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Effect of temperature on excitation energy transfer and upconversion phenomena in Er:YVO$_4$ single crystals

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Abstract

Investigation of excitation and decay of Er^{3+}in YVO$_4$ single crystals has been carried out at temperature range from 5 to 500 K. In the limit of low Er^{3+} content, the temperature dependence of the ^{4}S$_{3/2}$ decay is not consistent with predictions of multiphonon relaxation model. In heavily doped crystals the ^{4}S$_{3/2}$ decay is governed by cross relaxation process, whose rate grows steadily with increasing temperature. An efficient upconverted luminescence near 550 nm following a cw and short pulse (5 ns) excitation of the ^{4}I$_{9/2}$ level in the system under study has been recorded and analysed. Contribution of the excited state absorption to these phenomena has been considered.

Keywords: Crystal growth; Optical properties; Luminescence

1. Introduction

In recent years the optical properties of YVO$_4$ crystals doped with Er^{3+} have been studied intensively to evaluate their laser potential at various wavelengths [1–3]. However, it is known that the real potential of this system strongly depends on dynamics of the relaxation to lower states, optical excitation, and upconversion mechanism. Upconversion mechanism may consist of the processes: ground states absorption (GSA), excited state absorption (ESA), energy transfer, electric and magnetic dipole transition and multiphonon relaxation. The absorption spectra, emission spectra and fluorescence dynamics of Er^{3+}:YVO$_4$ have been presented and analysed in detail [1]. The general characterisation of multiphonon relaxation in YVO$_4$ has been reported [2]. The absorption cross-sections (S_{ESA}) from ^{4}I$_{13/2}$ level of Er:YVO$_4$ have been registered experimentally [4]. In this study, the temperature dependence of ^{4}S$_{3/2}$ decay in the range 5–500 K has been investigated and compared with predictions of multiphonon relaxation model. The upconverted green luminescence spectra following the excitation of ^{4}I$_{9/2}$ level of Er^{3+} by a cw laser diode and by short pulse duration (5 ns) has been observed. The contribution of ESA processes in upconversion phenomena has been assessed. The influence of temperature on the upconverted integrated green luminescence intensity has been discussed.

2. Experimental details

Yttrium vanadate single crystals doped with Er^{3+} were grown by Czochralski method. The samples containing 0.5, and 4 at % of Er were used in this study. Absorption spectra were measured with a Varian model 2300 absorption spectrophotometer. The upconversion luminescence spectra were excited by 3 W laser diode emitting at 808 nm or by Continuum OPO model Surelite I pumped by third harmonic of Nd: YAG laser. The sample luminescence was dispersed by 1 m double grating monochromator, detected by photomultiplier and analysed by a Stanford Model SRS 250 Boxcar integrator. In luminescence decay measurements a digital oscilloscope Tektronix model TDS 3052 has been used. For low temperature measurements, the samples were mounted in Oxford Model CF 1204 continuous flow liquid helium cryostat equipped with a temperature controller.

3. Results and discussion

3.1. Multiphonon relaxation

In Fig. 1 we present the temperature dependence of

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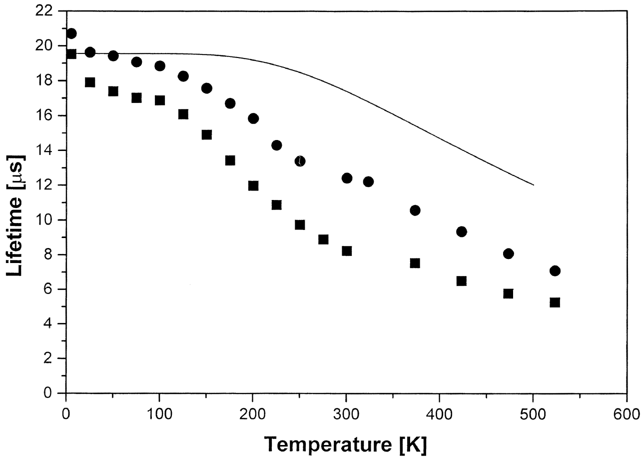

Fig. 1. Temperature dependence of luminescence lifetime of the $^4S_{3/2}$ level of Er^{3+} in YVO_4 crystal. Data indicated by solid circles and squares for samples containing 0.5 at % and 4 at % of erbium, respectively. See text for the explanation of theoretical line.

luminescence lifetime of the $^4S_{3/2}$ level of Er^{3+} in YVO_4. Experimental data are indicated by solid circles and squares for the samples containing 0.5 at % and 4 at % of erbium, respectively. The samples were excited by OPO at 523 nm into the level $^2H_{11/2}$. The lifetimes of Er^{3+} for heavy doped YVO_4 are shorter due to concentration quenching effect. The obtained data are consistent with data presented previously for room temperature and at 77 K [1,2]. We made an attempt to interpret the obtained experimental data using the phenomenological approach of Riseberg and Moos [5]. In this approximation the temperature dependence of the multiphonon relaxation rate is given by:

$$A_{ph} = A_0(\overline{n_i} + 1)^{p_i} \tag{1}$$

Where A_0 is spontaneous rate, n_i denotes the average occupation number of ith mode as given by:

$$\overline{n_i} = \frac{1}{\exp(\hbar\omega/kT) - 1} \tag{2}$$

The expected temperature dependence of $^4S_{3/2}$ lifetime has been drawn according to the formula:

$$\tau = \frac{12A_r(^2H_{11/2})\exp\left(-\frac{\Delta E}{kT}\right) + 4A_r(^4S_{3/2})}{12\exp\left(-\frac{\Delta E}{kT}\right) + 4} + A_0\left(\frac{\exp\frac{\hbar\omega}{kT}}{\exp\frac{\hbar\omega}{kT} - 1}\right)^p \tag{3}$$

where: A ($^2H_{11/2}$), A_r ($^4S_{3/2}$) denote the values of the radiative transition rates as given in [1], $\Delta E = 709$ cm^{-1} is the energy gap between $^2H_{11/2}$ and $^4S_{3/2}$ levels. A_0 denotes the spontaneous multiphonon transition rate, $\hbar\omega = 890$ cm^{-1} is the maximum of phonon energy [6] participating in multiphonon relaxation, and $p = 4$ is the number of phonons needed to cover the energy gap between $^4S_{3/2}$ and $^4F_{9/2}$ levels. For low energy phonons the high order of the process is needed, and the probability of such process is expected to be very low. A_0 has been calculated from the inverse of luminescence lifetime measured at 5 K. The solid line in Fig. 1 presents the dependence predicted on the basis of calculated radiative transition rates. It can be seen that the theoretical approach cannot predict the experimental temperature dependence of lifetime for the $^4S_{3/2}$ level. The experimentally determined lifetime decreases quickly with increasing temperature, especially in low temperature region. This may be caused by interaction of active ions with structural defects, but the reason of observed discrepancy is not clear yet.

3.2. Luminescence upconverted spectra

In Fig. 2 we present the upconverted green luminescence spectra excited by cw laser diode emitting at 808 nm, and by short pulses (duration 5 ns) of OPO emitting at 795 nm and exciting the $^4I_{9/2}$ level of Er^{3+}. Luminescence intensity after the pulse excitation presented by dotted line was definitely weaker than that after cw excitation. The upconverted $^4S_{3/2}$ decay was a single exponential, and rise time was not observed. The luminescence from $^4I_{9/2}$ level has not been observed, because the energy gap to low lying $^4I_{11/2}$ is only 2200 cm^{-1}. Under cw excitation, the metastable $^4I_{11/2}$ and $^4I_{13/2}$ levels are populated and, both the ion–ion interaction and ESA processes can occur.

3.2.1. Excitation with short pulse

During the short pulse excitation the populations of low lying $^4I_{11/2}$ and $^4I_{13/2}$ levels are too low to contribute to the upconversion process by ESA. Therefore, we suppose

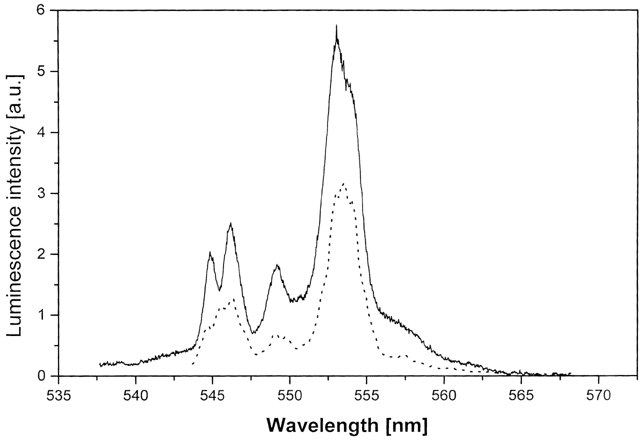

Fig. 2. Room temperature upconverted luminescence spectra excited by cw laser diode emitting at 808 nm (solid line) and by short pulse (5 ns) emitting at 785 nm — dotted line for the sample containing 4 at % of erbium.

that only the ESA from $^4I_{9/2}$ level may be responsible for this upconversion phenomenon.

In order to confirm the participation of the ESA processes under short pulse excitation, the excitation spectrum of $^4S_{3/2}$ luminescence was recorded at room temperature. The sample was excited by tuneable OPO in the range 780–870 nm and detected at 532 nm. The resulting excitation spectrum is presented in Fig. 3 by dashed line with the absorption cross-section from ground state S_{GSA} spectrum (solid line) in the same wavelength domain. ($S_{\mathrm{GSA}}=a/N$, where a — absorption coefficient, and N — number of ions/cm^3). The obtained excitation spectrum is broader than absorption spectrum and unresolved because the emission line of OPO in this region is as large as 7 nm.

From the analysis of the energy level diagram of Er^{3+} in YVO$_4$ presented in [1], we have built the absorption cross-section from excited states S_{ESA} spectra corresponding to $^4I_{9/2}$–$^2H_{9/2}$ transition after pumping around 800 nm using the expression presented in [7].

$$\sigma_{\mathrm{ESA}}^{J-J'}(\lambda)=\bar{\lambda}S_{\mathrm{calc}}(J-J')\sum_{i,j}\frac{f_i}{2J'+1}\cdot\frac{1}{\pi}\cdot\frac{\Delta\lambda/2}{(\lambda-\lambda_{ij})^2+(\Delta\lambda/2)^2} \quad (4)$$

where: f_i is the Boltzmann factor for ith 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 Er^{3+} ion in YVO$_4$, for the $^2H_{9/2}$ were taken from Table 3 in [1]. Those for $^4I_{9/2}$ multiplet were not observed previously. They have been derived in this work from absorption spectrum recorded at 5 K and they are 12 347, 12 408, 12 445, 12 479, 12 574 cm^{-1}. $\Delta\lambda$ is the linewidth of ESA line assumed to have a Lorentzian profile and the same as of GSA line around 800 nm i.e. $\Delta\lambda=0.75$ nm; $\bar{\lambda}$ is the average wavelength of the transition $\bar{\lambda}=8.27\times10^{-5}$ cm. S_{calc} has been calculated by using the expression:

$$S_{\mathrm{calc}}=C(n)S\left(^4I_{9/2}-J'\right) \quad (5)$$

where

$$C(n)=\frac{(n^2+2)^2}{9n}\frac{2\pi^3e^2}{3hc} \quad (6)$$

and

$$S(^4I_{9/2}-J')=\sum_{t=2,4,6}\Omega_t|\langle^4I_{9/2}\|U^{(t)}\|J'\rangle^2 \quad (7)$$

S is the electric–dipole transition strengths, n — refractive index, $U^{(t)}$ are matrix elements and Ω_t are Judd–Ofelt parameters. S_{calc} was calculated taking to account Ω_t parameters from [1] and $C(n)=0{,}0283$ for YVO$_4$ ($n=2.02$). In this calculation it is assumed that all transitions between the Stark components have the same intensity and the same polarization.

The resulting spectrum is presented in Fig. 3 by bold line. It can be seen that the excitation spectrum coincides with the ESA transition lines rather than with those of GSA transition.

3.2.2. Excitation by cw pump laser

The dependence on temperature of the upconverted green integrated luminescence intensity, excited by a cw laser diode emitting at 808 nm is presented in Fig. 4. From the analysis of absorption spectra of $^4I_{9/2}$ level recorded at 5 K and at room temperature, we suppose that the increase of integrated luminescence intensity with increasing temperature in the 5–140 K region is caused by an increase of the absorption coefficient. Slow decrease of the integrated luminescence intensity with increasing temperature in the 140–300 K region may be caused by strong decrease of the quantum efficiency of $^4S_{3/2}$ with increasing temperature (see Fig. 1).

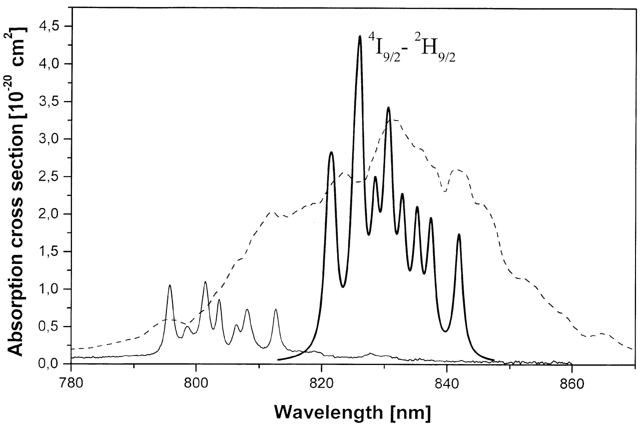

Fig. 3. Room temperature excitation spectrum of $^4S_{3/2}$ luminescence of Er^{3+} in YVO$_4$ — dashed line with S_{GSA} spectrum (solid line). For the comparison, the calculated spectrum for $^4I_{9/2}$–$^2H_{9/2}$ transition is presented — bold line.

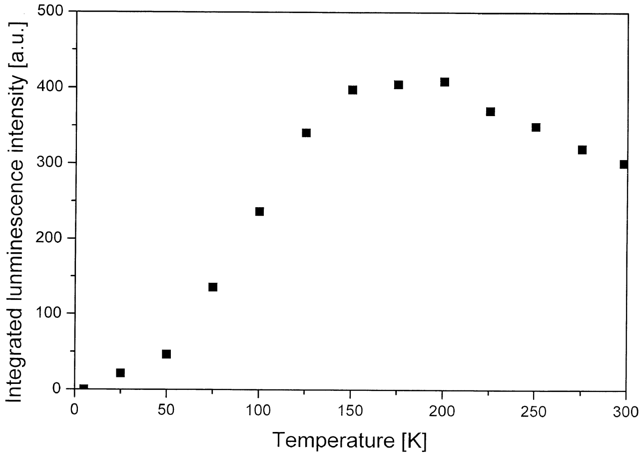

Fig. 4. Temperature dependence of the upconverted integrated luminescence intensity excited at 808 nm by a cw diode laser for the sample containing 4 at % of erbium.

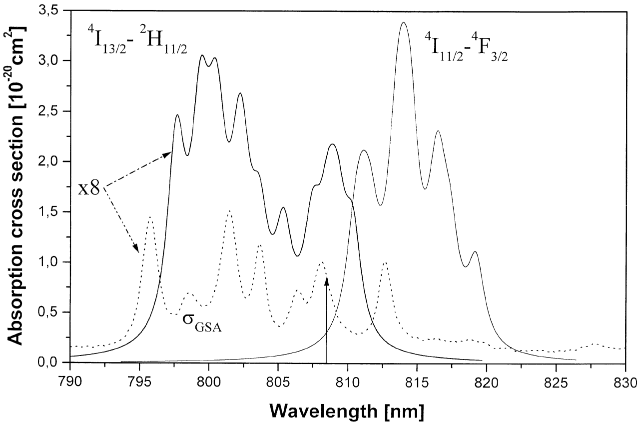

Fig. 5. Calculated S_{ESA} spectra for $^4I_{13/2}$–$^2H_{11/2}$ and $^4I_{11/2}$–$^4F_{3/2}$ transition of Er^{3+} in YVO_4. For the comparison, the S_{GSA} for $^4I_{15/2}$–$^4I_{9/2}$ transition is presented by dotted line. The solid arrow indicates the wavelength of excitation.

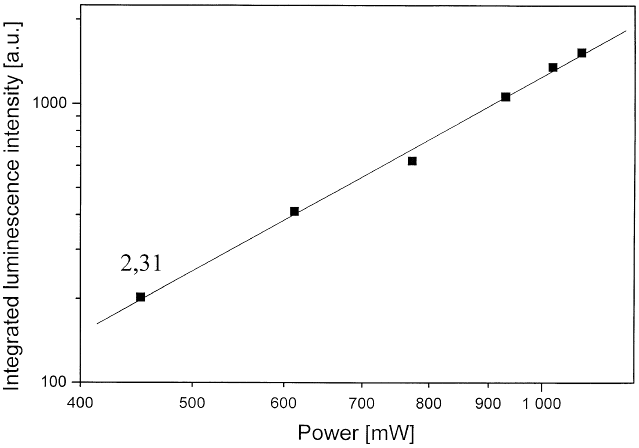

Fig. 6. Integrated luminescence intensity for transition originating in the $^4S_{3/2}$ of Er^{3+} in YVO_4 versus the power of excitation at 808 nm for the sample containing 4 at % of erbium. The straight line follows power dependence with the *n*-value indicated.

In order to assess the possibility of ESA from $^4I_{11/2}$ and $^4I_{13/2}$ levels, which are populated after cw excitation at 808 nm the S_{ESA} spectra corresponding to $^4I_{13/2}$–$^2H_{11/2}$ and $^4I_{11/2}$–$^4F_{3/2}$ S_{ESA} transitions were built using the method described above. The resulting S_{ESA} spectra (solid lines) are reported in Fig. 5 with the S_{GSA} for $^4I_{15/2}$–$^4I_{9/2}$ transition (dotted line). The calculated S_{ESA} spectra for $^4I_{13/2}$–$^2H_{11/2}$ are in very good agreement with that measured experimentally [5]. It can be seen, that the S_{ESA} for $^4I_{13/2}$–$^2H_{11/2}$ transition overlap strongly the S_{GSA} and they are of the same order to magnitude. The S_{ESA} for $^4I_{11/2}$–$^4F_{3/2}$ transition is one order of magnitude higher than the S_{ESA} for $^4I_{13/2}$–$^2H_{11/2}$ transitions, but the overlap with the S_{GSA} is weak. Thus, we suppose that the probability of occurrence of ESA by excitation at 808 nm for both described transitions has the same order. It was reported [8] that in Er^{3+}doped fluorozirconate glasses, ESA processes were the principal processes for the upconversion emission around 550 nm under 800 nm excitation.

In Fig. 6 the integrated luminescence intensity for transition originating from the $^4S_{3/2}$ level of Er^{3+} are plotted versus the power of cw excitation at 808 nm. Experimental data are denoted by square symbols and the straight line follows power dependence with the n value indicated. A value of n equal to 2.31 indicates that, the upconvesion process may involve two-photon sequential absorption.

4. Conclusion

The temperature dependence of the $^4S_{3/2}$ decay is not consistent with predictions of multiphonon relaxation model. In excitation into $^4I_{9/2}$ with short pulse the ESA from $^4I_{9/2}$ level may be responsible for upconverted green luminescence phenomenon. In an excitation by cw pump laser mainly the metastable $^4I_{11/2}$ and $^4I_{13/2}$ levels are populated and, ESA from both the levels can occur. We suppose that the ESA processes from $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ levels of Er^{3+}in YVO_4 govern the upconversion phenomenon under excitation around 800 nm.

Acknowledgements

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