VUV studies of host and Ce^{3+} emissions in $YAlO_3$

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Cerium activated yttrium aluminum perovskite (YAP:Ce) is a well known commercial scintillator material [1]. Although it has been established that the dominant mechanism of scintillation light production in YAP:Ce is due to radiative recombination of charge carriers via Ce^{3+} ion [2] there are other competing mechanisms involving excitons, traps, and uncontrolled defects producing various so-called "host" emissions that still remain controvercial and unclear.

In this report we present new results of VUV studies on YAP performed at Superlumi station of Hasylab at DESY. We will demonstrate that spectroscopic studies involving VUV synchrotron light can be used to study various processes and channels of energy transfer from the host to activator ions in scintillator materials.

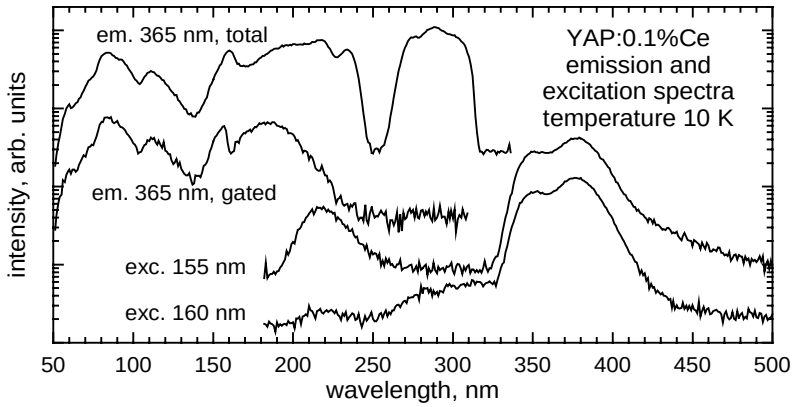

Figure 1: Uncorrected emission (resolution 4.32 nm) and excitation (resolution 0.32 nm) spectra of YAP:0.01%Ce. The spectra were shifted to aid presentation. The emission spectra were measured with the excitation wavelength set at 155 nm and 160 nm. The integrated ("total") and time resolved ("gated") excitation spectra were measured with the emission wavelength set at 365 nm (maximum of Ce-emission). For details see text. Temperature was 10 K

In Fig. 1 we present "total" and "gated" excitation spectra of the well known Ce^{3+} emission also shown in the same figure. The “total” spectrum was measured with the signal accumulated between the consecutive synchrotron pulses (192 ns) while the “gated” spectrum was measured within a 40 ns time window triggered by a synchrotron pulse with 150 ns delay. We note that the "total" spectrum shows a structure between 200 and 330 nm corresponding to Ce^{3+} *f-d* bands split by the low symmetry crystal field component. Interestingly the *f-d* bands are missing in the "gated" spectrum indicating that all the processes of energy transfer triggered by excitation below 200 nm and represented by a structured band between 50 and 140 nm, an "excitonic" peak at about 160 nm and a band at 180 nm, are relatively slow.

In particular the band peaking at 180 nm visible in the "total" spectrum and clearly resolved in the "gated" spectrum for the first time, is likely to represent the transition to the localized level overlapping continuum of conduction band states (e.g. *4f-6s* transition at Ce^{3+}). This transition, followed by autoionization, leads to slow recombination involving traps (see the report by Szupryczynski et al. in the same volume [3]).

The structure in the band below 140 nm (exactly the same in the two spectra) is due to spectral characteristics of the Al grating of the primary monochromator and does not reflect any real physical processes. The high signal at these wavelengths is, nevertheless, indicative of strong sensitivity to VUV excitation and, 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 providing both fast and slow components in the scintillation time profiles. This notion is further supported by the emission spectra shown in Fig. 2 showing that in the Ce-activated samples emission spectrum under VUV excitation is always dominated by Ce-emission.

Interestingly the emission spectra shown in Fig. 1 under excitation by two close wavelengths in the range of the "host" peak show different contributions of two "host" emissions peaking at 220 and 300 nm. These emissions have been studied before [4].

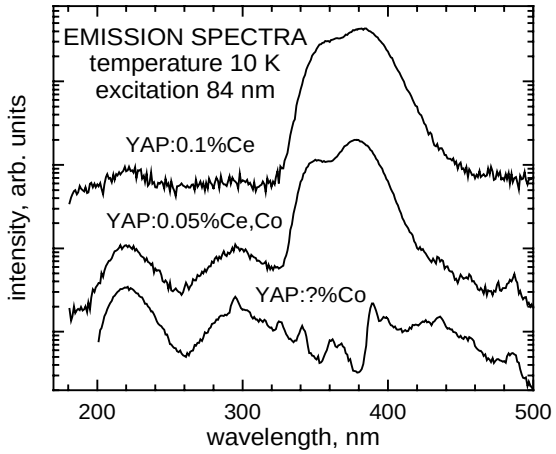

Figure 2: Uncorrected VUV excited emission spectra of YAP:0.1%Ce, YAP:0.05%Ce,Co and YAP:Co (no Ce). Resolution was 4.32 nm. The spectra were shifted to aid presentation. In addition to the dominant Ce^{3+} emission band peaking at about 365 nm in samples activated with Ce there are two "host" emissions at 220 and 300 nm and a number of Co lines in the YAP:Co sample. Temperature was 10 K

In Fig. 2 we show emission spectra of the three different samples, YAP:0.1%Ce, YAP:0.05%Ce,Co and YAP:Co (concentrations of Co in the two last samples was not known). We note that both "host" emissions at 220 and 300 nm dominate the spectrum of the sample that did not contain any Ce (YAP:Co). We note also that Ce-activated samples show a dominant Ce^{3+} band at 365 nm and that the intensities of "host" emissions decrease with the increasing concentration of Ce. Clearly the recombination via Ce ions establishes itself as a dominant mode of decay of electron-hole pairs generated by VUV synchrotron radiation.

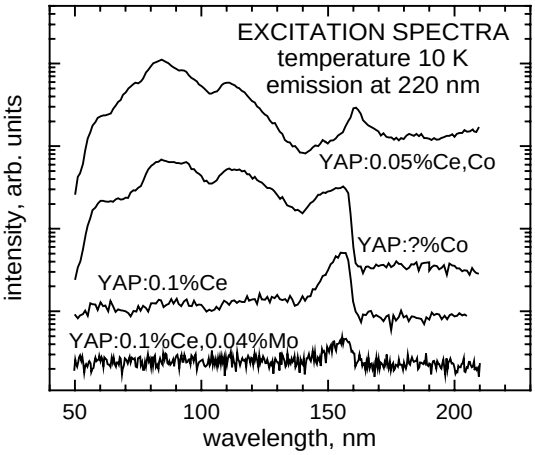

Figure 3: Uncorrected excitation spectra (resolution 0.32 nm) of the 220 nm "host" emission in different samples of YAP. The spectra were shifted to aid presentation. Note that the VUV contribution to the spectra drops in samples containing Ce.

In Fig. 3 we present excitation spectra of the 220 nm "host" emission in four different samples of YAP; YAP:Co, YAP:0.1%Ce,Co, YAP:0.1%Ce and YAP:0.1%Ce,0.04%Mo. The highest contribution at VUV wavelength is shown by the spectrum of the sample with no Ce (YAP:Co). Actually the intensity is so high that the spectrum shows distortions due, very likely, to saturation effects. From the spectra we conclude that the intensity at VUV drops with the increasing concentration of Ce indicating, consistently with the emission spectra shown in Fig. 2, that there is a competition for electron-hole pairs between Ce ions and "host" centers and that Ce ions win. For a high enough concentration of Ce the spectrum consisits of only one relatively narrow band peaking at about 155 nm, close to the bandgap of the material. It is reasonable to assume that VUV excitation creates free electron-hole pairs that are consecutively captured by Ce and/or "host" recombination centers and that 155 nm excitation (160 nm in the case of the 300 nm "host" emission) generates directly excitons later captured by defects responsible for the "host" emissions.

Interestingly the intensity of "host" peaks and emissions is much weaker in YAP:0.1%Ce,0.4%Mo. This observation is consistent with better scintillator performance of Mo-codoped sample reported recently [5].

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