*Nonexponential decay of Ce-emission in $Rb_3Lu(PO_4)_2$:Ce and $Cs_3Lu(PO_4)_2$:Ce

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Ce^{3+} ion is one of the most effective activators. It has been studied in a number of solid state hosts and has a long history of successful applications - mostly in the field of scintillation detectors. Cerium-activated, wide bandgap materials are a subject of interest primarily due to their relatively fast, short-wavelength emission that originates in parity-allowed transitions from the lowest level of the excited *5d* configuration of the Ce^{3+} ions down to the $^2F_{5/2}$ and $^2F_{7/2}$ terms of the *4f* configuration of these ions. Some initial results on the optical spectroscopy of $Rb_3Lu(PO_4)_2$:1%Ce crystals have been already published [1]. In the excitation spectrum of the Ce^{3+} *d-f* emission the *f-d* excitation bands (in the 220 - 350 nm wavelength range), the "host" peak (at about 175 nm), and intensive VUV band (in 50 –160 nm range) have been identified. At room temperature, all of these excitations lead to a Ce emission identical to that measured under x-ray excitation. At T = 10 K, the shape of the Ce emission is somewhat different – the spin-orbit splitting of the ground state of these ions becomes perceptible, and the spectrum is slightly shifted. It was found that, in fact, the RT spectra are distorted due to "radiation trapping" – the effect in which one ion emits a photon that can be reabsorbed by another similar, unexcited ion before the photon can leave the material.

In this report we present results of luminescence decay measurements for $Cs_3Lu(PO_4)_2$:1%Ce and $Rb_3Lu(PO_4)_2$ activated with 1 and 4 % Ce. Figure 1 shows the RT and low-temperature pulse shapes of the Ce^{3+} d-f emission (410nm) excited by 330 nm synchrotron radiation. This wavelength was chosen to produce a direct *f-d* excitation of the activator ions. Although directly excited Ce-emission decay is usually single exponential, this is not the case for the materials investigated. All of the observed pulses are non-exponential. They can, however, be reasonably well fit with two-exponentially decaying curves. A similar fitting procedure was also needed for the scintillation pulses (not presented here). The dominant emission pulse components have decay time constants in the range of 30 – 40 ns, more or less similar to the corresponding scintillation components. In fact, this is the initial part of each pulse that is non exponential and can be approximated by a combination of a dominant component and a much faster component of about 5 – 10 ns. Such a decay pattern suggests that part of Ce ions lose their excitation energy by a transfer to some type of quenching centers and that modest migration of energy among Ce ions takes place. This represents the intermediate state between the following [2] two limiting cases:

A) No migration of energy among donors (Ce ions) and the presence of energy transfer to acceptors (quenching centers). Because of the random distribution of acceptors, some donors will find acceptors in very close proximity. These donors will decay rapidly by energy transfer causing an initial fast decay. As time progresses, only the more distantly separated donor-acceptor pairs remain excited, and the decay rate decreases with increasing time. It, however, never reaches the "isolated" value of $1/\tau_R$ (where τ_R is the radiative life-time of the donors). The decay of donors is non-exponential at all times.

B) Very fast migration of energy among donors in comparison to the donor-acceptor transfer rate. In this case, the excitation migrates between so many donor ions that it continuously senses the average environment of acceptors. The decay of donors is exponential with a decay rate faster than $1/\tau_R$. This is usually the typical mechanism of concentration quenching.

In the intermediate case between A) and B) the decay of donors is non-exponential at the beginning stage and finally becomes exponential within a few τ_R periods. When the migration rate increases, the radiative decay of the donors becomes exponential at earlier times. Additionally, both the migration and donor-acceptor energy transfer rates depend on temperature, and usually an increase with increasing temperature is observed.

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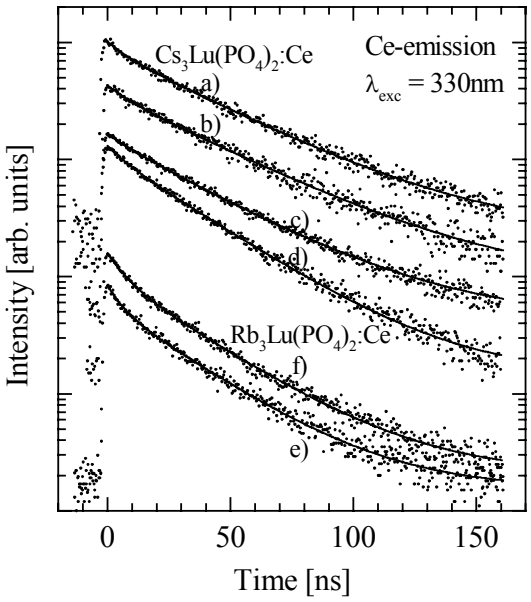

Figure 1.

Pulse shapes of *f-d* (330 nm) excited Ce-emission of: $Cs_3Lu(PO_4)_2$:Ce (a, b) and $Rb_3Lu(PO_4)_2$:Ce (c - f);

a) 1%Ce, RT, $I(t) = 834\cdot\exp(-t/40.7) + 156\cdot\exp(-t/6.7) + 23$
b) 1%Ce, 10K $I(t) = 356\cdot\exp(-t/42.1) + 64\cdot\exp(-t/8.8) + 9$
c) 1%Ce, RT, $I(t) = 1444\cdot\exp(-t/37.9) + 166\cdot\exp(-t/9.4) + 44$
d) 1%Ce, 10K, $I(t) = 1097\cdot\exp(-t/31.1) + 200\cdot\exp(-t/6.6) + 14$
e) 4%Ce, RT, $I(t) = 552\cdot\exp(-t/30.4) + 273\cdot\exp(-t/5.4) + 15$
f) 4%Ce, 10K, $I(t) = 763\cdot\exp(-t/.31.7) + 437\cdot\exp(-t/7.0) + 16$

For the $Cs_3Lu(PO_4)_2$:1%Ce sample both decay time constants are somewhat longer at low temperature (b) than at RT (a). The shortening of the emission pulse at RT can be explained either by thermal quenching of the Ce-luminescence or by an increase of Ce-Ce and/or Ce-quenching center energy transfer rates. While the first hypothesis has a limited chance of being true (since the Ce-emission thermal quenching for most materials occurs at much higher temperatures) the second is quite probable. It is also worth noting that the scintillation pulse, although it maintains a non-exponential shape, it is considerably longer. This is most probably due to a delay of lattice to Ce-ion energy transfer, caused by charge trap mediation in the recombination of electron-hole pairs – an effect quite widespread among recombination-based scintillators.

In contrast, for the $Rb_3Lu(PO_4)_2$:1%Ce sample both decay time constants substantially increase with increasing temperature and the RT dominant component is (within the range of experimental and fitting errors) characterized by the same decay time constant as it is in the case of scintillation. The first feature suggests that for this material, due to an increasing overlap at higher temperatures of the Ce absorption and emission bands, the radiation trapping effect dominates over an energy-transfer-based quenching. The similarity of the scintillation and directly excited Ce-emission pulses suggests the presence of a rapid lattice-activator energy transfer – an extremely desirable feature for all scintillators.

At higher activator levels, an energy-transfer-induced quenching becomes more pronounced. While at low temperature, for the $Rb_3Lu(PO_4)_2$:4%Ce sample, the emission pulse (f) is nearly identical to that observed for the 1 % Ce-doped material (d), at room temperature (e) a slight decrease of both time constants is observed instead of the increase recorded for the 1 % Ce-doped sample (c). A presence of rapid lattice-activator energy transfer for the 4 % Ce-doped sample is also confirmed by the proximity of the scintillation and *f-d* excited Ce-emission pulses.

Due to numerous interesting processes such as the rapid host-Ce ions energy transfer, Ce-Ce and Ce-quenching center energy migration, as well as radiation trapping, these materials certainly deserve more attention from the fundamental research point of view. Accordingly, future studies will involve a wider range of activation levels and focus on such issues as quenching center identification and the detailed investigation of energy transfer processes.

References

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