Mechanisms of up-conversion excitation of blue emission in YAG:Tm, Yb

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Abstract

Trivalent ytterbium ions were used as sensitizers for the 1D_2 and 1G_4 blue emitting thulium levels. The evolution of the population of the 1D_2 , 1G_4 , 3H_4 , and 3F_4 levels of Tm^{3+} and the $^2F_{5/2}$ level of Yb^{3+} were investigated after short resonant excitation into these levels in YAG:Tm, Yb crystals. We observed upconversion fluorescence with a fast cooperative process followed by a slower step-by-step-process.

Introduction

The realization of laser emission from high energy levels of rare-earth ions in crystals is a difficult problem due to the lack of suitable pump sources. A way to overcome this difficulty would be to up-convert the infrared pump excitation by energy transfer between the activator ions or by using a sensitizer. Earlier experiments [1] indicated that Yb might be a good sensitizer for the blue emission of Tm. However the interest in this sensitization was diminished by the lack of pump sources in the range 930-970 nm where Yb has a strong absorption band. The progress in powerful laser diodes emitting in this range renewed the interest in Yb sensitized systems. However the practical use of this up-conversion sensitization needs a deep knowledge of the dynamic and spectral properties of the system. We report here about the investigation of up-conversion of infrared radiation to the 1D_2 and the 1G_4 levels of Tm, Yb:YAG (Figure 1). The concentration of dopants varied from 1 to 3 at. % for Tm and from 5 to 20 at. % for Yb.

Fig. 1. Relevant energy levels and transfer processes in Tm and Yb in YAG

Experimental results

We have investigated the temporal behaviour of luminescence from various levels of Tm (1D_2 , 1G_4 , 3H_4 , and 3F_4 , Figure 1) and from $^2F_{5/2}$ Yb when pumping into Yb or Tm levels (except of 3F_4) with short dye, Ti:sapphire or OPO laser pulses.

Complex energy transfer takes place from Yb to Tm and vice versa:

- luminescence from all these levels of Tm is present when pumping into Yb with 940 nm radiation
- when pumping into 3H_4 , 1D_2 - and 1G_4 -Tm emission occurs only in Yb codoped crystals
- Yb emission is excited when pumping the various levels of Tm.

Under $^2F_{5/2}$ Yb pumping the luminescence decay of 1D_2 , 1G_4 , and 3H_4 shows a peculiar behaviour, to our knowledge not reported previously. The temporal evolution of luminescence consists of a fast spike (where the time $t_{\max}$ corresponding to the maximum emission intensity $I_{\max}$, ranges from 4 to 25 μ s) followed by a slow rise and decay (with $t_{\max}$ from 18 to 240 μ s). The values of $t_{\max}$ for the fast and the slow process and the ratio $I_{\max, \text{fast}}/I_{\max, \text{slow}}$ depend on the Yb and Tm concentrations and on the emitting level: at high concentrations the values of $t_{\max}$ are smaller for both processes and $I_{\max, \text{fast}}$ is larger than $I_{\max, \text{slow}}$ (Figure 2).

Similar behaviour was observed for the 1D_2 and 1G_4 Tm and $^2F_{5/2}$ Yb emission (Figure 3) when pumping into 3H_4 or for the $^2F_{5/2}$ Yb emission after excitation into 1D_2 or 1G_4 . The fluorescence intensity from the investigated levels is nonlinear with the pumping intensity. The power dependencies are different for the various levels as well as for the fast and slow parts of the decay curve. In the sample with 1% Tm and 10 % Yb the exponent of the 1G_4 fast emission process is about 2.2, while for the slow process the exponents are 1.1 for 3F_4 , 1.3 for 3H_4 , 3.4 for 1G_4 , and 3.8 for 1D_2 .

Discussion

The observed pump wavelength and concentration dependence implies that different up-conversion and depopulation processes are responsible for the fast and slow features observed in emission. The feed mechanism for the fast process is most likely a cooperative up-conversion excitation [2] into 1G_4 by which two excited Yb ions transfer simultaneously their excitation to a Tm ion. The depopulation of 1G_4 is also rather complicated and involves a three-ion process with an excitation of two Yb ions as well as an energy transfer within the Tm system. The dominant process seems to be the up-conversion (1G_4 , 1G_4) $\rightarrow$ (1D_2 , 3F_3), although the high efficiency of this process at relatively low Tm concentrations is surprising. The slow process could be due to a step-by-step (APTE) up-conversion [1] in which isolated Yb ions transfer successively their energy to various levels of a given Tm ion. A computer simulation based on a rate equation system gives a fairly well description of the observed behaviour with the parameters measured from the fluorescence decay curves of the various levels. In this analysis we used for the step-by-step Yb to Tm transfer an $\exp(-\beta \Delta E)$ dependence [3] for the various steps. Here, ΔE describes the mismatch between Yb and Tm energy gaps for each step of transfer.

The large efficiency of the cooperative process seems surprising when regarding earlier estimations [4] which expect an efficiency several orders of magnitude lower than for the step-by-step process. This discrepancy might arise from the model of coupling: a strong short range interaction would lead to a dramatic increase of the rate of the cooperative processes. This correlates with other features of the process which suggest that the cooperative up-conversion takes place within nearest neighbours (n.n.) ensembles of two Yb ions and one Tm ion.

Fig. 2. Room temperature temporal behaviour of Tm $1D_2$, $1G_4$, $3H_4$, $3F_4$ and Yb $2F_{5/2}$ emission when pumping Yb $2F_{5/2}$ in different YAG:Tm, Yb-crystals. The time scale is the same for all decays.

Fig. 3. Temporal behaviour of emission of $2F_{5/2}$ Yb in YAG: Tm, Yb when pumping in Tm $1D_2$, $1G_4$, and $3H_4$. The other conditions are as in Figure 2.

Also a rapid migration within Yb excited levels (i.e. high Yb concentration) would help to have the two n.n. Yb donor ions excited at the same moment. The possible presence of a superexchange interaction between the three ions of the ensemble, similar to that observed for several n.n. rare-earth ion pairs, could give consistency to our model.

Conclusions

The existence of the fast process in the population of the $1D_2$ or $1G_4$ level when pumping in Yb, coupled with the slow rise of the population of $3F_4$ indicates inversion of population between these levels immediately after pumping, with potential for pulsed up-conversion laser emission.

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