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Upconversion-induced blue, green and red emission in Ho^{3+}:BaY_2F_8

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Abstract

An analysis of infrared to visible upconversion in Ho^{3+}:BaY_2F_8 is given. Excitation at 888 nm into the $^5I_8 \rightarrow {}^5I_5$ transition leads to intense visible emission in the blue, green and red spectral range. Based on the energy levels of Ho^{3+} in BaY_2F_8, and the pump intensity dependencies of the observed emissions, an excitation scheme is presented.

Keywords: Ho^{3+}:BaY_2F_8; Upconversion; Excited state absorption; Cross relaxation; Energy transfer

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1. Introduction

In the last decade, upconversion processes in various rare earth (RE) doped materials are intensively investigated in order to obtain efficient visible lasers for application in the fields of information processing, displays or medicine. In upconversion processes, photons of lower energy are converted into a higher-energy photons by means of internal energy transfer processes. This could be a promising solution for obtaining visible solid state lasers pumped with infrared laser diodes, which are nowadays commercially available for many spectral regions.

The trivalent holmium is a promising ion for upconversion applications because of its energy levels structure, which allows and favours a lot of upconversion processes. Especially in crystalline matrices with low energy phonons, a variety of energy levels are not strongly quenched by multiphonon decay, and thus, can act as initial levels for upconversion and excited state absorption transitions, which populate higher energy levels. One of such crystals is BaY_2F_8 (BYF), for which the phonon energy is about 360–380 cm^{-1} [1]. This crystal is monoclinic with cell parameters $a = 0.6983$ nm, $b = 1.0519$ nm, $c = 0.4264$ nm, $\alpha = \gamma = 90°$ and $\beta = 99.676°$ [2]. The Ho^{3+} ion substitutes the Y^{3+} sites of C_2 symmetry and is surrounded by eight fluoride ions [2].

There are several studies about spectroscopic and laser characteristics of BYF, either singly doped with RE ions (e.g. Er^{3+} [3,4], Tm^{3+} [3] and Ho^{3+} [1,3,5]), or codoped with Yb^{3+} [6,7]. For Ho^{3+} doped crystals, these studies concentrate on the laser emission in the infrared spectral range around 2.1 and 2.9 μm, corresponding to the transitions $^5I_7 \rightarrow {}^5I_8$ and $^5I_6 \rightarrow {}^5I_7$, respectively, and on upconversion processes due to Ho^{3+}–Yb^{3+} energy transfer [3,5,6,8]. Basic spectroscopy as well as theoretical and experimental studies on the concentration quenching in Ho^{3+}:BYF were made by Tkachuk et al. [4]. To our knowledge, there are no publications dealing with upconversion processes in singly Ho^{3+}-doped BYF.

In this paper we investigate some spectroscopic characteristics of the system and the upconversion mechanism under infrared pumping, especially at 888 nm ($^5I_8 \rightarrow {}^5I_5$ transition). Emission in the blue, green and red spectral region is observed and a scheme of the processes involved is proposed.

2. Experimental set-up

The BYF crystal investigated was grown by the Czochralski method with a Ho^{3+} concentration of 1 at% (1.28×10^{20} ions/cm^3). The room temperature absorption measurements were performed with a CARY 2400 spectrophotometer. The emission measurements were performed after excitation with a Ti-sapphire laser (Spectra-Physics 3900S) operating between 730 and 1000 nm. The emitted light was detected by a S1 photomultiplier, which was placed behind a 0.5-m monochromator (Spex 1870). All spectra were normalised in accordance with the spectral response of the detection system. For the excited

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state absorption measurements, a double modulation technique with two lock-in amplifiers was used; the setup is described in detail in [9]. A halogen lamp (250 W) and a frequency doubled Nd:YVO$_4$ (Spectra-Physics Millenia X) operating at 531 nm were used as probe and pump beam, respectively. Here, the 0.5 m monochromator was used in combination with a Si diode. It can be shown, that for the simultaneously measured $\Delta T = I_u - I_p$ and $T = I_u$ spectra, where I_p and I_u are the lamp transmission signals for the pump beam applied and not applied to the crystal, respectively, the following equation holds [9]:

$$\frac{\Delta T}{T} = An_e L \left[\sigma_{\mathrm{GSA}} + \sum_i \frac{n_i}{n_e} (\sigma_{\mathrm{EM},i} - \sigma_{\mathrm{ESA},i}) \right]$$

where A is the gain constant of the second lock-in amplifier, n_e is the number of excited ions, n_i is the number of ions in the i-th multiplet and σ_{GSA}, σ_{EM}, and σ_{ESA} are the ground state absorption, stimulated emission, and excited state absorption cross section, respectively.

For the low temperature measurements, the crystal was placed in a closed-cycle cryostat. For the transmission measurements at low temperature, the same halogen lamp and 0.5 m monochromator in combination with a InSb diode was used. For the measurements of the decay kinetics, an optical parametric oscillator (GWU-OPO) pumped by the third harmonic of a Nd:YAG laser (Spectra-Physics GCR 130), a 0.25 m monochromator (Spex minimate) and a S1 photomultiplier were used. The decay curves were summed up with a digital oscilloscope (Le Croy 9360) in order to increase the signal to noise ratio.

3. Results and discussion

In Fig. 1 the low-temperature (15 K) absorption bands corresponding to the transitions $^5I_8 \rightarrow {}^5F_3$ (around 480 nm), $^5I_8 \rightarrow {}^5S_2, {}^5F_4$ (around 535 nm), $^5I_8 \rightarrow {}^5F_5$ (around 640 nm), and $^5I_8 \rightarrow {}^5I_5$ (around 885 nm) are presented. For a better understanding and assignment of possible cross-relaxation and excited state absorption processes, the energetic positions of the Stark levels of the involved multiplets were determined from low temperature absorption and emission spectra, the results are listed in Table 1.

In order to find the most efficient upconversion at room temperature for Ho^{3+}:BYF, several pump wavelengths were tested and consequently several schemes for upconversion mechanisms were analysed. Upconverted visible emission was observed after excitation around 750 nm, around 888 nm and around 965 nm. Visible emission after excitation around 750 nm was also observed in Ho^{3+}:YLiF$_4$ [10]. Although in this spectral region a weak absorption band according to the $^5I_8 \rightarrow {}^5I_4$ transition exists, the main process was ascribed to the $^5I_7 \rightarrow ({}^5S_2, {}^5F_4)$ excited state absorption utilising an avalanche-like excitation mechanism. The excitation around 965 nm is not resonant to any ground state absorption, but resonant to the $^5I_7 \rightarrow {}^5F_5$, $^5I_5 \rightarrow {}^3K_8$, and $^5F_5 \rightarrow {}^5G_4$ excited state absorption transitions. However, the detailed excitation scheme in these cases needs to be further investigated. The most intense emission in the visible range is obtained after excitation around 888 nm. This observation is consistent with the ground state absorption and $\Delta T/T$-spectra for Ho^{3+}:BYF (see Fig. 2). At 888 nm (11261 cm^{-1}), there is a strong peak in the absorbance spectrum according to the transition from the ground state to the 3rd Stark level of the $^5I_5$ multiplet (see Table 1). In the $\Delta T/T$-spectrum, this absorption peak does not occur. This indicates, that it is overlapped by a strong ESA transition between the 0th Stark level of the $^5I_5$ multiplet at 11 238 cm^{-1} and the 9th Stark level of the $({}^5F_1, {}^5G_6)$ multiplet at 22 493 cm^{-1} (see Table 1).

In the room temperature emission spectrum (Fig. 3)

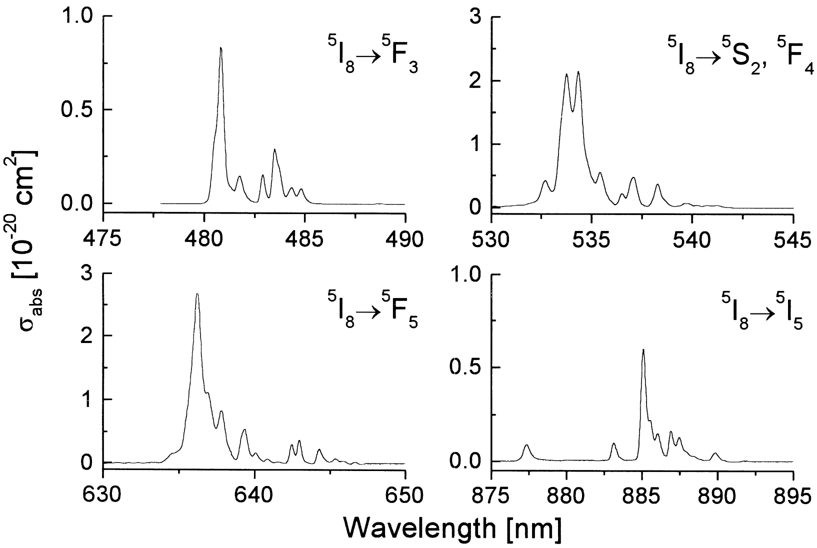

Fig. 1. Absorption cross-sections for the transitions $^5I_8 \rightarrow {}^5F_3$, $^5I_8 \rightarrow ({}^5F_4, {}^5S_2)$, $^5I_8 \rightarrow {}^5F_5$, and $^5I_8 \rightarrow {}^5I_5$ at 15 K.

Table 1
The energetic positions of the Stark levels for Ho^{3+}:BaY_2F_8 crystal[a]

Multiplet	Stark levels positions	No. of levels expected	No. of levels found
$^5I_8$	0, 19, 38, 48, 75, 119, (126), (184), 190, 232, 268, 303, 346, 371	17	14
$^5I_7$	5064, 5096, 5109, 5124, 5140, 5153, 5178, 5191, 5199, 5217, 5232, 5289, 5318	15	13
$^5I_6$	8670, 8685, 8695, 8701, 8707, 8711, 8715, 8740, 8745, 8755, 8800, 8810, 8848	13	13
$^5I_5$	11238, 11255, 11261, 11267, 11274, 11286, 11291, 11298, 11323, 11397	11	10
$^5I_4$	13226, 13262, 13352, 13363, 13370, 13383, 13400, 13408, 13416	9	9
$^5F_5$	15482, 15495, 15221, 15553, 15564, 15623, 15641, 15646, 15679, 15701, 15718	11	11
$^5S_2 + {}^5F_4$	18528, 18564, 18577, 18619, 18639, 18676, 18714, 18735, 18772, (18801), 18825, 18863, (18920)	14	13
$^5F_3$	20647, 20671, 20682, 20708, 20757, 20798, 20811	7	7
$^5F_2 + {}^3K_8$	21092, 21134, 21164, 21181, 21217, 21253, 21272, 21382, 21417, 21428, 21458, 21497, 21533, 21556	22	14
$^5F_1 + {}^5G_6$	22148, 22183, 22220, 22255, 22342, 22373, 22416, 22451, 22493, 22540, 22659, 22731	16	12
$^5G_5$	24022, 24064, 24124, 24153, 24158, 24184, 24234	11	7

[a] The values in parentheses are uncertain.

recorded for 888 nm excitation, emission bands due to the transitions $^5F_3 \rightarrow {}^5I_8$ (blue emission around 490 nm), $^5S_2 \rightarrow {}^5I_8$ (green emission around 545 nm), $^5F_5 \rightarrow {}^5I_8$ (red emission around 655 nm) and $^5S_2 \rightarrow {}^5I_7$ transition (infrared emission around 750 nm) are present. In the normalised spectrum the relative integrated intensities of the above bands are approximately 0.03:1:0.03:0.15. In order to describe the upconversion mechanism, some additional characteristics of the emission were investigated. The number of photons involved in the upconversion processes leading to the visible emission was derived from the intensity dependencies of the blue, green and red emission on the excitation power ($I_{em} \propto I_p^n$) by two methods. From the integrated intensity of the corresponding components in the spectra, we determine $n = 1.9$, 1.6 and 1.5 for the blue, green and red (650 nm) emission, respectively (the error in the determination is approximately 0.1). In Fig. 4, $I_{em}(I_p)$ is depicted in a double logarithmic scale. In the second method, the temporal evolutions of the $^5F_3$, $^5S_2$ and $^5F_5$ population were recorded after chopped continuous wave excitation at 888 nm (characteristics not shown here). From the steady state population values taken for different excitation powers we determine $n = 1.9$, 1.6 and 1.4 for blue, green and red emission, respectively (the error in the determination is approximately 0.1). Both sets of values are very close to each other, implying a small experimental error. The slopes are nearly independent from the excitation power in the investigated range. The slope values are different for the three emission components, suggesting different mechanisms for populating the corresponding luminescent multiplets. Taking into account the above described observations and the Ho^{3+} energy level diagram, the following excitation scheme for the observed up-converted emission is proposed (see Fig. 5).

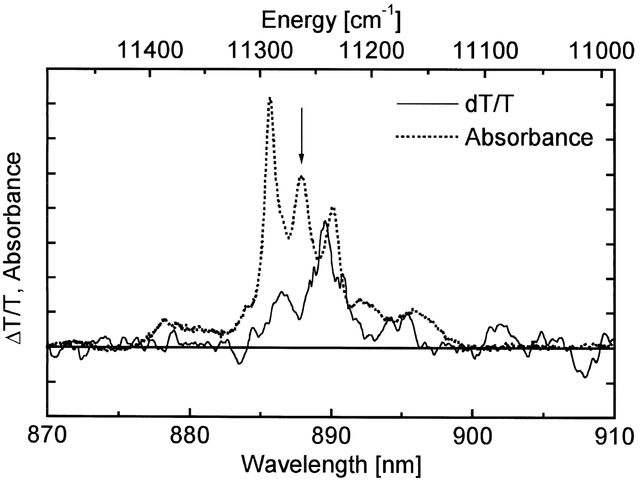

Fig. 2. $\Delta T/T$ spectrum (explanation see text) in the region of the $^5I_8 \rightarrow {}^5I_5$ absorption around 888 nm at room temperature in comparison with the absorbance spectrum. Both spectra are not normalised. The arrow marks the optimum excitation wavelength for the upconverted emission.

The upconversion process leading to the blue emission starts with the $^5I_8 \rightarrow {}^5I_5$ GSA followed by the $^5I_5 \rightarrow {}^5F_1$ ESA transition. Fast phonon de-excitation populates the $^5F_3$ level, from which blue emission ($^5F_3 \rightarrow {}^5I_8$) takes place. This is supported by the quadratic dependence of the blue emission on the pump intensity.

The green (545 nm) and infrared (750 nm) emission both occur from the $^5S_2$ level. This level is populated from

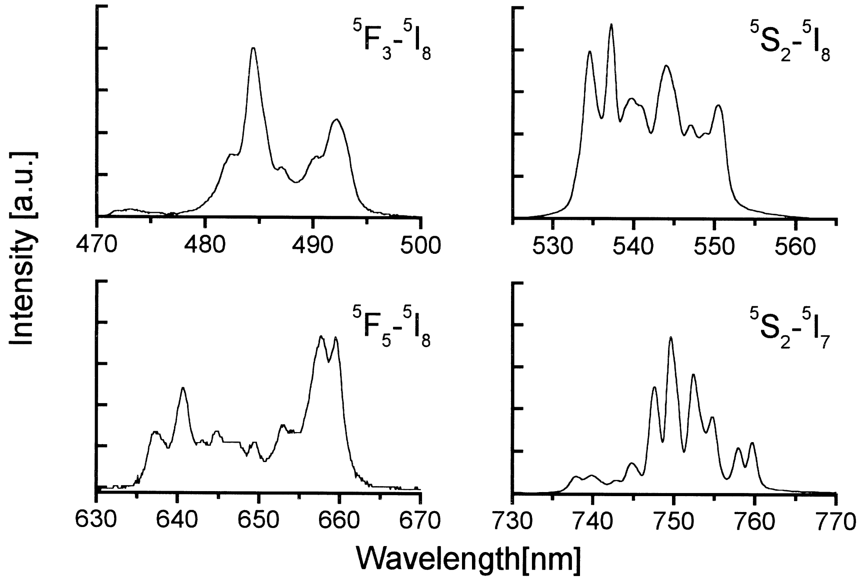

Fig. 3. Emission spectra of the Ho^{3+}:BaY_2F_8 crystal recorded at 300 K ($\lambda_{exc}=888$ nm).

the $^5F_3$ level by multiphonon decay and also by the cross relaxation process s1 [($^5F_3$, $^5I_5$)→($^5S_2$, $^5I_4$)]. In this case, the slope of the process would be 2. However, radiative decay from the $^5F_3$ level as well as the cross relaxation process s4 [($^5I_5$, $^5I_8$)→($^5I_7$, $^5I_7$)] take place and reduces the slope to about 1.8 in the low pump power limit. A further reduction occurs because of the cross relaxation process s2 [($^5F_3$, $^5I_8$)→($^5F_5$, $^5I_7$)], which bypasses the $^5S_2$ level. A detailed modelling of the involved processes is in progress.

The emission around 650 nm corresponds to the $^5F_5 \rightarrow {}^5I_8$ transition. There are several possible ways for the population of the $^5F_5$ level. One of these processes is the multiphonon relaxation from the $^5S_2$ multiplet. However, it cannot be the only process, because the slopes characterising the green and red emission differ. So, additional processes must be taken into account. Most favourable is the cross-relaxation process s2 [($^5F_3$, $^5I_8$)→($^5F_5$, $^5I_7$)], which follows the initial two step absorption. Another possible process is non-resonant ESA of the excitation radiation (888 nm) from the $^5I_7$ multiplet. This requires the population of the $^5I_7$ level. This is possible by the cross relaxation processes s2 and s3 [($^5S_2$, $^5I_8$)→($^5I_4$, $^5I_7$)] as well as s4 [($^5I_5$, $^5I_8$)→($^5I_7$, $^5I_7$)]. However, the process s4 requires the assistance of phonons and seems to be less probable. Anyway, the $^5I_7$ multiplet has a very long lifetime and thus can act as a suitable initial level for ESA.

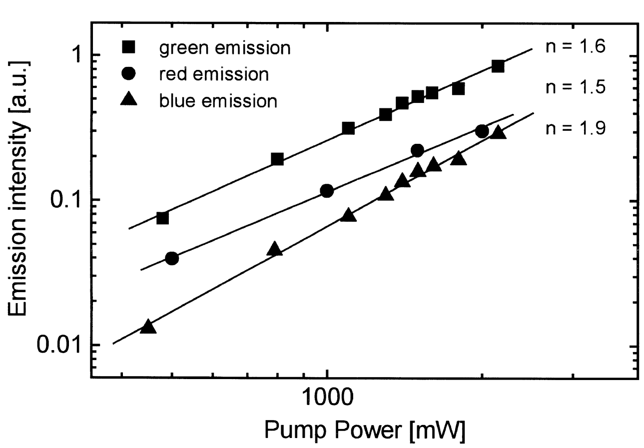

Fig. 4. Power pump dependencies at room temperature for the $^5F_3 \rightarrow {}^5I_8$ (blue), $^5S_2 \rightarrow {}^5I_8$ (green), $^5F_5 \rightarrow {}^5I_8$ (red) transitions for Ho^{3+}:BaY_2F_8 ($\lambda_{exc}=888$ nm).

In the above described processes leading to the visible emission a variety of non-radiative decay paths, multiphonon as well as cross relaxation processes, take place. Thus, the radiative and experimental lifetimes of the involved energy levels are expected to differ strongly. The radiative lifetimes, derived from Judd-Ofelt calculations, of the $^5S_2$ and $^5F_5$ are 530 and 317 μs, respectively [4]. The experimental values for this two levels are 270 and 55 μs at room temperature giving a quantum efficiency of approximately 50 and 17%, respectively, thus indicating the influence of multiphonon decay and energy transfer processes. The radiative lifetime of $^5F_3$ is estimated to be 295 μs using the Ω_i values from [4]. However, the experimentally observed lifetime is only around 2–3 μs at room temperature giving a quantum efficiency of approximately 1%. This shortening of the lifetime implies that this level is depopulated not only radiatively but also to a large extend by non-radiative decay. The energetic distance between the $^5F_3$ level and the $^5F_4$ level is 1875 cm^{-1} (see Table 1). Thus, the number of phonons required to bridge the energy gap is about 5 and a significant multiphonon decay rate is expected.

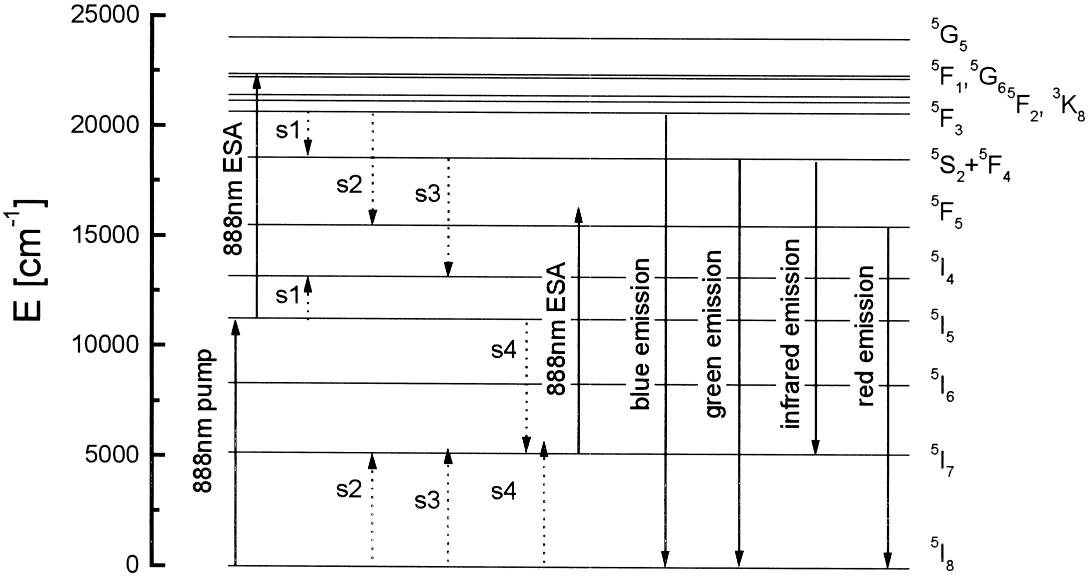

Fig. 5. Energy level and excitation scheme for Ho^{3+}:BaY_2F_8 after excitation at 888 nm.

For a better understanding and description of all processes involved which lead to the visible emission of Ho^{3+}:BYF some more experimental work (temperature and concentration dependencies) as well as theoretical modelling would be necessary. This work is in progress.

4. Summary

We have checked the possibility to get the upconversion emission for Ho^{3+}:BYF after continuous wave excitation in the range from 730 to about 1000 nm. The most intense visible emission is observed after excitation into the $^5I_5$ multiplet (around 888 nm). Blue, green, and red components are present in the upconverted emission spectrum, from which the green one is of the highest intensity. The slopes of the power dependencies of the above components are different from each other, indicating different population mechanisms of the luminescent levels. Various combinations of two step absorption, cross-relaxation, multiphonon decay as well as resonant and non-resonant excited state absorption processes are involved. This preliminary study shows that an efficient upconverted green emission is observed at room temperature for Ho^{3+}:BYF. Further investigations are necessary in order to describe the system microscopically as well as to evaluate the possibility to realise laser oscillation in this system.

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