Luminescence and energy transfer processes in $La_2Be_2O_5$:Pr

A.J. Wojtowicz and M. Malinowski[1]

Institute of Physics, N. Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[1]*Institute of Micro- and Optoelectronics, Warsaw Univ. of Technology, Koszykowa 75, 00-662 Warsaw, Poland*

Potential applications of wide bandgap materials activated with rare earth (RE) ions in opto- and microelectronics belong to such diverse areas as lighting and display phosphors, radiation detectors, light emitting diodes and solid state lasers [1]. The tremendous progress that we witness in all those areas would not be possible without extensive work carried out at synchrotron facilities all over the world. In particular an intense VUV excitation and superb instrumentation available at Superlumi station of Hasylab in Hamburg provide an exceptional opportunity to study luminescence and various energy transfer processes that occur in systems comprising the solid state host material and the rare earth activator ion.

The Pr^{3+} ion with its fast and efficient UV *d-f* emission and rich *f-f* energy structure sustaining various cooperative interactions leading to efficient up- and down-conversion clearly is one of the prime subjects of such a research. In 1999 at Superlumi station of Hasylab we started a program of studies on various materials activated with Pr. One of these materials is $La_2Be_2O_5$:Pr (LBO:Pr). Although strong pump-induced absorption due to transient color centers and excited state absorption prevent lasing in the visible part of the spectrum in LBO:Pr [2] the material could still be of interest for other applications such as those involving infra-red to blue and orange to blue up-conversion [3] and/or fast UV *d-f* emission. In this note we report initial results that we obtained during the last experimental session at Superlumi station in July 1999.

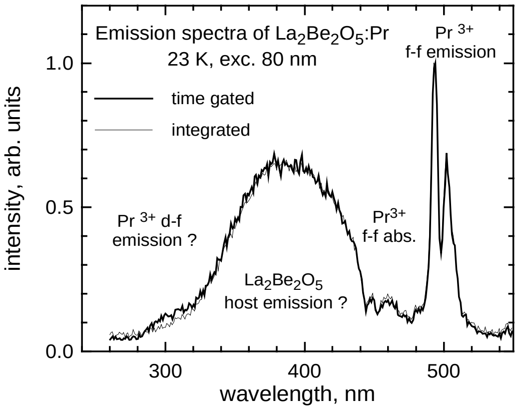

Figure 1: Uncorrected emission spectra of Pr-activated $La_2Be_2O_5$ crystals at 23 K. The excitation wavelength was set at 80 nm. For designation of the curves see text.

In Fig. 1 we present two emission spectra of $La_2Be_2O_5$:Pr under 80 nm excitation at 23 K, designated “time gated” (thick solid line) and “integrated”. (thin solid line). The “integrated” spectrum was measured with the signal accumulated during the time between the consecutive synchrotron pulses (192 ns) while the second, “time gated” spectrum, was measured within a 40 ns time window triggered by a synchrotron pulse with no delay. The spectra were scaled to aid comparison. We note that the traces overlap closely except at around 300 nm. Larger signal accumulated during a shorter 40 ns time window may indicate a relatively higher contribution of shorter components due to, most likely, *d-f* emission from the Pr^{3+} ion. The broad band peaking at around 390 nm resembles a “host emission” band typical of undoped oxide and fluoride lattices and due to radiative decay of self-trapped excitons or excitons trapped at some defects or impurities [5]. Sharp features distorting the longer wavelength side of the “host emission” band at about 440 to 480 nm are due to *f-f* absorption lines of Pr^{3+} ($^3H_4$-^3P_J, [2,4]) and, finally, emission lines at around 500 nm are due to downward *f-f* transitions from the lowest level of the $^3P_0$ multiplet [2,4].

These assignments are supported by the excitation spectra of various emissions identified in Fig. 1 and shown in Fig. 2. These spectra have not been corrected and, therefore, the structure in the VUV reflects mostly the spectral variations of the synchrotron flux introduced by the grating of the primary monochromator. Nevertheless the relatively high signal in VUV (high VUV response) can be reasonably associated with energy transfer mechanisms that enable the material to scintillate efficiently. Unfortunately such a high response is missing in the excitation spectrum of the *d-f* emission (trace a). This explains why there is almost no *d-f* emission under 80 nm excitation (Fig. 1). On the contrary the spectra b) and c) show much higher VUV response, although the host emission is excited more efficiently in the “host peak” (probably of excitonic origin) at about 200 nm. The high VUV response of the *f-f* emission suggests that Pr^{3+} ions are efficient recombination centers of electron-hole pairs generated by ionizing radiation but, at the same time, the relaxation losses of the recombining e-h pair prevent efficient excitation of the higher lying *d*-levels. The different appearance of the host peak in traces b) and c) can be explained, most likely, by the second order effects (compare the VUV peak at 110 nm). The presence of *f-d* bands in the excitation spectrum of the *f-f* emission can be explained by the population of ^3P_J terms by downward cascade transitions following excitation into *d*-levels (trace b). The weak *f-d* band in trace c is most likely due to some contribution of the *d-f* emission at 430 nm. We note also that the position of the host peak allows to make a rough estimate of the bandgap energy in $La_2Be_2O_5$. This energy should be close to 6.2 eV.

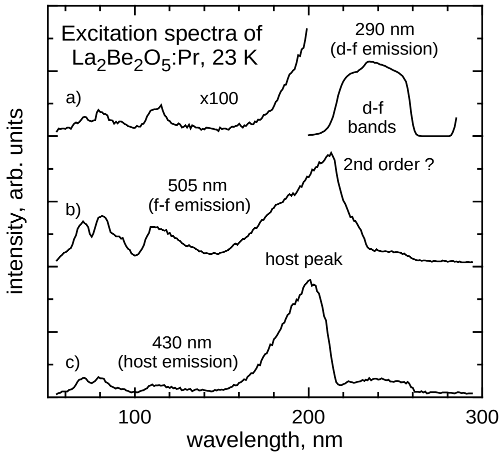

Figure 2: Uncorrected excitation spectra of $La_2Be_2O_5$:Pr at 23 K. The consecutive traces were shifted vertically. The emission wavelengths were set at 290 nm (trace a, the excitation spectrum of the d-f emission), 505 nm (trace b, f-f emission), and 430 nm (trace c, host emission). The d-bands (trace a) are probably distorted because of the high concentration of Pr (1%). Note the weak VUV response of the d-f emission (factor 100) and very high VUV response of the f-f emission.

Finally in Fig. 3 we present the emission spectra obtained under excitation into *f-d* bands at 250 nm designated "integrated". (thick solid line) and "time gated" (thin solid line). The spectra were scaled to aim comparison. The traces overlap in the range of the *d-f* emissions but differ in the range of the *f-f* emissions suggesting that the decay time of *f-f* emissions must be significantly longer than that of the *d-f* emissions. We note that the *d-f* emission bands in $La_2Be_2O_5$:Pr cover wide range of wavelengths in UV from about 280 to 420 nm.

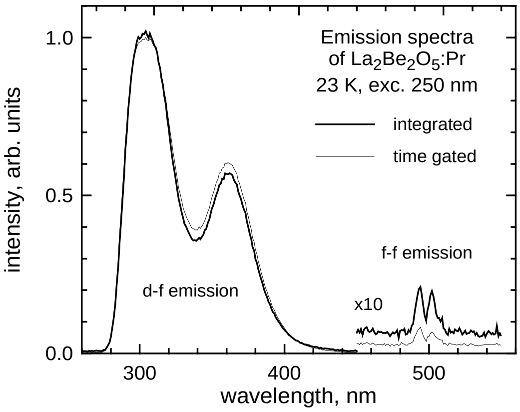

Figure 3: Uncorrected emission spectra of $La_2Be_2O_5$:Pr at 23 K. The excitation wavelength was set at 250 nm. For designation of the curves see text.

We have also measured time profiles under UV and VUV excitations for various emission wavelengths and temperatures. In particular under the 250 nm excitation the time profile measured at 300 nm shows a single exponential decay with a time constant of about 20 ns. The decay time does not change too much with temperature up to 300 K. These results will be fully reported later.

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