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VUV-UV-visible luminescence of Nd$^{3+}$, Er$^{3+}$ and Tm$^{3+}$ and energy distribution in LiLuF$_4$ single crystal host

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Abstract. It is the aim of this contribution to provide an overview of luminescence spectra and decay characteristics of Nd$^{3+}$, Er$^{3+}$ and Tm$^{3+}$ centers in LiLuF$_4$ single crystal including possible energy transfer mechanisms towards and away from the Nd$^{3+}$ 5d excited state. Single crystal doped with the mentioned RE ions were prepared by micro-pulling-down technique. Excitation and emission spectra and fast decay kinetics in VUV spectral region are completed with radio- and photoluminescence spectra and decay kinetics in UV-visible region.

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 [1, 7, 8]. Wide band-gap fluoride hosts can be used for this purpose and the Nd$^{3+}$ ions can act as suitable emission centers to obtain fast nanosecond emission around 180-190 nm due to 5d-4f transition of Nd$^{3+}$. Also other rare earth ions, namely Er$^{3+}$ and Tm$^{3+}$, exhibit 5d-4f emission in such hosts shifted to even shorter wavelengths around 160-170 nm [2, 3].

Previous measurements of luminescence and decay characteristics of doubly doped LiLuF$_4$ samples point to some energy losses mechanism [4]. It is the aim of this paper to provide an overview of the energy loss mechanism drawing the energy away from the 5d$^1$ excited state of Nd$^{3+}$. Overall scheme of energy transfer and conversion processes including their concentration dependences 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 [5] 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, 1, 10, and 30 mol% of Er$^{3+}$ or Tm$^{3+}$.

The experiments were performed at the DESY Synchrotron in Hamburg (Germany) using the SUPERLUMI experimental station [6] of HASYLAB. With this setup the high-resolution excitation and emission spectra in the range of 35-750 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 intensity of the synchrotron radiation and spectral dependence of excitation monochromator throughput. Using deconvolution procedure (SpectraSolve package, Ames Photonics) the decay curves were fitted by multiexponential functions. Luminescence, RL and absorption characteristics in VUV were combined with those in UV-visible where the latter were measured at spectrometer Shimadzu 3101PC and spectrofluorometer 199S in Prague.

3. Results and discussion

To identify the main process of energy losses from 5d\(^{1}\) Nd emission level, radioluminescence (RL) spectra in VUV and UV were measured. If there is some energy transfer between Nd and Er or Tm ions, the differences in emitted sum of light in VUV and UV region must be observed. RL spectra were measured in Sendai for VUV (35-250 nm) and in Prague for UV region (200-750 nm). VUV measurement is not corrected and due to this fact is not possible to glue together the spectra for Nd emission at 180, 230 and 260 nm. From these VUV spectra we can use the information that the same concentration dependence for those peaks was observed and the ratio of the intensity between 180 nm VUV and 230 and 260 nm UV Nd peaks is constant with different concentration of dopants. In the light of the fact that the ratio of intensities was constant, the Nd peaks at 230 and 260 nm from corrected UV spectra were used for further evaluations.

To identify the energy transfer process from Nd to Tm(Er), it will be studied: the absolute and relative sum of light emitted from 5d\(^{1}\)-4f and 4f-4f, the overlap of the emission and absorption peaks and concentration dependence.

Figures 1 and 2 present the RL emission spectra for different Tm\(^{3+}\) and Er\(^{3+}\) concentrations. The absolute sum of the energy emitted from the 5d\(^{1}\)-4f + 4f-4f transitions can be calculated from the RL spectra. With the increasing concentration of Er(Tm) small increase of intensity in the Nd 5d\(^{1}\)-4f transitions ended at 230 and 260 nm could be observed. This points to the energy transfer from Er (Tm) to Nd. At the concentrations higher than 10% the concentration quenching takes place and all the emission intensity decreases rapidly.

**Figure 1.** Radioluminescence spectra of LuLiF\(_4\) :Nd 1%, Er x%, RT.

**Figure 2.** Radioluminescence spectra of LuLiF\(_4\) :Nd 1%, Tm x%, RT.
The ratio between overall intensity emitted from Nd 5d\(^1\)-4f and other 4f-4f transitions gives us an idea about the relative amount of energy emitted from the samples and possible energy transfer from Er and Tm to 5d\(^1\) state of Nd. Changing of the intensity in Nd peaks proves this transfer.

The result in table 1 shows that Nd-only doped sample emits the 30 % energy from Nd 5d\(^1\) (interval 210-273 nm) and 70 % (interval 274-620 nm) from all other 4f states. With the increasing Er concentration the 5d\(^1\) energy decreases and the 4f emission intensity increase. In the case of Tm, we observe the decrease of the Nd 5d\(^1\) emission for concentration 0.1 and 1% and for higher concentrations the 5d\(^1\) emission intensity increase. The decrease of this intensity points to energy transfer not from dopants to Nd, but from Nd to dopants on the 4f-4f level. All is complicated by the concentration quenching process.

**Table 1.** Sum of relative/absolute RL response of LuLiF\(_4\):Nd 1%, Tm x%, Er x %, emitted from 5d\(^1\) and 4f states.

<table>
<thead>
<tr>
<th>Dopant, interval</th>
<th>Tm, Er concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Tm, 210-273 nm(^a)</td>
<td>1.4</td>
</tr>
<tr>
<td>Tm, 274-620 nm(^a)</td>
<td>3.9</td>
</tr>
<tr>
<td>Tm, 210-620 nm(^a)</td>
<td>4.8</td>
</tr>
<tr>
<td>Er, 210-273 nm(^a)</td>
<td>1.4</td>
</tr>
<tr>
<td>Er, 274-620 nm(^a)</td>
<td>3.3</td>
</tr>
<tr>
<td>Er, 210-620 nm(^a)</td>
<td>4.8</td>
</tr>
<tr>
<td>Tm, 210-273 nm(^b)</td>
<td>30.4</td>
</tr>
<tr>
<td>Er, 210-273 nm(^b)</td>
<td>30.4</td>
</tr>
</tbody>
</table>

\(^a\) Absolute response (arb. units).
\(^b\) Relative response, sum 210-620 nm=100% (%).

In the table 1, there are integral values of radioluminescence responses with increasing concentration of Tm\(^{3+}\) and Er\(^{3+}\). The absolute values of the intensities in the range from 210 nm to 276 nm are integrated and compared with the same integral values in range from 273 nm to 620 nm. The sum of these two values represents 100% of luminescence intensity in range from 210 nm to 620 nm. These intensities give us an idea about the amount of luminescence emitted from 5d\(^1\) to 4f states and from the 4f to 4f states. It is obvious that there are only small differences in the 5d\(^1\) region for small concentrations of dopants. Generally, for the higher concentrations the concentration quenching practically kills all the luminescence.

For 0.1 and 1% Er concentration an increase of intensity in the first interval (table 1) could be observed. This process is observed only for 0.1% Tm concentration (table 1). This means that the emission from the Nd 5d\(^1\) region is higher for the doped samples that the emission of the undoped ones. This points to mentioned energy transfer from dopants to Nd at 5d\(^1\) level. From the 1% concentration of Tm (Er) the decrease of the luminescence intensity on both intervals could be observed. This behavior shows that energy transfer process from dopants to Nd is reduced by another process.

This process could be explained by the overlap of the emission peak of Nd at 260 nm with Tm and Er absorption bands at 263 nm, 256 nm respectively. These overlaps caused the decrease of the intensity in these 5d\(^1\) Nd bands (figure 3). From figure 3 we can nicely see that the Nd 5d\(^1\)-2H\(_x\) transition, which ends at 260 nm, is tunneling by the 4f-4f transitions of Er and Tm starts at \(^4\)D\(_{5/2}\), \(^3\)P\(_2\) respectively. Also the other absorption bands in this area could contribute to this tunneling.
3.1. Mechanism of energy transfer and energy loss in (Nd, Er) and (Nd, Tm) doped LiLuF₄

Nice proof, that there is energy distribution process, is shown on figure 4, 5. There are no Er³⁺ (Tm³⁺) absorption bands around 180 nm, but one has to take into account that radiative deexcitation of 5d₁ level of Nd³⁺ can finish not only at the 4I ground state multiplet, but also at higher lying 4F and 2H multiplets, which can explain fast emission bands at about 230 nm and 260 nm, figure 4, 5. The decay time of the 230 nm and 260 nm emissions is identical with that measured in the 180 nm band; 18.18 ns, 18.25 ns which proves that all the three peaks are related to transitions starting from the same 5d₁ level. It is also worth noting in figure 8 that under excitation at 145 nm the 230 nm and 260 nm bands contain noticeable part of slow components. These are other evidences and support the idea that the energy transfer Er³⁺-Nd³⁺ to Nd 5d₁ level does exist.

Figure 3. RL spectra combine with absorption measurement. Overlap of Nd 5d⁻¹-4f transition with 4f energy levels of Er³⁺ and Tm³⁺.

Figure 4. Emission spectra in UV under excitation at 160 nm into 4I₉/₂⁻5d₂ absorption band of Nd³⁺, LuLiF₄: Nd 1%, Er 1%, RT.

Figure 5. Emission spectra in UV under excitation at 145 nm into 5d level of Er³⁺, LuLiF₄: Nd 1%, Er 1%, RT.
In case that the 230 nm and 260 nm fast emission bands related to the deexcitation of 5d$^1$ excited state of Nd$^{3+}$ are overlapped with the 4f-4f absorption band of Er$^{3+}$($^4D_{5/2}$) an energy transfer from Nd$^{3+}$ 5d$^1$ state to nearby lying Er$^{3+}$ ion can occur, figure 3.

The situation in (Nd, Tm) doped LiLuF$_4$ samples is quite analogous. Under the excitation at 145 nm the 230 nm and 260 nm bands contain same part of slow components. None-zero intensity of the slow component in the latter spectrum is due to the fact that the Tm$^{3+}$ HS emission is still excited even at 160 nm. Emission decay in 230 nm and 260 nm is again in the nanosecond time scale (14.85 ns, 14.45 ns) and the decay time value is the same as for the 180 nm band.

Under excitation at 145 nm (to the Er) the Nd 180 nm band contains noticeable part of slow components. In figure 6 there is the concentration dependence of this time and the shortening of decay time with the increasing concentration could be observed. These are other evidences and support for the idea that energy transfer Er$^{3+}$-Nd$^{3+}$ does exist.

![Figure 6](image_url)

**Figure 6.** Concentration dependence of Nd 5d$^1$ decay time at 180 nm under excitation at 145 nm to Er$^{3+}$, LuLiF$_4$: Nd 1%, Er x%, Tm x%, RT.

### 4. Conclusions

Radioluminescence from the 5d state of Nd$^{3+}$ consists of the broad bands at about 182 nm, 230 and 260 nm which are ascribed to transitions ending at the $^4I_9$, $^4F_5$ and $^2H_9$ multiplets, respectively. Absolute intensity of this RL emission is higher for samples doped by Er$^{3+}$ and Tm$^{3+}$ then the single doped ones. The appearance of additional slower decay components in Nd$^{3+}$ emission also point to radiative or nonradiative energy transfer from codoping ions to Nd$^{3+}$. These observations prove that energy transfer from dopants to Nd at 5d$^1$ level exists.

RE ions have 4f-4f absorption bands in 230-270 nm spectral regions which, in the case of the overlap with the above mentioned 5d-4f transitions of Nd$^{3+}$, caused the unwanted energy transfer from 5d level of Nd$^{3+}$ towards mentioned 4f-4f states of Er$^{3+}$ and Tm$^{3+}$. Behavior of the integral value of the RL intensity in the regions 210-273 nm and 274-620 nm together with the luminescence decay times explain the energy losses in Nd peaks due to energy transfer from Nd to Er$^{3+}$ and Tm$^{3+}$. Finally we discovered that the unwanted energy transfer from Nd to dopants at 4f level exists.

All these processes are very concentration dependent and concentration quenching cause that their investigation is possible only in region of very small concentrations.
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