Core-level excitation and excitonic processes in heavy ternary fluorides

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Recent advances in high-energy physics calorimetry, X-ray imaging, and time-resolved medical diagnostics have created a strong demand for ultrafast scintillator materials capable of delivering a major fraction of their scintillation response within the first nanosecond following excitation. In the search for such materials, we synthesized powder samples, determined their crystal structures, and, in selected cases, grew small single crystals of a set of novel heavy ternary fluorides, including $CsLu_2F_7$, Cs_2HfF_6, $CsTaF_6$, $BaLuF_5$, $BaLu_2F_8$, Ba_2HfF_8 etc. These compounds possess high stopping power and a high effective atomic number Z_{eff}, as well as a wide band gap that facilitates the observation of ultrafast Cherenkov radiation, cross-luminescence, and intraband luminescence. The synthesized compounds were studied by high temporal resolution spectroscopy techniques, employing excitation by a pulsed electron beam at the Institute of Physics in Tartu (IRF~60 ps) and VUV photons at the synchrotron radiation beamlines FinEstBeAMS at MAX IV (IRF~180 ps) and P66 at DESY (IRF~130 ps). The guiding objective of this study was to identify energy relaxation processes responsible for the branching between the two types of intrinsic emission, namely fast cross-luminescence and relatively slow excitonic emission.

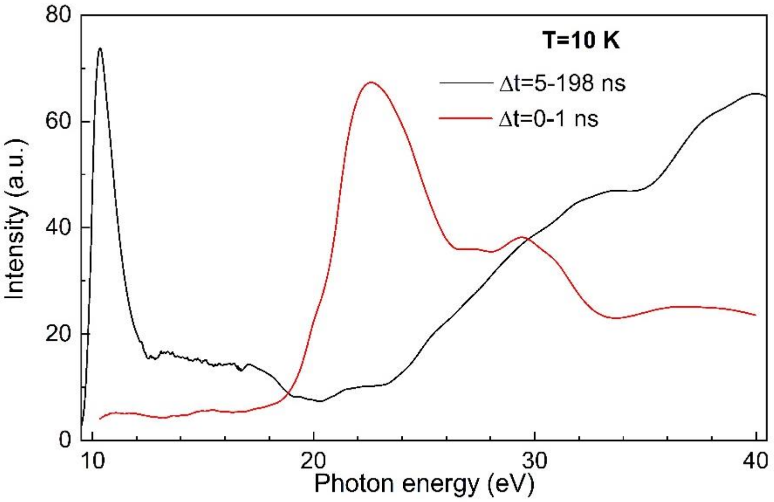

Figure 1. Excitation spectra of fast and slow decay components recorded for the 290 nm emission of $BaLuF_5$ at T=10 K.

For the first time, a correlation between core-level excitation and excitonic processes in heavy ternary fluorides has been reliably established. An exceptionally intense luminescence of an excitonic origin was discovered in several of the investigated materials (Cs_2HfF_6, $CsTaF_6$). This emission is attributed to excitons whose electron component is localized in the 5d states of the heavy elements Hf or Ta while the hole component resides in the F 2p states. The position of the excitonic band in the excitation spectrum of the emission was found to depend strictly on the energy position of the heavy-element d states in the electronic band structure. No cross-luminescence could be detected in these compounds. In contrast, in compounds exhibiting relatively weak excitonic emission, cross-luminescence is clearly observable ($CsLu_2F_7$, $BaLuF_5$, Ba_2HfF_8). Time-resolved excitation spectra reveal that the excitation efficiency of the fast component associated with cross-luminescence increases gradually starting from a threshold energy characteristic of Cs or Ba core level excitation and then decreases significantly at higher excitation energies where the creation of two or more excitons by a single incident photon becomes possible. This behaviour directly evidences competition between core-band excitation and excitonic relaxation channels, as illustrated for $BaLuF_5$ (Fig. 1) The mechanisms governing the interaction between core-level excitations and excitons will be discussed, and application prospects of novel cross-luminescent materials will be considered.