VUV spectroscopy of wide bandgap materials
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A B S T R A C T
In this paper we will present VUV spectroscopy experiments performed at the Superlumi station of Hasylab, DESY, Hamburg, on samples of BaF₂ crystals activated with Ce and BaF₂ (Ba,La)F₂ crystals activated with Er. The results of these experiments include time resolved luminescence and luminescence excitation spectra obtained under wavelength selective VUV and UV excitation by pulsed synchrotron radiation.

We will reveal the information provided by the VUV/UV excitation spectra of the Ce³⁺ 5d⁰ → 4f as well as Er³⁺ 4f⁰¹⁰ → 4f⁰¹¹ and 4f¹⁰ emissions on energy transfer mechanisms from the fluoride host to the rare earth ion. We will demonstrate that the fast energy transfer channels involve bound excitons while the generation of free electrons and holes leads to slower processes dependant on hole and/or electron trapping.

We will demonstrate that differences between the excitation spectra of the 5d → 4f emission in Ce and 4f¹⁰ → 4f¹¹ emission in Er activated BaF₂ are generated by the coupling of the 4f⁰ → 5d transition to the 4f¹⁰ core of the Er³⁺ ion. We will also identify the additional band, absent for Ce, which is due to the exchange split high spin (HS) state of the 4f¹⁰5d configuration responsible for the slow decay of the excited Er³⁺ ions in BaF₂ and (Ba,La)F₂.

Finally we will provide evidence and explain why the dominant VUV 4f¹⁰ → 4f¹¹ Er³⁺ emission in BaF₂ is spin-forbidden and slow while in the mixed (Ba,La)F₂ crystals it is spin-allowed and fast.

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1. Introduction
The surge of interest in VUV spectroscopy of solid state materials is largely due to new and demanding applications such as UV and VUV solid state lasers, fast and efficient scintillators and new “quantum-cutting” phosphors driven by mercury-free discharge radiation. At the forefront of materials considered for these attractive new applications are wide bandgap materials activated with rare earth ions.

An important additional incentive is provided by disparity between easily accessible model programs providing energies for a large number of emission and absorption lines of rare earth ions and scarce experimental results especially in the UV and VUV spectral ranges. We note that the so-called “extended Dieke’s” diagram based on model calculations partly verified by experiment and covering energies above 40,000 cm⁻¹ has been established only recently [1,2]. Experimental verification for some of these energies is still missing [3].

We also note that the VUV excitation spectra of rare earth emissions reflect various mechanisms of energy transfer from the host to the ion enabling evaluation of e.g. scintillator materials. The annual Hasylab reports published on-line provide numerous examples, see e.g. 1.

In this paper we report experimental studies of UV and VUV luminescence from Ce and Er activated crystals of BaF₂ and Er activated mixed crystals of (Ba,La)F₂ using wavelength selective, pulsed synchrotron radiation. The results that we have obtained confirm and extend earlier studies of other fluorides [3], as well as provide some new experimental observations, such as fast and efficient VUV emission from (Ba,La)F₂:Er.

2. Crystals and experimental set-ups
The Ce and Er doped samples of BaF₂ and (Ba,La)F₂ were cut from larger boules grown by Optovac Inc. (North Brookfield, MA, USA) using the Bridgman method. The concentration of Ce in the melt was 0.015 and 0.05 mol% for the Ce-doped boules of BaF₂. The 0.05 mol% boule was co-doped with Na (0.2 mol%) to minimize interstitial fluorine compensation. The Er concentrations in Er-doped boules of BaF₂ were 0.05 and 0.2 mol% in the melt. The (Ba,La)F₂ boule contained 30 mol% of La and 0.2 mol% of Er. The samples were not subjected to any chemical reducing procedure. They
were of high optical quality, clear, displayed no color, no inclusions and no indication of oxygen contamination.

The VUV/UV experiments (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, was also given by Zimmerer [4].

For excitation we have used a primary 2 m normal incidence monochromator in 15° McPherson mounting, equipped with the holographic concave grating (1200 groves/mm), coated by emission (323.5 nm) measured at 10 K from the sample of BaF$_2$:3. Experimental results and discussion

In Fig. 1 we present time resolved excitation spectra of the Ce emission 323.5 nm) measured at 10 K from the sample of BaF$_2$:0.05 mol%Ce, 0.2 mol%Na at 10 K. The spectra have been corrected using a salicylate standard. Resolution was 0.12 nm, step 0.5 nm. Black line, signal accumulated in the time window set at 2-42 ns (“fast” spectrum), red line, 150–190 ns (“slow” spectrum). For details see text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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For excitation we have used a primary 2 m normal incidence monochromator in 15° McPherson mounting, equipped with the holographic concave grating (1200 groves/mm), coated by Al $+$ MgF$_2$ (50–330 nm). The resolution was 0.32 nm.

For emission we have used two monochromators: the home-made 0.5 m Pouey VUV monochromator (f/2.8, fixed resolution of 1.1 nm), 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). Resolution of this monochromator depended on the adjustable slit width and the grating inserted.

We have used three gratings, one having 1200 g/mm (2.7 nm/mm) and blazed at 300 nm and two others having 300 g/mm (10.8 nm/mm) and blazed at 300 and 500 nm, respectively.

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The lowest HS d-level and terminating at consecutive lowest states of the 4f11 configuration. Arrows indicate calculated positions of d-bands corresponding to transitions from 0.1 nm. To expose fine details part of the spectrum was multiplied by a factor of 20 at 10 K. Excitation was 153 nm (maximum of LS band). Resolution was 1.1 nm, step was set at 0.5 and 0.01 nm, respectively. Black arrows indicate positions of the relevant 4f11 levels. For details, see text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The lowest energy, high spin (HS) d-level of the 4f105d Er3+ configuration.

It is interesting to note a peak and a corresponding indentation at 133.9 nm in the red and black line spectra shown in Fig. 2. This observation strongly suggests that there are two separate processes providing excitation of VUV and VIS Er emissions that compete for the excitation photons. We identify these two processes as direct Er3+ d-excitation leading mostly to d–f VUV emission and an Er-bound exciton exciting f–f VIS emission of Er3+ [9].

None of the spectra shown in Fig. 2 reveals a significant VUV sensitivity suggesting a lack of good response to ionizing radiation. A very weak VUV signal at 547 nm is, as revealed by the emission spectrum under VUV excitation (not shown), mostly due to the STE emission and not to emission from Er ions.

The 163.5 nm emission band, dominating the spectrum shown in Fig. 3, is generated by the slow spin forbidden optical transition between the lowest energy, high spin (HS) d-level of the 4f115d Er3+ configuration [10] and the ground state of the 4f11 Er3+ configuration by an electron moved to the lowest energy 5d orbital. The transition energies are therefore increased by energies corresponding to transitions between the consecutive states (3I6, 3F7, 3F6) of the 4f10 configuration (Ho3+ ion), producing higher lying bands in the excitation spectrum of the Er3+ d–f emission.

The bands shown in Fig. 2 have been labeled by the J-values corresponding to the consecutive 4f10 states reached by a given transition. The lowest states of the Er3+ 4f115d configuration must have a total spin S equal to 5/2 or 3/2 hence we have used the "LS" label to designate a spin 3/2 level and a spin-allowed transition band (the ground state is 4I15/2, spin 3/2) while "HS" designates a spin 5/2 level and a spin-forbidden transition band.

The arrows in Fig. 2 indicate energies of 4f11 levels calculated by Piatkowski [12] in the framework of the free ion approximation by diagonalization of the appropriate energy matrix. M.F. Reid's f-shell empirical programs were used to evaluate the energy parameters. The experimental values of only low energy levels (up to 35,000 cm−1) from the absorption spectrum of BaF2:0.2 mol% Er were included in the calculations which provided, nevertheless, theoretical energies for all the states of the 4f11 configuration. The root mean square deviation between the experimental and calculated energies was 90 cm−1.

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Of the five states, 2F(2)5/2, 2F(2)7/2, 2G(2)7/2 and 2G(2)9/2, only one, 2F(2)5/2, fits some sharp line features in the spectra. None of the remaining four states is expected to play any role. In particular the 2G(2)7/2 levels overlap the centers of strong allowed d-bands and any contribution from them is highly unlikely. Even if there is some weak absorption into one of those levels, it must be immediately depleted nonradiatively into the overlapping d-level as the configuration coordinate parabola of the d-level intersects the f-level parabola near its minimum.

In Fig. 3 we show time-integrated emission spectrum under 153 nm excitation (d-band) at 10 K. The spectrum has not been corrected for spectral sensitivity of the set-up. To aid presentation two different vertical scales have been used to expose fine details of the spectrum. The arrows indicate calculated positions of bands corresponding to transitions originating at the lowest d-level and terminating at the lowest levels of the 4f11 configuration. The agreement between experimental and calculated positions of bands in the VUV range of wavelengths is reasonably good.

In Fig. 4 we present a time-integrated excitation spectrum of the 4S3/2–4I15/2 green Er emission at 10 K for the sample of (Ba,-La)F2:0.2 mol% Er. The spectrum resembles the spectrum measured for VUV emissions in Er-activated BaF2 and shown in Fig. 2
of 143.2 nm and the (LS, larger splittings we expect a lower transition energy, hence a red with the spin-orbit coupling, for splitting of the 5d(e) levels. For low symmetry crystal field component is responsible, together change (increase) the low symmetry crystal field component. The presence of compensating fluorine interstitial ions is expected to brought about by a large La co-doping; the resultant massive pres-

133.9 nm. The shift of d-bands reflects the change in crystal field 4f105d state multiplied by a factor of 10 in order to expose a weak spin-forbidden band on the short wavelength side of the first spin-allowed band peaking at 157 nm. We note that positions of all the bands in (Ba,La)F2 are shifted in comparison to BaF2: the (HS, J = 8) band peaks at 164.6 instead of 162.1 nm, the (LS, J = 8) band peaks at 157 instead of 153 nm, the (LS, J = 7) band peaks at 148.5 instead of 143.2 nm and the (LS, J = 6) band peaks at 138.1 instead of 133.9 nm. The shift of d-bands reflects the change in crystal field brought about by a large La co-doping; the resultant massive presence of compensating fluorine interstitial ions is expected to change (increase) the low symmetry crystal field component. The low symmetry crystal field component is responsible, together with the spin-orbit coupling, for splitting of the 5d(e) levels. For larger splittings we expect a lower transition energy, hence a red shift of relevant absorption bands, as observed experimentally.

We note that shifts of d-levels results in the change in relative positions of 4f11 levels. Calculated positions of the five relevant 4f11 levels are shown by arrows. We observe that the two 4G(2)/2 levels no longer overlap the maxima of LS bands but fall between two of the 2F(2)/2 levels, which, in BaF2, was positioned half way between the LS and HS bands, now overlaps the LS band. In Fig. 5 we show the time resolved VUV/UVM emission spectra of (Ba,La)F2:Er under excitation into the 157 nm, spin-allowed band where the black line presents “fast”, and a red line - “slow” time window spectra. There is also shown a time-integrated emission spectrum under excitation into the 165 nm spin-forbidden band. The “slow” spectrum clearly demonstrates that most of the emission is fast (the decay time is 46 ns) but there is also a slowly decaying band at 170 nm at the longer wavelengths side of the dominant “fast” band at 162.3 nm that becomes visible for longer delays. The “slow” band at 170 nm dominates the spectrum under the 165 nm excitation corresponding to the spin-forbidden transition to the lowest HS state of the 4f105d configuration, as expected.

We observe that in both materials, BaF2:Er and (Ba,La)F2:Er, the VUV emission resulting from direct excitation into the lowest energy (HS, J = 8) level, is slow, as expected. This is no longer the case for higher d-level excitations. In BaF2:Er excitation into the 153 nm LS band is followed by relaxation and slow emission from the (HS, J = 8) level. In (Ba,La)F2:Er excitation into the LS band at 157 nm band corresponding to the (LS, J = 8) level, is followed by a fast, spin-allowed emission from the same level with almost no relaxation to the lower (HS, J = 8) level.

The obvious conclusion must be that relaxation between the lowest LS and HS levels is strongly enhanced when the 2F(2)/2 level is positioned between them. This is the case in BaF2 but in (Ba,-La)F2, where stronger lower symmetry crystal field component shifts the lowest d-levels downwards, is not.

In Fig. 6 we show a simple configuration coordinate model for the three relevant electronic states of the Er3+ ion in BaF2 and (Ba,-La)F2, 4f11 2F(2)/2, 4f105d (HS, J = 8) and 4f105d (LS, J = 8). We assume that all the 4f11 states, in particular the ground state 4I15/2 (not shown) and the 4F(2)/2 level (black solid line) assume equilibrium positions for the same value of the configuration coordinate, namely zero. The equilibrium positions of the two lowest energy 4f105d state parabolas were chosen to fit experimental values of appropriate transitions from absorption (excitation) and emission spectra. From the figure it is clear that in BaF2 the 4F(2)/2 level

Fig. 4. Time integrated excitation spectrum of Er emission at 550 nm in (Ba,La)F2:0.2 mol%Er at 10 K. Resolution was 0.32 nm, step 0.5 nm. The red line shows part of the spectrum multiplied by 10 to expose the low intensity HS band peaking at 165 nm. Arrows indicate calculated positions of 4f11 levels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Uncorrected VUV/UVM emission spectra of (Ba,La)F2:0.2 mol%Er at 10 K. Black and red lines present time resolved emission spectra under 157 nm (LS band) excitation. Resolution was 1.1 nm, step 0.1 nm. Blue line presents time integrated emission spectrum under 165 nm excitation (HS band). Resolution was 1.1 nm, step 0.05 nm. Arrows indicate calculated positions of d-bands corresponding to transitions originating from the lowest LS level and should be compared to positions of the spin-allowed “fast” bands (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Configuration coordinate diagrams showing energies of two 4f105d states, (HS, J = 8) and (LS, J = 8), and one 4f11 state, 4F(2)/2 of Er3+ ion in BaF2 (left), and (Ba,La)F2 (right). The parabolas of the excited 4f11 state and the ground 4f11 state, 4I15/2, assume minimum energy at zero. The equilibrium positions of d-states parabolas have been shifted to fit experimental transition energies from excitation and emission spectra. Note the shifts of d-level electronic energies responsible for relative position of the 4f11 level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
them. In (Ba,La)F₂ situation is different and nonradiative relaxation contribute to the nonradiative transition (relaxation) between the two d-levels must be, and apparently is, much slower.

4. Summary and conclusion

In this paper we have presented selected examples illustrating the significance of VUV spectroscopy in studies of wide bandgap materials activated with rare earth ions.

VUV/UV excitation spectra help to identify and evaluate various channels of energy transfer from the host to the emitting ion. We have pointed out that, in addition to direct excitation of the ion, there is also a fast and efficient channel involving excitons bound to the ion. Direct optical excitation into the band corresponding to this process is followed by fast and efficient emission with no delay and no rise time. On the contrary, free excitons are unlikely to transfer their energy to the ions creating, instead, self-trapped excitons (STE).

We note that for the rare earth bound exciton a significant fraction of energy is lost to lattice relaxation so that, consequently, no VUV/UV emission can be excited and observed.

The VUV excitation with photon energies exceeding bandgap energy generates free electron-hole pairs that may be consecutively trapped and recombined in the vicinity of the rare earth ion with transfer of recombination energy to the ion. Since the intermediate step in this process involves the rare earth bound exciton no high energy 4f⁻¹5d or 4f⁰ levels can be excited. Consequently the Ce⁴⁺ ion with its near UV d−f transition stands a chance to be good radiative recombination center while Er⁵⁺, emitting in the VUV/UV, does not.

The VUV excitation spectra provide, therefore, a convenient test revealing how good a given material is in response to ionizing radiation. This is important in applications involving detection of gamma and/or X-ray radiation.

We have demonstrated that comparison between excitation spectra of light (here Ce) and heavy (Er) rare earth ions reveals interesting and important differences in their electronic structure.

The excitation spectra of heavy ions reveal additional weak bands corresponding to spin-forbidden transitions from the ground state to the exchange split HS states of the 4f⁰−15d configuration. Unlike for the Ce⁴⁺ ion, for which the structure of excited states is fully described by the crystal field split d-level, in Er⁵⁺ the excited states of the 4f⁰5d configuration are determined by excited states of the d-electron as well as of the 4f⁰ configuration, changing the number and positions of bands in the excitation (absorption) spectrum.

We have also demonstrated that studies of VUV emission and excitation spectra can provide important information concerning radiative and nonradiative relaxation of highly excited rare earth ions. In particular we have demonstrated that nonradiative relaxation between consecutive LS and HS energy levels of the Er⁴⁺ 4f⁰5d configuration may be relatively slow. In consequence it is possible to observe fast and efficient emission from the LS level as in Er activated (Ba,La)F₂. In BaF₂:Er, where d-levels are shifted because of modified crystal field, fast nonradiative relaxation from the LS to HS level is facilitated by a 4f¹¹ 2F(2)15/2 level located almost exactly halfway between them. Consequently the VUV emission of BaF₂ is dominated by slow, spin-forbidden transition between the HS level of the 4f⁰5d configuration and the ground state 4f¹¹ 4I₁₅/₂.

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