at room and cryogenic temperatures in YAP and YAG. The spectra are not corrected and, in particular, the "structure" in the VUV below 140 nm is due to spectral characteristics of the set-up and does not reflect any true physical processes.

The bands that dominate the spectra are typical of f-d transitions of Ce$^{3+}$ and Pr$^{3+}$ ions. So, the trace a reveals the two well known f-d bands of Ce$^{3+}$ at 240 and 310 nm. The traces b and c (excitation spectra of Pr$^{3+}$ d-f emission in YAP and YAG) are dominated by two broad bands peaking at 185 and 214 nm in YAP, and at 238 and 290 nm in YAG. These bands correspond to the $^3$IH$_4$--$^4$f$^5$d transitions of Pr$^{3+}$. At vacuum ultraviolet (VUV) wavelengths below 200 nm the spectra reveal also the so-called "host" peaks at about 160 nm (YAP) and 185 nm (YAG) and a "structure" at VUV below 140 nm. The "host" peaks and the high sensitivity at VUV wavelengths have previously been associated with the occurrence of energy transfer mechanisms that enable the material to scintillate efficiently. Excitation spectra of Ce$^{3+}$ and Pr$^{3+}$ d-f emissions had been also measured at 10 K but since there were no important differences the spectra are not presented here.

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The 4f$^2$ electron configuration of Pr$^{3+}$ exhibits a rich energy level structure that supports numerous f-f transitions. Some of these transitions in the visible have been extensively studied in the past using resonance or shorter wavelength visible excitation. As shown in Fig. 2 a far UV and VUV wavelength excitation can also be used to excite a visible 490 nm f-f emission. Traces b' and c' represent spectra measured at room temperature for YAP and YAG crystals, respectively. Traces b'' and c'' represent the same spectra measured at 10 K.

Interestingly, for both YAP and YAG, the Pr$^{3+}$ 490 nm f-f emission can be efficiently excited by wavelengths that belong to f-d bands, "host" peaks and VUV tail as in the case of the d-f emission, although their relative contributions vary with temperature. The mere presence of f-d bands proves that the $^5$P$_1$ level is fed by the energy transfer from the Pr$^{3+}$ 4f$^5$d levels. Nevertheless relatively higher contributions of the "host" peak and VUV tail clearly show that the $^5$P$_1$ levels are also populated by an additional energy transfer from the host material with no mediation of 4f$^5$d levels. We note also that there is a distinct difference between spectra taken at different temperatures. While at room temperature the spectrum is...
dominated by intraionic $f-d$ transitions, the "host" peak and VUV tail dominate the low temperature spectrum. The relative contributions of the "direct" (intraionic) and "host-related" energy transfer channels vary with temperature.

In Figs. 3 and 4 we present luminescence spectra under UV and VUV excitations. The spectra of YAP:Ce, YAG:Pr and YAP:Pr in Fig. 3 were obtained under the UV excitation into $f-d$ absorption bands at room and cryogenic temperatures. We note that the spectra are dominated by the strong broad $d-f$ bands as in the case of X-ray excitation (Fig. 1) although there is, obviously, no indication of "host" emissions. In addition to Pr$^{3+}$ $d-f$ emission bands there also are strong (or weak) lines representing $f-f$ emission at about 490 nm in agreement with the excitation spectra presented in Fig. 2. In particular there is almost no $f-f$ emission at 490 nm at 10 K in YAP:Pr (see the trace c') while in YAP:Pr the ratio of $d-f$ and $f-f$ emissions does not vary with temperature (compare traces b and b'). The origin of the weak broad band at around 400 nm (traces b and b') will be discussed later.

In Fig. 4 we present luminescence spectra under the 85 nm VUV excitation measured at room and cryogenic (8 K) temperatures. With the sole exception of the 8 K spectrum of YAP:Pr (trace b) the spectra are dominated by $d-f$ emission bands. The 8 K and 300 K spectra of YAP:Ce$^{3+}$ are fairly typical showing the characteristic spin-orbit split Ce$^{3+}$ doublet ($^2F_{5/2}$, $^2F_{7/2}$) (traces a and a'). In the case of Pr$^{3+}$ doped YAG and YAP the trends observed under $f-d$ excitation are reversed; the ratio of $d-f$ and $f-f$ emissions is almost independent of temperature in YAG:Pr while in YAP:Pr at low temperature the contribution of $f-f$ emission to the spectrum is unusually large (trace b'). To summarize we note that VUV excitation promotes Pr$^{3+}$ $f-f$ emission at 490 nm while at higher temperature the relative contribution of $d-f$ emissions increases. The VUV excitation also promotes an additional wide emission band localized at the wavelengths between 300 and 500 nm ("host" emissions). The shape and even the peak wavelength of this band varies with temperature suggesting that in fact it may well be not a single band but a combination of two or more bands. The origin of these emissions is not firmly established but it is quite likely to be due to radiative decay of an exciton trapped on some kind of a defect or impurity. In the case of YAG:Pr$^{3+}$ a "host" emission is hidden under much stronger and overlapping Pr$^{3+}$ $d-f$ emission bands.
Finally, in Fig. 5 we show the emission time profiles obtained under various wavelength VUV and UV excitations. Traces (a, d, g) represent pulse shapes of the Ce$^{3+}$ and Pr$^{3+}$ d-f emissions in YAP:Ce, YAP:Pr, and YAG:Pr, respectively, measured at 10K under direct excitation into f-d absorption bands. Thin solid lines show single-exponential fits to experimental points that yielded the following decay time constants: ~23 ns (YAG:Pr$^{3+}$), ~7.6 ns (YAP:Pr$^{3+}$), and ~17 ns (YAP:Ce$^{3+}$). These decay time constants are probably very close to the corresponding radiative lifetimes. Note that the Pr$^{3+}$ radiative lifetime is much shorter in YAP than in YAG, and that the Ce$^{3+}$ radiative lifetime in YAP falls between the two lifetimes of Pr$^{3+}$ (in YAP and YAG). This is consistent with the well known dependence of the Einstein coefficient A on the emission wavelength.\(^{20}\)

The time profiles of the Ce$^{3+}$ and Pr$^{3+}$ d-f emissions in YAP:Ce, YAP:Pr, and YAG:Pr were also measured at room temperature but, since they are less likely to truly reflect the radiative lifetimes we have chosen not to present them here. The decays were, nevertheless, single-exponential, although the decay time constants assumed different values. In YAP these values increased to 8.3 ns (Pr$^{3+}$) and 18.8 ns (Ce$^{3+}$); the most likely reason of this effect being the radiation trapping caused by the increased overlap between emission and absorption bands at elevated temperatures. Similar behaviour was found for many materials.\(^{21}\)

Interestingly we observe a different behaviour in YAG:Pr$^{3+}$, where a decay time constant decreases with temperature reaching 14.5 ns at 300K. A likely reason is increased thermal quenching caused by a relatively low d-f energy gap (~10,000 cm$^{-1}$).\(^{18}\) Another explanation involves thermally activated autoionization of an electron occupying the highly lying 4f$^5$5d levels of Pr$^{3+}$ ions that overlap the conduction band of YAG.\(^{22}\) Autoionized electrons are then unable to return to the 5d levels and the only deexcitation route for the exciton bound to the Pr$^{3+}$ ion is radiative or nonradiative energy transfer to the f-f energy levels. As a consequence there is an increased f-f emission at higher temperatures, as observed (see Fig. 3, traces c and c').

In order to study the host-to-activator ion energy transfer the time profiles of d-f emission under the VUV excitation at various temperatures were measured. Traces c and b represent time profiles of the Ce$^{3+}$ d-f emission measured under the 85 nm excitation at 7 and 300 K, respectively. These profiles display longer decay times (at about 29 ns) and higher backgrounds (the background of the 7 K profile being about 7 times higher). Interestingly both profiles show also rise times of about 1 and 3 ns at 7 and 300 K, respectively. Temperature dependent decay and rise times in YAP:Ce and LuAP:Ce have been studied before and interpreted in the frame of a model including recombination center (Ce$^{3+}$) and electron traps.\(^{23}\)

We note the similar behaviour for Pr$^{3+}$ doped YAP and YAG. In both materials the decay time constants are longer for VUV excitation and at higher temperatures (10 to 12.5 ns increase between 10 and 300 K for YAP and 23 to 32 ns increase for YAG). We also observe longer rise times and higher backgrounds. To give an example we present traces e and h for YAP and YAG, respectively. More experimental data and a detailed quantitative analyses of these results will be presented elsewhere.

4. CONCLUSIONS

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. It has been firmly well established that in a number of Ce-activated modern scintillator materials it is the recombination of charge carriers via the Ce$^{3+}$ ions that provides the dominant mechanism of scintillation light production. In this Communication we find that also Pr activation in YAG and YAP leads to effects that are readily explained in the frame of the same model. These effects include high VUV sensitivity, presence of the “host” peaks in the excitation spectra, longer and temperature dependent decay and rise times, and higher background in time profiles. The process of charge carrier recombination via Pr$^{3+}$ is more complex than in the case of Ce-activation because higher lying levels that are due both to 4f$^5$5d and 4f$^6$ configurations are active. Although VUV-excitation of Pr-activated YAG and YAP leads to emission dominated by the Pr$^{3+}$ d-f emission the Pr$^{3+}$ f-f emission is also observed. We find that in addition to nonradiative or radiative 4f$^5$5d$\rightarrow$4f$^6$ energy transfer also a direct recombination of e-h pairs via 4f$^6$ Pr$^{3+}$ levels provides an efficient mechanism of light production in these materials.

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