Concentration Dependence Study of VUV-UV-Visible Luminescence of Nd^{3+} and Gd^{3+} in $LuLiF_4$

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Abstract

An overview of absorption and luminescence characteristics of Nd^{3+} and Gd^{3+} centers in a $LiLuF_4$ single crystal host is provided. Single crystals doped with the above rare earth ions were prepared by micro-pulling-down technique in the form of rods a few cm long with a diameter of about 2 mm. Excitation and emission spectra and fast decay kinetics in VUV and UV spectral regions were measured at room temperature. The observed absorption and emission peaks are due to the 5d-4f and 4f-4f optical transitions of Nd^{3+} and Gd^{3+} centers. Concentration dependence of the decay kinetics is also discussed.

1. Introduction

R&D of new, fast scintillators is a very topical problem due to the demanding new applications in the medical, security and scientific fields. Fast scintillators emitting in VUV spectral region can be coupled with position-sensitive detectors filled with photosensitive gases or with other VUV-sensitive detectors and used in special imaging techniques [1]. Wide band-gap fluorides are the best single crystal host for this purpose, and the Nd^{3+} ion provides fast 5d-4f emission around 180-190 nm in the host lattices like LaF_3, $LiYF_4$, $LuLiF_4$, BaY_2F_8 and others [2-4], while the oxide hosts are not suitable for this purpose due to the overlap of the lowest lying 5d levels with the 4f ones [5]. High energy shifted Nd^{3+} emission, i.e. the weak crystal field of the host, is attractive due to increasing sensitivity of the above mentioned photosensitive gases towards higher energies in VUV region. Due to low energy yield of single Nd^{3+}-doped crystals the codoping with other rare earth (RE) ions, namely Er^{3+} or Tm^{3+}, has been recently studied as a tool to improve energy transfer from the host to Nd^{3+} emission centers and to consequently increase the light yield [6,7].

In this paper, the absorption and luminescence spectra and emission decays are provided for the Gd^{3+}, (Nd^{3+}, Gd^{3+}) doped $LiLuF_4$ host. This host was chosen because of the elevated density of 6.17 g/cm^3 and easy crystal growth enabled by its congruent melting [8]. The possibility of enhancing energy transfer to the Nd^{3+} center by Gd^{3+} codoping is explored. Concentration dependences of emission spectra and decays are discussed as well.

2. Experiment

The Nd^{3+} and (Nd^{3+}, Gd^{3+}) doped $LuLiF_4$ and $GdLiF_4$ samples were prepared in Tokuyama Co. by micro-pulling-down technique [9] in the form of rods a few cm long with a diameter of about 2 mm from which the polished plates 2x8x1 mm in size were prepared for the experiments.

Concentrations of the RE dopants in the melt were 1% or 4% of Nd^{3+} codoped with 1%, 4% and 10% of Gd^{3+} respectively. The concentration is described by the atomic percentage of RE's referred to Lu.

Luminescence spectra and decays of Nd and Gd-doped $LuLiF_4$ and undoped $GdLiF_4$ were measured at the DESY Synchrotron in Hamburg (Germany) using the SUPERLUMI experimental station of HASYLAB [10]. With this setup the high-resolution spectra in the range of 50-650 nm were recorded where integral, fast (0-10 ns gate with respect to the excitation pulse) and slow (85-95 ns gate with respect to the excitation pulse) emission components are provided. Emission and excitation spectra were measured by the microsphere-plate detector (MSP, for VUV) or microchannel plate detector (MCP, for UV) [10]. All the measurements were performed at room temperature (RT).

Emission spectra are not corrected for spectral dependence of sensitivity of the detection part, while the excitation ones are corrected for spectral dependence of excitation intensity. This correction can induce artifacts below some 70 nm due to low excitation intensity. More specifically, the excitation spectra were corrected for the intensity of synchrotron radiation and spectral dependence of excitation monochromator throughput using acetylsalicylate [11]. The luminescence decays curves were fitted by multiexponential functions using the convolution procedure and least square sum fitting routine (SpectraSolve package, Ames Photonics). VUV characteristics were further completed with the UV-visible absorption and radioluminescence (RL) spectra measured at spectrometer Shimadzu 3101PC and custom-made 5000M fluorometer model, Horiba Jobin Yvon, respectively, in Prague. RL was measured under X-ray excitation (40 kV, 15 mA).

3. Results and discussion

Gd doped $LuLiF_4$

The absorption spectra of $GdLiF_4$ and (Nd,Gd)-doped $LuLiF_4$ in Fig. 1 show peaks related to 4f-4f transitions of the Nd^{3+} and Gd^{3+} centers. There is practically no absorption of Gd^{3+} above 320 nm, and there is no or very little overlap of the Nd^{3+} and Gd^{3+} absorption peaks between 200-600 nm. With increasing concentration of the dopants the absorption amplitude in all peaks increases and no other effect is observed.
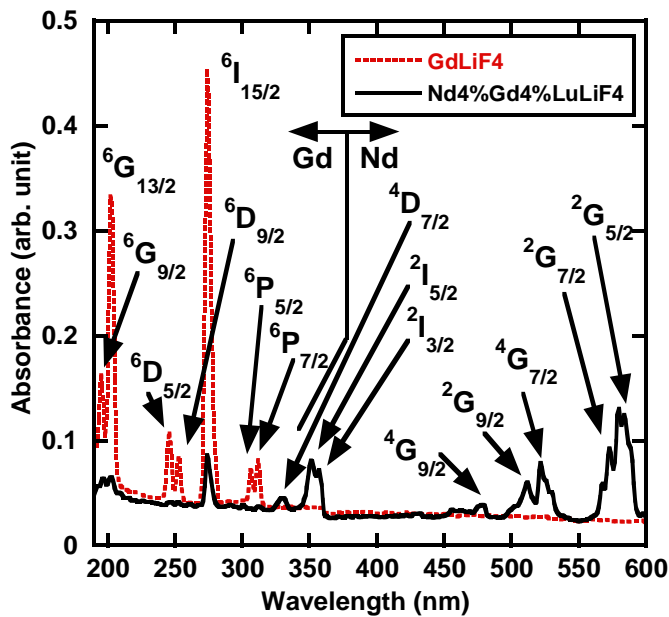

Fig. 1 Absorption spectra of $GdLuLiF_4$ and $LuLiF_4$: Nd4%, Gd4%, 1 mm thick samples; correction for reflectance was not made.

Fig. 2 presents RL spectra for different Nd3+ and Gd3+ concentrations. Luminescence from 5d1 state of Nd3+ at 240 and 260 nm is ascribed to the transition ending at the 4Fx and 2Hx multiplets,

and the same nanosecond decay time values have been measured in the 180, 240 and 260 nm bands (see below). With increasing concentration of Gd a small decrease in emission intensity in the Nd 5d1-4f transitions at 230 and 260 nm could be observed. With increasing concentration of Gd3+ the emission intensity of Nd3+ above 340 nm decreases. The Gd3+ has no absorption bands in this spectral range and it is not clear what causes such an effect. Samples with 4% Nd concentration have practically equally intense luminescence as those with lower concentration. These results point to some kind of energy transfer or additional concentration quenching effect on 4f-4f emissions of both ions, which will further increase the total emission energy loss.
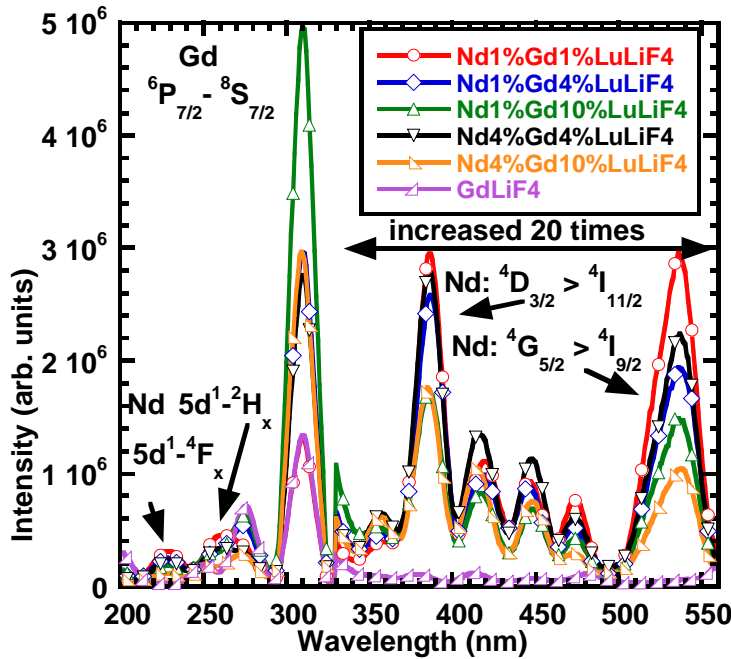
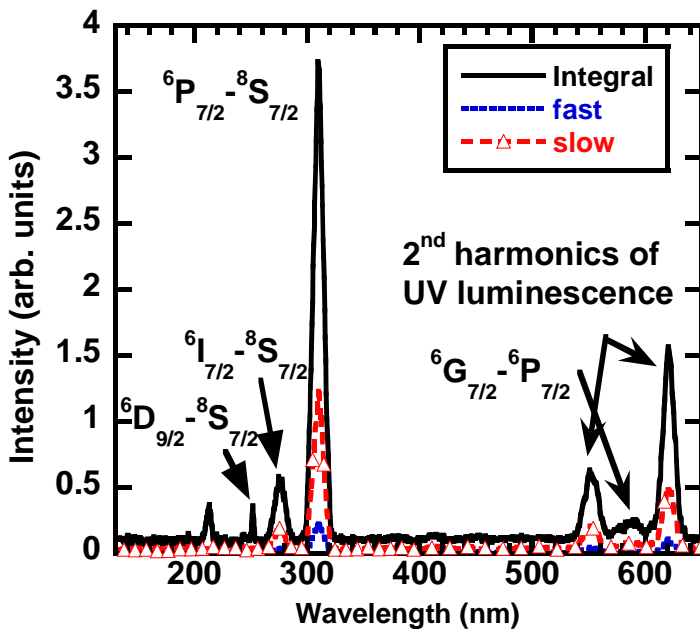Fig. 2 Radioluminescence spectra of LuLiF$_4$: Nd x%, Gd x%, RT.

Fig. 3 Emission spectra of GdLiF$_4$, exc=126 nm, RT.

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In Fig. 3 the line spectrum of Gd^{3+} ions is presented under excitation into the band edge of the $GdLiF_4$. The emission lines are ascribed to Gd^{3+} transitions, only the 212 nm line does not have an appropriate interpretation as it is considerably low-energy shifted from the nearest $^6G_{7/2}$-$^8S_{7/2}$ (at 203 nm) transition. The peaks at 551 and 621 nm are 2nd harmonic of the 275 and 312 nm UV lines, but between them there is the hint of $^6G_{7/2}$-$^6P_{7/2}$ transition between higher 4f levels of Gd^{3+} [12].
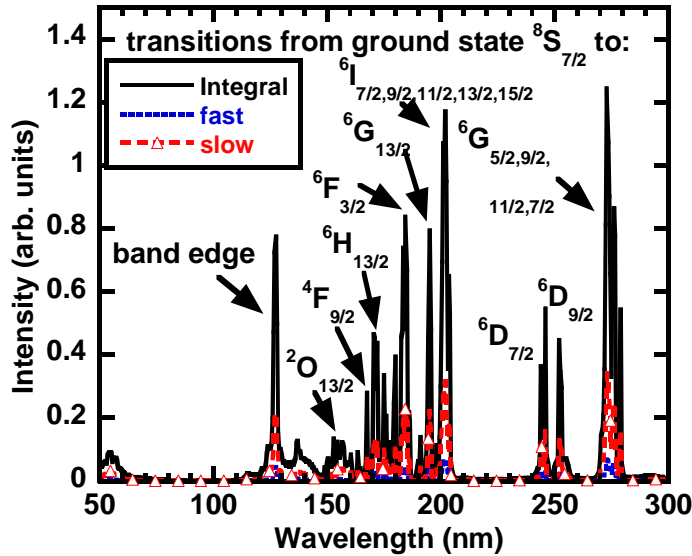

Fig. 4 Excitation spectra of $GdLiF_4$, em=312 nm, RT.

Excitation spectrum of the leading 312 nm line from Fig. 3 is displayed in Fig. 4 and it reflects plentiful level structure of Gd^{3+} transitions, see also [12]; the position of the band edge at about 126 nm is consistent with [13,14].

Nd, Gd-doped $LuLiF_4$

Under the band-to-band excitation, the PL spectrum in Fig. 5 shows a mixture of the Nd^{3+}-related and Gd^{3+}-related transitions.
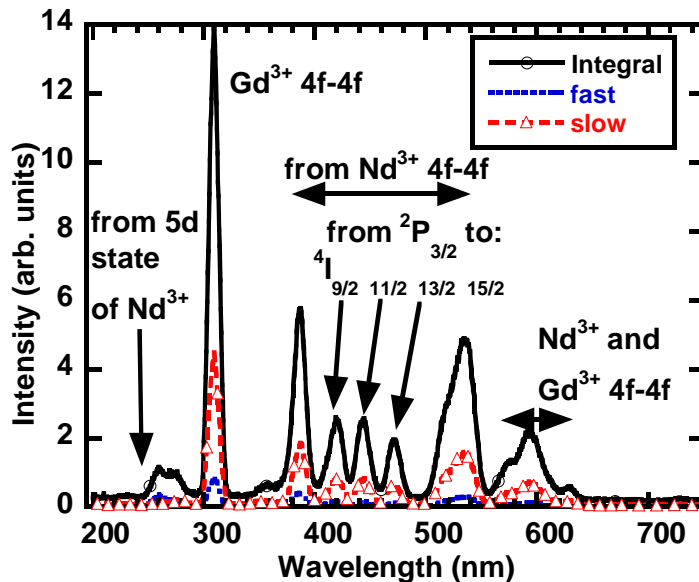

Fig. 5 Emission spectra of Nd1%Gd1% $LuLiF_4$, exc=124 nm, RT.

Excitation spectrum of the Gd^{3+} 312 nm emission in Fig. 6(a) shows very clearly the band edge of $LuLiF_4$ host; in the excitation spectrum of 5d-4f emission of Nd^{3+} Fig. 6(b), the band edge is masked by a strong 4f-5d excitation band of Nd^{3+} within 125-170 nm.
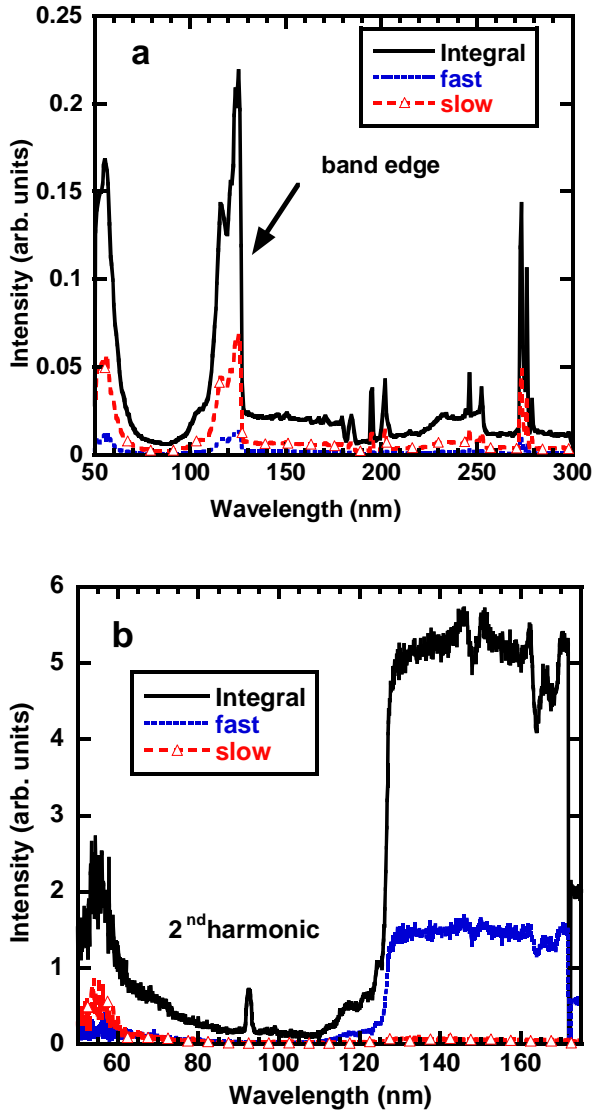
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Fig. 6 Excitation spectra of Nd1%Gd1% LuLiF$_4$ at RT, a) Gd^{3+} 4f-4f emission line em=312 nm, b) Nd^{3+} 5d-4f emission, em=185 nm.

PL decay was measured for several exc/em combinations: under the direct excitation of Nd^{3+} the fast 5d-4f emission in Fig. 7(a) shows a single exponential decay and a decay time of 19 ns. When the same emission is excited via the host band edge at 120 nm Fig. 7(b), the decay shows a rising part with the rise time of about 7 ns and decay time of 20 ns.

While the decay time is consistent with the previous measurements of this kind in Nd-doped LuLiF$_4$, it is not clear what is the origin of the 7 ns rise time in the decay under 120 nm excitation. Most probably it is due to an energy transfer from the host.
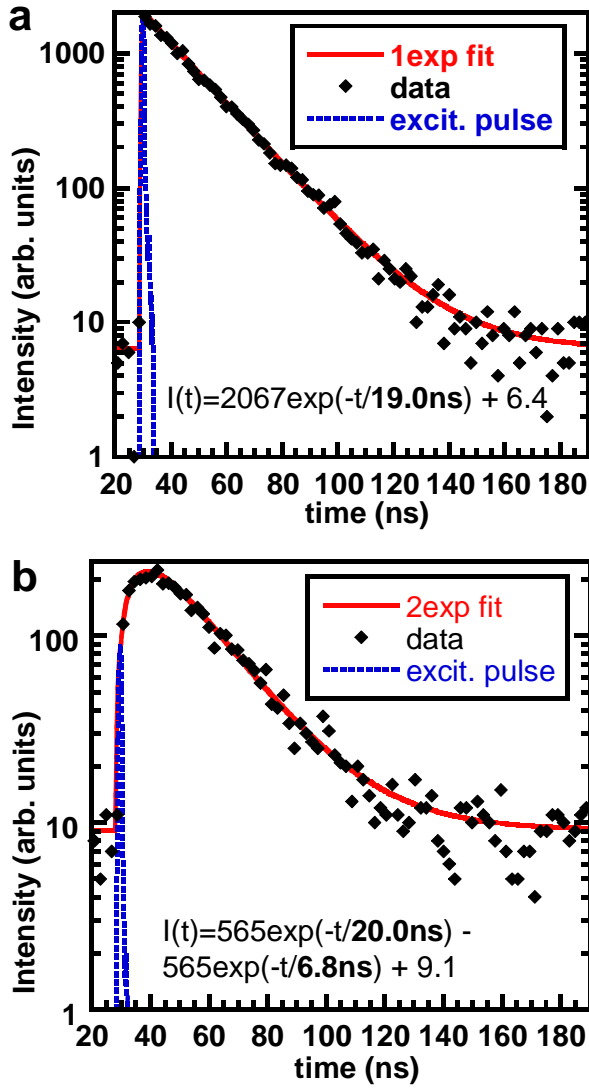
a

I(t)=2067exp(-t/**19.0ns**) + 6.4

b

I(t)=565exp(-t/**20.0ns**) - 565exp(-t/**6.8ns**) + 9.1

Fig. 7 Decays of the Nd^{3+} 5d-4f emission at 185nm under (a) exc=138 nm, (b) exc=120 nm; Nd 1% Gd 1% $LuLiF_4$ sample.

For higher Gd concentration, the analogous PL spectra were studied as in the case of Nd1% Gd1% sample in Fig. 6. Apparently, with increasing Gd concentration the Nd^{3+} emission lines are getting relatively weaker with respect to that of the Gd^{3+} at 312 nm. Direct excitation into the 4f-5d absorption band of Nd^{3+} (ex=128 nm) shows a fast 5d-4f emission band of Nd^{3+} peaking at 180 nm.

For Nd 1% Gd 4% concentration, the excitation spectrum of 312 nm line is analogous to Fig. 6(a). Apparently, excitation at the band edge is becoming relatively weaker with respect to excitation within the Gd^{3+} 4f-4f transitions around 200 nm and 275 nm, but in an absolute way it may be even more intense with respect to the Nd1% Gd1% sample in Fig. 6(a) if the measurement conditions are the same.

For Nd1% Gd4% sample, the fast 5d-4f decays in the 185 nm band of Nd^{3+} under excitation at 128 and 120 nm were measured. Under direct excitation into 4f-5d excitation band of Nd^{3+} at 128 nm the decay time is evaluated of 17.9 ns, i.e. slightly shorter with respect to Fig. 7(a) which might be the sign of an onset of energy transfer towards the Gd^{3+} whose concentration is four times higher compared with Fig. 7(a). Also, the energy transfer from the host is accelerated, as the rise time is shorter (2.9 ns) with respect to Fig. 7(b) (6.8 ns) so that its relation to the Gd^{3+} concentration cannot be excluded.
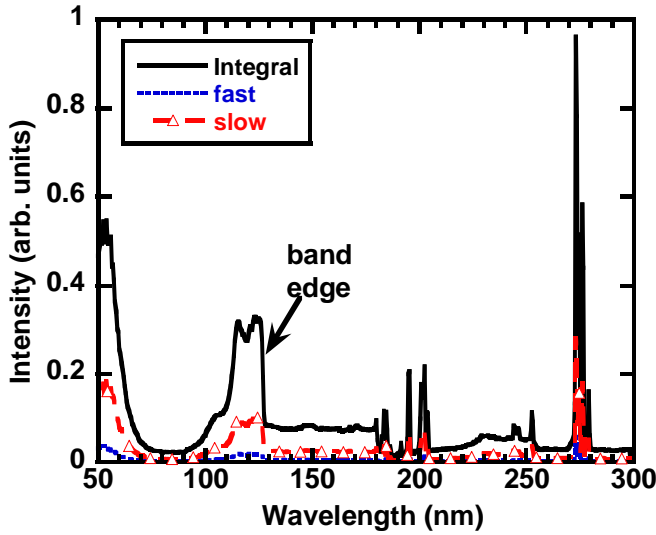
Fig. 8 Excitation spectra of Gd^{3+} line, em=312nm Nd 1% Gd 4% LuLiF$_4$, RT.

In Fig. 8 the excitation spectrum of 312 nm line is shown, analogous to Fig. 6(a). Apparently, excitation at the band edge is getting relatively weaker with respect to excitation within the Gd^{3+} 4f-4f transitions around 200 nm and 275 nm, but in the absolute way it may be even more intense with respect to the Nd1% Gd1% sample in Fig. 6(a) if the measurement conditions are the same. It is interesting to note that both in Fig. 6(a) and Fig. 8 there is clear excitation of 312 nm Gd^{3+} line in the 4f-5d excitation band of Nd^{3+} within 130-170 nm, i.e. energy is transferred from 5d state of Nd^{3+} to the Gd^{3+} 4f-4f lines most probably due to the overlap between 5d-4f 180 nm emission of Nd^{3+} and Gd^{3+} 4f-4f lines around 183-185 nm. This behavior is consistent with the above mentioned Nd^{3+} 5d-4f shortening of decay time.

Excitation spectrum of Nd^{3+} pertaining to the emission line at 415 nm is shown in Fig. 9; the energy transfer from Gd^{3+} pertaining to 4f-4f levels is apparent most probably due to good overlap of Nd^{3+} $^2L_{17/2}$ at about 31800-32200cm^{-1} and of Gd^{3+} $^6P_{7/2}$ level at about 32200 cm^{-1} (311 nm).
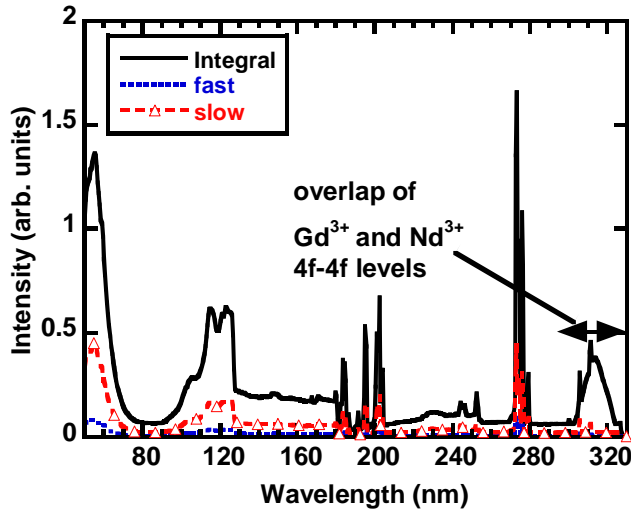

Fig. 9 Excitation spectra of Nd^{3+} at 410 nm pertaining to 4f-4f emission line, $^2P_{3/2}$-$^4I_{11/2}$ for Nd 1% Gd 10% LuLiF$_4$.

Decay curves of 5d-4f Nd^{3+} emission at still higher Gd10% concentration continue in the trend observed in the Nd1% Gd4% sample; the decay time value further decreases to 15.5 ns and the transfer from the host is further accelerated.

Fast 5d-4f decay times in the 185 nm band of Nd^{3+} are shown in Tab. 1. Under direct excitation into 4f-5d excitation band of Nd^{3+} at 128 nm, the dependence of decay time on different concentration of Gd is shown. The decay time is slowly decreasing from 19.0 to 15.5 ns with increasing concentration of Gd^{3+} ions. Also the energy transfer from the host under 120 nm

excitation is accelerated as the rise time in Tab. 1 is decreasing from 6.8 ns to 0.6 ns. With respect to samples with concentration of Gd around 10% further acceleration of the decay is observed, which can be understood in terms of the onset of the concentration quenching of the Nd^{3+} ions themselves.

	concentration (%) Nd^{3+} / Gd^{3+}				
	1/1	1/4	1/10	4/4	4/10
decay time 128nm – 185nm	19	17.9	15.5	16.1	14.9
decay time 120nm – 185nm	20	17.7	14.8	16.2	12.7
rise time 120nm – 185nm	6.8	2.9	0.6	0.8	0.4

Tab. 1 Dependence of decay time and rise time of LuLiF$_4$ samples doped with different concentration of Nd^{3+} and Gd^{3+}; the concentration is described by atomic percentage of REs referred to Lu.
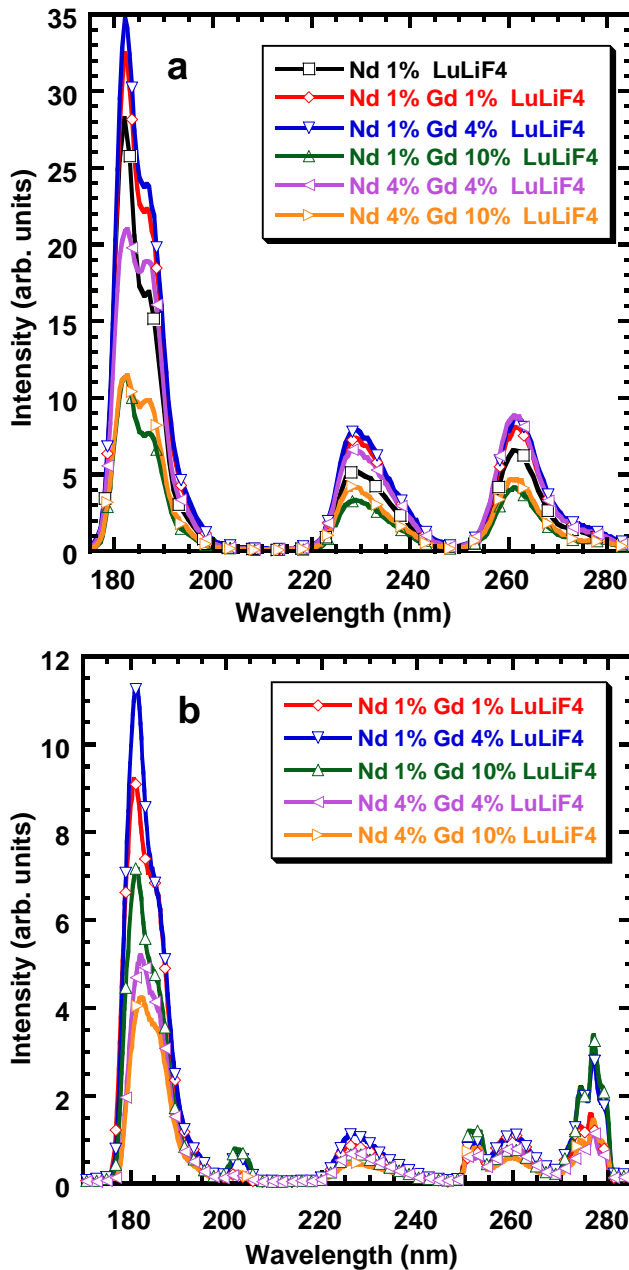

Fig. 10 Photoluminescence (a) and radioluminescence (b) spectra of Nd, Gd doped LuLiF$_4$, exc=160nm (a), X-ray, RT.

The dependence of photoluminescence and radioluminescence intensity of the doubly doped samples is presented in Fig. 10. The most intense PL and RL is observed for Nd1% Gd4% sample. There is an overlap of Nd^{3+} emission and Gd^{3+} absorption band around 185 nm. It is obvious that the increasing concentration of Gd^{3+} reduces the Nd^{3+} luminescence due to energy transfer from Nd^{3+} to Gd^{3+} centers. At the same time, the highest scintillation efficiency of Nd1% Gd4% sample points to the improved energy transfer to the 5d state of Nd^{3+}, which is due to Gd presence in the sample. Higher Nd concentration causes an additional concentration quenching effect and does not result in an increase in intensity luminescence intensity.

From the application point of view, so far, the $Nd:LuF_3$ single crystal is the best in terms of light yield and stopping power [15] followed by the $Nd,Gd:LuLiF_4$ one. However, large LuF_3 crystals are extremely difficult to grow due to incongruent melting and their cost is very high. Therefore, if the light yield of $Nd,Gd:LuLiF_4$ can be further improved, it might show the best figure-of-merit.

4. Conclusions

The undoped $GdLiF_4$ sample displays all the expected Gd^{3+} emission lines starting from $^6P_{7/2}$, $^6I_{7/2}$ and $^6D_{9/2}$ at about 311nm, 275 nm and 255 nm, respectively and also the transition $^6G_{7/2}$-$^6P_{7/2}$ at about 590 nm. In the excitation spectrum of the 311 nm line, a rich spectrum of the higher excited states of Gd^{3+} is nicely shown and the band edge of the material appears at about 127 nm at RT.

The essential features of the doubly doped Nd, Gd $LuLiF_4$ can be surveyed as follows:

Under the 124 nm excitation into the band edge of the host, relative intensity of the Nd^{3+} 4f-4f lines within 380-550 nm decreases with increasing concentration of Gd^{3+}, and the decay time of 5d-4f emission decreases as well which point to the energy transfer from the 5d state of Nd^{3+} into the Gd^{3+} lines around 183-185 nm and from 4f-4f states of Nd^{3+} to Gd^{3+} ones in spectral region of 210-290 nm. This conclusion is further supported by the appearance of the fingerprint of the 130-170 nm positioned excitation band of the 5d-4f emission of Nd^{3+} in the excitation spectrum of the Gd^{3+} 311 nm emission line.

Under the excitation into the band edge (exc=120 nm) there is several ns rise time in the decay of the Nd^{3+} 5d-4f 185 nm emission which is getting shorter with the increasing Gd^{3+} concentration.

Increase in Nd concentration from 1% to 4% in the samples with constant Gd10% concentration results to the distortion and further acceleration of 5d-4f Nd^{3+} decay at 185 nm which points to the onset of the concentration quenching in the Nd subsystem as such.

Further energy transfer from the Gd^{3+} belonging 4f-4f levels to the Nd^{3+} ones appears due to a good overlap of Nd^{3+} $^2L_{17/2}$ at about 31800-32200cm^{-1} with the Gd^{3+} $^6P_{7/2}$ level at about 32200 cm^{-1} (311 nm).

The Nd1% Gd4% sample shows the highest Nd^{3+} photoluminescence and radioluminescence intensity in the VUV region (em=185 nm) which is a proof of the positive effect of Gd^{3+} ion in the energy transfer towards Nd^{3+} center in the scintillation mechanism. Yet higher concentration of Gd^{3+} makes the energy transfer away from Nd^{3+} 5d state dominating and at the same time increase in Nd^{3+} above a few percent causes an additional concentration quenching as well.

We project fine concentration tuning of Nd and Gd dopants which might further increase the scintillation efficiency. Moreover, Czochralski growth of the optimized crystal composition is also planned, which should further improve the crystal quality and consequently the scintillation efficiency as well.

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