ELSEVIER

Journal of Luminescence 60&61 (1994) 870–873

JOURNAL OF
LUMINESCENCE

Up- and down-conversion processes in Yb^{3+}–Tm^{3+}–Ho^{3+} doped $Gd_3Ga_5O_{12}$ garnet

A. Brenier*, L.C. Courrol, C. Pédrini, C. Madej, G. Boulon

Laboratoire de Physico-Chimie des Matériaux Luminescents, Unité de Recherche Associée au CNRS No. 442, Université Claude Bernard-Lyon I, 43 Bd du 11 November 1918, 69622 Villeurbanne cedex, France

Abstract

The sensitization of the Ho^{3+} 2 μm laser emission by the Yb^{3+}–Tm^{3+}–Ho^{3+} ions in $Gd_3Ga_5O_{12}$ host is presented. We have analyzed both down- and up-conversion processes and we have measured the up-conversion quantum yield. Various models are used to model the excited state dynamics.

1. Introduction

Adequate sensitization of the Ho 2 μm laser emission is usually obtained from the $^5I_7 \rightarrow {}^5I_8$ transition of Ho^{3+} ions in different hosts with the sensitizers: Cr^{3+}, Er^{3+} and Tm^{3+} ions. The two former ones allow efficient flash lamp pumping while the latter is well adapted for laser diode pumping at around 800 nm. As can be seen in Fig. 1 Ho–Tm sensitization by means of Yb^{3+} ions is also attractive because of the possibility of laser diode pumping between 920 and 975 nm where powerful laser diodes are now available and because Yb^{3+} ions have only one excited state ($^2F_{5/2}$) with no possibility of excited absorption. The different down-conversion channels are labelled 1, 2, 3 and 4 in Fig. 1. But the drawback of sensitizers is the introduction of new energy losses. One of them is the Ho → Tm back transfer, labelled 5 in Fig. 1, which can be an important source of losses when the Tm concentration increases and which was presented in a previous work [1]. Another source of losses is the up-conversion processes occurring from the Yb and Ho or Tm infrared levels to the Tm and Ho visible levels.

We have shown that efficient Tm → Ho energy transfers occurs in $Gd_3Ga_5O_{12}$ (GGG) [2] and we have recently found that Yb → Tm and Yb → Ho energy transfers lead to an enhancement of the Ho 2 μm fluorescence. Due to the presence of 3 ions two of which (Tm and Ho) have several involved electronic levels the excited state dynamics under short pulse excitation into Yb ions is rather complicated with both up- and down-conversion process appearing.

All materials were single crystals grown in our Laboratory by using the Czochralski method. To analyze the fluorescence dynamics we cannot use the rate equations because Grant's procedure [3] can only be applied in the case of a very fast energy diffusion among donors and the decays were not found to be exponential. We therefore, used standard models like Inokuti–Hirayama and Yokota–Tanimoto models which allow one to

---

* Corresponding author.

0022-2313/94/$07.00
SSDI 0022-2313(93)E0360-A

describe the decay rates of the donors, but also other models like Chandrasekhar's procedure [4] and the transfer function method [1] which permit one to also describe the dynamics of the acceptors.

2. Down-conversion processes

– $^2F_{5/2}(Yb) \to {}^3H_5(Tm)$ and $^2F_{5/2}(Yb) \to {}^5I_6(Ho)$ energy transfers are indicated by channels 1 and 2 in Fig. 1: the time evolution of the Yb fluorescence is correctly described by the Yokota–Tanimoto expression with critical radius R_0 equal to 10.9 and 11.4 Å and transfer efficiencies close to unity for GGG:5% Yb, 5% Tm and GGG:5% Yb, 3% Ho samples, respectively.

– $^5I_6(Ho) \to {}^3H_5(Tm)$ energy transfers, indicated by channel 3 in Fig. 1, have been detected corresponding to a 90% quantum yield.

– $^3F_4(TM) \to {}^3I_7(Ho)$ energy transfers have been studied in detail in a previous paper [1]. It has been shown that the two emitting levels are in thermal equilibrium. From the fits of the experimental temporal evolutions of the $^5I_7$ and $^3F_4$ fluorescences we were able to determine the critical radius R_0 of forward and backward energy transfers: they are of the same order of magnitude as the radii obtained by Dexter's classical method based on the overlap of absorption and emission spectra only in the case for which we take into account a diffusion process. As an example for the backtransfer Ho → Tm we have found in GGG:1% Tm, 0.5% Ho, R_0 = 8.4, 7.2 and 11.6 Å from spectroscopic data, with and without diffusion, respectively.

3. Up-conversion processes

The excitation of the Yb ions is also followed by anti-Stokes emissions coming from both upper Tm levels at 820 nm ($^3F_4$) and 481 nm ($^1G_4$) and upper Ho levels at 548 nm ($^5S_2$–$^5F_4$) and 665 nm ($^5F_5$). As can be seen in Fig. 1, two or three-step nearly resonant up-conversion processes have been observed and, in addition, the power dependence of the intensities of fluorescence at the top of their time evolution have been mentioned near the ground states. We expected that n should be an

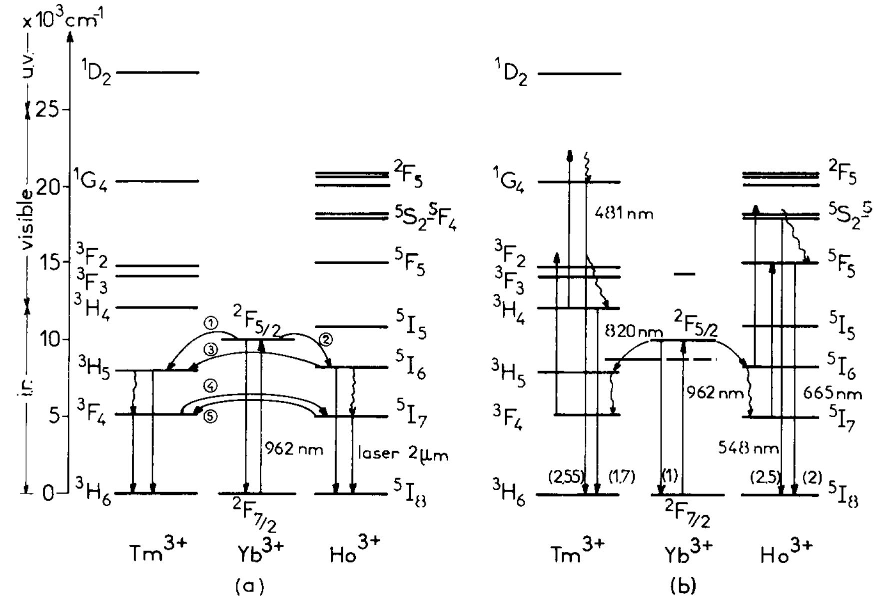


Fig. 1. (a) Down-conversion process in GGG:Yb:TM:Ho sample under Yb ion pumping, (b) up-conversion processes in GGG:Yb:Tm:Ho sample under Yb ion pumping.

integer but non-integer values 2.5 for the Ho^{3+} green emission and 2.55 for the Tm^{3+} blue emission, probably reveal a mixture of two- and three-photon processes.

The up-conversion quantum yield from Yb ions to a particular Ho or Tm level was obtained using an integrating sphere. The results are shown in Table 1.

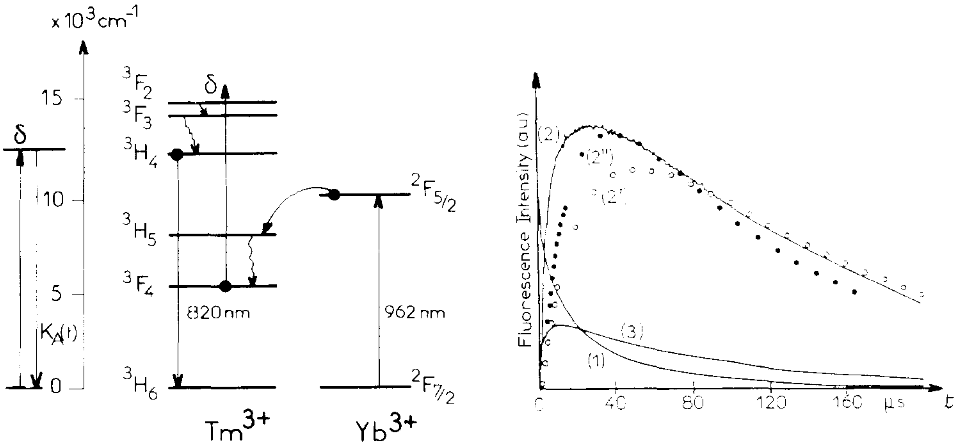
We turn now to the dynamics of the up-conversion energy transfer in Yb–Ho and Tb–Tm bidoped samples. A tentative model of the initial rise-times of all the anti-Stokes fluorescences has been constructed. We only give in this paper the treatment of the $^3H_4 \rightarrow {}^3H_6$ red transition as shown in Fig. 2. The population $N_A(t)$ of the $^3H_4$ acceptor levels is described in the framework of the fluorescence transfer function method [1] in terms both of $K_A(t)$, the response of the acceptor level to an excitation, described by an Inokuti–Hirayama expression and of $e(t)$ the source of excitation by the following relation:

$$N_A(t) = \int_0^t e(t - t')K_A(t')\,dt'. \tag{1}$$

If $e(t)$ is taken as the product of the $^2F_{5/2}$ (Yb) and $^3F_4$ (Tm) populations, the model is not able to reproduce the experimental data in Fig. 2. We think that this is due to the fact that our model supposes the same yield of up-conversion transfer for all Yb–Tm ion pairs whatever the interatomic distance. In fact, because of the fluctuations of ion

Table 1
Up-conversion quantum yields after infrared excitation into Yb ions

Crystal	Level	Quantum yield (%)
5% Yb, 0.5% Ho	$^5S_2$ $^5F_4$	2.7
5% Yb, 3% Ho	$^5S_2$ $^5F_4$	4.4
5% Yb, 5% Tm	$^3H_4$	6.0
5% Yb, 5% Tm	$^1G_4$	0.03
5% Yb, 5% Tm, 0.5% Ho	$^3H_4$	5.1



(a) (b)

Fig. 2. (a) Yb–Tm up-conversion transfer in GGG:5% Yb:5% TM sample: example of the $^3H_4 \rightarrow {}^3H_6$ Tm transition. (b) Time evolution of the $^3H_4 \rightarrow {}^3H_6$ emission: Curve (1): Experimental data of the $^3H_4 \rightarrow {}^3H_6$ fluorescence after a direct δ excitation into $^3H_4$ level. $K_A(t)$ is the response of the acceptor level to the excitation. Curve (2) and circles (2′) and (2″): after excitation into to Yb ions. Curve (2): experimental data of the $^3H_4 \rightarrow {}^3H_6$ fluorescence. Circles (2′): from a model which does not take into account the fluctuations of positions of donors and acceptors. Circles (2″): from a model taking into account partially the fluctuations of positions of donors and acceptors. Curve (3): time evolution of the source $e(t)$ used to obtain circles (2′).

distributions in the regions of the crystal where the ion pairs are closer, the coefficient of transfer is higher and a more important contribution to the up-conversion process is expected. Then using Chandrasekhar's procedure to describe the source of excitation which can now be represented as

$$e(t) = \int\int a(\phi, \phi')\, N_{\mathrm{D}\phi}(t) N_{\mathrm{D}'\phi}(t)\, \mathrm{d}\phi\, \mathrm{d}\phi', \qquad (2)$$

where $N_{\mathrm{D}\phi}$ and $N_{\mathrm{D}'\phi}$ are the donor and acceptor populations created by the Yb ions belonging to one class of donor ions having the same total transfer rate ϕ on each acceptor ion. The up-conversion probability $a(\phi, \phi)$ is an unknown function whose value was 1 in the previous model. Taking a larger probability $a(\phi, \phi) = \phi$ in (2) and inserting this into (1) we obtain curve 2″ in Fig. 2. The experimental and calculated rise times are now much better.

4. Conclusion

We have shown that efficient down-conversion energy transfer from the initially excited Yb ions to both the Tm and Ho ions occurs. We have also studied up-conversion processes and measured the quantum yield of the energy losses. In addition, we have shown that a good description of the up-conversion dynamics must take into account the fluctuations of the distribution of the donor and acceptor pain distances.

References

[1] A. Brenier, G. Boulon, C. Madej, C. Pédrini and L. Lou, J. Lumin. 54 (1993) 271.
[2] A. Brenier, C. Madej, C. Pédrini, G. Boulon, J. Phys.: Condens. Matter 3 (1991) 203, 7887.
[3] J.C. Grant, Phys. Rev. B 4 (1971) 648.
[4] S. Chandrasekhar, Rev. Mod. Phys. 15 (1943) 1.