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The up-conversion processes in Ho^{3+} doped $LiTaO_3$

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Abstract

The up-conversion processes in Ho^{3+} doped lithium tantalate were investigated under continuous wave excitation into the $^5F_5$, $^5I_4$ or $^5I_5$ multiplets and with the energy due to the $^5I_6 \rightarrow {}^5S_2$ transition, which is not resonant with the ground state absorption. The most intense green emission originating from the $^5S_2$ multiplet is observed after excitation into the $^5F_5$ and $^5I_4$ multiplets. The excited state absorption spectrum, emission spectra, dependencies of emission intensity on the excitation power as well as possible mechanisms of excitation are presented. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ho^{3+}; Lithium tantalate; Excited state absorption; Up-conversion; Insulators; Optical properties; Luminescence

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1. Introduction

In up-conversion processes quanta of the excitation light (usually from IR or NIR range) are converted in the optical material into quanta of a higher energy (usually in the visible range). It is expected that these processes can be applied in new optical devices such as all-solid-state lasers for VIS range, IR-detectors, solid-state displays or in new efficient phosphors. Because of a suitable Ho^{3+} energy level scheme which enables a variety of excited state absorption and cross-relaxation processes, holmium doped materials are promising for applications. However, for many years investigation of up-conversion processes focused first of all on Ho-Yb doped materials [1–4]. Recently the number of works dealing with up-conversion in singly-doped holmium materials increased [5–13] and for instance a new efficient photon-avalanche pumping scheme was reported for some of them [10–12].

In this paper we investigate the up-conversion processes in $LiTaO_3$:Ho^{3+} crystals. The host crystal is well known (isostructural to $LiNbO_3$) and widely applied as a nonlinear crystal with very good electro-optical properties [14]. For both $LiNbO_3$ and $LiTaO_3$ optical properties were investigated for crystals doped with rare earth ions (Nd, Er, Pr, Tm, Er, Dy) and for some of them laser oscillation has been achieved [15,16]. Recently spectroscopic properties of Ho^{3+} doped $LiTaO_3$ were investigated and the energy level scheme as well the results of Judd-Ofelt analysis and transition rates for main transitions were reported in Ref. [17]. The up-conversion mechanism after excitation into the $^5F_5$ multiplet and its temperature dependence were studied in Ref. [13]. In this work the excited state absorption (ESA) measurements of $LiTaO_3$:Ho^{3+} crystal are presented. We discuss and compare the up-conversion processes leading to the green emission from the $^5S_2$ multiplet after excitation into some spectral regions where ESA bands occur, i.e. around 650, 760 and 980 nm.

2. Experimental

The crystal investigated was grown by the Czochralski technique with 0.5% mol Ho^{3+} in the melt (9.5×10^{19} ions/cm^3). The up-converted emission was investigated after excitation with the 647.1-nm line of a krypton laser or after excitation at about 760, 890 or 980 nm with a continuous wave (cw) Ti:sapphire laser pumped by a frequency doubled Nd:YVO_4 laser (Spectra Physics Millenia X). The emission spectra were recorded in a conventional set-up consisting of a 1/2-m SPEX or 1-m double-

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grating monochromator, an Si-diode or an S-1 type photomultiplier, a lock-in amplifier (Stanford Research), and a personal computer. The spectra were afterwards corrected according to the spectral sensitivity of the set-up used. The excited state absorption (ESA) measurements were performed at RT by a pump and probe technique in the cw regime. The detailed description of the method can be found elsewhere [18]. Briefly described, in this experiment the transmission signal is measured by a lock-in amplifier for the crystal probed with a halogen lamp only (transmission signal I_u) and for the crystal simultaneously excited with a laser at a certain wavelength absorbed in the crystal and probed with a halogen lamp (transmission signal I_p). As a pump laser wavelength we used either 890 nm (Ti:sapphire) or 531 nm (SHG of Nd:YVO_4). As an ESA spectrum we shall denote the difference spectrum ($I_u - I_p$) measured by a second lock-in amplifier and afterwards normalised to the transmission signal ($I_u \approx I_p$). For a qualitative estimation one can roughly assume that in the ranges of the positive signal ground state absorption (GSA) and stimulated emission (SE) dominate, while in the range of negative signal mainly ESA dominates. From the transmission spectrum of the unpumped crystal (I_u) the ground state absorption bands were derived.

3. Results and discussion

Within the energy diagram schema of trivalent holmium (Fig. 1) there are few possible pumping mechanisms leading to the up-converted emission from the luminescent levels: $^5G_4$ ('violet' component ~390 nm), $^5F_3$ ('blue' ~485 nm), $^5S_2$, $^5F_4$ ('green' ~550 nm and 'infrared' ~750 nm), $^5F_5$ ('red' ~650 nm). Depending on the pumping scheme (up-conversion mechanism) and properties of the host (rate of non-radiative processes) different relative intensities between the above emission components have been observed in the up-conversion emission spectra for thus far investigated holmium materials [6–9,12].

In order to evaluate the possibility of up-conversion pumping by absorption from holmium excited states in $LiTaO_3$:Ho^{3+} we have measured the ESA spectrum in the range from 450 to 1050 nm (Fig. 2, bottom layer). For comparison, bands of GSA derived from the transmission spectrum measured simultaneously in the same set-up are also shown (Fig. 2, top layer). We have assigned the main ESA transitions (depicted in Fig. 2a) on the basis of the energy level scheme for $LiTaO_3$:Ho^{3+} [17]. In many spectral regions the ESA transitions from $^5I_7$ and $^5I_6$ multiplets can overlap. The populations of these levels

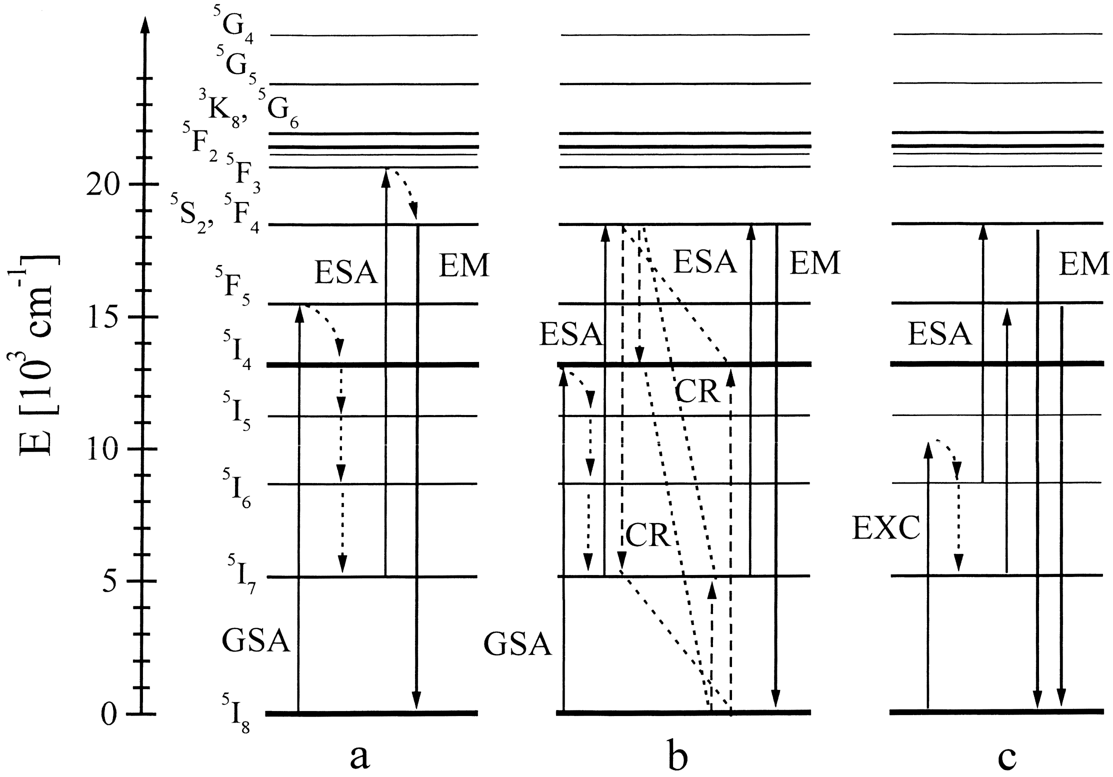

Fig. 1. Schematic energy diagram of Ho^{3+} levels in $LiTaO_3$ and possible up-conversion mechanisms resulting in the green emission from the $^5S_2$ multiplet: (a) for excitation into $^5F_5$ multiplet; (b) for excitation into the $^5I_4$ multiplet; (c) for excitation at 980-nm wavelength. The processes involved: CR, cross relaxation; EM, emission; ESA, excited state absorption; EXC, excitation; GSA, ground state absorption.

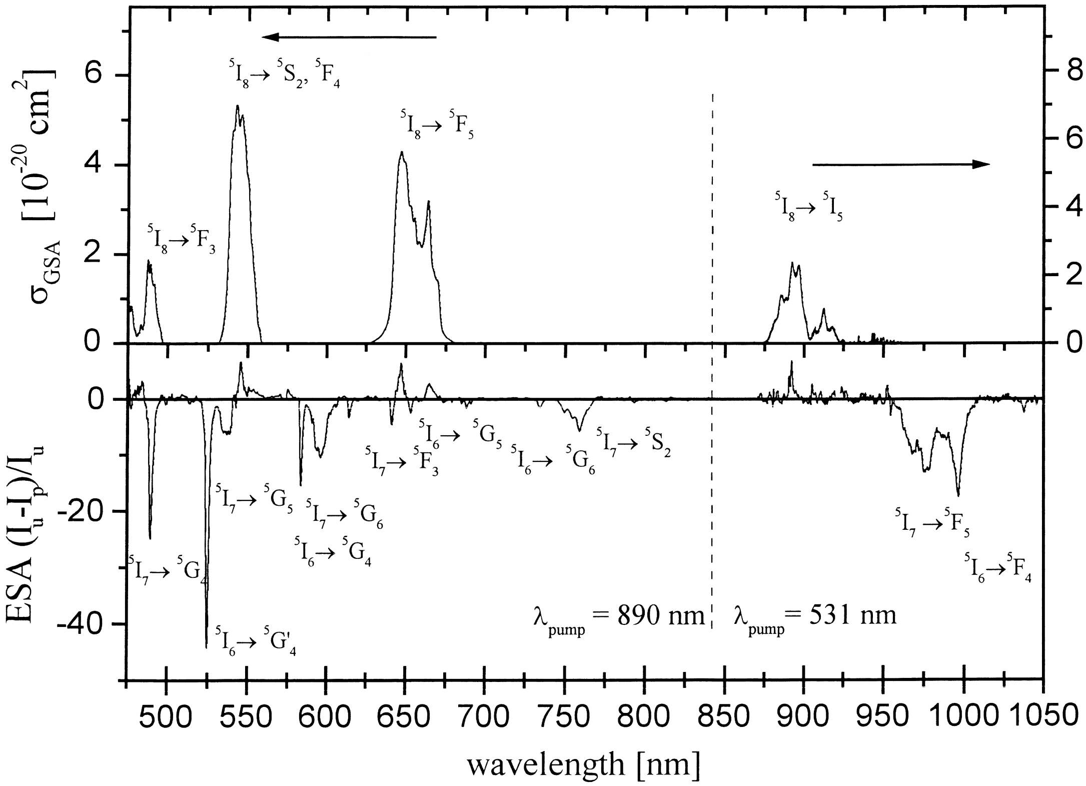

Fig. 2. The ESA spectrum of the LiTaO$_3$:Ho^{3+} crystal recorded at RT in a cw regime (bottom layer) with the pump laser wavelength 890 nm (left, up to 850 nm) or 531 nm (right). For comparison a part of GSA spectrum (RT) is shown at the same spectral range (top layer). The propagation vector of the excitation was parallel to the optical axis of the crystal ($\vec{k}\|\vec{c}$, α polarisation).

under the experimental pumping conditions are not known, hence an exact analysis of ESA spectrum and direct determination of the cross-sections [18] of the involved transitions is not possible. Some more information could be gained from measurements of ESA in a time-resolved regime or from theoretical considerations (J-O analysis) and simulations (rate equation analysis) performed for every spectral range.

We distinguish in our spectrum few spectral regions where the relatively strong ESA processes can lead to the up-conversion of excitation radiation, i.e. ~490, 525–540, 584–613, 642–690 nm (overlapping of ESA and strong GSA), 730–765 nm (overlapping of strong ESA and weak GSA) and 950–1020 nm. It is perhaps worth mentioning, that excitation at the wavelength around 584 nm was reported recently for YAlO$_3$:Ho [10] and Ho-doped fluoride glass [11] to result with the photon-avalanche. However, the excitation source for this experiment (tuneable dye laser) is not widely accessible yet. In the present work we focus on the excitation experiments in the spectral ranges of 642–690, 730–765 and 950–1020 nm, which are nowadays already covered by commercially available laser diodes and thus of possible practical interest.

The excitation within the range of 642–660 nm, where the GSA to the $^5F_5$ multiplet overlaps with the ESA (possible overlap of both $^5I_6 \to {}^5G_5$ and $^5I_7 \to {}^5F_3$ transitions) was obtained with the krypton laser (647.1-nm line). This excitation brings about a green emission from the $^5S_2$ multiplet (Fig. 3). The intensity of this emission depends significantly on the temperature [13]. Luminescence intensity decreases about ten times from ~10 to 300 K [13], although the lifetime of the $^5S_2$ multiplet decreases only ~30% in this temperature range [17]. This behaviour implies that the intensity of the up-converted luminescence depends probably not only on the contribution of non-radiative transitions from $^5S_2$. The mechanism of up-conversion is also very sensitive to the temperature due to non-radiative decay processes from intermediate levels, e.g. $^5I_6$ and $^5I_7$, and due to the required energy match between levels involved in the GSA- and ESA-processes. This behaviour should be further investigated, ESA spectra should be taken also at other temperatures to determine the matching conditions and the temperature dependencies of lifetimes of all involved levels should be known. The serious limitation with respect to the optimisation of the up-conversion process at the moment is the only one excitation wavelength available for this spectral range (krypton laser line, 647.1 nm). By using this excitation the

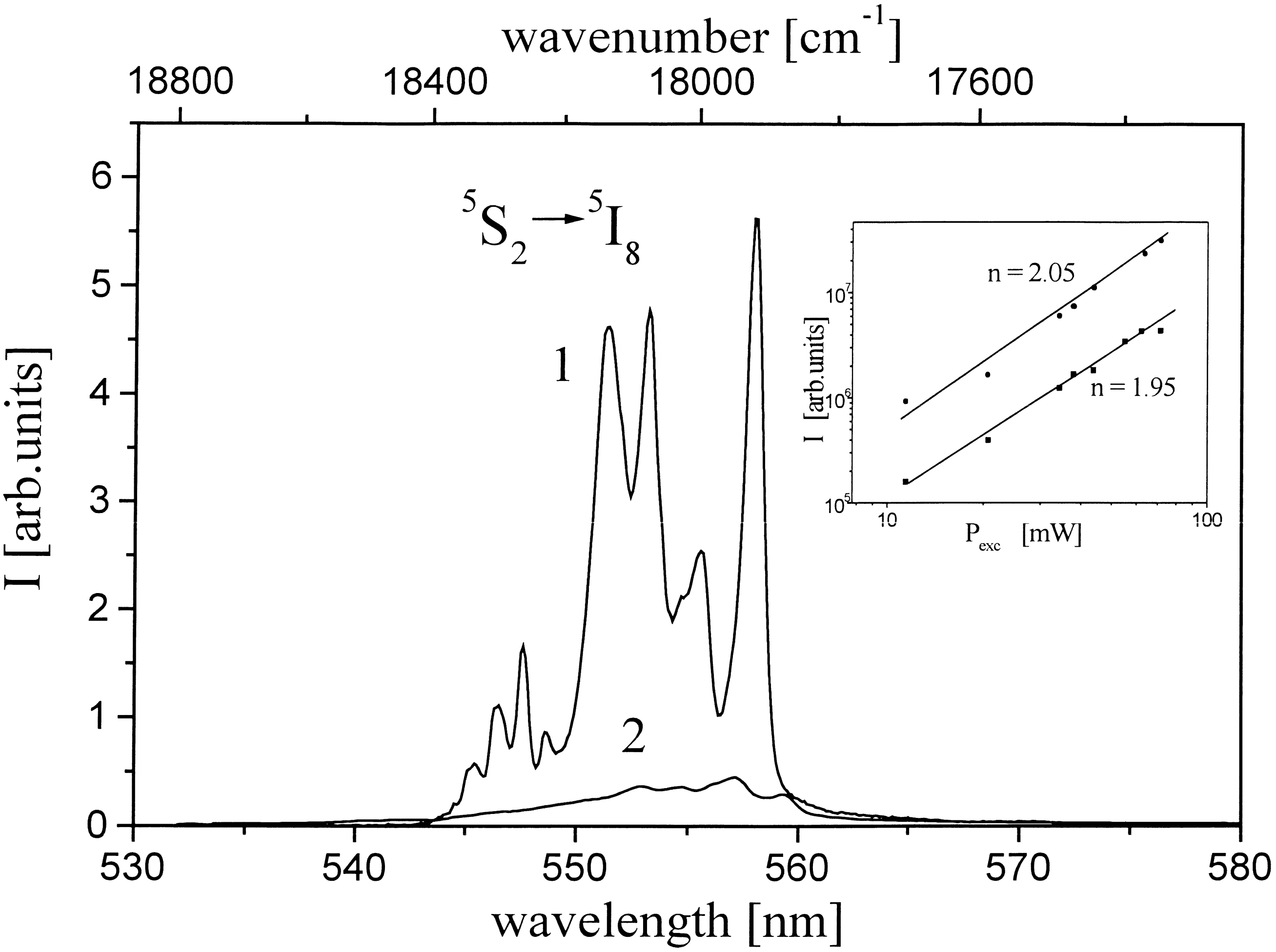

Fig. 3. Emission spectrum of LiTaO$_3$:Ho^{3+} crystal recorded at 15 K (1) and at RT (2) when exciting into $^5F_5$ multiplet (λ_{exc}=647.1-nm line of krypton laser). In the inset the dependence of the up-converted green emission intensity on the excitation power is shown (log-log scale), n=1.95 at RT, 2.05 at 15 K.

optimal conditions for obtaining the most intense green emission at room temperature are possibly not fulfilled. The dependence of the intensity of up-converted emission measured as a function of the intensity of excitation characterises to a certain extent the mechanism of processes investigated. The expected dependence is expressed as $I_{out}\sim I^n_{exc}$ [19] where I_{out}, I_{exc} are the output and excitation intensity, respectively, n is the number of photons absorbed per one photon emitted. In the case of resonant excitation of the emitting level (directly or through energy transfer) n equals to unity [1], for two-photon processes n=2 [1,6,8], for processes involving more photons n is larger (e.g. up to five-photon processes were found in Er-doped systems [19]). The intensity of up-converted luminescence (exc. into the $^5F_5$ multiplet at 647.1 nm) measured by us as a function of excitation power and depicted in the double logarithmic scale gives the slope of the linear fit near to two, independently of the temperature (Fig. 3, inset). From the slope obtained, energy level scheme and ESA spectrum, two processes populating the $^5S_2$ multiplet could be taken into account: excitation by ESA from the $^5I_7$ multiplet to the $^5F_3$ multiplet followed by the non-radiative relaxation to the $^5S_2$ multiplet (Fig. 1a) and/or excitation by ESA from the $^5I_6$ multiplet to the $^5G_5$ multiplet followed by the non-radiative relaxation. However, additional measurements of kinetics of this process and its modelling with rate equations [13] imply, that mainly the former mechanism contributes to the green emission.

In the spectral range around 760 nm, the strong ESA bands overlap with very weak GSA bands due to the transition from the ground $^5I_8$ to the $^5I_4$ multiplet. The absorption bands in this range are practically not measurable for samples of a few millimetre length and of dopant concentration in the typical range used for investigations. Indeed, the probability of this electric dipole absorption transition is very low due to the appropriate matrix elements [20]. As this transition is also magnetic dipole forbidden, one could expect a very inefficient pumping process in this spectral range. Despite this, an intensive green up-converted emission is observed after cw excitation into the $^5I_4$ multiplet around 760-nm wavelength. In the emission spectrum (Fig. 4a) bands due to the strong green emission from the $^5S_2$ and to the weak red emission from the $^5F_5$ multiplet are observed. The mechanism of excitation in this case seems to be complex. We have measured the temporal dependencies of the green emission for different excitation powers as well as the dependence of emission spectrum on the excitation power. From the integrated intensity of the green band in the spectrum and from the intensity of temporal dependencies taken in the steady state we have determined the dependence of the emission intensity on the excitation power (Fig. 4, inset). The slope of the appropriate linear fit is ~1.5, i.e. significantly lower than 2. We suppose that in that case the green emission is induced in a few-step process (Fig. 1b). In the first step the weak ground state absorption (GSA) $^5I_8 \rightarrow {}^5I_4$ populates the $^5I_4$ multiplet and due to the non-radiative relaxation also the $^5I_7$ multiplet. In the next step the ESA transition $^5I_7 \rightarrow {}^5S_2$ takes place. Further population of the $^5I_7$ multiplet can be due not only to the relaxation from the $^5I_4$ multiplet but also to the following cross relaxation processes: $({}^5S_2, {}^5I_8) \rightarrow ({}^5I_7, {}^5I_4)$ and/or $({}^5S_2, {}^5I_8) \rightarrow ({}^5I_4, {}^5I_7)$. Hence the ESA from the $^5I_7$ multiplet is enhanced and finally leads to the efficient population of the $^5S_2$ multiplet and to the green emission. Due to the contribution of cross relaxation processes the mechanism is described no longer by an integer number n of photons involved in the up-conversion. The green up-converted emission after excitation into the $^5I_4$ multiplet was reported up to now for only few other holmium-doped materials [6–9,12]. It was also reported that the slope of the power dependence was lower than two (1.8 in Ref [8], 1.3 in Ref. [9], 1.6 in Ref. [12]). The more detailed description of this process, which can be of general validity for Ho^{3+} doped materials, requires some additional experimental investigations (e.g. dependence on dopant concentration and on the temperature) as well as a theoretical modelling.

In some Ho^{3+}-doped materials the excitation into the $^5I_5$ multiplet (around 890 nm) brings about a strong green or/and red up-converted emission [6–8,10]. The emission was ascribed as due either to the direct two-step absorption

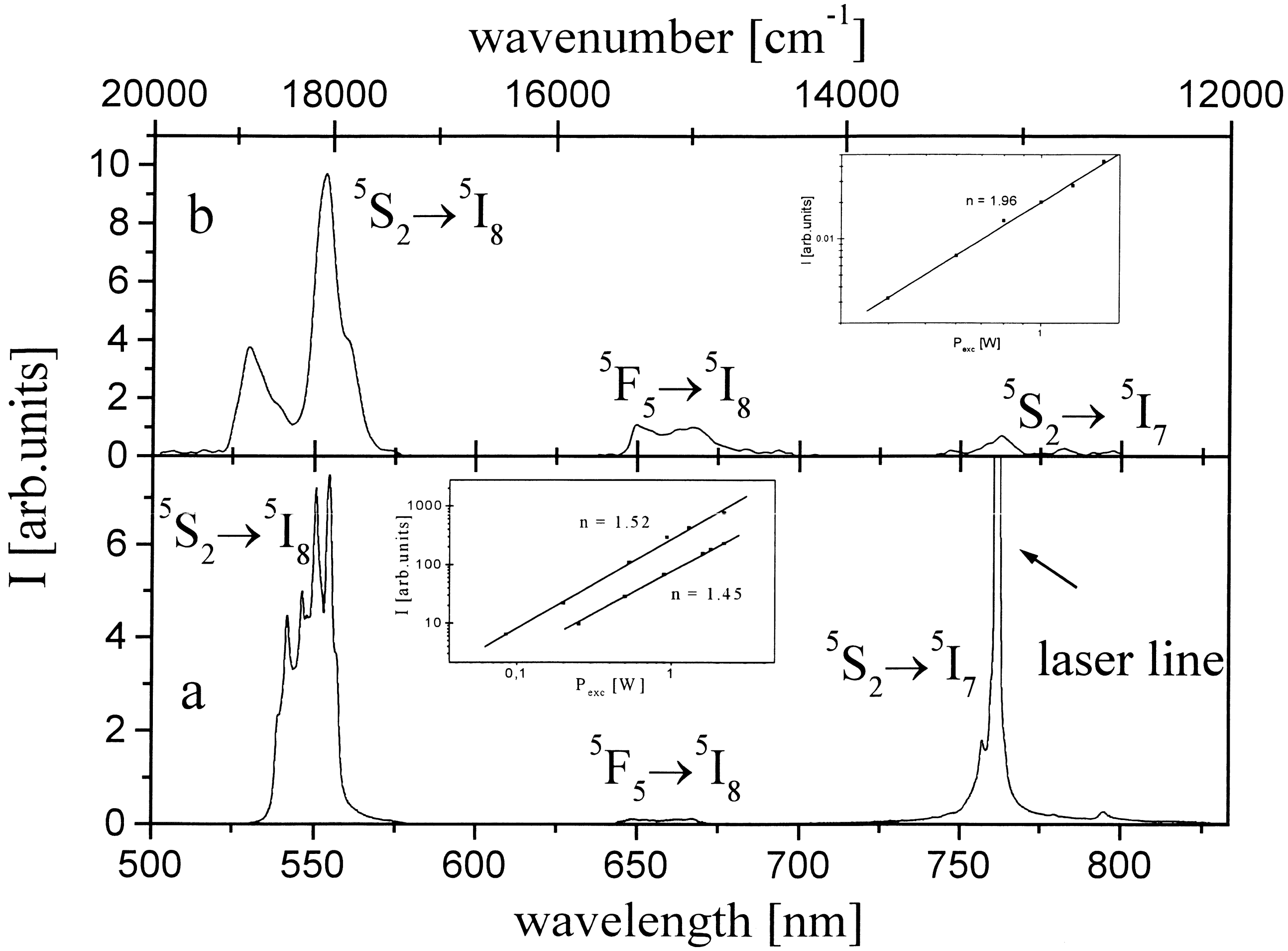

Fig. 4. Emission spectrum of $LiTaO_3$:Ho^{3+} crystal recorded at RT when (a, bottom layer) exciting into $^5I_4$ multiplet (760 nm) and when (b, upper layer) exciting with the energy matching the $^5I_6 \rightarrow {}^5S_2$ ESA transition (980 nm). The band around 530 nm at the upper spectrum is most probably an artifact due to the second harmonic of the Nd:YVO_4 laser used in the experimental set-up. The dependencies of the green emission intensity on the excitation power are shown in the insets: (a) slope values $n=1.45$ and 1.52 obtained from the recorded emission spectra or from the temporal dependencies, respectively; (b) slope $n=1.96$.

(ESA) from the $^5I_5$ multiplet [6,7], to the energy transfer up-conversion [10] or to both mechanisms taking place [8]. In the case of our crystal there is practically no ESA in this spectral range so a direct two-step absorption is not expected. Actually, none of the higher lying Stark levels of $^5G_6$ or $^5G_5$ is in resonance with the energy of such a transition. Even if thermal broadening and populating of the involved multiplets could make this transition possible, the obstacle for ESA from this level in our case is its very short lifetime (0.5 μs [13]) and multiphonon relaxation to the lower-lying levels [13,17]. Indeed, using the excitation wavelength around 890 nm we observed a green emission of a very low intensity, practically not measurable and of no practical importance.

Much brighter emission (but not so intense as by excitation at 647.1 or 760 nm) was observed after the excitation at wavelength around 980 nm. Excitation energy in this case is not strictly resonant with any of the GSA transitions (Fig. 1c) but it matches well the ESA transitions (Fig. 2) $^5I_7 \rightarrow ^5F_5$ or/and $^5I_6 \rightarrow ^5F_4$. In the emission spectrum (Fig. 4b) the relative intensity of the 'red' emission from the $^5F_5$ multiplet is stronger than recorded by excitation with the 760 nm, suggesting that the $^5I_7 \rightarrow ^5F_5$ ESA populates this multiplet in addition to the non-radiative decay from the $^5S_2$ multiplet. However, the mechanism leading to the green emission must be the $^5I_6 \rightarrow ^5F_4$ ESA transition followed by the non-radiative decay to the $^5S_2$ multiplet. The dependence of the intensity on the excitation power gives a slope of ~2 (Fig. 4b, inset), which is in agreement with the expected excitation schema (Fig. 1c). For this mechanism the way of building the initial population of the $^5I_6$ multiplet is not quite clear. The same question arises for photon-avalanche process [10,21], in which the excitation energy is not in resonance with the GSA but with ESA from a certain metastable state. It is supposed that the weak vibronic states of the nearest GSA levels participate in photon-avalanche mechanism [21]. In our case of excitation around 980 nm there are no features characteristic for a typical avalanche process (existence of cross relaxation processes populating the metastable stable, threshold of the process, characteristic shape of the temporal dependence with a bending point), thus the observed intensity is not very high.

4. Summary

By using different excitation wavelengths (647.1, 760, 890 and 980 nm) we investigated up-conversion processes resulting in the green and red up-converted emission in $LiTaO_3:Ho^{3+}$. The strongest green emission is observed when exciting within the $^5F_5$ and $^5I_4$ multiplets, whereas the weakest is within the $^5I_5$ multiplet. The up-conversion processes investigated are characterised by the numbers of involved photons n ~2 (excitation at 647.1 and around 980 nm) or ~1.5 (excitation at 760 nm). The behaviour observed for our crystal with the excitation around 760 nm seems to be of general validity for Ho-doped materials and can be of possible practical application.

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