Up-conversion fluorescence in MBE-grown Nd$^{3+}$-doped LaF$_3$/CaF$_2$ waveguides

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Abstract

The up-conversion fluorescence, at low temperature, of Nd$^{3+}$-doped LaF$_3$ planar waveguides grown on (1 1 1) oriented CaF$_2$ substrates by Molecular Beam Epitaxy is reported. The up-converted emissions excited with a tunable Ti: Sapphire laser are observed in UV-blue, green and orange regions corresponding to the $^4D_{3/2} \rightarrow ^4I_{11/2}$ ($J = \frac{2}{3}, \frac{1}{3}$, and $\frac{1}{2}$), $^4G_{7/2} \rightarrow ^4I_{9/2}$ and $^2G_{7/2} + ^2G_{5/2} \rightarrow ^4I_{9/2}$, $^4G_{7/2} \rightarrow ^4I_{11/2}$ transitions, respectively. The up-converted emission at 381 nm ($^4D_{3/2} \rightarrow ^4I_{11/2}$), due to a three-photon process, gives rise to the most intense luminescence. The green and orange up-converted luminescences originate from an energy transfer process involving two Nd$^{3+}$ ions in the $^4F_{3/2}$ excited state while two successive energy cross-relaxations are suggested for the UV-blue emission. The maximum intensity is obtained for Nd$^{3+}$ content of 1 at% for all the emissions observed. The up-conversion fluorescences are observed for different samples doped in the range 0.5–5 at%. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Up-conversion luminescence; Nd$^{3+}$; LaF$_3$ waveguide films; MBE-growth

Short-wavelength solid-state lasers have attracted much attention in recent years due to a wide range of applications including optical data storage, color displays, infrared sensors and biomedical diagnostics. Rare earth doped up-conversion materials have proven to be some of the most efficient candidates for obtaining visible or UV lasers upon infrared light excitation and up-conversion laser action has been demonstrated with various rare earth ions including Er$^{3+}$, Tm$^{3+}$, Ho$^{3+}$, Nd$^{3+}$, and Pr$^{3+}$, both at low and room temperatures [1].

Planar or channel waveguides and optical glass fibers have a greater potential to obtain high-temperature up-conversion emission and laser operation compared to bulk materials, due to the high confinement of excitation light in these guided configurations. The wave-guiding properties of Nd-doped LaF$_3$ thin films elaborated on CaF$_2$ substrates by MBE have been demonstrated elsewhere [2]. Recently, we have demonstrated the first laser operation at 1.06 μm in these waveguides [3]. In this paper, we report infrared to UV, green and orange up-converted emissions in these epilayered layers, originating from three- and two-photon up-conversion mechanisms.

All the experiments were carried out at 25 K. After excitation of the thin films by a Ti: sapphire laser tuned around 800 nm, up-conversion luminescences of Nd$^{3+}$ were observed mainly in three spectral regions: between 350 and 420 nm corresponding to the transitions of $^4D_{3/2} \rightarrow ^4I_{9/2}$ ($J = \frac{2}{3}, \frac{1}{3}$, and $\frac{1}{2}$) (Fig. 1); from 510 to 540 nm due to $^4G_{7/2} \rightarrow ^4I_{9/2}$ transition; and from 570 to 600 nm resulting from two transitions $^4G_{7/2} \rightarrow ^4I_{11/2}$ and $^2G_{7/2} + ^2G_{5/2} \rightarrow ^4I_{9/2}$. The fluorescence spectra have been obtained for different samples with Nd$^{3+}$ content ranging from 0.5 to 5 at%. The maximum of luminescence intensity has been obtained for a Nd concentration of 1 at%. For all the samples the most intense upconverted emission is the UV fluorescence at 381 nm.

Excitation spectra for the up-conversion emissions were obtained in two spectral ranges corresponding to the $^4I_{9/2} \rightarrow ^4F_{5/2}, ^4F_{7/2}$ and $^4I_{9/2} \rightarrow ^4F_{3/2}$ transitions of Nd$^{3+}$ by monitoring the $^4D_{3/2} \rightarrow ^4I_{11/2}$ transition at...
Fig. 1. $^{4}D_{3/2}$ → $^{4}I_{13/2}$ up-conversion spectrum for the 1 at% Nd$^{3+}$-doped LaF$_3$ layer grown on CaF$_2$(1 1 1) substrate recorded at 25 K.

Fig. 2. Excitation spectra for 381 and 524 nm up-conversion lines as well as 901 nm IR emission lines for LaF$_3$: 1 at% Nd$^{3+}$/CaF$_2$(1 1 1) sample at 25 K.

Fig. 3. Log–Log plots for different upconversion emissions as a function of incident laser powers for LaF$_3$: 1 at% Nd$^{3+}$/CaF$_2$(1 1 1) at 25 K.

Table 1

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Nd$^{3+}$ concentrations (at%)</th>
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</thead>
<tbody>
<tr>
<td>$^{4}D_{3/2} \rightarrow ^{4}I_{13/2}$</td>
<td>0.5  1.0  2.5  5.0</td>
</tr>
<tr>
<td>$^{4}G_{7/2} \rightarrow ^{4}I_{9/2}$</td>
<td>88    68    41     25</td>
</tr>
<tr>
<td>$^{4}G_{7/2} \rightarrow ^{4}I_{9/2}$</td>
<td>142   116   61     33</td>
</tr>
<tr>
<td>$^{2}G_{7/2} + ^{4}G_{5/2} \rightarrow ^{4}I_{9/2}$</td>
<td>152   118   63     34</td>
</tr>
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</table>

381 nm and the $^{4}G_{7/2} \rightarrow ^{4}I_{9/2}$ transition at 524 nm for the sample doped with 1 at% Nd (Fig. 2). For comparison, the excitation spectrum recorded for infrared emission at 901 nm, corresponding to the $^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$ transition, is also shown in Fig. 2. The principal excitation lines are similar for different emissions, indicating energy transfer processes.

Fig. 3 shows the dependence of the intensity of the up-converted emission intensities on the laser intensity by monitoring the emission peaks at 381, 524 and 578 nm. According to the slopes of the fitted straight lines in the logarithmic plots, a three-photon process produces the UV emission from the $^{4}D_{3/2}$ level, while a two-photon process is responsible for the green and orange emissions from the $^{4}G_{7/2}$ and $^{2}G_{7/2} + ^{4}G_{5/2}$ levels.

The fluorescence rise and decay curves for the up-conversion emissions and the infrared emission of the $^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$ transition were measured with a digital oscilloscope. The decay times for green and orange up-conversion emissions are very close to each other, while that for the blue emission is much shorter. At long time delays, signals approach exponential decays. The corresponding decay times have been measured and are given in Table 1. The decay times obtained are very different from the intrinsic lifetimes of Nd$^{3+}$ in LaF$_3$ bulk crystal [4] (35 μs, 110.5 and 29.2 ns corresponding to the $^{4}D_{3/2}$, $^{4}G_{7/2}$ and $^{2}G_{7/2} + ^{4}G_{5/2}$ levels, respectively) for the three levels studied in this work. Therefore, successive absorption cannot be the predominant process since in that case the measured decay time corresponds to the intrinsic lifetime of the level. The effective mechanisms should be some kind of energy transfer and/or energy cross-relaxation between different Nd$^{3+}$ ions.

From the energy levels of Nd$^{3+}$ in LaF$_3$ crystals [5], it can be seen that there exist different resonant energy transfer processes capable of populating the green, orange and UV up-conversion upper levels. The up-conversion mechanisms can be described as follows (Fig. 4): after the pump laser excites the ground state Nd$^{3+}$ to the $^{4}F_{3/2}$ or $^{2}H_{9/2} + ^{4}F_{5/2}$ level depending on the pump wavelength selected (1), two adjacent excited Nd$^{3+}$ ions in $^{4}F_{3/2}$ state interfere with each other inducing two energy transfer processes (2) and (2'). In a third step, an additional cross-relaxation process involving two Nd$^{3+}$ ions excited in $^{4}F_{3/2}$ and in $^{4}G_{7/2}$ states excites one ion to
the upper $^2L_{15/2}$ state and the other relaxes to the $^4I_{11/2}$ level (3). According to energy levels of Nd$^{3+}$, this third step is also resonant. Thus, for the populated $^4G_{7/2}$ level, there exists a competition between the energy cross-relaxation to upper level, radiative transition to the ground state, and nonradiative decay to the $^2G_{7/2} + ^4G_{5/2}$ levels. Since the third energy transfer is resonant, it could be very efficient. This is probably the reason for the efficient three-photon up-conversion in the UV-blue region. This mechanism is confirmed by a rate equation analysis [6].

In conclusion, efficient UV, green and orange up-conversion luminescence has been demonstrated under IR excitation at 25 K in Nd$^{3+}$-doped LaF$_3$ thin films elaborated by MBE on CaF$_2$ (1 1 1) substrates. The UV-blue fluorescence from the $^4D_{3/2}$ level of Nd$^{3+}$ is the most intense up-converted emission and corresponds to a three-photon process. Other up-conversion emissions in the green and orange regions are ascribed to the $^4G_{7/2} \rightarrow ^4I_{9/2}$ and $^2G_{7/2} + ^4G_{5/2} \rightarrow ^4I_{9/2}$, $^4G_{7/2} \rightarrow ^4I_{11/2}$ transitions, respectively.

Energy transfer processes involving two Nd$^{3+}$ ions excited in the $^4F_{3/2}$ state are suggested for the green and orange up-conversions, while a third cross-relaxation energy transfer involving two Nd$^{3+}$ ions excited in the $^4F_{3/2}$ and $^4G_{7/2}$ states is proposed to populate the $^4D_{3/2}$ level. The maximum intensity is obtained with 1 at% doped samples.

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References