VUV-excited emission time profiles of $YAlO_3$:Ce, Co

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Although cerium activated yttrium aluminum perovskite (YAP:Ce) is a widely used commercial scintillator material [1] it has only recently been noted that its notorious underperformance (25-38 ns scintillation decay time at room temperature instead of 17 ns) is caused by uncontrolled traps that accompany Ce-radiative recombination centers [2]. Assuming that most of the holes are captured by Ce^{3+} ions immediately after excitation the fraction of electrons that goes to traps and not to Ce^{4+} ions is determined by trap concentrations and electron capture cross sections of Ce^{4+} ions and the traps. Then the only way to improve the material is to reduce trap concentrations. If, on the contrary, one assumes that effective hole and electron capture rates are comparable this fraction could be reduced by deliberately introducing a new shallow trap that would have a large cross section for electrons and would compete effectively with deeper traps. Obviously it would also be necessary to have the shallow trap lifetime short enough not to interfere with the scintillation time profile.

Led by these ideas we started a joint program to study an effect of intentional codopants in Ce-activated YAP. The Co ion is the first case that we studied in this context. The results of spectroscopic studies and, in particular, a new UV/VIS emission from the Co^{2+} ion in YAP:Ce, Co have been reported in [3]. In this note we would like to concentrate on VUV-excited Ce-emission time profiles of YAP:Ce, Co.

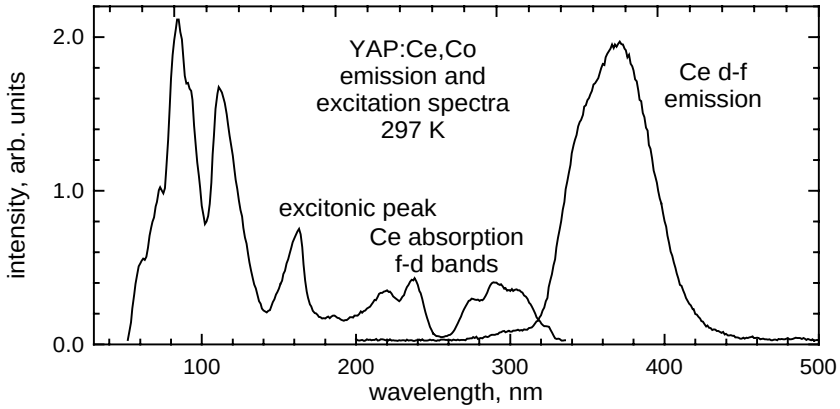

Figure 1: Uncorrected emission (resolution 5.8 nm) and excitation (resolution 0.31 nm) spectra of YAP:Ce, Co. The emission spectrum was measured with the excitation wavelength set at 163 nm (excitonic peak). The excitation spectrum was measured with the emission wavelength set at 369 nm (maximum of Ce-emission). For details see text and [3]. Temperature was 297 K

As shown in Fig. 1 the emission and excitation spectra of YAP:Ce, Co do not reveal any gross changes that could be attributed to Co. The emission spectrum, measured under the 163 nm excitation (excitonic peak) consists of the well known broad emission band of Ce^{3+} peaking at about 369 nm. The excitation spectrum shown in the figure was measured with the emission wavelength set at 369 nm The structure between 200 and 330 nm in this-spectrum comprises the five Ce^{3+} *f-d* bands split by the low symmetry crystal field component. The structure in the VUV below 140 nm reflects the spectral characteristics of the primary monochromator (Al grating) and does not correspond to any real physical processes. Nevertheless the high signal at these wavelengths is indicative of strong sensitivity to VUV excitation. Also, since the VUV photons at these wavelengths provide over the bandgap excitation of the host material, the Ce ions must be efficient radiative recombination centers.

To study traps in YAP:Ce, Co we have measured a number of time profiles of Ce-emission under VUV and *f-d* excitations at various temperatures. In Fig. 2 we show two representative profiles. The dashed and solid

line profiles were obtained under *f-d* (238 nm) and VUV (84 nm) excitations, respectively. The *f-d* excited profile shows no rise time and a decay time constant of 18.8 ns (within experimental error equal to the radiative lifetime of the excited Ce^{3+}) while the VUV-excited profile shows a rise time (3.1 ns) and a longer decay time constant (at 30.3 ns) that are indicative of traps [2].

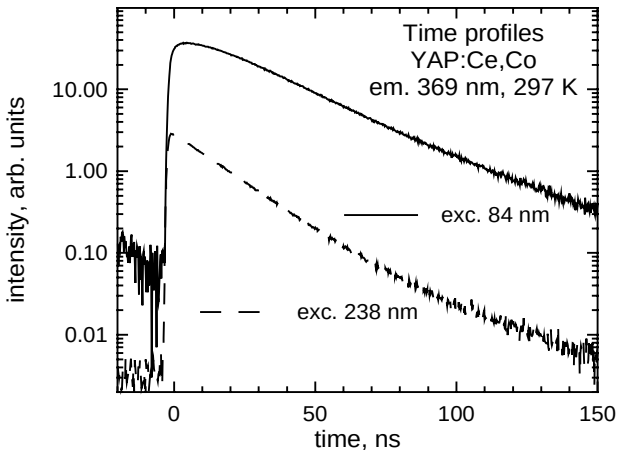

Figure 2: Emission time profiles of YAP:Ce, Co under 238 and 84 nm excitations. The emission monochromator was set to 369 nm, temperature was 297 K.

A simple one-trap model predicts [2] that a trap can modify a rising or a decaying part of the emission time profile introducing a characteristic time τ (trap lifetime),

$$\tau = (s \cdot \exp(-E/kT))^{-1}, \qquad (1)$$

where E is the trap depth, s the frequency factor, and k the Boltzman constant. This formula can be used to extract trap parameters by plotting the decay and rise time constants found from the fits to profiles measured at different temperatures on the Arrhenius diagram and by using the appropriate straight line fits, as shown in Fig. 3.

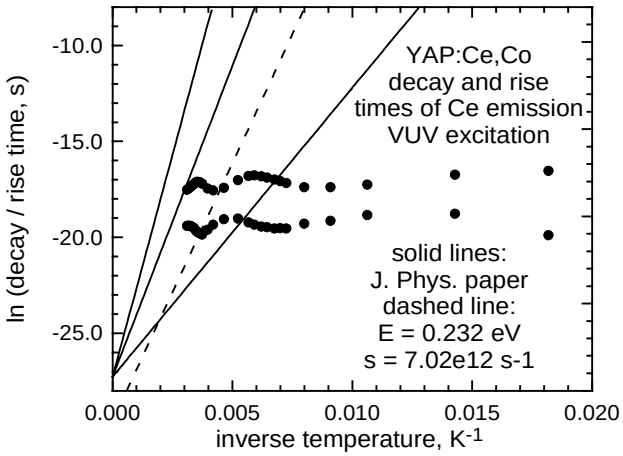

Figure 3: Decay and rise time constants agains the inverse temperature. Points on the diagram were obtained from the fits to measured Ce-emission profiles (84 nm excitation). Solid lines were plotted using trap parameters obtained earlier [2]. The dashed line represents a straight line fit to selected points.

The solid lines were calculated from trap parameters obtaine from other experiments (thermoluminescence, scintillation light against temperature) and on the other YAP sample (Union Carbide) [2]. Clearly the results obtained from emission time profiles suggest that the shallowest trap parameters have changed (from 0.13 eV, $7 \cdot 10^{11} s^{-1}$, Union Carbide, to 0.232 eV, $7 \cdot 10^{12} s^{-1}$ dashed line, this work). We note, however, that earlier Hasylab experiments on the same Union Carbide sample failed to provide any evaluation of the shallowest trap parameters (the possible explanation could be the much higher Ce-concentration, 0.3% against 0.05%) [4]. Therefore, we are reluctant to claim that by Co-doping we have succeded in introducing an intentional electron trap. We note also that, as presented in [3], since Co assumes a role of a radiative recombination center (stable or quasistable 2+ and 3+ charge states), it is not very likely to perform as the shallow electron trap. Obviously more studies are needed to clarify the situation.

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