VUV and UV emissions from Er$^{3+}$ in (Ba,La)F$_2$

A.J. Wojtowicz, S. Janus, P. Palczewski and M. Witkowski

Insytut Fizyki, Uniwersytet M. Kopernika, Grudziądzka 5, 87-100 Toruń, Poland

The recent surge of interest in the VUV and UV luminescence and spectroscopy of inorganic solid state materials activated with rare earth ions has been motivated by applications such as scintillators, solid state lasers and mercury free phosphors. Also availability of excellent synchrotron facilities devoted to VUV (Superlumi and HIGITI stations, Hasylab, DESY, Hamburg) and support for experimental groups from the EC, provide an additional incentive for researchers to collect some missing experimental data that have been, in the past, difficult to obtain and scarce. Likewise in 2007 we have continued studies of wide bandgap materials at Superlumi and, in particular, we have performed new experiments on Er-activated BaF$_2$[1,2].

These experiments have shown that all the VUV and UV emissions in BaF$_2$:Er are parity- and/or spin-forbidden and slow, as reported earlier for other fluorides (see e.g. [3]). The conclusion was that the parity-allowed 4f$^{10}$5d $\rightarrow$ 4f$^{11}$ emission originates mostly in the lowest energy high-spin (HS) level of the 4f$^{10}$5d configuration (2S+1=6), as proposed earlier by A. Meijerink and coworkers [3]. Since this transition terminates at the low-spin (LS) $^4$I$_{15/2}$ ground state level of the 4f$^{11}$ configuration (2S+1=4), it is spin-forbidden and, consequently, the corresponding VUV emission at 163.5 nm must be slow.

In 2008 we have conducted similar studies of the mixed (Ba,La)F$_2$:Er crystals. Unexpectedly, we have discovered that the dominant VUV emission peaking at about 162.5 nm, shown in Figure 1, is relatively fast and unquenched (45 ns at 10 K and 35 ns at room temperature).

Note the large difference between fast and slow emissions for all bands (except the 170 nm) suggesting short decay times, as corroborated by a direct time profile measurement shown in Figure 2.

It is interesting to note that at room temperature the excitation into any of the three identified LS bands corresponding to higher excited states of the 4f$^{10}$5d configuration generates fast emissions (with 35 ns decay time) while at 10 K fast emissions (with 45 ns decay time) require the excitation into the lowest LS band at 157 nm. The excitation into any other of the
shorter wavelengths LS bands is followed by emission characterized by a completely different spectrum, consisting of slowly decaying sharp lines. The positions of these lines, as shown in Figure 3, fit nicely the calculated energies of transitions originating at the \( ^2G_{7/2} \) state at 66,122 cm\(^{-1}\) (the best fit position of the \( ^2G_{7/2} \) level). The emission from the \( ^2G_{7/2} \) state has been never, to the best of our knowledge, reported before.

The \( ^{1}I_{15/2} \) level energies used to calculate arrow positions in Figure 1 and 2, have been obtained in the free ion approximation by D. Piatkowski who used the M.F Reid’s f-shell empirical programs to evaluate the parameters necessary for diagonalization of the relevant energy matrix [4]. Since only the low energy levels (up to 35,000 cm\(^{-1}\)) have been included in the calculations, it is interesting to compare the calculated value (which is 66,022 cm\(^{-1}\)) with the best fit value of 66,122 cm\(^{-1}\). We note that the difference is reasonable (the root mean square deviation between the calculated and experimental line positions was 90 cm\(^{-1}\)).

The \( ^{1}I_{15/2} \) level in BaF\(_2\) must be effectively, although unexpectedly, involved in the nonradiative relaxation between the two LS 4f\(^{11}\)5d levels (despite no difference in the spin quantum number, see discussion in [3]). Note that these two levels involve the d-electron in the same orbital; the difference in energy between these levels being mostly due to difference in energy between the \( ^1I_8 \) and \( ^1I_7 \) states of the 4f\(^{10}\) configuration [5]. The expected relatively small change in the configuration coordinate may therefore explain the slow nonradiative relaxation in the absence of the \( ^2G_{7/2} \) level, at least for low temperatures. Note, however, that the position of the \( ^2G_{7/2} \) level, at 66,120 cm\(^{-1}\), is actually somewhat below the 4f\(^{10}\)5d level, at 67,570 cm\(^{-1}\). As a simple configuration coordinate model shows this is enough to promote, at low enough temperature, some occupation of the \( ^2G_{7/2} \) level and emission, as observed [4]. At higher temperatures a direct nonradiative relaxation between the 4f\(^{10}\)5d levels is faster and spin-allowed emission from the lower LS level dominates the spectrum.

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**References**


