

ENERGY TRANSFER MECHANISMS AND EXCITED STATE DYNAMICS OF Yb^{3+} , Tm^{3+} AND Ho^{3+} DOPED $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ SINGLE CRYSTALS

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The transfer mechanisms occurring in ytterbium, thulium and holmium doped gadolinium gallium garnet crystals are presented. Various models are used to modelize the up- and down-conversion processes. They lead to a good description of the excited state dynamics and provide information about the efficiencies of the transfers.

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1. Introduction

The eye-safe 2 μm laser emission is usually obtained from the $^5I_7 \rightarrow ^5I_8$ transition of Ho^{3+} ions imbedded in crystals or glasses. The fluorescence of holmium is usually sensitized by other ions like Cr^{3+} , Er^{3+} and Tm^{3+} [1-4]. The two former ones allow efficient flash lamp pumping while the latter is well adapted for laser diode pumping at around 800 nm. The Ho 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 with no possibility of excited state absorption. We have shown in a previous work [5, 6] that efficient $\text{Tm} \rightarrow \text{Ho}$ energy transfers occur in $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) and in the present paper we study energy transfers $\text{Yb} \rightarrow \text{Tm}$ and $\text{Yb} \rightarrow \text{Ho}$ in GGG which lead to an enhancement of the Ho infrared fluorescence.

The counterpart of the presence of sensitizers is that they can introduce the same kind of energy losses. We have analyzed previously in detail the $\text{Ho} \rightarrow \text{Tm}$ back-transfer which can be an important source of losses when the Tm concentration increases [7] and this process is shortly presented here. Another usual source of losses is the up-conversion processes which are identified in this work, occurring from the Yb and Ho or Tm infrared levels towards the Tm and Ho visible levels.

We have measured the quantum yields and analyzed the excited state dynamics induced by very short pulsed excitations.

All the materials studied here were single crystals grown in our laboratory by using the Czochralski method. Single, double and triple doped samples were obtained containing various rare earth ion concentrations. The real concentrations of the dopants and their coefficients of segregation k (around 1.2 for the three dopants) were determined knowing the crystallized fraction of the melt $g(l)$ at a point l along the axis of the crystal.

To analyze the fluorescence dynamics, we are not allowed to use the rate equations because the Grant's procedure [8] can be applied only in the case of a very fast energy diffusion among donors and the decays were not found exponential. We therefore used standard models, like Inokuti-Hirayama [9] and Yokota-Tanimoto [10] models which allow one to describe the decay rates of the donors, but also other models like the Chandrasekhar's procedure [11, 5, 6] and the transfer function method [12, 7] which permit to describe also the dynamics of the acceptors.

2. Direct Yb \rightarrow Tm and Yb \rightarrow Ho energy transfers

These transfers were studied in double-doped systems after excitation of Yb³⁺ ions in the $^2F_{5/2}$ level at 962 nm. These non-resonant transfers are sketched

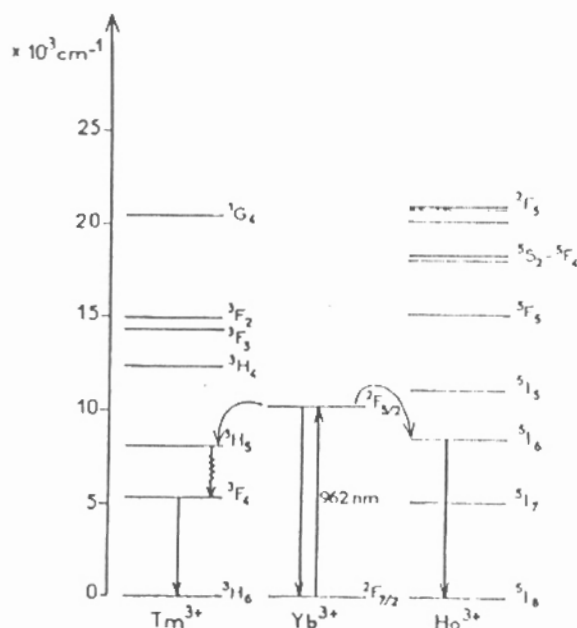


Fig. 1. Energy level scheme of ions and direct Yb \rightarrow Tm and Yb \rightarrow Ho energy transfers.

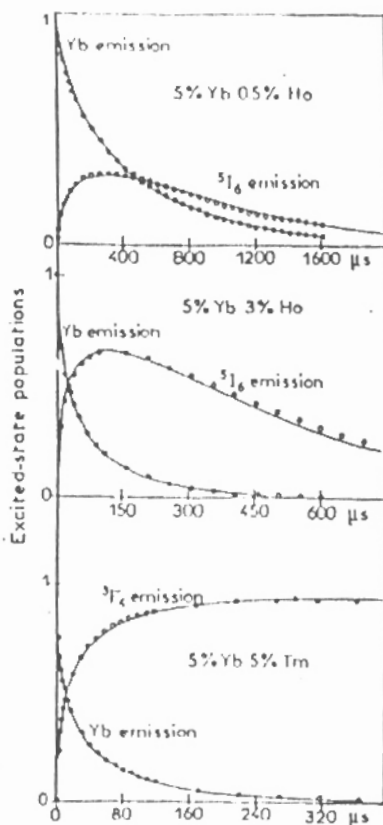


Fig. 2. Time-dependence of the ${}^2F_{5/2}$ (Yb), 3F_4 (Tm) and 5I_6 (Ho) emissions after a short excitation in Yb. The circles are the results of the fits.

in Fig. 1 and the decay profiles of the ${}^2F_{5/2}$ (Yb), 5I_6 (Ho) and 3F_4 (Tm) emitting levels are shown in Fig. 2.

The time evolution of the Yb fluorescence is correctly described by the Yokota-Tanimoto expression [10]:

$$N_D(t) = \exp \left[-\gamma t - bt^{1/2} \left(\frac{1 + 10.87x + 15.50x^2}{1 + 8.743x} \right)^{3/4} \right] \quad (1)$$

with

$$b = (4/3)\pi^{3/2} C_A R_{DA}^3 \gamma^{1/2},$$

$$x = D(Yb-Yb) R_{DA}^{-2} \gamma^{-1/3} t^{2/3},$$

$$D(Yb-Yb) = k C_{Yb}^{4/3},$$

where $1/\gamma = 1.47$ ms is the experimental time-constant of the decay of the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ fluorescence obtained in GGG:5% Yb, C_{Yb} and C_A are the Yb and Tm or Ho concentrations, $D(Yb-Yb)$ is the Yb diffusion constant and R_{DA}

represents the critical radius of the Yb/Ho or Yb/Tm dipole-dipole interaction. The characteristics of transfers are indicated in Table I, where it can be seen that the transfer efficiencies are close to unity for the concentrations considered.

TABLE I

Characteristics of direct Yb \rightarrow Tm and Yb \rightarrow Ho energy transfers.

Crystal	$C_{\text{Tm}}, C_{\text{Ho}}$	R_0 [Å]	k [$10^{-39} \text{ cm}^6 \text{ s}^{-1}$]	η_T [%]
GGG:5%Yb, 5%Tm	8.74×10^{20}	10.90	0.300	0.96
GGG:5%Yb, 3%Ho	4.64×10^{20}	11.40	0.558	0.97
GGG:5%Yb, 0.5%Ho	7.43×10^{19}	12.96	0.760	0.83
GGG:5%Yb, 5%Tm, 0.5%Ho				0.99

The dynamics of the acceptors was described very nicely (Fig. 2) by the relation

$$\dot{N}(t) = -N'/\tau' - (N/\tau + \dot{N}) \quad (2)$$

using the identity relation

$$\dot{N}(t) = -N/\tau + (N/\tau + \dot{N}), \quad (3)$$

where the population N of the donor Yb was calculated by the Yokota-Tanimoto model and the population N' of the acceptor is deduced from the solution of (2) [5].

3. Tm \rightarrow Ho energy transfers

In the Yb-Tm-Ho tridoped sample in addition to the previous transfers we detected the transfer:



This transfer is clearly seen by comparison of the ${}^5I_6(\text{Ho})$ decay time in the Yb-0.5% Ho bidoped sample and in the Yb-Tm-0.5% Ho tridoped one, after a short excitation in the ${}^3F_5(\text{Ho})$ level. It is much shorter in the latter sample, corresponding to a 90% transfer quantum yield.

The kinetics of the forward and backward ${}^3F_4(\text{Tm}) \leftrightarrow {}^5I_7(\text{Ho})$ energy transfers in Tm/Ho bidoped GGG have been studied in detail in a previous paper [7]. The $\text{Tm}^{3+}/\text{Ho}^{3+}$ system is very convenient for diode pumping near 800 nm in the ${}^3H_4(\text{Tm})$ level since an efficient Tm \rightarrow Tm cross-relaxation mechanism drives the energy towards the ${}^3F_4(\text{Tm})$ level followed by the ${}^3F_4(\text{Tm}) \rightarrow {}^5I_7(\text{Ho})$ transfer (Fig. 3). The efficiency of the latter is reduced by the ${}^5I_7 \rightarrow {}^3F_4$ back-transfer. We analyzed the kinetics of the 5I_7 and 3F_4 levels with a model taking into account a random distribution of the ions in the crystal as well as the diffusion of the energy between the ions. Fluorescence "transfer function" method [12] has been used in the analysis. The decay profiles of the ${}^5I_7(\text{Ho})$ and ${}^3F_4(\text{Tm})$ after an excitation in the ${}^3H_5(\text{Tm})$ level are shown in Fig. 4. At short time the short decay of the donors is correlated to the short rise time of the acceptors and at long time the decays

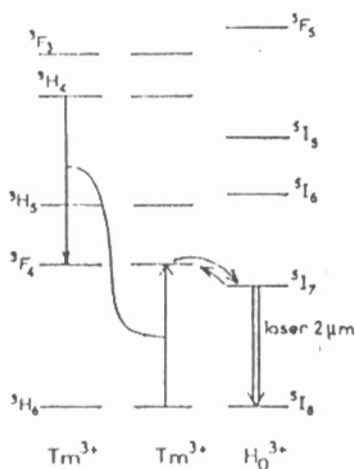


Fig. 3. Energy levels and transfer mechanisms in the Tm^{3+} , Ho^{3+} codoped systems.

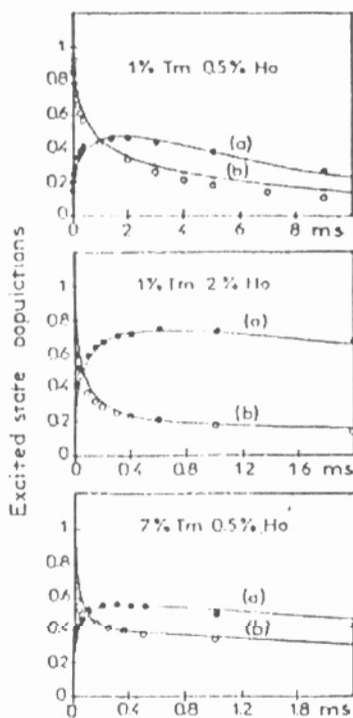


Fig. 4. Kinetics of the $^5I_7(Ho)$ (curves (a)) and $^3F_4(Tm)$ (curves (b)) after a δ excitation in the $^3H_5(Tm)$ level.

of donors and acceptors are similar, indicating 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 of the transfer and of the back-transfer. They are compared to the ones that were obtained from the calculation of the overlap between the absorption and the emission of donors and acceptors, respectively [6]. We can see in Table II that the critical

TABLE II

Critical radii (\AA) of the ion-ion interaction assuming dipole-dipole mechanism and diffusion among the donor ions. In parenthesis is given the critical radius obtained from a model without diffusion.

From the spectra independent of crystal	From the fits		
	7% Tm 0.5% Ho	1% Tm 0.5% Ho	1% Tm 2% Ho
Ho \rightarrow Ho	17.9		
Ho \rightarrow Tm	8.4	9.7 (12.2)	7.2 (11.6)
Tm \rightarrow Ho	15.1	26.7 (31.9)	18 (19.7)
Tm \rightarrow Tm	13.3		6.5 (19.3)
			18 (21.5)

radii, obtained from the fits, of the forward transfer Tm \rightarrow Ho and back-transfer Ho \rightarrow Tm after an excitation in the 3H_5 level, are of the same order of magnitude (the dispersion is about 25%) as the radii obtained from spectroscopic data, except for the heavily Tm doped sample (7% Tm) in the case of the Tm \rightarrow Ho forward transfer. In the latter case a discrepancy occurs because of the fast diffusion among the Tm ions which is not taken into account by the Yokota-Tanimoto treatment.

4. Up-Conversion processes and anti-Stokes emissions

The excitation of the Yb ions is also followed by anti-Stokes emissions coming from the upper Tm and Ho levels: 820 nm (3H_4 (Tm)), 481 nm (1G_4 (Tm)), 548 nm (${}^5S_2 - {}^5F_4$ (Ho)), 665 nm (5F_5 (Ho)), (Fig. 5). These processes were neglected in the excited state dynamics described in the previous sections because they are rather weak.

The up-conversion quantum yield from Yb ions towards a given Ho or Tm level was obtained using an integrating sphere. The results are gathered in Table III.

We also measured the power dependence of the fluorescences. While the Yb ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ fluorescence varies linearly with the density of excitation as expected, it was found a quadratic dependence for the ${}^3H_4 \rightarrow {}^3H_6$ infrared fluorescence of Tm and for the ${}^5S_2 \rightarrow {}^5I_8$ green and ${}^5F_5 \rightarrow {}^5I_8$ red fluorescence of Ho, and a cubic dependence of the ${}^1G_4 \rightarrow {}^3H_6$ blue fluorescence of Tm. This behaviour confirms the two-step or three-step up-conversion processes indicated in Fig. 5.

We turn now to the dynamics of up-conversion energy transfers in Yb/Ho and Yb/Tm bidoped samples and we consider here the two following up-conversion

TABLE III
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

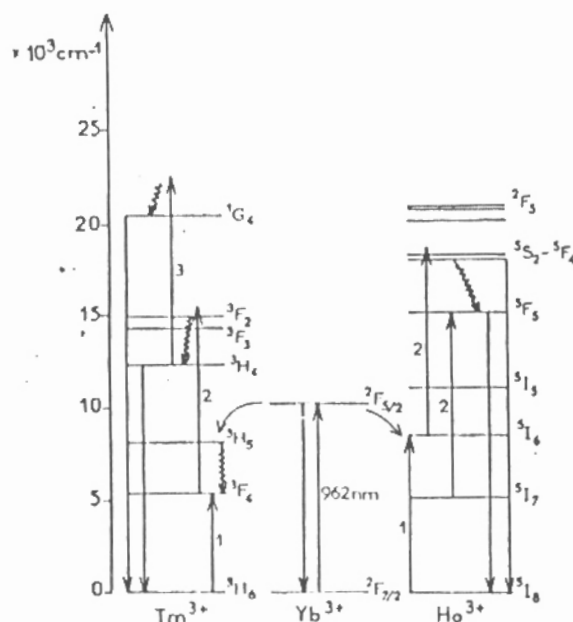
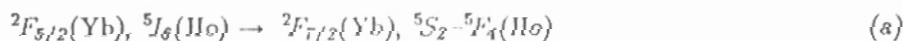


Fig. 5. Up-conversion processes and anti-Stokes emissions after a short excitation in Yb. The sequence of transfers in time is indicated by numbers of the side of each transition induced by the inter-ionic interaction.

processes:



Process (a) is nearly resonant and process (b) is obtained after relaxation of excitation from 3F_2 and 3F_3 levels to 3H_4 state.

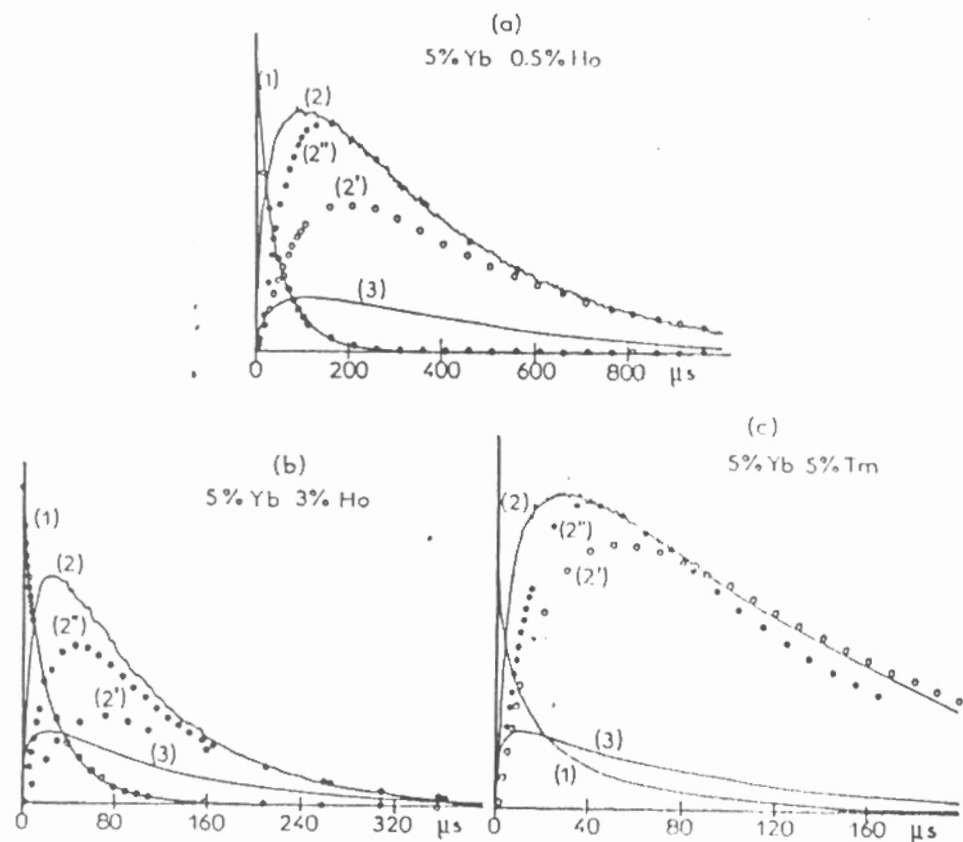


Fig. 6. Time evolution of the 5S_2 - ${}^5F_4 \rightarrow {}^5I_6$ (Ho) fluorescence (a) and (b) and ${}^3H_4 \rightarrow {}^3H_6$ (Tm) fluorescence (c). Curves and circles (1) — after a direct δ excitation. Curves (2) and circles (2') and (2'') — after excitation into the Yb ions. Curves (3) — the time evolution of the source $\epsilon(t)$ used to obtain circles (2'). The solid lines are for experimental data, the circles are from the models.

A tentative of modelisation of the time evolution of the 5S_2 - 5F_4 (Ho) and 3H_4 (Tm) fluorescences after excitation of the Yb ions in bidoped systems was described in detail in a forthcoming paper [15]. The population of the acceptor levels (5S_2 - 5F_4 (Ho) and 3H_4 (Tm)) is described in the framework of the fluorescence "transfer function" method [7] in terms of $K_A(t)$, the response of the acceptor level to an excitation, described by an Inokuti-Hirayama expression, and of $\epsilon(t)$, the source of excitation. If $\epsilon(t)$ is taken as the product of populations ${}^2F_{5/2}$ (Yb) and 5I_6 (Ho) or ${}^2F_{5/2}$ (Yb) and 3F_4 (Tm), it can be seen in Fig. 6 that the model is not able to reproduce the experimental data, in particular the rapid rise time. We think that it is due to the fact that our model supposes the same yield of up-conversion transfer for all the Yb/Ho or Yb/Tm ion pairs whatever the interatomic distance.

In order to take into account the fluctuations of ion distribution, we have used the Chandrasekhar's procedure to describe the source of excitation which can now be represented as:

$$e(t) = \int \int a(\phi, \phi') N_{D\phi}(t) N_{D'\phi}(t) d\phi d\phi', \quad (4)$$

where $N_{D\phi}$ and $N_{D'\phi}$ are the donor and acceptor populations created by the Yb excited ions belonging to a class of donor ions having the same total transfer rate ϕ on each acceptor ion. $a(\phi, \phi')$ is an unknown function whose value was unity in the previous model. Taking $a(\phi, \phi') = \phi$, we obtain the curves (2'') in Fig. 6. The experimental rise times are now much better described. So despite of the fact that the model is not rigorous, it proves that a good description of up-conversion dynamics must take into account the fluctuations of distribution of relative positions of the donor/acceptor ions.

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in the previous model and representing the up-conversion probability. In order to obtain a faster rise time from expression (2) we have to give a larger weight in expression (11) to the products $N_{D\phi}(t)N_{D'\phi}(t)$ having a large ϕ . That means that the excited Yb ions which are close to acceptor ions in a part of the crystal will have simultaneously a large yield ϕ of transfer (1) or (2) and a large probability of up-conversion $a(\phi, \phi')$. Taking $a(\phi, \phi') = \phi$ in expression (11) inserted in expression (2), we obtain the circles (2'') in Fig. 9. The experimental rise times are now much better. So despite the fact that our model is not rigorous it proves that a good description of up-conversion dynamics must take into account the fluctuations of distribution of relative positions of the donor/acceptor ions.

V. CONCLUSION

We have shown that efficient down-conversion energy transfers drive the pump energy into Yb ions towards the 3I_7 2- μm emitting laser level of the Ho^{3+} ions. We have measured the quantum yield of the up-conversion energy losses in the Yb-Ho and Yb-Tm bidoped samples. They are not more than 4.4% in our condition of excitation.

In the triply Yb-Tm-Ho-doped sample the up-conversion energy losses in Ho^{3+} ions are even weaker (Fig. 5) because they are quenched by the resonant $^5I_6(\text{Ho}) \rightarrow ^3H_5(\text{Tm})$ transfer. Moreover, efficient cross-relaxation mechanisms down-convert the up-converted energy from the upper Ho and Tm energy levels to the ground state, since the fluorescence time dependence of the former is not exponential when they are directly excited. The counterpart of the addition of Tm ions in the material is the storage of a fraction of the energy into the $^3F_4(\text{Tm})$ level.

We have shown that both up-conversion and down-conversion dynamics cannot be described correctly if the fluctuations of distribution of the donor and acceptor positions are not taken into account.

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