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The $^1S_0$ emission from the minor site of Pr^{3+} in $(Ba,La)F_2:Pr$

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HIGHLIGHTS

- ► Pr f-f and f-d time resolved emission spectra were measured.
- ► Emission from the minor La-site of Pr^{3+} in $(Ba,La)F_2:Pr$ was identified.
- ► Configuration coordinate diagrams of the Pr^{3+} in different sites were proposed.

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ABSTRACT

In this paper we present and discuss results of detailed spectroscopy studies of Pr^{3+} luminescence from the $(Ba,La)F_2$:0.2 m%Pr crystals under UV and VUV synchrotron excitation.

We have measured time resolved emissions from the minor site Pr^{3+} in $(Ba,La)F_2:Pr$ at 10 and 300 K. The spectra clearly show the $^1S_0$ emission from the Pr^{3+} ions in some low symmetry Pr-sites (we designate them La-sites) previously identified in higher concentration (0.3 m%Pr and more) crystals. However most of emission from the Pr activated $(Ba,La)F_2$ crystals originates in Pr^{3+} ions in other sites which produce an efficient d-f emission. As demonstrated by excitation spectra, the emission from some of these sites (denoted as Ba-sites) closely resembles the d-f emission from BaF_2.

The La-site, time resolved and long delay emission spectra are dominated by hypersensitive transitions from the $^1S_0$ and $^3P_0$ levels to lower energy levels of the $4f^2$ configurations. Only these transitions contribute to the photon cascade emission desired for some mercury free phosphor applications.

1. Introduction

Rare earth activated wide bandgap materials are essential for many applications such as phosphors, lasers and scintillators. One of the most interesting cases is activation by Pr^{3+} ions. Usually Pr activation leads to materials showing fast and efficient 4f5d UV emission under ionizing radiation (scintillators) or visible photon cascade under selective VUV excitation (quantum cutting, mercury free lighting phosphors).

The cascade emission from Pr^{3+} in fluoride hosts (two visible emission photons from a single incident vacuum ultraviolet photon) has been reviewed by Piper et al. (1973) and, more recently by Kuck et al. (2005). In these papers the authors show that the necessary condition for efficient cascade emission is the presence of the emission originating at the $^1S_0$ level of the Pr^{3+} ion. Rodnyi et al. (2005) report that, depending on the Pr-activation level, BaF_2 crystals may show: 1) narrow line emissions originating at the $^1S_0$ level and $^3P_0$ (cascade) emissions that follow the $^1S_0 \rightarrow {}^1I_6$ transition (for BaF_2:3 m%Pr) or, 2) fast d-f and slow $^3P_0$ f-f (cascade) emissions originating at the lowest level of the 4f5d configuration (for BaF_2:0.3 m%Pr). They propose that for the 3 m%Pr sample the lowest 5d level of the Pr^{3+} in the dominant site is above the $^1S_0$ level while for the 0.3 m%Pr sample it is below the $^1S_0$ level and suggest that Pr-clustering, originally suggested by Levey et al. (1984), in the higher Pr-concentration sample is responsible for the large change in the crystal field and corresponding shifts of d-levels.

In this paper we focus on the $^1S_0$ emission from some Pr-sites in the $Ba_{0.8}La_{0.2}F_{2.2}$:0.2 m%Pr crystal. However, since Pr-concentration in this crystal is below 0.3 m% Pr, the Pr-clustering does not seem very likely. Nevertheless, we note that in such $(Ba,La)F_2$ mixed crystal, 20% of Ba-sites are occupied by La^{3+} ions and 20% of interstitial sites are filled with excess fluorine ions and there are plenty of reasons for which some highly distorted, low symmetry site (we will designate it La-site) may occur.

2. Samples and experimental set-up

The Pr doped samples of $(Ba,La)F_2$ were cut from larger boules grown by Optovac Inc. (North Brookfield, MA, USA) using the

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Bridgman method. The concentration of Pr in the melt was 0.2% mol.

The VUV/UV measurements (luminescence and excitation spectra) were performed at the Superlumi station of Hasylab on the Doris III storage ring in Desy, Hamburg, Germany.

A detailed description of Superlumi's experimental facilities, available online,[1] was also given by Zimmerer (2007). For excitation a primary 2 m normal incidence monochromator in 15° McPherson mounting, equipped with the holographic concave grating (1200 groves/mm), coated by Al + MgF2 (50–330 nm) is used. The resolution was 0.32 nm.

For emission one of the two monochromators could be used: the homemade 0.5 m Pouey VUV monochromator (f/2.8, the resolution of 1.1 nm, fixed slit widths) equipped with the solar blind Hamamatsu R6836 photomultiplier (115–300 nm) for VUV, and the Acton Research 0.3 m Czerny-Turner monochromator "Spectra Pro 300i" (f/4) equipped with the Hamamatsu R6358P photomultiplier for longer wavelengths spectra (200–800 nm). The resolution of this monochromator depended on the adjustable slit widths and the grating inserted. The choice was between three gratings, one having 1200 groves/mm (2.7 nm/mm) and blazed at 300 nm and two others having 300 groves/mm (10.8 nm/mm) and blazed at 300 and 500 nm, respectively.

3. Experimental results and discussion

In Fig.1 we present time resolved emission spectra under excitation at 160 nm (higher energy high spin (HS) triple d-band (see Fig. 2). There are significant differences between the fast (40 ns time window, 2 ns delay, black solid line) and the slow (40 ns time window, 150 ns delay, red solid line) emissions. The fast gate spectrum shows the structured broad band with features at 230.9, 259.5, 275 nm that, very likely, result from transitions originating at the lowest HS d(e)-level and terminating at the consecutive lower lying $4f^2$ energy levels. After change of the scale of the slow emission (by the factor of 10 in the range 200–340 nm) we have observed the weak features at 249, 271, 337 nm (blue solid line in Fig. 1). Moreover both fast and slow gate spectra show a band at 403.5 nm (black and red solid lines in Fig. 1). All of these features are due to f-f emissions from the $^1S_0$ state to some lower lying $4f^2$ energy levels.

The black and red arrows in Fig. 1 show the positions of lines calculated by one of us (MEW) using the adopted Cowan code, (Cowan, 1981) and published formulas (see Wybourne, 1965), and due to transitions originating at d and $^1S_0$ levels, respectively, and terminating at consecutive lowest states of the $4f^2$ configuration. Because of the lack of inversion symmetry, the slow emission spectra in Fig. 1 are dominated by hypersensitive transitions (J must be even and $\Delta J = \pm 2$) from the $^1S_0$ level to $^3F_2$ (249 nm), $^1G_4$ (271 nm), $^1D_2$ (337 nm) and $^1I_6$ (403.5 nm) levels of the $4f^2$ configuration.

The fast gate spectrum originates in the lowest state of the 4f5d configuration and terminates at $^3H_4$ (230.9 nm), $^3H_6$ (259.5 nm), $^3F_4$ (275 nm) and $^1D_2$ (351.5 nm) levels of the $4f^2$ configuration.

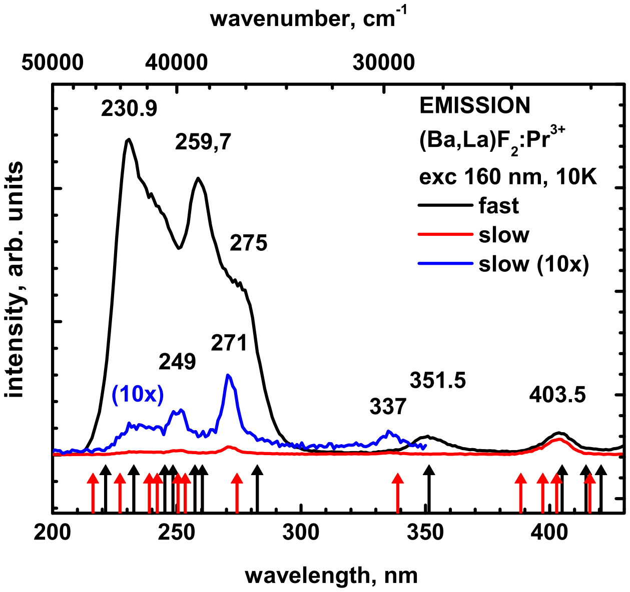

Fig. 1. Time resolved emission spectra at 10 K, res. 5.4 nm, step 1 nm. Excitation 160 nm. Black line, fast emission (2–42 ns time window), red line slow emission (150–190 ns time window). Note the change of scale for the slow emission (10x, blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To identify sites responsible for all those emissions, we have measured time resolved excitation spectra of selected emissions; at 351.5 nm (fast, d → $^1D_2$), and 403.5 nm (slow, $^1S_0$ → $^1I_6$), as shown in Fig. 2. The fast 351.5 nm spectrum (top panel in Fig. 2) contains three bands at 136, 158 and 205 nm representing, respectively, Pr^{3+}-trapped exciton, d(t) and d(e) bands of Pr^{3+} in a Ba-site, typical of BaF_2 (see Wojtowicz et al., 2011). Consequently, the 351.5 nm and some of other fast emissions shown in Fig. 1, are due to Pr^{3+} ions in Ba-sites. No $^1S_0$ emission has been detected in BaF_2 (Wojtowicz et al., 2011). We note that the shift between the gravity centers of d(t) and d(e) bands is equal to 14500 cm^{-1} and is close to the value of 10 Dq in BaF_2.

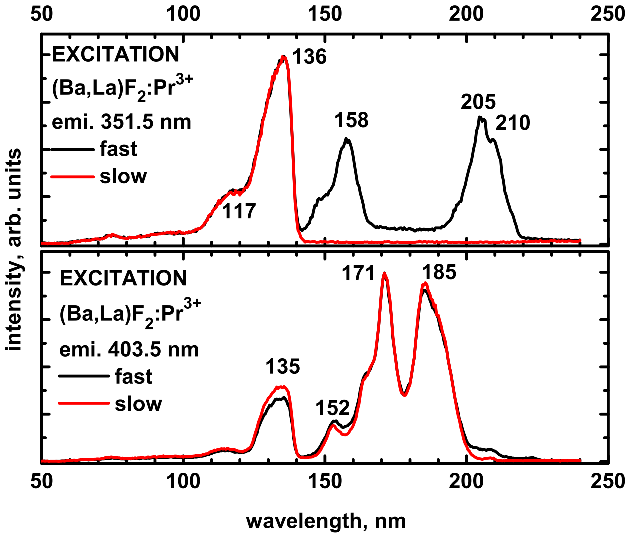

Fig. 2. Time resolved excitation spectra at 10 K, res. 0.32 nm, step 0.5 nm. Top panel: emission wavelength set at 351.5 nm. Black line represents fast emission (2–42 ns), red line, slow emission (150–190 ns). Bottom panel: emission wavelength set at 403.5 nm. Black line depicts fast emission (2–42 ns), red line, slow emission (150–190 ns). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The more interesting is the 403.5 nm spectrum (lower panel in Fig. 2), which does not show any fast contribution. Four bands at 135, 152, 171 and 185 nm do not match bands of Pr^{3+} in Ba-site suggesting that they are due to Pr^{3+} ions in some heavily distorted sites. We will designate these sites as La-sites. Note that the

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