High energy $4f^{11}$ and $4f^{10}5d$ levels of Er^{3+} in BaF_2

A.J. Wojtowicz and S. Janus

Institute of Physics, N. Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland

The interest in the VUV spectroscopy of wide bandgap materials has been generated by applications such as scintillators, solid state lasers and mercury free phosphors. Preliminary, low resolution experiments performed on Er-activated BaF_2, at Superlumi station of Hasylab, DESY, Hamburg, Germany, have already been published in 1999 [1]. Nevertheless, since the interpretation given therein did not take into account the possibility that some of the observed VUV and UV emission lines may originate in the hypothetical highly lying doublet state $^2F(2)_{5/2}$ [2,3], new experiments have been planned and performed in 2007.

In this report we will present direct evidence that the $^2F(2)_{5/2}$ state levels do exist at about 63,400 cm^{-1}, as predicted by theory [2]. As presented earlier, the competition between Er-bound exciton and Er^{3+} $4f^{10}5d$, $4f^{11}$ ($^2F(2)_{5/2}$) levels is responsible for strong variations of the complex pattern of VUV, UV and VIS emission lines with relatively small changes in the excitation wavelength [3]. In this report we will also demonstrate that competition between $^2F(2)_{5/2}$ and two states of the $4f^{10}5d(e)$ configuration (HS, high spin; and LS, low spin) is responsible for the strong variation of this pattern with temperature.

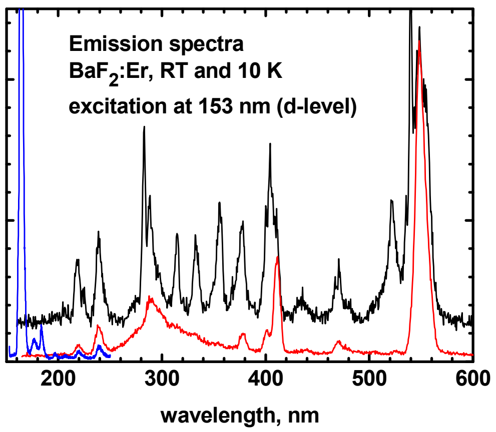

Figure 1: Emission spectra. Black line 297 K, res. 2.7 nm, red line, 10 K, res. 2.7 nm, blue line 10 K, res. 1.1 nm, VUV monochromator and photomultiplier (for the description of the experimental set-up see [4,5].

In Fig. 1 we show the emission spectra under the excitation at one of the three d-bands (153, 144, 134 nm) associated with the spin-allowed transitions from the Er^{3+}ground $4f^{11}$ level ($^4I_{15/2}$) to the LS (low spin) levels of the $4f^{10}5d$ configuration. Since the 10Dq crystal field splitting is large (about 16,000 cm^{-1}) and the energy differences between these levels are much smaller (4500 and 4600 cm^{-1}, respectively) we assign them, following van Pieterson et al [6], to states in which one electron of the original $4f^{11}$ ground state configuration is moved to the same d(e) orbital while the remaining 10 f-electrons are left in the $^5I_8$, $^5I_7$, $^5I_6$ states of the Ho^{3+} ion, respectively. We note that at RT, under the excitation into the wavelengths falling between the LS d-bands almost all of the VUV and UV emission lines below 380 nm disappear [1,3]. The explanation involves an Er-bound exciton (see [1,3]) and follows the idea of Yang and DeLuca who proposed that the energy transfer from the host to the ion is accompanied by a large energy loss due to the lattice relaxation [7]. We also note that most, but not all, of these lines disappear at 10 K.

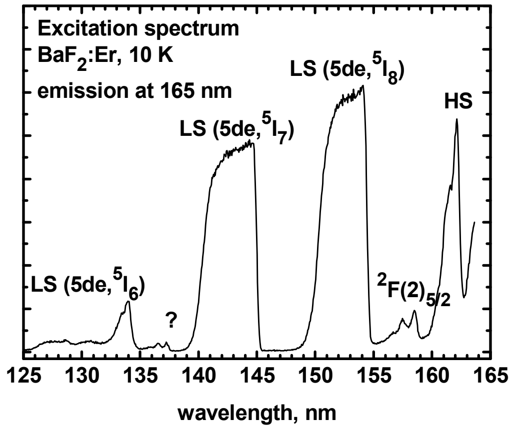

Figure 2: Uncorrected excitation spectrum at 10 K, res. 0.32 nm, step 0.05 nm. Emission was set at 165 nm (at the long wavelength tail of the HS emission at 163.5 nm).

In Fig. 2 we present the excitation spectrum of the HS emission at 163.5 nm (see blue line in Fig. 1) at 10 K. The detection monochromator was set at 165 nm to enable a good measurement with no scattered excitation light of the HS excitation band at 163.5 nm. The spectrum shows, beside the HS band, two high intensity, saturated bands at 153 and 143 nm and a low intensity band at 134 nm quenched, most likely, by competing excitonic transitions at 125-135 nm. These three bands are assigned to transitions involving $^5I_8$, $^5I_7$, $^5I_6$ states of the $4f^{10}$ configuration of the Ho^{3+} ion, left behind by an electron promoted to the d(e) orbital at the Er^{3+} ion. The most interesting, and previously unreported feature is, however, represented by weak bands at about 156.6, 157.5 and 158.5 nm. These bands must be due to the $^2F(2)_{5/2}$ state, energy of which has been calculated to be 63,345 cm^{-1} [2]. In addition we observe a set of three bands, labeled by a question mark in Fig. 2, at 135.9, 136.6 and 137.3 nm that may, presumably, be due to one of the other unreported doublets, such as $^2G(2)_{9/2}$, $^2G(2)_{7/2}$, $^2F(1)_{5/2}$, and $^2F(1)_{7/2}$ energies of which are unknown at this time.

It is interesting to note that the presence of the intermediary level between the two d-levels must facilitate the fast relaxation between them thus promoting the emission from the lowest HS level. Nevertheless, since one can reasonably expect large equilibrium position difference between the two states (one of which involved d-orbital while the other does not), the energy difference between the minimum energies of the two parabolas may be much less than the difference between the corresponding vertical transitions. Consequently, at high enough temperatures one can expect some emissions in the range of 300-400 nm due to transitions from the $^2F(2)_{5/2}$ level to a number of doublet levels of the Er^{3+} ion at 25-40,000 cm^{-1} that disappear at lower temperatures, as observed.

Unfortunately we have not been able to measure the appropriate spectra at RT and we are left with the less conclusive evidence from the relatively low quality experiments at 10 K shown in Fig. 3.

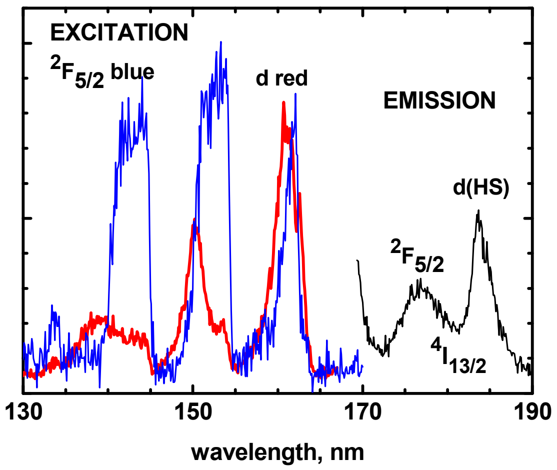

Figure 3: Emission and excitation spectra of BaF_2:Er at 10 K. Black line: emission, res. 1.1 nm, step 0.1 nm, excitation 152 nm. Blue line: excitation, res. 0.32 nm, step 0.1 nm, emission set at 177 nm. Red line: excitation, res. 0.32 nm, step 0.1 nm, emission set at 184 nm. Temperature was 10 K.

The emission spectrum shown in Fig. 3 was measured at wavelengths above the dominating emission band at 163.5 nm corresponding to transition between the HS d-level and the ground state of the Er^{3+} ion, $^4I_{15/2}$. The spectrum shows two lines, at 176.6 and 184 nm. The 184 nm line is 6800 cm^{-1} below the 163.5 nm line so it must be due to the transition from the HS d-level to the second lowest $4f^{11}$ level of the Er^{3+}, $^4I_{13/2}$. The second band, at 176.6 nm (56,600 cm^{-1}) may, therefore, correspond to the transition originating at $^2F(2)_{5/2}$, since 56,600 + 6800 = 63,400 cm^{-1}, 157.7 nm. The blue and red lines show excitation spectra of these two emission bands at 176.6 and 184 nm. We note the larger contribution of the blue spectrum at wavelengths corresponding to two doublets at 157 and 137 nm, identified in Fig. 2.

This work was supported by DESY and the European Community under Contract RII3-CT-2004-506008 (IA-SFS). The support and hospitality of Prof. G. Zimmerer and Dr G. Stryganyuk of Hasylab is also gratefully acknowledged.

References

[1] W. Drozdowski, J. Glodo, and A.J. Wojtowicz, VUV and UV luminescence in BaF_2:Er, Hasylab Annual Report, Hamburg, 1999 (http://hasyweb.desy.de/science/annual_reports/1999_report/part1/contrib/42/621.pdf).

[2] R.T .Wegh, E.V.D. van Loef, G.W. Burdick, and A. Meijerink, Luminescence spectroscopy of high-energy levels $4f^{11}$ levels of Er^{3+} in fluorides, Mol. Phys. 101 (2003) 1047-1056

[3] A.J. Wojtowicz, VUV spectroscopy of BaF_2:Er, accepted for publication in Optical Materials.

[4] G. Zimmerer, Nucl. Instr. Meth. Phys. Res. A 308 (1991) 178.

[5] http://hasylab.desy.de/facilities/doris_iii/beamlines/i_superlumi/index_eng.html

[6] L. van Pieterson, M.F. Reid, and A. Meijerink, Phys. Rev. Lett. 88 (2002) 067405-1.

[7] K.H. Yang, J.A. DeLuca, Phys. Rev. B 17 (1978) 4246.