Red laser-induced up-conversion mechanisms in Ho^{3+} doped LaF₃ crystal

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Abstract

In this work, the up-conversion properties of the Ho^{3+}-doped LaF₃ upon excitation by a cw red dye laser are reported. Ten groups of emission lines have been detected over a wide spectral range from 13 000 to 22 000 cm^{-1}. Five of them are up-conversion emissions arising from four energy levels: $^5G_4$, $^5G_6$, $^5F_3$ and $^5S_2(^5F_4)$. The strongest up-conversion was observed for the green emission corresponding to the $^5S_2(^5F_4) \rightarrow {}^5I_8$ transition. The up-conversion mechanism is a sequential two-photon absorption via the $^5I_7$ level upon excited state absorption (ESA) excitation. However, when excited into ground state absorption (GSA) transitions; two energy transfers involving either two Ho^{3+} ions excited in the $^5F_5$ multiplet or one in $^5F_5$ and the other in $^5I_6$ multiplets were suggested. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been a renewed interest in up-conversion studies of the rare-earth ions in various materials including crystals, glasses and thin films due to the development of the high power laser diodes and the requirement for short wavelength emitting solid state lasers. The LaF₃ crystal is a promising host material with which up-conversion laser operation has been obtained when doped with Nd^{3+} ions [1,2].

LaF₃ has a trigonal crystal structure with a space-group of F_{3c1}, and the site symmetry of La^{3+} is C_2 [3]. Since the impurity ions replace the La^{3+} ion, there is no such problem as charge compensation. Previous investigation had shown that the maximum lattice phonon energy in LaF₃ is about 350 cm^{-1} [4,5]. Generally, the low phonon energy presents an advantage in obtaining high up-conversion efficiency because of a small multiphoton relaxation rate. The absorption and fluorescence spectra for the Ho^{3+} ion in LaF₃ have been studied at 1.5 K, and the energy level diagram has been established by Caspers and colleagues [6]. Weber et al. have calculated the radiative transition probabilities for the Ho^{3+} ion in this crystal [7]. Recently, up-conversion fluorescence of Ho^{3+} in LaF₃ was reported by Reddy using two laser excitation at 640 and 800 nm [8]. Up-conversion from the three energy levels $^5G_5$, $^5F_3$ and $^5S_2(^5F_4)$ has

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been observed at room temperature. The up-conversion mechanisms at 640 nm excitation were explained by both a sequential two-step excitation via $^5I_6$ level and an energy transfer process involving two Ho^{3+} excited to the $^5F_5$ and $^5I_6$ levels.

In this paper, we report the efficient up-conversion fluorescence of the Ho^{3+}-doped LaF_3 crystal induced by a cw red dye laser continuously tuned between 15 200 and 16 200 cm^{-1}. The up-conversion fluorescence has been detected in several wavelength regions resulting from four energy levels: $^5G_4$, $^5G_6$, $^5F_3$ and $^5S_2(^5F_4)$. Due to the limitation of our experimental equipment, we could not record the emission arising from the $^5G_5$ multiplet. Since emissions from both the higher and the lower-lying levels ($^5G_4$, $^5G_6$) were detected, we can infer that the emission from $^5G_5$ level also exists. In accordance with the experimental results, the up-conversion mechanisms proposed in this work are somewhat different from those reported by Reddy [8].

2. Experimental

The samples used in this work were high-quality LaF_3 single crystals doped with 0.2% and 0.5% Ho^{3+} and grown by the Optovac company of the USA.

For the up-conversion study, a cw Argon ion laser (Spectra Physics 2000) pumped tunable dye laser (Spectra Physics 375) was employed to excite the samples. The dye was Kiton Red which enabled the laser to be tuned between 15 200 to 16 200 cm^{-1} with maximum power at about 15 600 cm^{-1}. The pumping laser was focused into the crystals with a 20 cm focal length lens. The emission signal was dispersed by a Coderg T800 three grating monochromator and detected by a EMI 9558 QB photomultiplier. The dynamic properties were measured using a Metrix oscillograph (OX 750-2). All the measurements were performed at liquid nitrogen temperature (77 K).

3. Results and discussion

Upon red laser excitation, we have observed ten groups of emission lines corresponding to ten different transitions of Ho^{3+} in LaF_3 : Ho^{3+} crystal. According to the transition character, five of the ten groups, $^5G_4 \rightarrow {}^5I_6$ (580 nm), $^5G_6 \rightarrow {}^5I_8$ (455 nm), $^5F_3 \rightarrow {}^5I_8$ (485 nm), $^5S_2(^5F_4) \rightarrow {}^5I_8$ (540 nm), $^5S_2(^5F_4) \rightarrow {}^5I_7$ (740 nm), are due to multiphoton excitation processes. Fig. 1 shows the green ($^5S_2(^5F_4) \rightarrow {}^5I_8$) and blue ($^5F_3 \rightarrow {}^5I_8$) up-conversions recorded with LaF_3 : 0.2% Ho^{3+}. The green emission is stronger than all the other transitions and gives the crystal a very intense green color. The blue up-conversion is almost ten times less intense than the green, and the others are even weaker. The sample doped with 0.5% Ho^{3+} shows the same emission spectra as the 0.2% Ho^{3+} sample. Several energy levels have been determined from the emission and excitation spectra, as shown in Table 1.

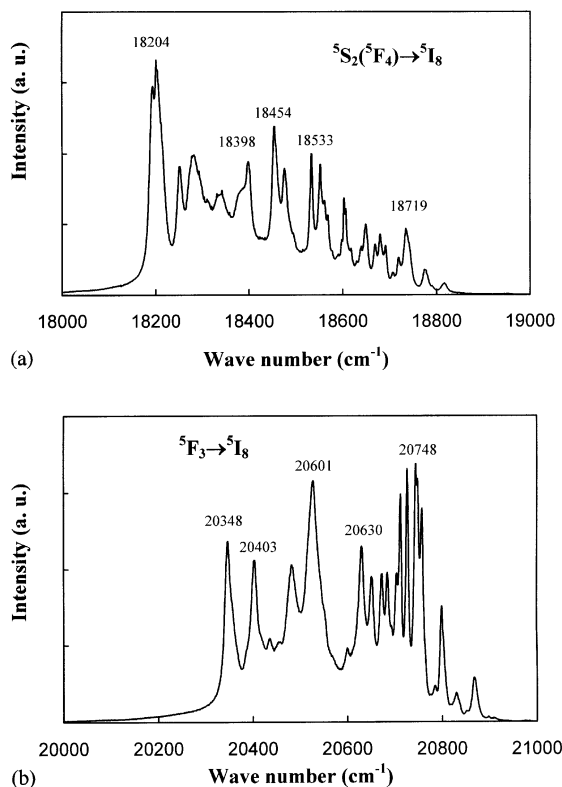The excitation spectra for the 0.5% and 0.2% Ho^{3+}-doped sample are shown in Fig. 2 (a and b)

(a)

(b)

Fig. 1. Emission spectra of the up–conversion fluorescence from the Ho^{3+} ions in LaF_3 at 77 K with laser excitation at 15 719 cm^{-1}: (a) $^5S_2(^5F_4) \rightarrow {}^5I_8$; (b) $^5F_3 \rightarrow {}^5I_8$.

Table 1
Energy level splitting of the Ho^{3+} ion in LaF_3 at 77 K

$^{2S+1}L_J$ Multiplet	Stark sublevels (cm^{-1})
$^5I_8$	0, 5, 42, 51, 69, 122, 145, 201, 215, 226, 261, 306, 321, 349, 387, 398, 409
$^5I_7$	5192, 5246, 5251, 5272, 5279, 5287, 5295, 5305, 5314, 5389, 5460, 5503, 5586, 5642
$^5I_6$	8728, 8732, 8755, 8767, 8779, 8784, 8790, 8812, 8834
$^5F_5$	15 592, 15 596, 15 604, 15 614, 15 626, 15 644, 15 717, 15 734
$^5F_4$, $^5S_2$	18 592, 18 603, 18 606, 18 623, 18 680, 18 693, 18 706, 18 724, 18 740, 18 780, 18 816
$^5F_3$	20 748, 20 758, 20 803, 20 831, 20 837, 20 873
$^5G_6$	22 259, 22 261, 22 267, 22 271, 22 276, 22 281, 22 288, 22 331, 22 364, 22 379, 22 393, 22 412
$^5G_4$	25 991, 26 014, 26 042, 26 060, 26 090, 26 102, 26 137, 26 150

Fig. 2. Excitation spectra of the Ho^{3+} red emission at 15 251 cm^{-1} and green emission at 18 204 $^{-1}$ at 77 K in LaF_3 : 0.5% Ho^{3+} (a) and LaF_3 : 0.2% Ho^{3+} (b).

for monitoring the red Stokes emission and green up-conversion. The blue emission from $^5F_3$ level has an excitation spectrum similar to that for the green emission, whereas for the others, the excitation spectra are similar to that of the red emission. There is not much difference between the two kinds of spectra, and we have noticed only that several excitation lines located at 15 556, 15 566, 15 612, 15 645 and 15 681 cm^{-1} are clearly enhanced in the excitation spectrum of the green emission (Fig. 2a). A careful analysis has shown that these lines result from an ESA transition: $^5I_7 \rightarrow {}^5F_3$. In the 0.2% Ho^{3+}-doped sample, the difference between the excitation spectra of the red and green emissions is more notable than that observed in the 0.5% Ho^{3+}-doped one (Fig. 2b). Those lines corresponding to the $^5I_7 \rightarrow {}^5F_3$ transition were reinforced compared to the rest of the lines. This phenomenon can be interpreted by the lower energy transfer probability at lower activator concentration. The assignments of the observed excitation lines are given in Table 2. These results have been confirmed by the red emission spectrum of the $^5F_3 \rightarrow {}^5I_7$ transition when excited with the argon ion laser at 21 837 cm^{-1} ($^3K_8$). All the lines mentioned above correspond to a specific line of the $^5F_3 \rightarrow {}^5I_7$ transition [9].
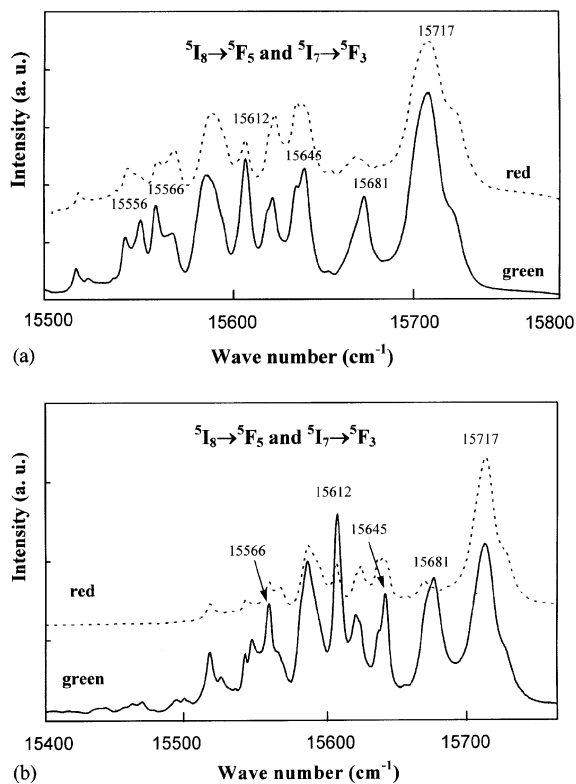
The fluorescence rise and decay properties of the up-conversion and red emissions were studied using cw laser excitation. The rise time for the green or blue ($^5F_3 \rightarrow {}^5I_8$) emission is very much different with excitation into the ESA or GSA, as shown in Fig. 3. For the green up-conversion at 18 204 cm^{-1}, a rise time of 11 ms was obtained with 15 681 cm^{-1} excitation, whereas two time constants with values of 0.3 and 4.6 ms were measured with 15 717 cm^{-1} excitation. The different rise times correspond to the different up-conversion mechanisms, which will be explained later by analyzing the up-conversion processes.

A log–log plot of the green and blue up-conversion intensities versus incident laser power exhibited a quadratic dependence with a slope of 1.7 under GSA excitation or 1.9 under ESA excitation (Fig. 4). This is a clear evidence for a two-photon

Table 2
Excitation lines observed at 77 K for $LaF_3 : 0.5\%$ Ho^{3+}

Transition	Energy (cm^{-1})	Stark sublevel transitions
$^5I_8 \rightarrow {}^5F_5$	15 522	5 − 1
	15 550	3 − 1
	15 564	4 − 4
	15 572	3 − 4
	15 592	1 − 1
	15 609	2 − 4
	15 626	1 − 5
	15 639	2 − 6
	15 644	1 − 6
	15 674	3 − 7
	15 717	1 − 7
	15 734	1 − 8
$^5I_7 \rightarrow {}^5F_3$	15 556	1 − 1, 2 − 3
	15 566	1 − 2, 4 − 5
	15 611	1 − 3
	15 645	1 − 5
	15 681	1 − 6

Fig. 3. Fluorescence-rise curves for the Ho^{3+} green emission under $15\,719\ cm^{-1}$: (a) and $15\,681\ cm^{-1}$ (b) for $LaF_3 : 0.5\%$ Ho^{3+} at 77 K.

excitation process. At higher excitation density, the experimental points deviate from a straight line. This phenomenon can be interpreted as a saturation effect when the excited state population becomes saturated. For other up-conversions, similar results were observed.

The spectroscopic and dynamic results have revealed that different up-conversion mechanisms are responsible for the up-conversion luminescence depending on either the excitation wave number being tuned on GSA or ESA lines. Part of the results obtained in this work cannot be explained by the up-conversion processes proposed by Reddy et al. [8]. Upon ESA excitation, a sequential two-step excitation via the $^5I_7$ level is proposed. Through a room temperature study with the 640 nm red laser excitation, Reddy et al. have suggested a successive absorption process involving the $^5I_6$ level as the intermediate level. According to our spectroscopic and fluorescence dynamics results, the successive absorption process is from $^5I_7$ level, rather than the $^5I_6$ level as suggested by Reddy [8]. Three reasons account for this conclusion. First, we have observed the excitation lines corresponding to the $^5I_7 \rightarrow {}^5F_3$ transition only for the green and blue $^5F_3$ up-conversions, and not for the $^5G_6$ up-conversin. Second, all the observed ESA lines correspond
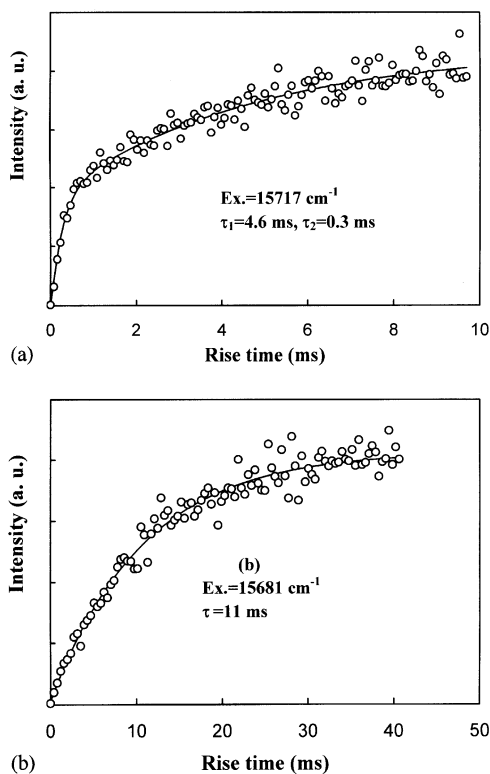
to an emission peak of the $^5F_3 \rightarrow {}^5I_7$ red emission when excited with a Ar^+ laser line at $21\,837\ cm^{-1}$. Third, the fluorescence rise time of the green up-conversion under ESA excitation, is about 11 ms and related to the lifetime of the $^5I_7$ level, whereas that for the $^5I_6$ level is about 5 ms [8].

When excited into the GSA transitions, two possible energy transfer processes were suggested:

$$^5F_5 + {}^5F_5 \rightarrow {}^5I_7 + {}^5G_4$$

and

$$^5F_5 + {}^5I_6 \rightarrow {}^5I_8 + {}^5G_5$$
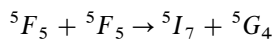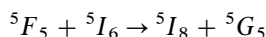
The first energy transfer is the proposed process to populate the $^5G_4$ level. We have observed a fluorescence rise time of about 300 µs for the yellow emission from $^5G_4$ level, corresponding to the fluorescence lifetime of the $^5F_5$ level [9]. The second
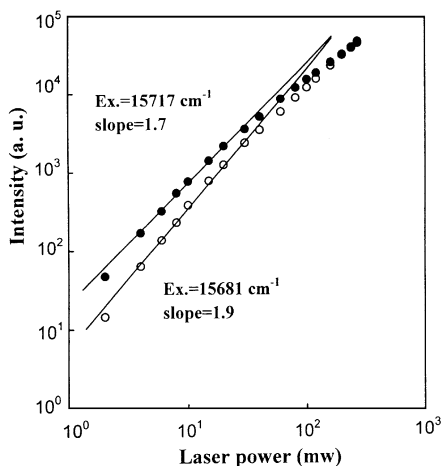
Fig. 4. Dependence of the green-emission intensity at 18 204 cm^{-1} as a function of the laser power at 77 K for LaF$_3$: 0.5% Ho^{3+}.
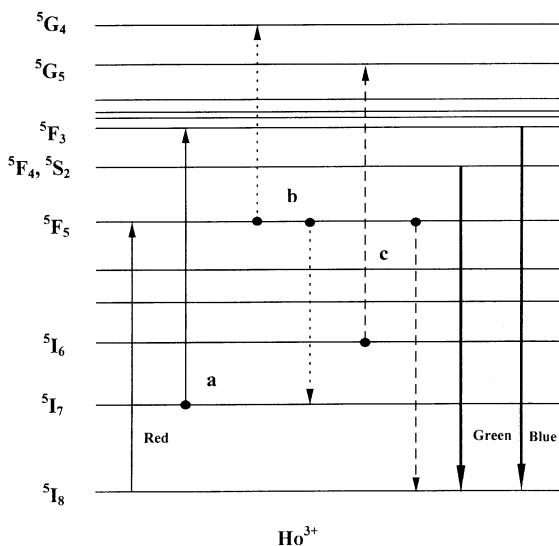

Fig. 5. Three excitation mechanisms for Ho^{3+} up-conversion in LaF$_3$: (a) successive absorption via the $^5I_7$ level; (b) energy transfer involving two ions excited in the same level $^5F_5$; (c) energy transfer involving two ions excited in two different levels.

energy transfer is responsible for the rise time of about 4.6 ms observed under GSA excitation for the green upconversion, corresponding to the 5 ms lifetime of the $^5I_6$ level. This is the reason that two

rise-time constants corresponding to the two energy transfer processes have been obtained under GSA excitation. Both energy transfers are resonant processes. All the three up-conversion processes are depicted in Fig. 5.

4. Conclusion

We have observed both efficient green up-conversion and several weaker up-conversions in Ho^{3+}-doped LaF$_3$ crystals upon cw red dye laser excitation at 77 K. The up-conversion mechanisms are different depending on whether the excitation is tuned to the ESA or GSA transitions. A sequential two-photon absorption via $^5I_7$ level is responsible for the green and blue ($^5F_3$) up-conversions with ESA excitation, whereas two energy transfer processes involving either two Ho^{3+} ions excited in the $^5F_5$ level or one in the $^5F_5$ and one in $^5I_6$ levels are suggested for GSA excitation.

Acknowledgements

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