VUV and UV luminescence in BaF_2:Er

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The interconfigurational $4f^{n-1}5d$-$4f^n$ transitions on rare earth ions have become a field of extensive studies quite recently, due to their potential application in scintillator materials and VUV lasers. As the $4f^{n-1}5d$ bands of heavier lanthanides lie in the VUV [1], more advanced setups are needed for spectroscopic measurements. The two superior stations of HASYLAB, SUPERLUMI and HIGITI, have already been involved in studies of such systems as $LiYF_4$:Er, BaY_2F_8:Er, and BaY_2F_8:Tm [2,3]. In this note we focus our attention on the BaF_2 crystal doped with 0.2% of erbium.

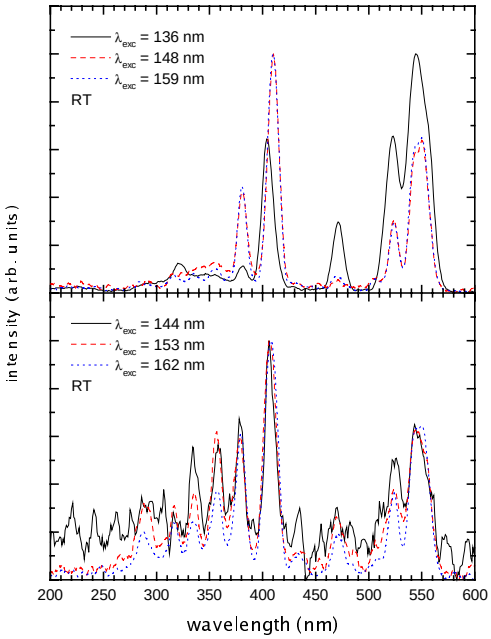

Figure 1: UV and VIS emission spectra of BaF_2:Er

A series of UV and VIS emission spectra of BaF_2:Er at various excitations ranging from 136 to 162 nm is presented in Figure 1. While the longer wavelength regions (375-600 nm) of all the spectra are quite similar regardless of the excitation wavelength, differences occur at shorter wavelengths. If the sample is excited at 144, 153, and 162 nm, distinct emission lines appear below 375 nm. These lines almost vanish at 136, 148, and 159 nm excitations.

The excitation spectra shown in Figure 2 explain the above observations. The sharp edge at 156 nm (upper window of Fig. 2) corresponds very well to the energy of the lowest $4f^{11}$-$4f^{10}5d$ transition on Er^{3+}, estimated as 64200 cm^{-1} by Loh [1] for CaF_2:Er. The bands below 156 nm may be thus ascribed to the $4f^{10}5d$ levels of Er^{3+}. The narrower peak at 162 nm is also associated with the $4f^{10}5d$ configuration and will be discussed later on. The excitation spectrum of the longer wavelength emission (lower window of Fig. 2) has its bands even at higher energies. The strongest one, peaking at 136 nm, was also observed by Yang and DeLuca [4] in excitation spectra of Nd^{3+}, Er^{3+}, and Tm^{3+} $4f^n$-$4f^n$ emission in trifluorides. They postulated an energy transfer from the host to the RE^{3+} ions, accompanied by a large energy loss (due to the lattice relaxation via formation of self-trapped hole centers, known as the V_K centers) that would not allow the $4f^{n-1}5d$ levels to be excited. However, the structure of the spectra measured by Yang and DeLuca was much simpler. In our spectrum we see three maxima at 136, 148, and 159 nm. As they correspond to the minima in the upper window of Fig. 2, we suppose that the excitation spectrum of the $4f^{11}$-$4f^{11}$ emission is actually a single broad band, which was transformed into a three-peak one by the competitive $4f^{11}$-$4f^{10}5d$ transitions at appropriate wavelengths. Therefore we ascribe the emission lines below 375 nm to the interconfigurational $4f^{10}5d$-$4f^{11}$, and above 375 nm to the intraconfigurational $4f^{11}$-$4f^{11}$ transitions on Er^{3+} ions.

Figure 3 shows the VUV and UV emission spectra of BaF_2:Er. Although in Ce- and Pr-doped BaF_2 the interconfigurational transitions produce fast luminescence, this is no longer true in case of Er-doped BaF_2. The time profiles of all emission lines in Fig. 3 show no fast component. The decay constants are much longer than 192 ns (which is the time between two consecutive bunches of electrons in the storage ring).

A possible explanation is given in the paper of Wegh *et al.* [3]. As they noted, in the ground state of Er^{3+} (configuration $4f^{11}$) there are three unpaired spins, so the spin multiplicity $2S + 1 = 4$. For the first excited state (configuration $4f^{10}5d$) two possibilities must be considered: $2S + 1 = 4$ if the spin of the $5d$ electron is antiparallel, or $2S + 1 = 6$ if parallel with the four unpaired spins left in the $4f^{10}$ core. This fact gives rise to a low-spin (LS) state and a high-spin (HS) one, with the latter located lower in energy according to the

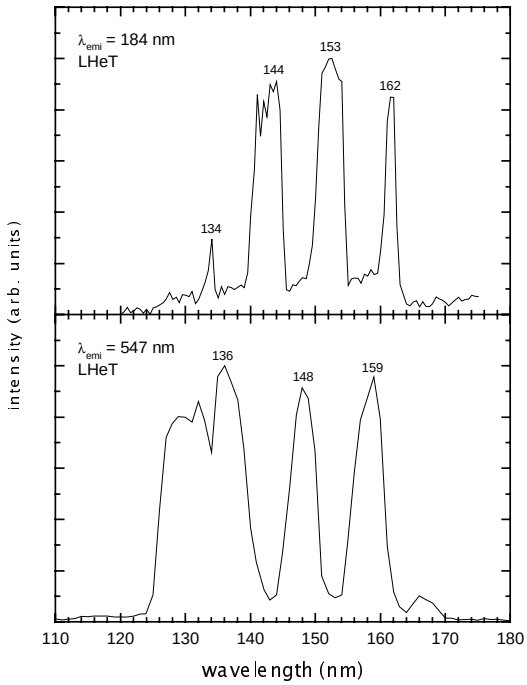

Figure 2: Excitation spectra of the Er^{3+} $4f^{10}5d$-$4f^{11}$ and $4f^{11}$-$4f^{11}$ emissions

Hund's rule. The $4f^{10}5d$-$4f^{11}$ emissions originating in the HS state are spin-forbidden, while these from the LS state are spin-allowed, thus the former should be relatively slow and the latter much faster [3].

Assuming that the lowest LS and HS levels of the $4f^{10}5d$ configuration are located at 64200 [1] and 61000 cm^{-1}, respectively, and taking the energies of the $4f^{11}$ levels from the paper of Pollack [5], we can calculate the wavelengths of all possible $4f^{10}5d$-$4f^{11}$ emissions. The position of the HS excited state was estimated from the excitation spectrum (upper window of Fig. 2), in which we associated this state with the 162 nm peak. Solid and open triangles in Fig. 3 denote the predicted positions of possible emission lines originating in the lowest LS or HS level: the spin-allowed transitions in the experimental range of Fig. 3 should peak at 156 (terminating at the $4f^{11}$ $^4I_{15/2}$ level), 174 ($^4I_{13/2}$), 185 ($^4I_{11/2}$), 194 ($^4I_{9/2}$), 204 ($^4F_{9/2}$), 218 ($^4S_{3/2}$), 222 ($^2H_{11/2}$), 238 ($^4F_{5/2}$), and 241 nm ($^4F_{3/2}$), while the spin-forbidden ones at 164 ($^4I_{15/2}$), 184 ($^4I_{13/2}$), 198 ($^4I_{11/2}$), 207 ($^4I_{9/2}$), 219 ($^4F_{9/2}$), and 239 nm ($^2H_{11/2}$).

Although the agreement between the expected and observed emission wavelengths is reasonably good, we question the presence of any inter-configurational transitions from the LS excited state in BaF_2:Er: *i)* there is no luminescence below 160 nm (which would have to originate in the LS state); *ii)* the emissions are slow; *iii)* besides the one at 174 nm, all the bands have appropriate transitions from the HS state assigned. These observations suggest, that all the observed $4f^{10}5d$-$4f^{11}$ emissions are spin-forbidden. The excitation into any of the LS excited levels of the $4f^{10}5d$ configuration must be thus followed by intersystem relaxation to the lowest HS excited state instead of the fast interconfigurational luminescence. The problematic slow emission at 174 nm, to which no spin-forbidden $4f^{10}5d$-$4f^{11}$ transition fits, may be associated with Er^{3+} ions in sites of symmetry other than trigonal, however this question remains open.

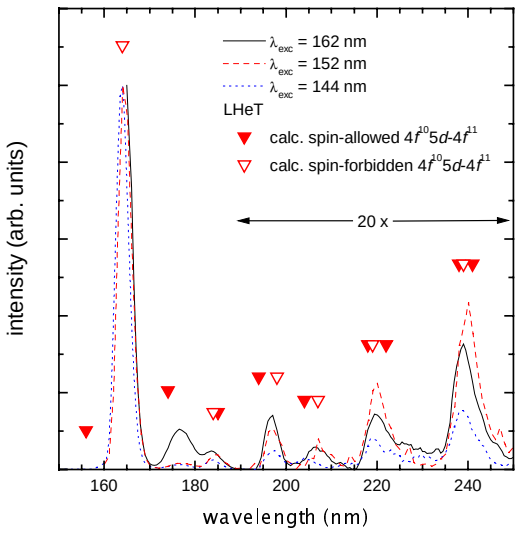

Figure 3: VUV and UV emission spectra of BaF_2:Er

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