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ADP011933

TITLE: Stokes and Anti Stokes Luminescence in LiTaO3:Ho

This paper is part of the following report:

TITLE: International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane, Poland on 9-12 October 2000

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Stokes and anti Stokes luminescence in $LiTaO_3$:Ho

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ABSTRACT

The paper deals with the excitation and decay of excited states of holmium in $LiTaO_3$ single crystals. Particular attention is paid to processes governing a population build up on the $^5S_2$ and $^5I_7$ metastable states whose quantum efficiencies are sufficiently high to be considered as initial levels for a laser transition. We observed for the first time, to our knowledge, an efficient conversion of the 647.1 nm light of a krypton ion laser into green luminescence in the material studied. Based upon analysis of excited state relaxation dynamics it is concluded that the mechanism involved is the excited state absorption from the long lived $^5I_7$ level. Efficient single wavelength excitation is due to coincidence of transition energies of the ground state absorption and excited state absorption.

Keywords: Stokes luminescence, $LiTaO_3$ single crystals, green luminescence.

1. INTRODUCTION

Anti Stokes luminescence, frequently referred as upconverted luminescence in rare earth doped solid matrices attracts much attention recently because it offers a potential of a visible laser emission. Numerous works deal with crystals and glasses doped with thulium or erbium. Upconversion in holmium doped matrices has been studied less extensively. Upconversion lasing in fluoride crystals doped with Ho + Yb [1], and in fluoride glass ZBLAN: Ho [2] has been achieved. Very recently upconversion phenomena in $YAlO_3$:Ho have been studied[3].

In this paper we report on luminescence of $LiTaO_3$ crystals with special attention paid to the red-to-green conversion processes.

2. EXPERIMENTAL

Single crystals of $LiTaO_3$:Ho were grown from congruent melt by the Czochralski method. Uniformly doped and good quality crystals have been obtained. The concentration of Ho^{3+} in the crystals studied was 0.3 and 0.5 at %. Absorption spectra were measured with a Varian model 2300 absorption spectrophotometer. The sample luminescence was exited by Argon laser emitting at 488 nm and Ti:sapphire laser emitting at 751 nm or by Krypton laser at 647.1 nm and dispersed by 1m double grating monochromator, detected by photomultiplier or InSb detector and analyzed by a Stanford Model SRS 250 Boxcar integrator.

3. RESULTS AND DISCUSSION

Room temperature luminescence spectrum of Ho^{3+} ion in $LiTaO_3$ is shown in Fig.1. The observed lines are not fully resolved and all are strongly inhomogeneously broadened. The electronic structure of Ho^{3+} ions is such that the visible and infrared transitions involve levels having a high multiplicity (2J+1) which gives a high number of Stark levels. This leads to strong levels overlapping. For some multiplets, additional peak splitting has been detected suggesting a multi-site occupancy of Ho^{3+} ions in $LiTaO_3$ lattice [4]. Green luminescence under the excitation by a krypton ion laser tuned to λ=647.1 nm was observed at room temperature. Obtained luminescence spectrum was identical as that recorded previously, when exciting into levels above $^5S_2$ level, and it was associated undoubtedly with the $^2S_2$ – $^5I_8$ transition of Ho^{3+} presented in Fig.1. In Fig.2 we present log-log plot of intensity of upconverted luminescence versus excitation power, recorded at 300K with a sample containing 0.5 % of holmium. Experimental data are shown by points whereas solid line indicates the power

Intl. Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals, Antoni Rogaski, Krzysztof Adamiec, Pawel Madejczyk, Editors, Proceedings of SPIE Vol. 4412 (2001) © 2001 SPIE · 0277-786X/01/$15.00

law behavior. Luminescence intensity is a nearly quadratic function of the excitation power (Slope ≅ 2), up to maximum available excitation power equal to 72 mW.

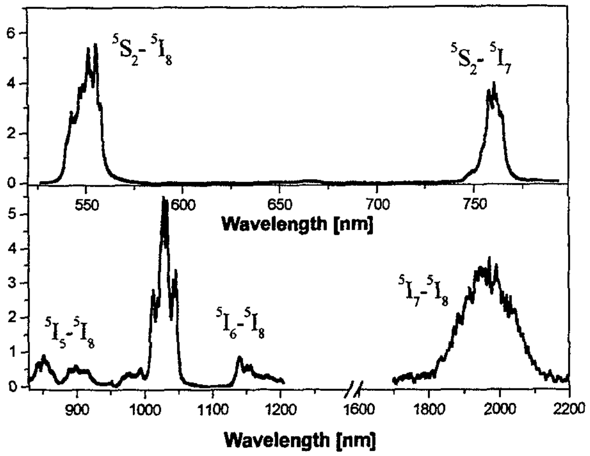

Fig. 1. Room temperature luminescence spectrum of Ho^{3+} ion in $LiTaO_3$.

In principle three mechanisms may be involved in the upconversion process, namely an absorption from an excited state (ESA), an excitation by energy transfer between activators and finally a photon avalanche, which combines ESA and an efficient cross relaxation. The latter mechanism is characterized by an excitation power threshold, above which the upconverted luminescence grows by orders of magnitude [6]. It can be seen in Fig. 2 that such a threshold has not been attained. Therefore a photon avalanche mechanism may be neglected in our case. We may neglect also the upconversion by energy transfer based on the observation that the lifetimes of excited states of Ho^{+3} in investigated samples do not differ indicating that an ion–ion interaction is weak. Thus, we consider mechanisms of upconversion processes from excited states.

To elucidate these mechanisms, from the analysis of the energy level diagram of Ho^{3+} in $LiTaO_3$ presented in [4], we have built the σ_{ESA} spectra corresponding to $^5I_7$–$^5F_2$ and $^5I_7$–$^5F_3$ transitions around 647 nm using the expression [5].

$$\sigma_{ESA}^{J-J'}(\lambda) = \bar{\lambda} S_{calc}(J-J') \sum_{i,j} \frac{f_i}{2J'+1} \frac{1}{\pi} \frac{\Delta\lambda/2}{(\lambda-\lambda_{ij})^2+(\Delta\lambda/2)^2} \tag{1}$$

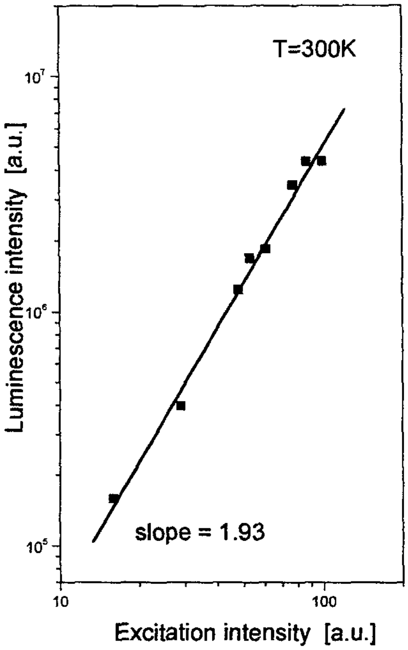

Fig. 2. Log-log plot of intensity of upconverted luminescence versus excitation power, recorded at 300K with a sample containing 0.5 % of holmium. The experimental data are shown by points whereas solid line indicates the power law behavior.

where: f_i is the Boltzmann factor for i-th crystal field level of the starting multiplet J of ESA transition. This factor has been approximated by 1/(2J+1); λ_{ij} are the expected wavelength position of ESA lines. In order to calculate λ_{ij}, the experimentally observed crystal-field energy levels of Ho^{3+} ion in $LiTaO_3$, for the $^5I_7$–$^5F_2$ and $^5I_7$–$^5F_3$ were taken from Table 3 in [4]. $\Delta\lambda$ is the linewidth of ESA line assumed to have a Lorentzian profile and the same as of GSA line around 647 nm i.e. $\Delta\lambda$=1nm; $\bar{\lambda}$ is the average wavelength of the transition $\bar{\lambda} = 6{,}34\times10^{-5}$cm and $\bar{\lambda} = 6{,}55\times10^{-5}$cm for the $^5I_7$–$^5F_2$ and $^5I_7$–$^5F_3$ respectively. S_{calc} has been calculated by using expression:

$$S_{calc} = C(n)S(J-J') \tag{2}$$

where:

$$C(n) = \frac{(n^2+2)^2}{9n} \frac{2\pi^3 e^2}{3hc} \tag{3}$$

and

$$S(J-J') = \sum_{t=2,4,6} \Omega_t \left|\langle J \| U^{(t)} \| J' \rangle\right|^2 \tag{4}$$

S is the electric – dipole transition strength, $U^{(t)}$ are matrix elements and Ω_t are Judd-Ofelt parameters. S_{calc} was calculated taking to account Ω_t parameters from [4], S_{calc}=0,3393 and 3,5824 for the $^5I_7$–$^5F_2$ and $^5I_7$–$^5F_3$ transitions respectively. C(n)=0,3219 for $LiTaO_3$ (n=2.175). In this calculation it is assumed that all transitions between the Stark components have the same intensity and the same polarization.

Calculated spectra are presented in Fig.3 by dashed line and solid line for the $^5I_7$–$^5F_2$ and $^5I_7$–$^5F_3$ transitions respectively. It can be seen

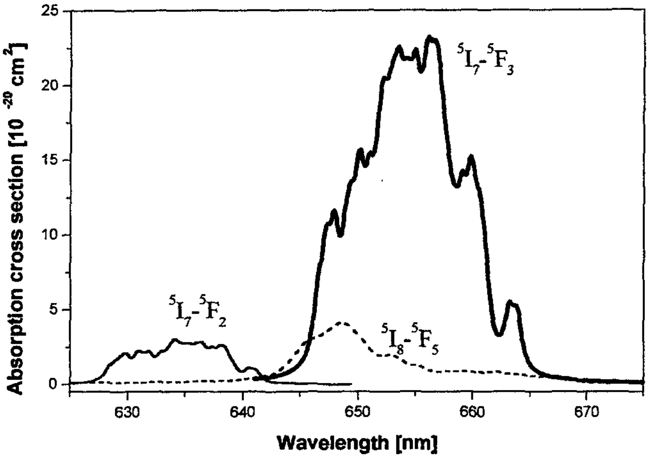

Fig. 3. Spectra of σ_{ESA} for the $^5I_7$ - $^5F_3$ transition (bold line) and σ_{ESA} for the $^5I_7$ - $^5F_2$ transition (solid line) with σ_{GSA} for the $^5I_8$ - $^5F_5$ transition (dash line) of Ho^{3+} in $LiTaO_3$.

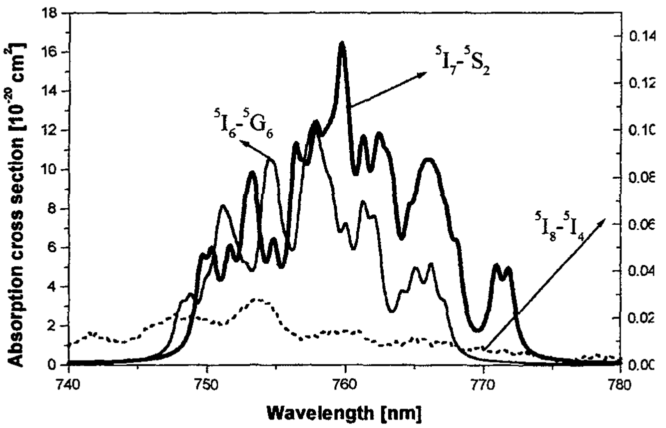

Fig. 4. Spectra of σ_{ESA} for the $^5I_7$ - $^5S_2$ transition (bold line) and σ_{ESA} for the $^5I_6$ - $^5G_6$transition (solid line) with σ_{GSA} for the $^5I_8$ - $^5I_4$ transition (dashed line) of Ho^{3+} in $LiTaO_3$.

that the σ_{ESA} spectrum for the $^5I_7$–$^5F_3$ transition overlaps that of σ_{GSA} for $^5I_8$–$^5F_5$ transition, which is presented by doted line in Fig.3. The overlap of σ_{GSA} with σ_{ESA} for the $^5I_7$–$^5F_2$ transition is weaker. Thus, we conclude that the ESA process from $^5I_7$ when exciting at 647nm may be appreciable. In order to assess the possibility of a mechanism of upconversion after pumping at 751nm into $^5I_4$ level, we have built the σ_{ESA} spectra corresponding to $^5I_6$–$^5G_6$, and $^5I_7$–$^5S_2$ transitions using the method described above. The resulting σ_{ESA} spectra for $^5I_7$–$^5S_2$ (solid line) and for $^5I_6$–$^5G_6$ (dashed line) transitions with the σ_{GSA} for $^5I_8$–$^5I_4$ transition (doted line) are reported in Fig.4. Both σ_{ESA} spectra for $^5I_7$–$^5S_2$ and σ_{ESA} for $^5I_6$–$^5G_6$ transitions overlap the σ_{GSA} spectrum, thus this mechanism of upconversion is likely to occur. The efficiency of this process is expected to be weak because the σ_{GSA} for $^5I_8$–$^5I_4$ transition is very small. However, a green luminescence under the excitation by cw Ti:sapphire laser emitting at 751nm was observed. Two proposed mechanisms of upconverted green luminescence by ESA after excitations at 647.1 and at 751 nm are presented in Fig.5.

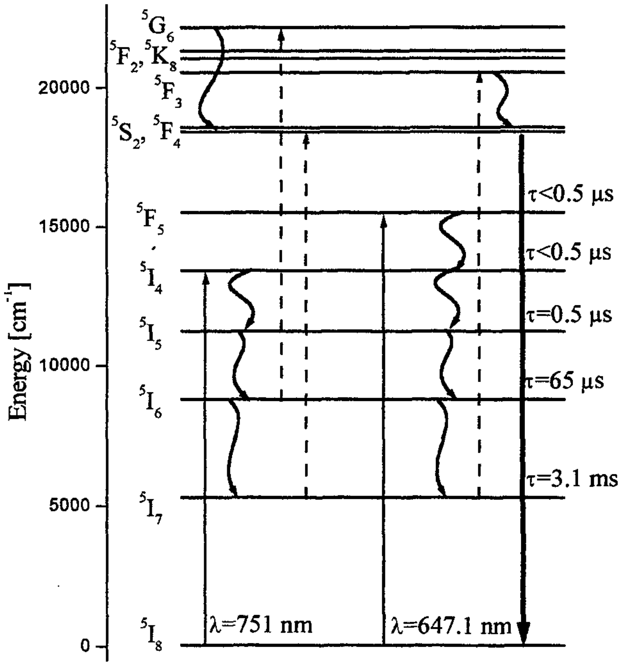

Fig. 5. Energy levels scheme of Ho^{3+} in $LiTaO_3$ crystal, and proposed mechanisms for upconversion green luminescence. GSA is indicated by solid arrows,non-radiative transitions by wave arrows, and ESA transitions by dashed arrows.

4. CONCLUSION

Excited state absorption of pumping light at 647 nm and 750 nm contributes adversely to population build up on the initial level of the $^5I_7 - {}^5I_8$ laser transition around 2 μm. On the other hand a strong ESA at 647 nm provides an excitation of the potential $^5S_2 - {}^5I_8$ laser transition in the visible.

ACKNOWLEDGMENTS

This work is supported by The Polish Committee for Scientific Research under grant No. 8T 11B 081 17

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