Intrinsic Luminescence in Yttrium Trifluoride

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Yttrium trifluoride (YF_3) doped by rare-earth ions is capable of producing efficient visible emissions under vacuum UV irradiation [1,2] and may be among good candidates of efficient phosphors. This material provides possibility for doping with rare earth ions due to its wide band gap (>10 eV) and suitable Y^{3+} sites where other trivalent rare-earth elements can be easily substituted without any additional charge compensation. However, the radiation resistance and formation processes of radiation defects inYF_3 under ionizing radiation (including VUV) are poorly studied so far. Also the luminescence properties of pure YF_3 need more attention.

Luminescence and excitation spectra as well as their temperature dependence were investigated using pulsed synchrotron radiation at the SUPERLUMI station. The excitation spectra were recorded with spectral resolution of 0.3 nm. The excitation spectra were normalized to equal quantum intensities of synchrotron radiation falling onto sample by means of sodium salicylate as reference. Luminescence spectra in the UV and visible range were recorded with a spectrograph SpectraPro-308i (Acton Inc.) equipped with a photomultiplier (Hamamatsu R6358P). The Pouey-type VUV monochromator together with a solar-blind photomultiplier (Hamamatsu R6836) were applied for the luminescence spectra detection in the VUV/UV spectral range. The spectral resolution of both analyzing monochromators was typically 11 nm. Emission spectra were not corrected for the spectral response of the detection systems. The excitation and emission spectra were recorded using time windows correlated with the excitation pulses of synchrotron radiation (delayed by δt). Namely time-integrated (TI) spectra as well as in the fast time window (FW length Δt = 12 ns, δt = 1.8) and the slow one (SW Δt = 95 ns, δt = 90 ns) were simultaneously recorded. The time resolution of detection systems was about 1 ns.

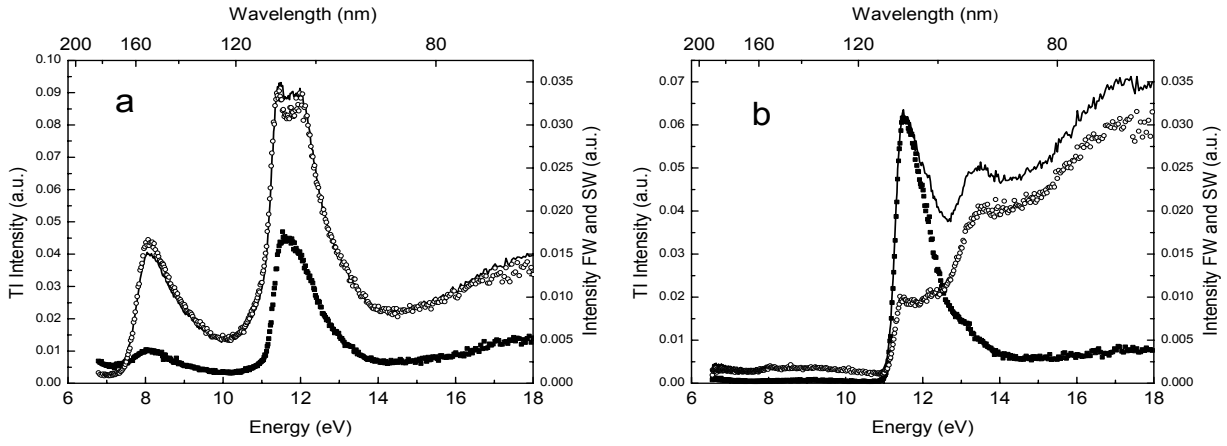

Figure 1: Excitation spectra for the time integrated (solid line), fast (solid squares) and slow (open circles) components of: 280 nm (4.4 eV) (a); and 220 nm (5.6 eV) (b) emissions.

Broad emission bands in VUV-visible spectral range were observed under excitation above 11 eV in YF_3 at 10 K. At least three emission bands were distinguished peaking at 5.6 eV (220 nm), 4.4 eV (280 nm) and 3.1 eV (400 nm). It was shown that the emission bands at 220 (5.6 eV) and 280 nm (4.4 eV) are intrinsic but the long wavelength emission at 400 nm (3.1 eV) has extrinsic nature. Observed intrinsic bands have a large Stokes shift (more than 5 eV), large widths (near 1 eV) and a

strong quenching at temperatures above 120 K. All these facts allow us assign the 4.5 eV and 5.6 eV emission to the radiative decay of self-trapped excitons in YF_3. The excitation spectra for the two intrinsic luminescence bands are shown on Fig.1. The relatively sharp excitation bands peaking at 11.6 eV (107 nm) were observed for both emissions. These excitation bands are located just below intrinsic absorption edge and correspond to the states of excitonic origin.

The question naturally arises whether the both luminescence bands originate from radiative decay of self-trapped excitons. A possible hypothesis is that two emission bands may arise from singlet and triplet spin states of STE and it, in turn, leads to two luminescence bands: singlet and triplet. It is known that singlet luminescence of STE has typical lifetimes in the few nanosecond range, which suggest allowed transitions form singlet excited state to the ground one. On the other hand transitions from the triplet to the singlet ground state are strictly forbidden and triplet luminescence of STE has lifetimes ranging from few-decade of nanoseconds up to several milliseconds [3 and ref. therein]. Luminescence bands of singlet and triplet STE can either have a coincident spectral position, or spectrally separated (triplet bands are about 1 or 2 eV below the singlet bands). Using the same argumentation the emission bands at 4.4 and 5.6 eV (280 and 220 nm) in YF_3 correspond to the triplet and singlet transitions of STE by analogy with alkali halides. However, each of these bands can be observed in the fast (FW) and slow (SW) time windows. The length of the FW was near 12 ns and this time coincides with the typical lifetime of luminescence of singlet STE, while the SW shows intensity of luminescence ranging from 95 up to 180 ns after excitation pulse and is dominated by the triplet luminescence of STE. It means that each of the STE luminescence bands exhibits components, which can be attributed to radiative decay of both singlet and triplet STE. Therefore emission bands could not be ascribed as pure singlet or triplet luminescence bands of STE. The second possibility is that the observed luminescence bands in YF_3 correspond to different configurations of STE. Presently we are not aware of any reliable data about the structure of STE in YF_3. Therefore one can only speculate that the STE in YF_3 may be in the form of V_k center plus electron, by analogy with LaF_3, where the existence of V_k centers has been identified through ESR and optical spectroscopy [4]. If at least two different sites for the V_k-type centers are possible in YF_3 then two different configurations of STE can occur leading to two different luminescence bands.

Finally, we would like to point out an interesting feature in the excitation spectra. For both luminescence bands it was observed that the fast (singlet) luminescence (FW) is preferentially excited in the region of the lowest energy exciton, just below of the band edge and poorly excited in the intra band region. This result is different of well-studied excitation spectra of STE luminescence for alkali halides [3,5] where triplet luminescence mostly excited in the excitonic region but singlet luminescence state is mainly formed on the recombination of electrons and self-trapped holes in band-to-band transitions. This fact shows that the structure and behavior of STE in YF_3 can be quite different in comparison with earlier investigated STE in alkali halides and other materials and further exploration of STE in YF_3 is required.

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