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Spectroscopy and kinetics of the population of monoclinic $KYb_{0.5}Y_{0.43}Tm_{0.07}(WO_4)_2$ crystals pumped by a pulsed Nd:YAG laser

S M Vatnik, A P Maiorov, A A Pavlyuk, D V Plakushchev

***Abstract*. The kinetics of pump radiation absorption and luminescence of monoclinic crystals of potassium-yttrium-ytterbium tungstate doped with thulium are studied. It is shown theoretically and experimentally that due to the 'excitation multiplication' caused by absorption of pump radiation from metastable states of thulium ions accompanied by cross-relaxation, above 50 % of a total number of thulium ions can occupy the $^3F_4$ level. The cross sections for stimulated transitions in the spectral region from 1600 to 2100 nm are calculated from luminescence spectra, and the gain in the crystal is estimated. The prospects of practical applications of the results obtained in the paper are discussed.**

***Keywords*:** *spectroscopy, population kinetics, laser pumping, optical amplifiers.*

1. Introduction

In the last years, solid-state lasers of new generation based on neodymium-doped media ($\lambda = 1.06$ μm) has been developed. The efficiency of these flashlamp-pumped lasers exceeds 8 % [1]. Upon cw pumping by semiconductor laser diodes and arrays, the optical efficiency of these lasers achieves 60 % [2, 3]. To convert radiation to other spectral ranges, methods of parametric generation [4] and SRS [5] are widely used, in particular, intracavity SRS self-conversion [6].

Of significant interest is the use of neodymium lasers for pumping solid-state active media. This has been realised in Refs [7, 8] where lasing of Ho : $BaYb_2F_8$ crystals in the two- and three-micron range pumped by a pulsed neodymium glass laser has been reported. Ytterbium ions in these crystals absorb the pump energy and transfer excitation to Ho ions. Note that pumping does not induce transitions of these ions from the ground and lower excited states, i.e., absorption of the pump radiation is independent, in the first-order approximation, of the energy state of holmium ions.

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If crystals doped (along with ytterbium) with other rare-earth elements absorb the pump radiation from excited states, the kinetics of absorption and populations of the energy levels can be fundamentally different from the kinetics studied in Refs [7, 8]. In our paper, we showed experimentally [for a $KYb_{0.5}Y_{0.43}Tm_{0.07}(WO_4)_2$ (7 %Tm : KYbW) crystal] and theoretically that in the presence of cross-relaxation processes, a considerable part of thulium ions can undergo transitions to the $^3F_4$ metastable state. In this case, the population of the $^3F_4$ level will rise exponentially during some time after the pump pulse onset. This effect is of interest for various practical applications, including the development of new laser systems and optical amplifiers operating in the two-micron range.

2. Model

Fig. 1 shows the energy level diagram of Yb-Tm ions, the main features of their interaction, and the mechanism of the exponential rise of the population of the $^3F_4$ level. At the beginning of the pump pulse, the thulium ions are in the ground state, while ytterbium ions are excited to the $^2F_{5/2}$ level. After a series of fast nonradiative transitions, a part of thulium ions undergo transitions to the $^3F_4$ metastable state, producing its initial ('start') population. Then, the 'excitation multiplication' occurs as follows.

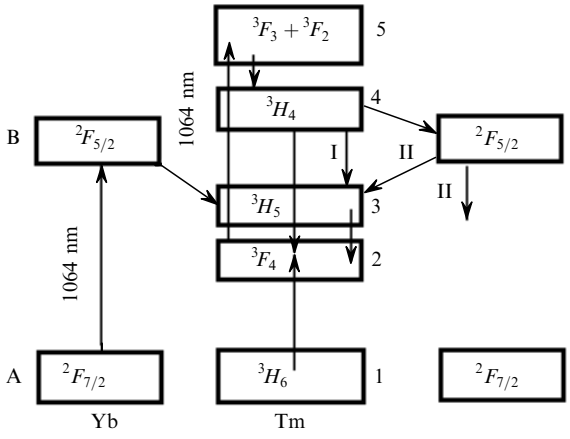

Figure 1. Energy level diagram and main energy-transfer channels in the system of interacting ions; A, B, 1 – 5 are the energy levels of Yb and Tm ions, respectively; I and II are the energy-transfer channels.

After absorption of a pump photon, the thulium ion undergoes transition from the $^3F_4$ metastable state to the $^3F_2$ level and relaxes nonradiatively to the $^3H_4$ level where cross-relaxation occurs [9], i.e., the thulium ion interacts with another ion, which is found in the $^3H_6$ ground state, resulting in the transition of the both ions to the $^3F_4$ metastable state. If the cross-relaxation efficiency is high, the absorption of the pump photon from the $^3F_4$ metastable state increases its population by unity, resulting in the exponential rise of the population of this level at the initial stage of pumping. Note that other energy-exchange channels (I and II in Fig. 1) can significantly reduce the cross-relaxation efficiency, however, the exponential rise of the population will also occur [see expression (7) below].

Later, when a great part of thulium ions underwent transitions to the $^3F_4$ level, the cross-relaxation efficiency will decrease due to depletion of the $^3H_6$ ground state. The population of the $^3F_4$ state will have a 'steady-state' value, which is determined by the lifetime of this state, up-conversion processes, the pump intensity, and by other parameters. Under some simplifying assumptions, which are unimportant for the further discussion, the rate equations describing these energy-exchange processes in the approximation of the pair interaction between ions have the form [9, 10]

$$\frac{dN_4}{dt} = \sigma_{25} I N_2 + k_{2124} N_2^2 - k_{4212} N_4 N_1 - \frac{N_4}{\tau_4}, \tag{1}$$

$$\frac{dN_2}{dt} = k_{BA13} N_1 N_B - \sigma_{25} I N_2 - 2(k_{2123} + k_{2124}) N_2^2 + 2k_{4212} N_4 N_1 + \beta_{42} \frac{N_4}{\tau_4} - \frac{N_2}{\tau_2}, \tag{2}$$

$$\frac{dN_B}{dt} = \sigma_{AB} I (N_A - N_B) - k_{BA13} N_1 N_B - \frac{N_B}{\tau_B}, \tag{3}$$

$$N_{Tm} = N_1 + N_2 + N_4, \qquad N_{Yb} = N_A + N_B. \tag{4}$$

Here, I is the pump intensity in units of the photon flux density; σ_{ij} is the cross section for transitions from the level i to the level j; k_{ijkl} is the kinetic constants of the interaction of ions $i \to j$ and $k \to l$; τ_i is the lifetime of the ith level; β_{42} is the relative fraction of the $4 \to 2$ transitions, including cascade processes $4 \to 3 \to 2$; and N_{Tm} and N_{Yb} are volume concentrations of thulium and ytterbium ions. All notations are identical to those used in Refs [9, 10].

A change in the pump intensity is determined by the relation

$$\frac{\partial I}{\partial z} = -I[\sigma_{AB}(N_A - N_B) + \sigma_{25} N_2], \tag{5}$$

where the z axis coincides with the propagation direction of the beam in a crystal.

Similarly to the results obtained in Refs [9, 10], we assume that fast nonradiative transitions occur from the levels B, 3 and 5 to the levels 2 and 4, and the efficient cross-relaxation takes place on the level 4, so that the populations of the levels B, 3–5 and their time derivatives can be neglected. In this case, the system of equations (1)–(3) is reduced to the equation

$$\frac{\partial N_2}{\partial t} = \sigma_{AB} N_A I + \eta \sigma_{25} N_2 I - 2[k_{2123} + (1-\eta) k_{2124}] N_2^2 - \frac{N_2}{\tau_2}, \tag{6}$$

where $\eta = k_{4212} N_1 \tau_4 / (1 + k_{4212} N_1 \tau_4)$ is the cross-relaxation efficiency [9], i.e., the fraction of ions involved in the cross-relaxation from the level 4. When the pump pulse duration is substantially shorter than the lifetime of the level 2, the three last terms in (6) can be neglected. The combined solution of equations (5) and (6) for 'thin' crystals, in which the absorbed pump power is much less than the incident pump power, gives the relation

$$\frac{\Delta I}{I} = \frac{\sigma_{AB} N_A L}{\eta} \left[\exp\left(\eta \sigma_{25} \int_0^t I dt \right) + \eta - 1 \right]. \tag{7}$$

Here, ΔI is the power absorbed by a crystal ($\Delta I \ll I$); L is the crystal thickness; and the Fresnel reflection loss is ignored. Note that relation (7) is valid at comparatively small populations of the level 2 when $N_2 \ll N_1$ because for N_2 comparable to N_1, the cross-relaxation efficiency η decreases due to the ground state depletion. In this case, a further increase in the crystal absorption is comparatively small (see also Fig. 3).

After the pump pulse termination, the intensity I in (6) vanishes, and we can easily obtain from (6) the kinetics of the population of the level 2, taking up-conversion processes into account:

$$\frac{N_2(t)}{N_2(0)} = \frac{\exp(-t/\tau_2)}{1 + k_{\Sigma Tm} N_2(0) \tau_2 [1 - \exp(-t/\tau_2)]}, \tag{8}$$

where $N_2(0)$ is the population of the level 2 at the initial moment, which corresponds in this case to the pulse termination time; and $k_{\Sigma Tm} = 2[k_{2123} + (1-\eta) k_{2124}]$ is the up-conversion coefficient [9, 10].

To determine the population of the levels 1–4 for an arbitrary crystal thickness and arbitrary duration of the pump pulse, one should solve the whole system of equations (1)–(5), which can be accomplished in principle numerically. The degree of correspondence of numerical calculations to the real population dynamics is not clear at present because one cannot expect *a priori* that the approximation of the pair interaction between ions will be sufficiently accurate in the case of intense pumping of the crystal [11].

3. Experimental

We fabricated plates of thickness 2.2 mm with a small ($\sim 2^\circ$) wedge from a 7 %Tm : KYbW crystal grown by the low-gradient Czochralski method from a solution in a $K_2W_2O_7$ melt [12, 13]. Polished surfaces of the plates were perpendicular to the crystallographic axis $\boldsymbol{b}$ with an accuracy of $\pm 3.^\circ$ The transmission spectra of samples were recorded with a Shimadzu spectrophotometer in the 400–3200-nm range. The luminescence spectra were detected in the 'forward scattering' geometry using an MDR-23U monochromator equipped with a measuring unit described in Ref. [10].

Fig. 2 shows the scheme of the experiments. Linearly polarised radiation from a pulsed Nd : YAG laser *1* was focused on the crystal surface *3* to a spot of diameter

230 ± 30 μm. The transmission kinetics and the luminescence spectrum and kinetics in the wavelength range from 1600 to 2000 nm were measured using appropriate filters and detectors. The transmission kinetics was detected with a FD256 photodiode connected via a matched load to a fast analog-to-digital converter. The time resolution of the measuring unit was 0.5 μs. The luminescence kinetics was measured using a PbSe photoresistor with a time resolution of 15 μs.

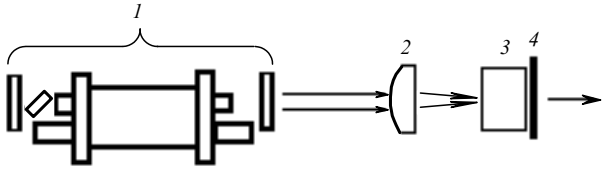

Figure 2. Scheme of the experiment: (*1*) Nd : YAG laser; (*2*) focusing lens; (*3*) crystal under study; (*4*) filter.

Our preliminary experiments showed that absorption of a sample was a maximum when the polarisation of the pump radiation was directed along the N_g axis of the optical indicatrix. All the data reported below were obtained for this orientation of the crystal. The cross-relaxation efficiency η, which enters in equations (6) and (7) as a parameter, was determined from comparative measurements of the relative intensity of luminescence of two crystals, 7 %Tm : KYbW and 15 %Tm : KYW [10]. Pumping was performed by a low-power 100-mW, 810-nm laser diode. The luminescence intensity normalised to the absorbed power proved to be identical, within the experimental error (~ 5 %), for both crystals, which suggests that they have the same cross-relaxation efficiency ~ 0.95 [10].

4. Results and discussion

Fig. 3 shows the shape of pump pulse in front of (P_{in}, curve *1*) and behind the crystal (P_{out}, curve *2*), as well as the time dependence of the absorption coefficient of the crystal calculated from the formula $C = (P_{in} - P_{out})/P_{in}^{max}$, taking into account the Fresnel reflection (curve *3*). The dashed curve is the approximation of the initial part of curve *3* according to equation (7). One can see that the absorption of the sample increases monotonically from 3 % at the pulse onset to ~ 75 % at the pulse termination. The initial part of this dependence (0 – 0.04 ms) is not shown because the intensity fluctuations P_{in} and P_{out} in this part caused by relaxation oscillations substantially exceed the average level.

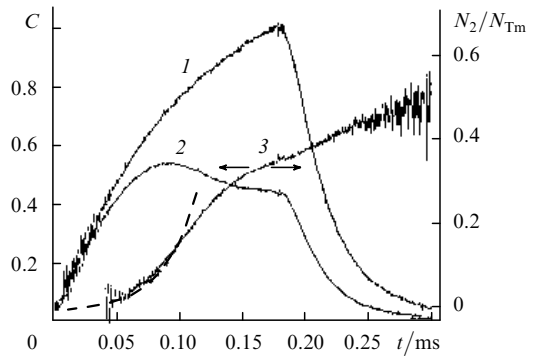

Figure 3. Normalised shapes of pump pulses in front of (*1*) and behind (*2*) the crystal, as well as the normalised time dependences of the absorption C of the sample and population N_2/N_{Tm} of the level 2 (*3*). The dashed curve is the approximation of C by equation (*7*).

Note that the only variable parameter of the approximation is the transition cross section σ_{25} because the other quantities appearing in (7), such as η and the initial absorption of the crystal $\sigma_{AB}N_A L = 0.030$ were determined experimentally. One can see from Fig. 3 that expression (7) agrees with the experimental dependence as a whole, however, because of significant variations in σ_{25} upon a change in the approximation region, we can obtain only the estimate of the cross section for this transition $\sigma_{25} = (1 - 3) \times 10^{-20}$ cm^2. We believe that some deviation of expression (7) from the experiment is mainly caused by the fact that the assumption about negligible population of the level 4 is not valid for the crystal under study. We will perform a more detailed analysis of the system of equations (1) – (5) by numerical methods elsewhere.

Fig. 3 also shows the relative fraction of thulium ions in the $^3F_4$ metastable state, which was calculated from the relation $N_2 = (C - \sigma_{AB}N_A L)/\sigma_{25}L$, where $\sigma_{25} = 2 \times 10^{-20}$ cm^2. According to this estimate, to the moment of the pump pulse termination, approximately 50 % of all thulium ions undergo transitions to the level 2.

Fig. 4 shows the time dependence of the luminescence intensity of the crystal. The dashed curve *2* shows the approximation of this dependence by equation (8) after the pump pulse termination using two fitting parameters $k_{\Sigma Tm}N_2(0)\tau_2 = 2$ and $\tau_2 = 1.50$ ms. Assuming that the upconversion coefficient of a 7 %Tm : KYbW crystal is the same as for a 15 %Tm:KYW crystal [10], i.e., $k_{\Sigma Tm} = 1.5 \times 10^{-18}$ cm^3 s^{-1}, we can easily obtain that $N_2(0)/N_{Tm} = 0.9$, in reasonable agreement with the data in Fig. 3. Note also that the lifetimes of the level 2 in 7 %Tm : KYbW and 15 %Tm:KYW crystals [10] are virtually the same.

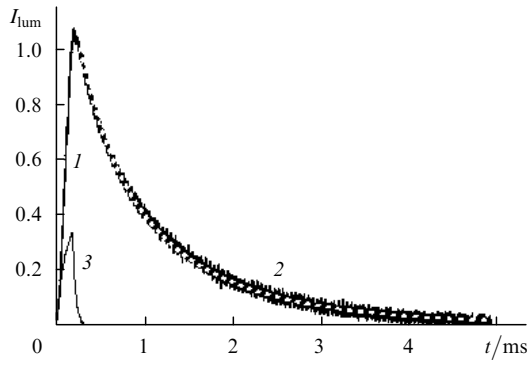

Figure 4. Time dependence of the normalised luminescence intensity I_{lum} for the $^3F_4 \rightarrow {}^3H_6$ transition (*1*) and its approximation (*2*) by formula (8), as well as the pump-pulse shape (*3*)

Fig. 5 shows the dependence of the cross section for stimulated $^3F_4 \rightarrow {}^3H_6$ transitions calculated by expression (14) from [10] using the results of measurements of luminescence of a 7 %Tm : KYbW crystal in the 'forward scattering' geometry neglecting reabsorption from the ground state. The maximum transition cross section $\sigma_{21} = 1.9 \times 10^{-20}$ cm^2 corresponds to the wavelength 1920 nm. In the

spectral range from 1890 to 1940 nm, the gain of the crystal under study at the end of the pump pulse was tentatively 60 %.

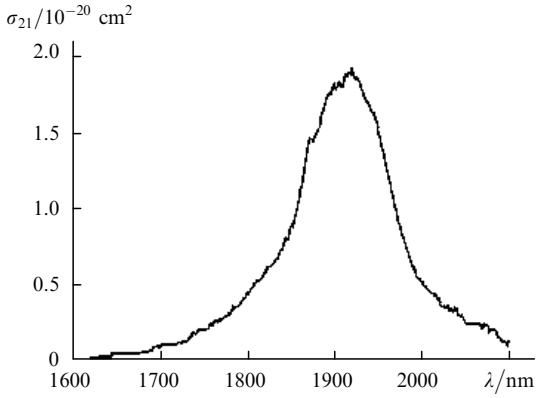

Figure 5. Dependence of the cross section for stimulated $^3F_4 \rightarrow {}^3H_6$ transitions on the wavelength calculated using the results of spectroscopic measurements.

According to our preliminary estimates, a 7 %Tm : KYbW crystal of thickness 1 cm absorbs up to 80 % of the pump energy and its gain in power in the spectral region from 1850 – 1970 nm should be no less than ten. We assume that, by appropriately optimising the crystal composition, we can develop prototypes of broadband amplifiers in the two-micron range with the gain of 10 – 20 dB/cascade, which can be used in optical communication systems, lidars, etc.

5. Conclusions

We have shown that the efficient cross-relaxation of thulium ions from the $^3H_4$ level in combination with absorption of the pump radiation from the $^3F_4$ level results in a significant population of this metastable level. Good agreement is obtained between theoretical and experimental dependences describing the kinetics of transmission and luminescence of the crystal. The possible practical applications of the results obtained in the paper are proposed. In our opinion, further studies of spectroscopic and kinetic characteristics of crystals upon high-power pumping are of significant interest for research and applications.

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