FLUORESCENCE DYNAMICS IN SOME SOLID-STATE LASER MATERIALS EMITTING IN THE INFRARED REGION: Ho3+ DOPED LiYF4 SINGLE CRYSTALS AND FLUORIDE GLASSES

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In the present work, we report on the optical properties of Er$^{3+}$ and Ho$^{3+}$ ions embedded in some solid-state materials. YLiF$_4$ single crystals are one of them. The other class consists of fluoride glasses, well-known for their wide range of transparency particularly in the mid-infrared region. Their compositions are the following:

- ZBLA:Er$^{3+}$:Ho$^{3+}$: 57ZrF$_4$ - 34BaF$_2$ - (5-x-y)LaF$_3$ - 4AlF$_3$ - xHoF$_3$ - yErF$_3$
- BAYT:Er$^{3+}$:Ho$^{3+}$: 20BaF$_2$ - 28.75AlF$_3$ - 22.5ThF$_4$ - (28.75-x-y)YF$_3$ - xHoF$_3$ - yErF$_3$
- BIZYT:Er$^{3+}$:Ho$^{3+}$: 30BaF$_2$ - 30InF$_3$ - 20ZnF$_2$ - (10-x-y)YF$_3$ - 10ThF$_4$ - xHoF$_3$ - yErF$_3$.

The study consists of recording and analyzing the experimental time-dependences of emitting level fluorescences in the infrared and visible ranges. The optical processes are described in terms of rate equations which apply because fast diffusion is generally involved between the Er$^{3+}$ sensitizers.

We have studied in details the emission processes in Er$^{3+}$ singly doped YLiF$_4$ single crystals [1,2] and shown that in heavily doped samples, energy transfer mechanisms occur through several modes including up-conversion and cross-relaxation transfers (right part of figure 1). The same dynamics is observed in the fluoride glasses. In particular, self-quenching mechanisms within Er$^{3+}$ ions of the green fluorescence originating from $^{4}S_{3/2}$, represented as $^{4}S_{3/2} ightarrow ^{4}I_{9/2} ightarrow ^{4}I_{15/2}$ and $^{4}S_{3/2} ightarrow ^{4}I_{15/2} ightarrow ^{4}I_{13/2}$, are shown to be very efficient as the Er$^{3+}$ concentration increases (table 1).

The infrared fluorescence processes of directly excited Ho$^{3+}$ ions were analyzed as a function of the Ho$^{3+}$ concentration. The increase of the $^{5}I_{7}$ level lifetime with Ho$^{3+}$ concentration in YLiF$_4$ and in fluoride glasses only at low concentrations, is interpreted by a reabsorption of the 2.3μm emission by the $^{5}I_{8}$ ground state. Such Ho$^{3+}$ concentration dependence is not observed for $^{5}I_{6}$. The high Ho$^{3+}$ concentration behaviour (> 1%) for $^{5}I_{7}$ is the same as for $^{5}I_{6}$: the decrease of the lifetime is due to the diffusion and trapping of energy.
A detailed analysis of the $\text{Er}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer mechanisms was carried out in $\text{YLiF}_4:\text{Er}^{3+}, \text{Ho}^{3+}$ single crystals for various laser excitations in the excited states of $\text{Er}^{3+}$ ions in the visible and infrared regions [3]. In fluoride glasses, these transfers were studied only under infrared laser excitation in the $^4I_{13/2}$ and $^4I_{11/2}$ levels. The fluorescence dynamics is well described by our models and therefore quite well understood. In the table 2 are gathered the quantum efficiencies of some energy transfers in the infrared. Special attention was drawn on the different excitation channels which populate $^5I_7$, lowest excited state of $\text{Ho}^{3+}$, owing to the prime interest of the $^5I_7 \rightarrow ^5I_8$ 2 $\mu$m infrared laser transition. Three main channels, called IR1, IR2 and RED are shown to be efficient, as indicated in the left part of the figure 1. The relative contributions of each channel of excitation to the $^5I_7$ level of $\text{Ho}^{3+}$ are calculated and are represented in table 3 as a function of the $\text{Er}^{3+}$ excitation level for three bi-doped $\text{YLiF}_4:50 \% \text{Er}^{3+}, x \% \text{Ho}^{3+}$ ($x = 0.5, 2, 5$) single crystals.

ACKNOWLEDGMENTS

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REFERENCES

1. R. RUBIN, A. BRENIER, R. MONCORGE and C. PEDRINI

2. A. BRENIER, J. RUBIN, R. MONCORGE and C. PEDRINI

3. J. RUBIN, A. BRENIER, R. MONCORGE and C. PEDRINI

![Diagram of energy transfer mechanisms](image)
Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Er$^{3+}$</th>
<th>Ho$^{3+}$</th>
<th>$\eta_T$ (%)</th>
<th>$\eta_T$ (%)</th>
<th>$\eta_T^*$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIZYT, % Er</td>
<td>0.1</td>
<td>1</td>
<td>8.5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>43</td>
<td>97</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

Table 2

Quantum efficiencies of energy transfers

(i) $\eta_T^1 : 4_1^{13/2} \rightarrow 5_1^7$ 
(ii) $\eta_T^2 : 4_1^{11/2} \rightarrow 5_1^6$ (excitation in $4_1^{9/2}$ of Er$^{3+}$) 
(iii) $\eta_T^* : 4_1^{11/2} \rightarrow 5_1^6$ (excitation in $4_1^{11/2}$ of Er$^{3+}$)

Table 3

<table>
<thead>
<tr>
<th>Exc</th>
<th>Ho$^{3+}$ concentration</th>
<th>0.5 %</th>
<th>2 %</th>
<th>5 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4_1^{13/2}$</td>
<td>IR$_1$</td>
<td>100 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$</td>
<td>100 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$</td>
<td>100 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$4_1^{11/2}$</td>
<td>IR$_1$ + IR$_2$</td>
<td>57%</td>
<td>43%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + IR$_2$</td>
<td>79%</td>
<td>21%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + IR$_2$</td>
<td>94%</td>
<td>6%</td>
<td></td>
</tr>
<tr>
<td>$4_1^{9/2}$</td>
<td>IR$_1$ + IR$_2$</td>
<td>92%</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + IR$_2$</td>
<td>82%</td>
<td>18%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + IR$_2$</td>
<td>66%</td>
<td>34%</td>
<td></td>
</tr>
<tr>
<td>$4_1^{9/2}$</td>
<td>IR$_1$ + PED</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + PED</td>
<td>35%</td>
<td>12%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + PED</td>
<td>26%</td>
<td>74%</td>
<td></td>
</tr>
<tr>
<td>$2_1^{11/2}$</td>
<td>IR$_1$ + IR$_2$</td>
<td>100 %</td>
<td></td>
<td>72%</td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + IR$_2$</td>
<td>72%</td>
<td>28%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR$_1$ + IR$_2$</td>
<td>88%</td>
<td>12%</td>
<td></td>
</tr>
</tbody>
</table>

Relative contribution of each channel of excitation to the $5_1^7$ level of Ho$^{3+}$ as a function of the Er$^{3+}$ excitation level.