



VUV-UV-visible luminescence of Nd^{3+} , Er^{3+} and Tm^{3+} in LiLuF_4 single crystal host

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ABSTRACT

An overlook of absorption and luminescence characteristics of Nd^{3+} , Er^{3+} and Tm^{3+} centers in LiLuF_4 single crystal is provided. Single crystal doped with the mentioned RE ions were prepared by micro-pulling-down technique in the form of few cm long rods with the diameter of about 2 mm. Excitation and emission spectra and fast decay kinetics in VUV spectral region were measured at SUPERLUMI station at synchrotron DESY, Hamburg and characterization was further completed in UV-visible region at conventional spectrophotometers. Observed absorption and emission peaks are ascribed to the 5d–4f and 4f–4f optical transitions in the doped rare earth ions. Concentration dependence of the decay kinetics is discussed.

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1. Introduction

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 (Schotanus et al., 1989). 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_2F_8 and others (Visser et al., 1993; Becker et al., 1998). 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 (Becker et al., 1998; Gesland et al., 1999). 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 (Wegh and Meijerink, 1999; Pieterse et al., 2002).

In LiYF_4 host the luminescence from 5d₁ state of Nd^{3+} shows the dominant band at about 190 nm due to transition 5d–4f_x (Visser et al., 1993). Luminescence of Er^{3+} and Tm^{3+} in LiYF_4 host shows the dominant 5d₁–4f_{15/2} spin-forbidden (HS) and spin-allowed (LS) transitions within 160–170 nm, with the decay times of the order of several nanoseconds (LS) and several microseconds (HS) (Wegh

and Meijerink, 1999; Zimmerer, 2007). In all three ions the 5d₁ based emission is accompanied by slow 4f–4f luminescence transitions in UV-visible region.

In this paper the absorption and luminescence spectra and emission decays will be provided for Nd^{3+} , (Nd^{3+} , Er^{3+}) and (Nd^{3+} , Tm^{3+}) doped LiLuF_4 host. This host was chosen due to elevated density of 6.17 g/cm³. Concentration dependences of emission spectra and decays will be discussed as well.

2. Experiment

The Nd^{3+} , (Nd^{3+} , Er^{3+}) and (Nd^{3+} , Tm^{3+}) doped LiLuF_4 samples were prepared by micro-pulling-down technique (Yoshikawa et al., 2007) in the form of few cm long rods with the diameter of about 2 mm from which the polished plates of 2 × 8 × 1 mm were prepared for the experiments. The concentrations of the RE dopants in the melt were 1% of Nd^{3+} codoped with 0.1, 1, 10, and 99% of Er^{3+} or Tm^{3+} .

The experiments were performed at the DESY Synchrotron in Hamburg (Germany) using the SUPERLUMI experimental station of HASYLAB (Becker et al., 1998; Gesland et al., 1999; Wegh and Meijerink, 1999; Zimmerer, 2007). With this setup the high-resolution spectra in the range of 90–600 nm were recorded. Emission and excitation spectra were measured by the microsphere-plate detector (MSP, for VUV) or microchannel plate detector (MCP, for UV). The samples were measured at room temperature (RT). Excitation spectra were corrected for the

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intensity of the synchrotron radiation and spectral dependence of excitation monochromator throughput. Using deconvolution procedure (SpectraSolve package, Ames Photonics) the decays curves were fitted by multiexponential functions. Luminescence and absorption characteristics in VUV were combined with those in UV-visible where the latter were measured at spectrometer Shimadzu 3101PC and spectrofluorometer 99S in Prague. Furthermore, transmittance and radioluminescence of some of the fluoride samples were also measured at a VUV setup in Sendai, Tokuyama Co. in Sendai.

3. Results and discussion

The transmittance and absorption measurements (Fig. 1.) show that with increasing concentration of dopants the absorption increases.

In all three ions the 5d₁ based emission is accompanied by 4f–4f luminescence transitions in UV-visible region. Luminescence from 5d₁ state of Nd³⁺ at 240 and 260 nm is ascribed to transition ending at the ⁴F_x and ²H_x multiplet and there are the same nanosecond decay times measured in the 180, 240 and 260 nm. Both ions (Er³⁺, Tm³⁺) show strong absorption bands at 256 nm, 260 nm respectively, which in principle can enable the cross-relaxation process from the Nd³⁺ 5d₁–4f to 4f–4f Er³⁺ (Tm) transitions (Duan et al., 2007).

Fig. 2a,b represents the radioluminescence spectra of samples with different concentration of RE ions. The decrease of intensity in the Nd³⁺ 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 which will increase further the total emission energy loss. There is practically no emission in the Er(Tm)99% doped samples.

The sum of energy emitted from 5d₁–4f + 4f–4f transitions can be calculated from the RL spectra. The result shows that singly-doped sample emits the same amount of energy from 5d₁ and 4f states. With growing codopant concentration the 5d₁ energy decrease and 4f emission grows (tables in Fig. 2 a,b).

The most serious drawback of these double doped systems is consists in the shortening of Nd³⁺ 180 nm emission decay time with increasing concentration of Er³⁺(Tm³⁺), see inset of Fig. 3. As

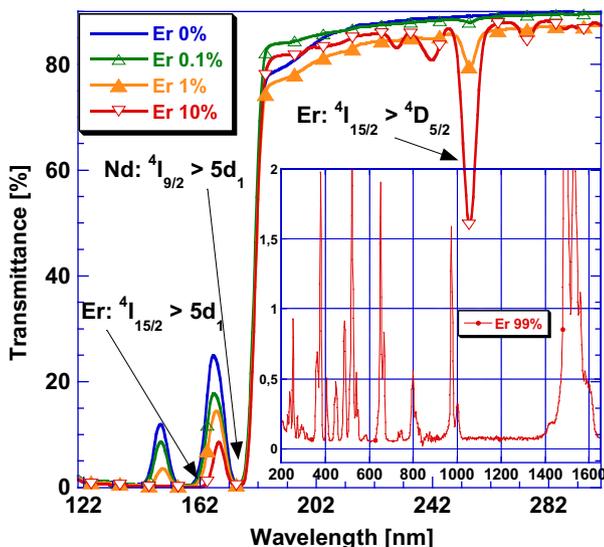


Fig. 1. Transmittance of LiLuF₄: Nd 1%, Er x%; 120–300 nm measured in Japan combine with absorption measurement 200–2600 nm from Prague.

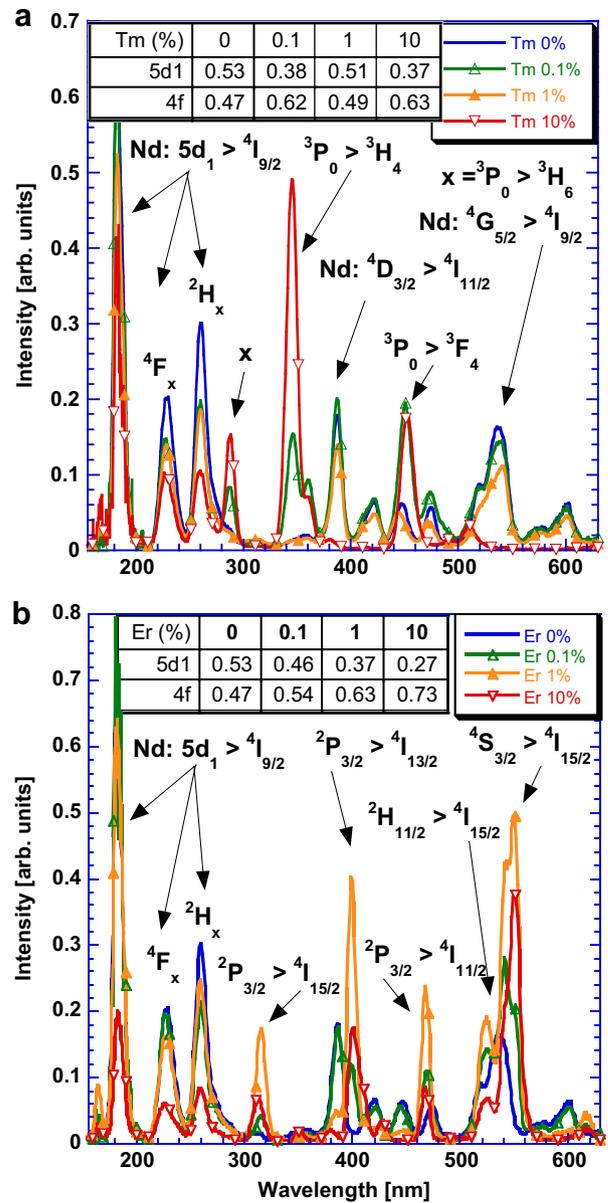


Fig. 2. Radioluminescence measurements combine 150–240 nm spectra from Japan and 210–650 nm spectra from Prague. Table represent sum of energy emitted from 5d₁ and 4f states. a) Emission bands of LiLuF₄: Nd 1%, Tm x%; b) Emission bands of LiLuF₄: Nd 1%, Er x%.

the decay time of 180 nm emission gets shorter even under 160 nm excitation, i.e. under the direct excitation of Nd³⁺ center it means that there is some energy transfer mechanism (probably the above mentioned cross-relaxation process) which brings away the energy from the 5d₁ excited state of Nd³⁺. Furthermore, additional concentration quenching in the 4f–4f transitions is evidenced in shortened decay times: ³P₀–³H₆ transition of Tm³⁺ at 287 nm shows decay times of 103, 63, 48 μs for 0.1, 1, 10% of Tm³⁺, respectively. Analogously, shortened decay times of ⁴S_{3/2}–⁴I_{15/2} transition of Er³⁺ at 551 nm shows values of 486, 265, 207 μs for 0.1, 1.0, 10% of Er³⁺, respectively.

Codoping with Er³⁺ and Tm³⁺ ions in LiLuF₄:Nd1% results in the appearance of additional slower decay components in Nd³⁺ emission, see Fig. 3, which point to radiative or nonradiative energy transfer from codoped ions to Nd³⁺.

In low concentration Tm and Er sample the decay time of Nd³⁺ emission at 180 nm is about 18.7 ns, perfectly consistent with Nd-

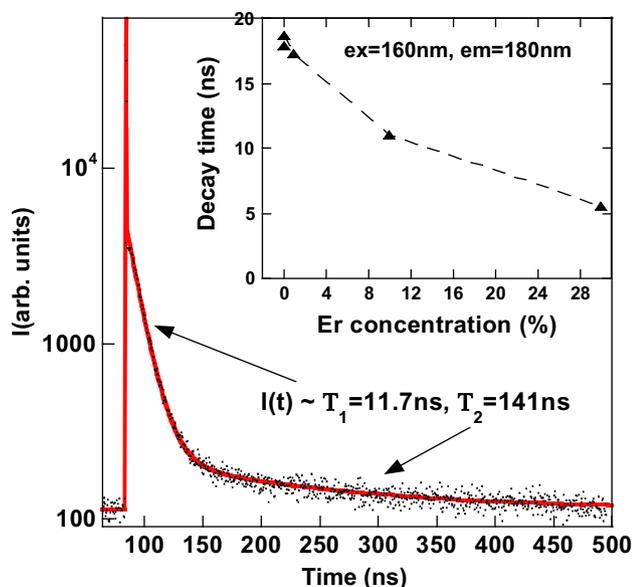


Fig. 3. PL decay of LiLuF₄:Er³⁺ 10%, Nd³⁺ 1%, ex = 145 nm, em = 180 nm. In the inset dependence of the decay time of Nd³⁺ 5d–4f emission on Er³⁺ concentration is given (Nd³⁺ 1%).

only doped samples. This agreement is also supported by total sum of energy emitted from 5d₁–4f + 4f–4f transitions calculated from RL spectra (tables in Fig. 2a,b). Energy transfer from Nd³⁺ to Er or Tm ions is minimal in these low concentrations.

The decay time of the 240 nm and 260 nm emissions is identical with that measured in the 180 nm band which proves the same starting 5d₁ level from which the deexcitation occurs for all the 180, 240 and 260 nm. Under excitation at 145 nm (directly to Er³⁺) the 240 nm and 260 nm bands contain noticeable part of slow components. These findings give further support for the hypothesis that energy transfer Er³⁺(Tm³⁺)–Nd³⁺ does exist but its quantitative evaluation requires further experiments.

4. Conclusions

At Er³⁺(Tm³⁺) concentration of about 10% there is clear decrease of the decay time value of Nd³⁺ fast VUV emission which decreases its intensity and points to nonradiative energy transfer away from the 5d₁ excited state of Nd³⁺. This highly unwanted phenomenon is

responsible for the deterioration of fast VUV light output and is tentatively ascribed to possible resonance of the 5d₁-originated Nd³⁺ emission at 240 and 260 nm and absorption bands of Er³⁺(Tm³⁺) in the same spectral region.

Concentration quenching in 4f–4f emission bands of Er³⁺ (Tm³⁺) is evidenced from their shortened decay times with increasing Er (Tm) concentration.

Appearance of slower components in fast Nd³⁺ emission decay under the excitation in the region of Er³⁺(Tm³⁺) 4f–5d absorption points to the presence of radiative or nonradiative energy transfer between these ions. At the same time observed anticorrelations (not shown here) in the excitation spectra of Er³⁺(Tm³⁺) and Nd³⁺ emission bands do not support such a hypothesis and additional experiments are needed to understand rather complex energy exchange mechanism among these ions.

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References

- Becker, J., Gesland, J.Y., Kirikova, N.Yu., Krupa, J.C., Makhov, V.N., Runne, M., Queffelec, M., Uvarova, T.V., Zimmerer, G., 1998. Fast VUV emission of rare earth ions (Nd, Er, Tm) in wide bandgap crystals. *J. Alloys Compounds* 275–277, 205–208.
- Duan, Ch., Tanner, P.A., Makhov, V.N., Kirm, M., 2007. Vacuum ultraviolet spectra and crystal field analysis of YAlO₃ doped with Nd³⁺ and Er³⁺. *Phys. Rev. B* 75, 195130.
- Gesland, J.Y., Khaidukov, N.M., Kirikova, N.Yu., Kirm, M., Krupa, J.C., Makhov, V.N., Uvarova, T.V., Queffelec, M., Zimmerer, G., 1999. VUV emission of stoichiometric Er³⁺ – and Tm³⁺ – containing fluoride crystals. *J. Electron Spectrosc. Relat. Phenomena* 101–103, 579–582.
- Pieterse, L., van., Reid, M.F., Burdick, G.W., Meijerink, A., 2002. 4f_n–4f_(n-1)5d transitions of the heavy lanthanides: experiment and theory. *Phys. Rev. B* 65, 045114.
- Schotanus, P., Dorenbos, P., van Eijk, C.W.E., Hollander, R.W., 1989. *IEEE Trans. Nucl. Sci.* 36, 132–136.
- Visser, R., Dorenbos, P., van Eijk, C.W.E., Meijerink, A., den Hartog, H.W., 1993. *J. Phys. Cond. Matter* 5, 8437–8460.
- Wegh, R.T., Meijerink, A., 1999. *Phys. Rev. B* 60, 10820–10830.
- Yoshikawa, A., Nikl, M., Boulon, G., Fukuda, T., 2007. Challenge and study for developing of novel single crystalline optical materials using micro-pulling-down method. *Opt. Mater.* 30, 6–10.
- Zimmerer, G., 2007. SUPERLUMI: a unique setup for luminescence spectroscopy with synchrotron radiation. *Rad. Measur.* 42, 859–864.