VUV-UV-Visible Luminescence of Nd\(^{3+}\), Er\(^{3+}\) and Tm\(^{3+}\) in Ternary Fluoride Single Crystals

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Fast scintillators emitting in VUV spectral region can be coupled with position-sensitive detectors filled with photosensitive gases or with the other VUV-sensitive detectors and used in special imaging techniques. Wide band-gap fluorides can be used for this purpose and the Nd\(^{3+}\) ion provides fast 5d-4f emission around 180-190 nm in the host lattices like LaF\(_3\), LiYF\(_4\), BaF\(_2\), BaY\(_2\)F\(_8\) and others [1]. Also other rare earth ions, namely Er\(^{3+}\) and Tm\(^{3+}\) can provide 5d-4f emission even further high energy shifted to 160-170 nm [1]. Such high energy shift is attractive due to increasing sensitivity of mentioned photosensitive gases towards higher energies in VUV region, but due to spin forbidden 5d-4f transition of Er\(^{3+}\) and Tm\(^{3+}\) the dominant part of this emission is released with microsecond decay times.

In this study 5d-4f and 4f-4f emission and decay kinetics characteristics of the Nd\(^{3+}\), Er\(^{3+}\) and Tm\(^{3+}\) singly and doubly doped LiLuF\(_4\) [2] and BaY\(_2\)F\(_8\) [3] hosts were studied in VUV spectral range at room temperature (RT) at SUPERLUMI I experimental station of HASYLAB. Measurements were completed by the absorption, radio- and photoluminescence measurements in VUV-visible spectral range in Institute of Physics, Prague and Tokuyama, Sendai. The Nd\(^{3+}\), (Nd\(^{3+}\), Er\(^{3+}\)) and (Nd\(^{3+}\), Tm\(^{3+}\)) doped LiLuF\(_4\) and BaY\(_2\)F\(_8\) samples were prepared by micro-pulling-down technique in Tokuyama and Tohoku university, respectively, in the form of few cm long rods with the diameter of about 2 mm from which the polished plates of 2x8x1 mm were prepared for the experiments. The concentrations of the RE dopants in the melt were 1% of Nd\(^{3+}\) codoped with 0.1-99% of Er\(^{3+}\) or Tm\(^{3+}\) in several concentration steps.

In LiLuF\(_4\) host the 5d\(_1\) based emission of all Nd\(^{3+}\), Er\(^{3+}\) and Tm\(^{3+}\) ions is accompanied by 4f-4f luminescence transitions in UV-visible region. Luminescence from 5d\(_1\) state of Nd\(^{3+}\) at 240 and 260 nm is ascribed to transition ending at the \(^{4}F_{5/2}\) and \(^{4}H_{6}\) multiplet and there are the same nanosecond decay times measured in the 180, 240 and 260 nm. Both ions (Er\(^{3+}\), Tm\(^{3+}\)) show strong absorption bands at 256 nm, 260 nm respectively, which in principle can enable the cross-relaxation process from the Nd\(^{3+}\) 5d\(_1\)-4f to 4f-4f Er\(^{3+}\) (Tm) transitions. Fig 1 represents an example of the radioluminescence spectra of samples with different concentration of Tm ions. The decrease of intensity in the Nd\(^{3+}\) 5d-4f emission bands with the growing concentration of codopants is obvious. Loss of intensity in 5d-4f bands is accompanied by the increasing intensity of 4f-4f emission lines. At higher
concentrations of Tm and Er ions there is an additional concentration quenching effect on 4f-4f emissions of both ions. The most serious drawback of these double doped systems consists in the shortening of Nd\textsuperscript{3+} 180 nm emission decay time with increasing concentration of Er\textsuperscript{3+} (Tm\textsuperscript{3+}), see the decay example and its concentration dependence in Fig. 2 and its inset, respectively. As the decay time of 180 nm emission gets shorter even under 160 nm excitation, i.e. under the direct excitation of Nd\textsuperscript{3+} center it means that probably the above mentioned cross-relaxation process brings away the energy from the 5d\textsubscript{1} excited state of Nd\textsuperscript{3+}. Furthermore, additional concentration quenching in the 4f-4f transitions is evidenced in shortened decay times: \(^{3}\text{Po-}^{4}\text{He}\) transition of Tm\textsuperscript{3+} at 287 nm shows decay times of 103, 63, 48 \(\mu\text{s}\) for 0.1, 1, 10\% of Tm\textsuperscript{3+}, respectively. Analogously, shortened decay times of \(^{4}\text{S}_{3/2}^{1/2}\) transition of Er\textsuperscript{3+} at 551 nm show values of 486, 265, 207 \(\mu\text{s}\) for 0.1, 1.0, 10\% of Er\textsuperscript{3+}, respectively.

The emission spectrum of the BaY\textsubscript{2}F\textsubscript{8}:Er\textsubscript{10\%} sample under 147nm excitation is shown in the fig. 2. Two 5d-4f luminescence transitions to the Er\textsuperscript{3+} ground state are observed. The fast luminescence originating from the spin-allowed low spin (LS) state and slow one from the spin-forbidden high spin (HS) state are peaking at 161 and 169nm, respectively, but each of them seems to contain both fast and slow components. The excitation spectrum for the 185nm Nd\textsuperscript{3+} emission of the Er-free BaY\textsubscript{2}F\textsubscript{8}:Nd\textsubscript{1\%} sample is also included.

Concluding, in both the LiLu\textsubscript{4} and BaY\textsubscript{2}F\textsubscript{8} single crystal hosts the emission characteristics of Nd\textsuperscript{3+}, Er\textsuperscript{3+} and Tm\textsuperscript{3+} centers were measured. In doubly doped systems, the cross-relaxation and energy transfer phenomena were evidenced and are the subject of continuing research. This research is supported by II-20052049 EC and I-20090104 EC projects of DESY Hamburg.

References

