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Cross-luminescence in mixed BaF₂-LaF₃ crystals

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BaF₂ crystals have attracted attention as fast scintillator after the discovery of fast UV luminescence. Despite of the nanosecond decay of well-known cross-luminescence [1] with the main emission bands at 5.6 and 6.35 eV, the effective response time of this scintillator is notably slowed by the self-trapped exciton (STE) emission peaked at 4.3 eV ($\tau \sim 620$ ns) at room temperature (RT) [2]. The contribution of the unwanted slow self-trapped exciton emission band can be considerably reduced by La - impurity doping as shown earlier [2]. Recent investigations of the mixed BaF₂- 0.1% LaF₃ crystals have revealed the new emission in the region of 7-8 eV [3]. The intensity of the new VUV emission increases together with the La doping concentration. Taking into account crystallographic-chemical considerations and experimental observations the new emission was tentatively assigned to the radiative electron transition from the charge compensating fluorine sub-band to the Ba 5p core band. In this study we applied time-resolved luminescence spectroscopy in order to study peculiarities of VUV emissions in BaF₂- 5% LaF₃ samples in more detail. Experiments were carried out using SUPERLUMI station and a luminescence setup connected to the BW3 beamline. Luminescence was recorded in time-integrated mode and in time-windows with a length Δt delayed by δt . The emission spectra were not corrected for sensitivity of the detection system.

Fig. 1a presents luminescence spectra of pure BaF₂ crystals and those of doped by LaF₃ excited by continuous X-rays and VUV photons. In accordance with [3] the weak VUV emission (note the logarithmic intensity scale) appears down to 8 eV in the doped samples. The onset of cross-luminescence excitation coincides with that observed for undoped samples and does not show significant temperature dependence as expected (Fig. 1b). These facts can be interpreted in an agreement with [3] that the Ba 5p holes participate in radiative recombination with electrons and not the respective core states of La ions. Moreover, in samples doped with LaF₃ the absorption edge in VUV is also shifted towards the lower energies by ~ 0.6 eV in respect of that in pure BaF₂. As can be seen on Fig. 1a, the short-wavelength edge of cross-luminescence exhibits also shift of similar size. Therefore, in La-doped BaF₂ the new sub-band formed from states of charge compensating fluorine interstitials is adjacent to the valence band consisting of 2p electronic states of F ions situated at their regular lattice sites.

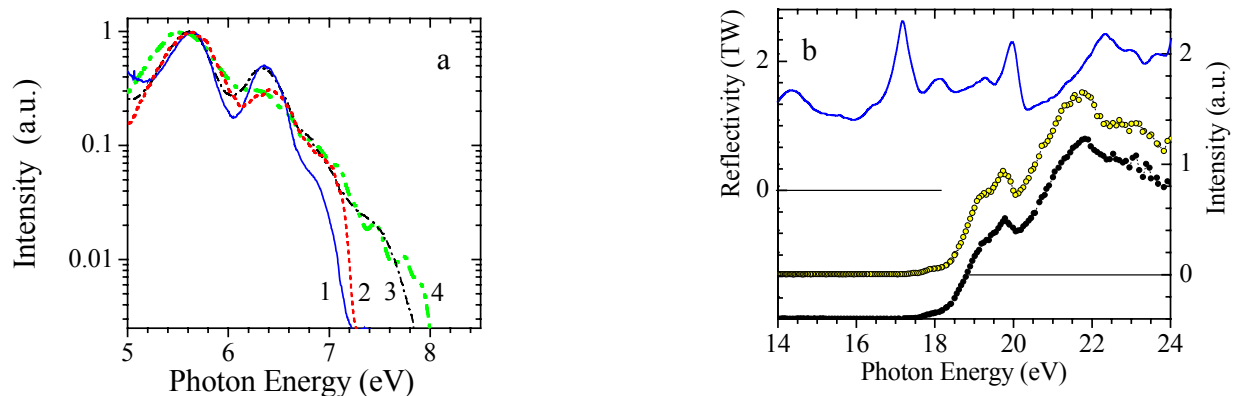


Figure 1: (a) Emission spectra of undoped BaF₂ crystal (1, 2) and BaF₂-5%LaF₃ (3,4). Crystals were excited by continuous x-ray (1,3) or by 21.9 eV photon pulses (2,4) at 300 K. (b) Time-resolved excitation spectra for 5.6 eV emission of BaF₂-LaF₃ at 300 K (o) and at 10 K (•). The spectra (also curves 1,3) were recorded within a time-window ($\delta t=0$ and $\Delta t=3$ ns). Blue line is the reflectivity spectrum at T=10 K.

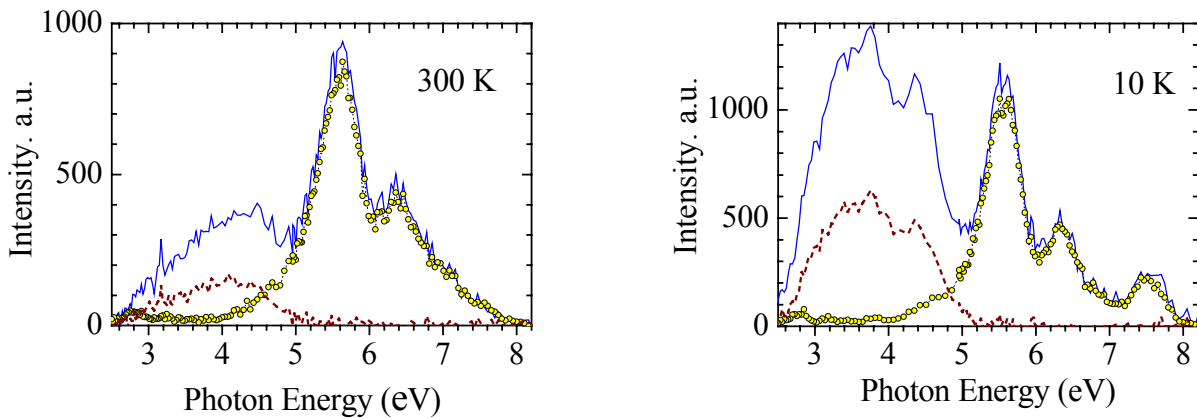


Figure 2: Emission spectra of BaF₂-LaF₃ crystal excited by 88.7 eV photons. The spectra were recorded in time-integrated mode (blue lines) and within a short time-window (symbols; $\delta t=0.12$ and $\Delta t= 1.5$ ns) and a long time-window (dashed line, $\delta t=54$ and $\Delta t=59$ ns).

It has been shown in [4] that weak VUV emissions can be conveniently studied under inner-shell excitation revealing much more details. In one hand such excitation is more bulk sensitive due to the reduced absorption coefficients in comparison with the energy region near intrinsic absorption edge. On other hand the experimental conditions are more favourable in the XUV region due to the reduced level of scattered VUV background, in particular using time-resolution in combination with undulator beam-lines like the BW3 at HASYLAB.

Fig. 2 demonstrates time-resolved emission spectra from a BaF₂- 5% LaF₃ crystal excited in the energy region of Ba 4d absorption. It is obvious that VUV emissions are pronounced in a better way than in Fig. 1a. In addition to the slow STE emission with maximum at 4.3 eV, the broad luminescence band extends to the UV region. This structure can be tentatively assigned to the superposition of emission centres due to imperfections introduced in the BaF₂ lattice by La impurity and radiation defects formed under XUV radiation. At RT the emission in the fast time-window has two maxima typical for cross-luminescence. The practically structureless tail extending to 8 eV originates from transitions of the fluorine interstitials sub-band. At 10 K a new band peaked at 7.6 eV becomes visible as was observed earlier in pure BaF₂ [4]. Its absence at RT and under low energy excitation (20 eV) shows that very unlikely it can be related to the sub-band formed from fluorine interstitials. Recent photoemission study of BaF₂ films at liquid nitrogen temperature provided an indication that the spin-orbit splitted (~ 2 eV) Ba 5p sub-bands might have a gap prohibiting hole relaxation. Therefore, similar interpretation applied for pure BaF₂ can be used in La doped crystals. As discussed in Ref. 4, the 7.6 eV emissions originates from the electron transitions from F 2p valence band to the lower Ba 5p_{1/2} sub-band while the main 5.6 eV cross-luminescence band belongs to the transitions F 2p – Ba 5p_{3/2}. At higher temperatures phonon assisted hole relaxation bridges this gap and the respective emission disappears.

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