

New UV/VIS emission from Ce and Co activated YAlO₃

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There is a continuous interest in near UV and blue emitting solid state materials in numerous areas such as phosphors, radiation detectors and active media for tunable lasers. Much of the work on UV and VUV emitting rare-earth activated solid state materials has been performed at Hasylab. In particular the superior experimental facilities of the Superlumi station at I-beamline covering VIS, UV and VUV spectral ranges make it possible to study wide bandgap (8-12 eV) materials. Only these materials are able to accommodate activator ions that produce fast and efficient UV and VUV emissions. Among these ions Ce, Pr, Nd, Tm and Er are clearly the best known and studied cases.

Open *d*-shell transition metal ions, unlike *f*-shell rare-earth ions, when introduced into the wide bandgap host material do not usually produce blue or near UV emissions. The only exception, as far as we know, is the Co²⁺ ion in the MgF₂ host [1]. In this note we report initial results of studies on the UV/VIS emission from yttrium aluminum perovskite, YAP, activated with Ce and Co. This emission, to the best of our knowledge, has not been observed and reported so far.

Cerium activated yttrium aluminum perovskite (YAP:Ce) is a well established commercial scintillator material that has found many applications [2]. Nevertheless it has been only recently understood that its notorious underperformance (25-38 ns scintillation decay time instead of 17 ns at room temperature) is caused by shallow traps that accompany Ce-radiative recombination centers [3]. In order to improve YAP:Ce we have started a joint program to study various intentional codopants in this material in order to identify an ion that would help to alleviate the influence of inadvertent impurities or defects on scintillation kinetics. The Co ion is the first case that we studied in this context.

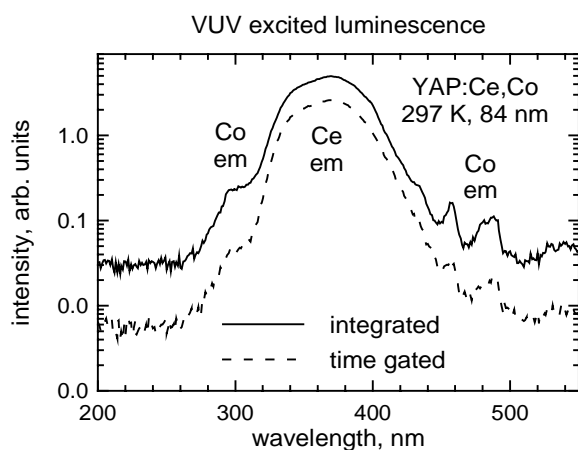


Figure 1: Uncorrected VUV excited emission spectra (resolution 5.8 nm) of YAP:Ce, Co. Solid line represents an “integrated” spectrum and dashed line represents “time gated” spectrum (see text).

In Fig. 1 we present emission spectra of YAP:Ce, Co under VUV excitation of 84 nm. The “integrated” spectrum was measured with the signal accumulated between the consecutive synchrotron pulses (192 ns) while the “time gated” spectrum was measured within a 30 ns time window triggered by a synchrotron pulse with no delay. The spectra comprise the well known broad emission band of Ce³⁺ peaking at about 369 nm and additional emission

lines at about 297, 430, 456 and 488 nm that must be due to Co-activation. Relatively larger contribution to the “time gated” spectrum at 369 nm indicates a larger contribution of a fast direct Ce³⁺ *d-f* component.

The excitation spectra shown in Fig. 2 have been measured with the signal accumulated between 0 and 192 ns and with the emission wavelength set at 360 nm (Ce emission) and 488 nm (Co emission). The structure between 200 and 330 nm in the Ce-spectrum corresponds to Ce³⁺ *f-d* bands split by the low symmetry crystal field component. Note that the *f-d* bands are missing in the Co spectrum indicating that there is no Ce emission at 488 nm and that there is no Ce-Co energy transfer. The structure in the VUV 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, both Ce and Co ions must be efficient radiative recombination centers. This notion is further supported by the emission spectra shown in Fig. 1.

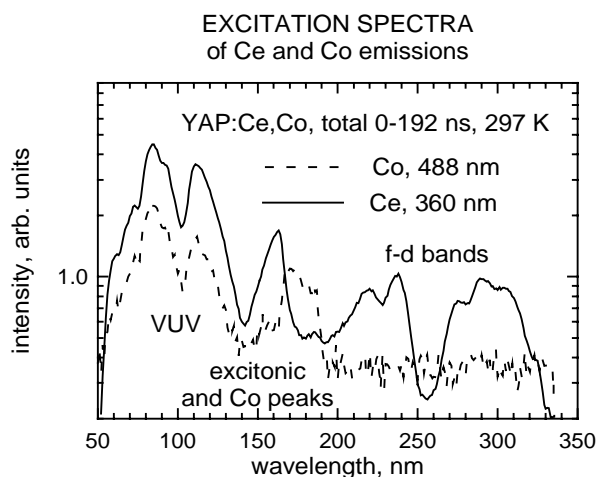


Figure 2: Uncorrected excitation spectra (resolution 0.31 nm) of Ce (360 nm, solid line) and Co (488 nm, dashed line) emissions of YAP:Ce, Co. Temperature was 297 K. Note the f-d, bands, excitonic and Co peaks and the VUV structure. See text for discussion.

Unlike the VUV structure below 140 nm the peaks between 140 and 200 nm are not generated by the spectral distribution of the VUV radiation from the primary monochromator. We conclude that the two peaks, at 163 and 182 nm, do reflect two separate processes that feed Ce and Co ions, respectively. The 163 nm peak has been previously assigned to the excitonic energy transfer channel from the host to Ce ions [3].

The emission spectra of YAP:Ce, Co under 163 and 182 nm are shown in Fig. 3. The differences between the two spectra clearly prove that under the 182 nm excitation there is an additional contribution that must be due to Co ions. Unfortunately we were not able to determine if the UV emission between 200 and 260 nm observed in MgF₂:Co [1] is absent or undetectable (low sensitivity below 260 nm).

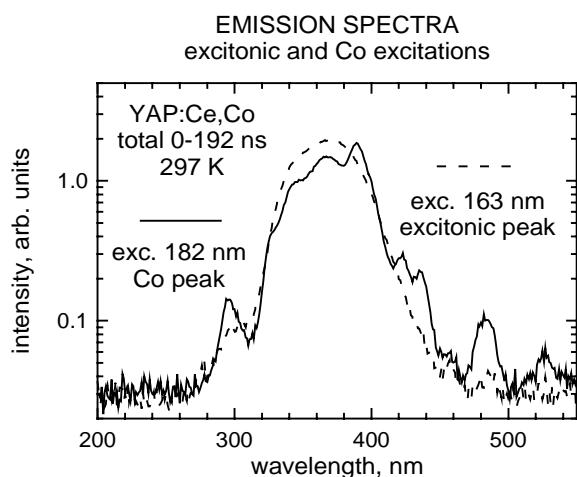


Figure 3: Uncorrected emission spectra (resolution 0.31 nm) of YAP:Ce, Co under excitonic (163 nm, dashed line) and characteristic Co (182 nm, solid line) excitations. The signal was accumulated between 0 and 192 ns. Temperature was 297 K.

The results presented in this note strongly suggest that both Ce and Co ions do introduce efficient and competing radiative recombination centers in YAP. The electronic configuration of Co is [Ar]3d⁷4s² and the third ionization potential at 34 eV is much higher than those of Al (28 eV) and Y (21 eV). Also, since the Co³⁺ and Co²⁺ radii at 0.63 and 0.72 Å are larger than Al³⁺ (0.51 Å) but less than Y³⁺ (0.89 Å) we conclude that the Co ion is capable of assuming the 3+

and/or 2+ charge states and that it substitutes for Y³⁺. Then there are two possibilities. The Co²⁺ ion may be stable introducing a hole bound at the shallow acceptor type level (simple acceptor, hole trap, no recombination [4]). Or the Co³⁺ is stable while the Co²⁺ is quasistable introducing a localized deep level in the forbidden energy gap (structured deep acceptor [4]). We also expect that a higher energy level corresponding to the excited state of the Co²⁺ ion (3d⁶4p¹) falls below the conduction band. The Co ion is then able to capture a hole (Co²⁺3d⁷ + h → Co³⁺3d⁶) and an electron (Co³⁺ + e → Co²⁺3d⁶4p¹). The UV Co emission would then be due to the 3d⁶4p¹ → 3d⁷ transition. Only the second option is consistent with all the experiments reported in this note.

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References

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