

Fluorescence dynamics of  $\text{YVO}_4:\text{Tm}^{3+}$ ,  $\text{YVO}_4:\text{Tm}^{3+}, \text{Tb}^{3+}$  and  $\text{YVO}_4:\text{Tm}^{3+}, \text{Ho}^{3+}$  crystals

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# Fluorescence dynamics of $\text{YVO}_4:\text{Tm}^{3+}$ , $\text{YVO}_4:\text{Tm}^{3+}, \text{Tb}^{3+}$ and $\text{YVO}_4:\text{Tm}^{3+}, \text{Ho}^{3+}$ crystals

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Received 20 May 1998

**Abstract.** The fluorescence dynamics of the  $^3\text{H}_4$  and  $^3\text{F}_4$  energy levels of  $\text{Tm}^{3+}$  in  $\text{YVO}_4$  single crystals codoped or not codoped with  $\text{Tb}^{3+}$  and  $\text{Ho}^{3+}$  ions was experimentally investigated and compared with classical energy-transfer models. In the  $\text{YVO}_4:1\% \text{Tm}^{3+}$  and  $\text{YVO}_4:1\% \text{Tm}^{3+}, 1\% \text{Ho}^{3+}$  crystals, the  $^3\text{H}_4$  state relaxes predominantly by internal cross-relaxation-type energy transfers, whereas in the  $\text{YVO}_4:0.5\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$  and  $\text{YVO}_4:1\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$  crystals the relaxation is dominated by direct energy transfers to the  $^7\text{F}_1$  state of the  $\text{Tb}^{3+}$  ions. In all of the codoped systems, strong energy transfers from the  $^3\text{F}_4$  state of the  $\text{Tm}^{3+}$  ions to the  $^7\text{F}_1$  and  $^5\text{I}_7$  states of the  $\text{Tb}^{3+}$  and  $\text{Ho}^{3+}$  codopants were evident. The electric dipole–electric dipole coupling parameter was evaluated for several cross-relaxation and direct-energy-transfer processes.

## 1. Introduction

$\text{YVO}_4$  is not an easy crystal to grow, but its excellent luminescence properties, when doped with rare-earth ions such as  $\text{Nd}^{3+}$  [1],  $\text{Tm}^{3+}$  [2, 3] and  $\text{Er}^{3+}$  [4, 5] and its reasonably good thermomechanical characteristics make it a very attractive laser material, in particular for applications requiring diode-pumped minilaser devices, and many studies are currently dedicated to it.

$\text{Tm}^{3+}$ -doped  $\text{YVO}_4$  is already known as a  $2 \mu\text{m}$  laser material [2] but it has been shown recently [3] that it can also be attractive in the eye-safe spectral region around  $1.5 \mu\text{m}$ . It is interesting not only because it is possible to pump the  $^3\text{H}_4$  emitting level directly using 800 nm high-power laser diodes, but also because it is characterized by large and broad absorption and stimulated emission cross-sections. A broad absorption spectrum around the pump wavelength is very convenient because it allows one to avoid thermoelectronic cooling of the laser diodes and a broad-band emission can be very useful when some wavelength tuning is needed.

In reference [3] we reported very briefly, along with other more extensive spectral data, some  $1/e$  fluorescence time constants measured for crystals doped singly with  $\text{Tm}^{3+}$

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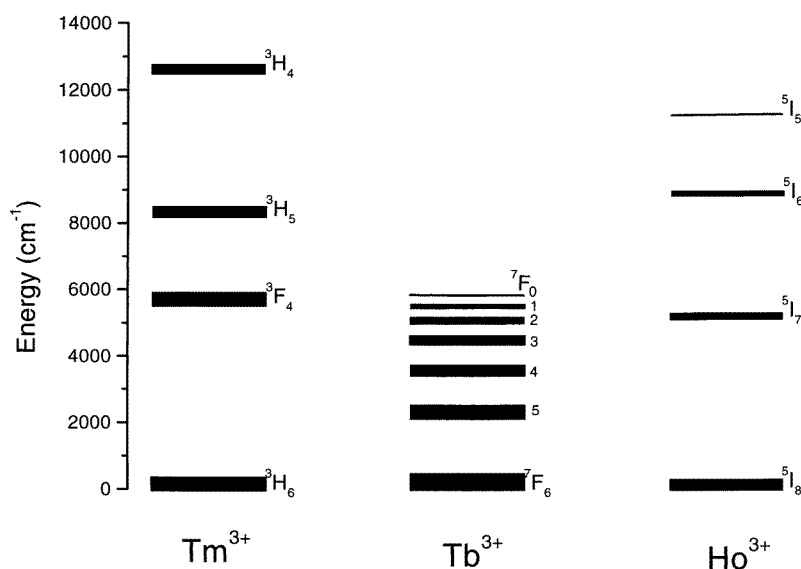
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ions and for crystals codoped with  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$  ions. Codoping with  $\text{Tb}^{3+}$  ions was investigated because it is necessary to reduce the fluorescence lifetime of the  ${}^3\text{F}_4$  terminal level of the  ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$  laser transition via  $\text{Tm} \rightarrow \text{Tb}$  energy-transfer processes, to avoid 'self-terminated' laser operation [6, 7].

In the present paper we describe and analyse the fluorescence dynamics within the  $\text{Tm}^{3+}$  ions and between the  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$  ions in more detail using the standard energy-transfer theories. In addition, we complete this work with a similar study carried out for the case of a crystal codoped with  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  ions, the latter also being known as efficient quenchers for the  ${}^3\text{F}_4$  metastable level [7].

**Table 1.** The actual concentrations of the dopants in the  $\text{YVO}_4$  crystals, as determined by ICP analysis.

Sample	% Tm/Y	% Tb/Y	% Ho/Y
Tm 1%	1.276		
Tm 0.5%, Tb 1%	0.674	0.789	
Tm 1%, Tb 1%	1.181	1.430	
Tm 1%, Ho 1%	1.289		1.346



**Figure 1.** Lower energy levels of  $\text{Tm}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ho}^{3+}$  of interest.

## 2. Experimental procedure

Yttrium vanadate single crystals doped with  $\text{Tm}^{3+}$  and codoped with  $\text{Ho}^{3+}$  or  $\text{Tb}^{3+}$  were grown using a  $\text{Pb}_2\text{V}_2\text{O}_7$  flux, which is considered a good solvent for growing vanadate crystals because of its ease of preparation and extremely low vapour pressure [8, 9]. The details of the crystal growth procedure have been reported in a previous paper [3]. The

dopants were added with nominal concentrations (with respect to that of  $Y^{3+}$ ) of 0.5%  $Tm^{3+}$ , 1%  $Tm^{3+}$ , (0.5%  $Tm^{3+}$ , 1%  $Tb^{3+}$ ), (1%  $Tm^{3+}$ , 1%  $Tb^{3+}$ ) and (1%  $Tm^{3+}$ , 1%  $Ho^{3+}$ ).

The crystals grew in the form of clear rods elongated in the direction of the crystallographic  $c$ -axis ( $5 \times 2 \times 2 \text{ mm}^3$ ) or in the form of small cubes ( $3 \times 3 \times 3 \text{ mm}^3$ ). The actual dopant contents in the crystals, as determined by conventional ICP analysis, are reported in table 1. Hereafter the crystals will be labelled with their nominal concentrations.

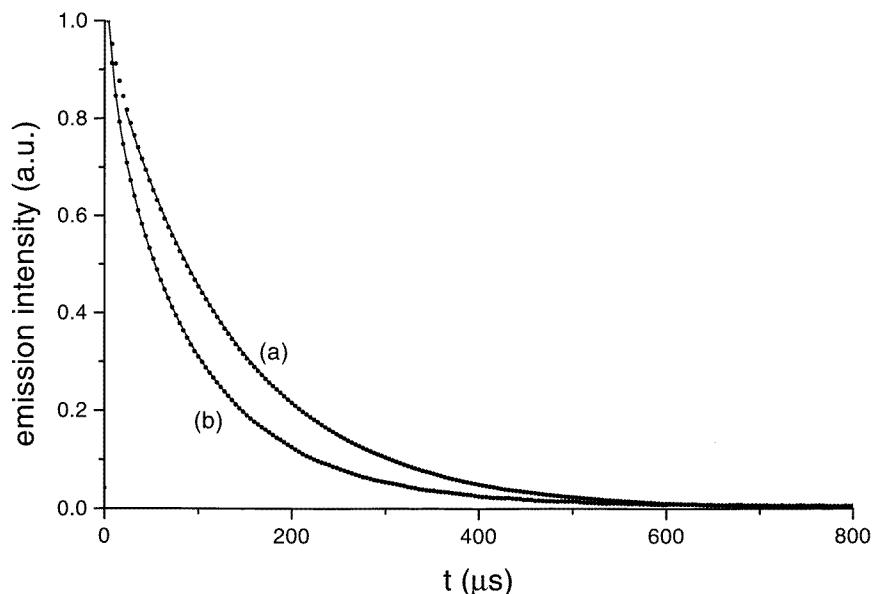
For the spectroscopic measurements, the samples were excited with a pulsed Raman-shifted Quantel dye laser (10 Hz, 10 ns) with a linewidth of  $0.2 \text{ cm}^{-1}$ . The infrared luminescence signals were detected and analysed by using a fast-response ( $0.5 \mu\text{s}$ ) North Coast germanium photodiode, coupled to a Lecroy 9400 digital oscilloscope to record fluorescence transients. All of the decay curves were measured at room temperature.

**Table 2.** Decay data for  $YVO_4:Tm^{3+}$ ,  $YVO_4:Tm^{3+}, Tb^{3+}$  and  $YVO_4:Tm^{3+}, Ho^{3+}$  crystals. The values in brackets are exponential decay times, estimated in the case of a non-exponential decay. The meanings of  $\tau_D$  and  $C_{DA}$  are given in the text.

State and crystal	Exponential		Inokuti–Hirayama	
	$\tau_{\text{decay}}/\mu\text{s}$	$\tau_{\text{rise}}/\mu\text{s}$	$\tau_D/\mu\text{s}$	$C_{DA}/10^{-50} \text{ m}^6 \text{ s}^{-1}$
$^3H_4$				
Tm 0.5%	133			
Tm 1%	(95)		136	0.18
Tm 0.5%, Tb 1%	(53)		102	1.9
Tm 1%, Tb 1%	(40)		89	0.96
Tm 1%, Ho 1%	(84)		125	0.18
$^3F_4$ (excitation in ( $^3F_2, ^3F_3$ ))				
Tm 1%	1150	80		
Tm 0.5%, Tb 1%	(110)		128	0.53
Tm 1%, Tb 1%	(60)		95	0.66
$^3F_4$ (excitation in $^3H_5$ )				
Tm 1%	1030			
Tm 0.5%, Tb 1%	(38)		(intermediate regime)	
Tm 1%, Tb 1%	(36)		(intermediate regime)	
$^5I_7$				
Tm 1%, Ho 1%	2560	81		

### 3. Structural, vibrational and electronic data

$YVO_4$  crystallizes at room temperature in the tetragonal  $I4_1/amd$  ( $D_{4h}^{19}$ ) space group [10]. There is only one yttrium site for which the lanthanide dopant can substitute. The yttrium site symmetry is  $D_{2d}$  and is coordinated by eight oxygen atoms. The vibrational properties of  $YVO_4$  have been studied in detail [11]. Internal modes of the  $VO_4^{3-}$  ion ranging from  $891$  to  $260 \text{ cm}^{-1}$ , and external modes ranging from  $310$  to  $157 \text{ cm}^{-1}$  have been observed and assigned. The Stark level structure of several manifolds of the  $Tb^{3+}$ ,  $Ho^{3+}$  and  $Tm^{3+}$  ions in  $YVO_4$  has been reported in [12] and is shown in figure 1.



**Figure 2.** Room temperature  ${}^3\text{H}_4$  fluorescence decays in (curve (a))  $\text{YVO}_4:0.5\% \text{Tm}^{3+}$  and (curve (b))  $\text{YVO}_4:1\% \text{Tm}^{3+}$  after 690 nm excitation. The solid lines are fits (a) to an exponential decay and (b) to the Inokuti–Hirayama model for electric dipole–electric dipole interaction. For the sake of clarity, not all of the data points have been plotted.

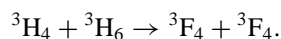
#### 4. Results and discussion

The results of the analysis of the room temperature decay curves for the  $\text{YVO}_4:\text{Tm}^{3+}$ ,  $\text{YVO}_4:\text{Tm}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{YVO}_4:\text{Tm}^{3+}$ ,  $\text{Ho}^{3+}$  crystals are collected in table 2; see also figures 2–5. In the following sections the data for the various crystals are discussed separately.

##### 4.1. $\text{YVO}_4:\text{Tm}^{3+}$ crystals

Following pulsed excitation at 690 nm into the ( ${}^3\text{F}_2$ ,  ${}^3\text{F}_3$ ) states, the room temperature decay curve of the luminescence from the  ${}^3\text{H}_4$  state in  $\text{YVO}_4:0.5\% \text{Tm}^{3+}$  (observation wavelength 1450 nm) is exponential, yielding a lifetime of the excited state of 133  $\mu\text{s}$  (figure 2). This value can be compared with the radiative lifetime of the  ${}^3\text{H}_4$  state (198  $\mu\text{s}$ ) calculated from the Judd–Ofelt intensity parameters [3]. The difference can be accounted for by weak multiphonon relaxation of the  ${}^3\text{H}_4$  state, as the  ${}^3\text{H}_4$ – ${}^3\text{H}_5$  energy gap can be bridged by about five 891  $\text{cm}^{-1}$  phonons. No cross-relaxation processes appear to be operative at this doping level.

On the other hand, the decay curve of the luminescence from the  ${}^3\text{H}_4$  state in  $\text{YVO}_4:1\% \text{Tm}^{3+}$  is weakly non-exponential. The decay appears to be faster at short times, indicating that energy-transfer processes are operative. In fact, the  ${}^3\text{H}_4$  state can be involved in the cross-relaxation process [13]:



The minimum energy mismatch for this process is 854  $\text{cm}^{-1}$  which can be bridged by the creation of one phonon, as a vibrational mode of 840  $\text{cm}^{-1}$  is present in the Raman

spectrum [11]. An exponential decay fits the data rather badly, with  $\tau = 95 \mu s$ . On the other hand, the decay curve can be fitted by the standard Inokuti–Hirayama (IH) model for electric dipole–electric dipole interactions between donor and acceptor [14] (figure 2). This model can be used to describe energy-transfer processes in complex crystals when the donor–acceptor transfer or the cross-relaxation is much faster than energy migration in the donor subset. More explicit models have been proposed and successfully applied to highly symmetric crystals [15]. In the present case, the fit to the IH model is excellent and gives a lifetime of the isolated donor ( $^3H_4$ ) state of  $\tau_D = 136 \mu s$ , in agreement with the result obtained for  $YVO_4:0.5\% Tm^{3+}$ , and a critical distance for the transfer of  $R_0 = 7.9 \text{ \AA}$ , corresponding to a dipole–dipole coupling parameter  $C_{DA} = 1.8 \times 10^{-51} \text{ m}^6 \text{ s}^{-1}$ . This value can be compared with a coupling parameter  $C_{DA} = 2.7 \times 10^{-51} \text{ m}^6 \text{ s}^{-1}$  obtained for the same cross-relaxation process in YAG [13]. We note that the present analysis of the decay curves differs from the one presented in reference [16], in which the non-exponential behaviour was not investigated.

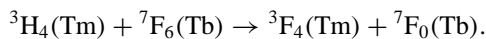
Pulsed excitation at 690 nm leads to a room temperature decay curve of the  $^3F_4$  state in  $YVO_4:1\% Tm^{3+}$  (observation wavelength 2000 nm) showing the presence of a rise time. The decay part can be fitted separately with an exponential curve, yielding  $\tau = 1.10 \text{ ms}$ . This compares reasonably well with the radiative lifetime of  $^3F_4$  (1.29 ms). The exponential shape of the decay does not rule out the presence of fast migration in the  $^3F_4$  state at this concentration. The small difference between the radiative and the experimental lifetimes can possibly be explained either on the basis of weak multiphonon relaxation or, more likely, of energy migration in the  $^3F_4$  subset and quenching by impurities or defects.

The whole curve can be fitted (although not perfectly) using a model accounting for an exponential rise followed by an exponential decay. The decay part is characterized by  $\tau = 1.15 \text{ ms}$ , which is similar to the value obtained above. The exponential rise time is close to  $80 \mu s$ , not far from the exponential fit of the decay of  $^3H_4$  in the same crystal. This result indicates that the  $^3F_4$  state is directly fed by  $^3H_4$ .

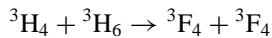
The decay curve of the  $^3F_4$  state after excitation in  $^3H_5$  for the  $YVO_4:1\% Tm^{3+}$  crystal is very nearly exponential. The fit gives  $\tau = 1.03 \text{ ms}$ . An exponential fit of the tail at long times is perfect, yielding  $\tau = 1.07 \text{ ms}$ . This observation is consistent with the presence of fast migration in the  $^3F_4$  subset, as pointed out above, and with a fast multiphonon decay from  $^3H_5$  to  $^3F_4$ ; this is reasonable, since the  $^3H_5$ – $^3F_4$  energy gap can be bridged by just three phonons.

#### 4.2. $YVO_4:Tm^{3+}$ , $Tb^{3+}$ crystals

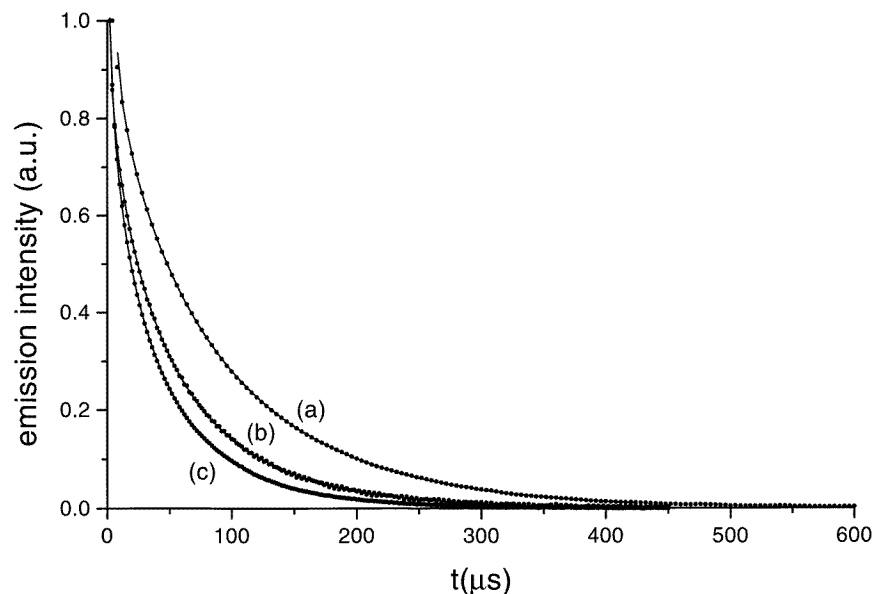
Following pulsed excitation at 690 nm into the ( $^3F_2$ ,  $^3F_3$ ) states, the room temperature decay curve of the luminescence from the  $^3H_4$  state in  $YVO_4:0.5\% Tm^{3+}$ ,  $1\% Tb^{3+}$  is definitely faster than for the  $YVO_4:0.5\% Tm^{3+}$  crystal. An exponential fit gives  $\tau = 53 \mu s$ . For this reason, it is reasonable to assume that the decay is dominated by the energy-transfer process



Presumably the internal cross-relaxation



does not contribute to the decay at this low  $Tm^{3+}$  concentration (see above). The data are fitted reasonably by the IH model for a dipole–dipole interaction in the absence of migration (figure 3). Presumably the fit is not perfect because of the simultaneous presence of the two energy-transfer processes. The IH fit gives for the internal decay of the isolated  $^3H_4$

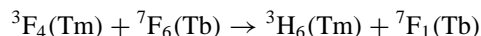


**Figure 3.** Room temperature  ${}^3\text{H}_4$  fluorescence decays in (curve (a))  $\text{YVO}_4:1\% \text{Tm}^{3+}$ ,  $1\% \text{Ho}^{3+}$ , (curve (b))  $\text{YVO}_4:0.5\% \text{Tm}^{3+}$ ,  $1\% \text{Tb}^{3+}$  and (curve (c))  $\text{YVO}_4:1\% \text{Tm}^{3+}$ ,  $1\% \text{Tb}^{3+}$ , after  $690 \text{ nm}$  excitation. The solid lines are fits to the Inokuti–Hirayama model for electric dipole–electric dipole interaction. For the sake of clarity, not all of the data points have been plotted.

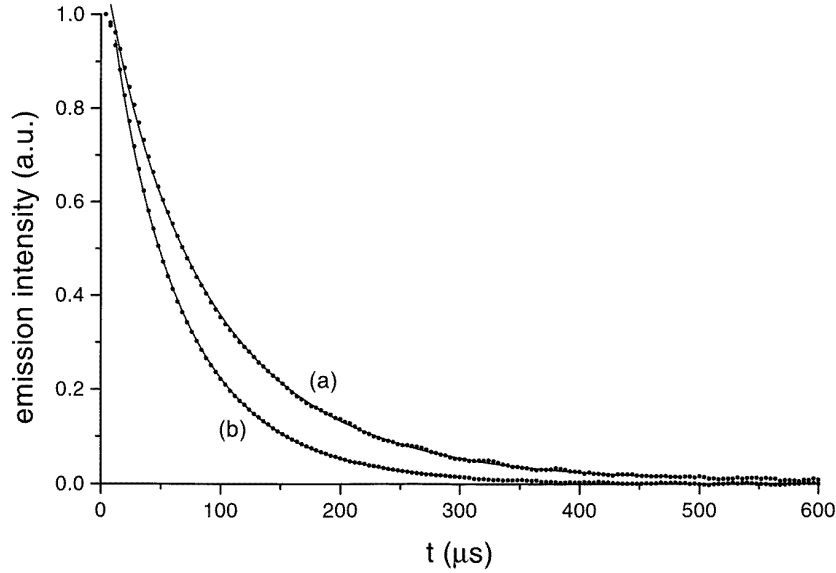
state  $1/\tau_D = 9.85 \times 10^3 \text{ s}^{-1}$ , i.e.  $\tau_D = 102 \mu\text{s}$ , and a critical distance (taking into account just the  $\text{Tm} \rightarrow \text{Tb}$  transfer) of  $R_0 = 11.1 \text{ \AA}$ , corresponding to a dipole–dipole coupling parameter  $C_{\text{DA}} = 1.9 \times 10^{-50} \text{ m}^6 \text{ s}^{-1}$ .

In the case of the  $\text{YVO}_4:1\% \text{Tm}^{3+}$ ,  $1\% \text{Tb}^{3+}$  crystal, the situation is similar to that for the more diluted  $\text{YVO}_4:0.5\% \text{Tm}^{3+}$ ,  $1\% \text{Tb}^{3+}$  (figure 3). Following excitation at  $690 \text{ nm}$ , an exponential fits the room temperature decay curve from  ${}^3\text{H}_4$  very badly, yielding  $\tau = 40 \mu\text{s}$ . The IH fit is worse than in the previous case; it gives parameters not very different from the ones obtained for the  $\text{YVO}_4:0.5\% \text{Tm}^{3+}$ ,  $1\% \text{Tb}^{3+}$  crystal, with  $1/\tau_D = 1.12 \times 10^4 \text{ s}^{-1}$ , i.e.  $\tau_D = 89 \mu\text{s}$ , and a critical distance (taking into account just the  $\text{Tm} \rightarrow \text{Tb}$  transfer) of  $R_0 = 9.7 \text{ \AA}$ . Presumably the fit gets worse because of the increased contribution of the internal cross-relaxation in this crystal.

Pulsed excitation at  $690 \text{ nm}$  gives rise to a much faster room temperature decay of the  ${}^3\text{F}_4$  state in  $\text{YVO}_4:0.5\% \text{Tm}^{3+}$ ,  $1\% \text{Tb}^{3+}$  than for  $\text{YVO}_4:1\% \text{Tm}^{3+}$  with no definite presence of a rise time. The decay is clearly non-exponential, as an exponential fit of the whole curve is bad, with  $\tau = 94 \mu\text{s}$ ; an exponential fit of the long-time tail gives  $\tau = 110 \mu\text{s}$ . An IH fit for a dipole–dipole interaction in the absence of migration is acceptable (figure 4), yielding  $\tau_D = 128 \mu\text{s}$ . Overall, the decay appears to be similar to the decay of  ${}^3\text{H}_4$  in the same crystal, suggesting that the  ${}^3\text{F}_4$  state is fed by  ${}^3\text{H}_4$ , and then decays rapidly, because of a very efficient quenching of  ${}^3\text{F}_4$  by the  $\text{Tb}^{3+}$  ions. In fact, the energy-transfer mechanism



is virtually resonant, with a minimum mismatch  $\Delta E = 6 \text{ cm}^{-1}$  [12]. Moreover, the transfer probability could be enhanced by migration in the  ${}^3\text{F}_4$  state. There is no possibility of back-transfer, as the  ${}^7\text{F}_j$  states of  $\text{Tb}^{3+}$  decay rapidly by multiphonon relaxation.



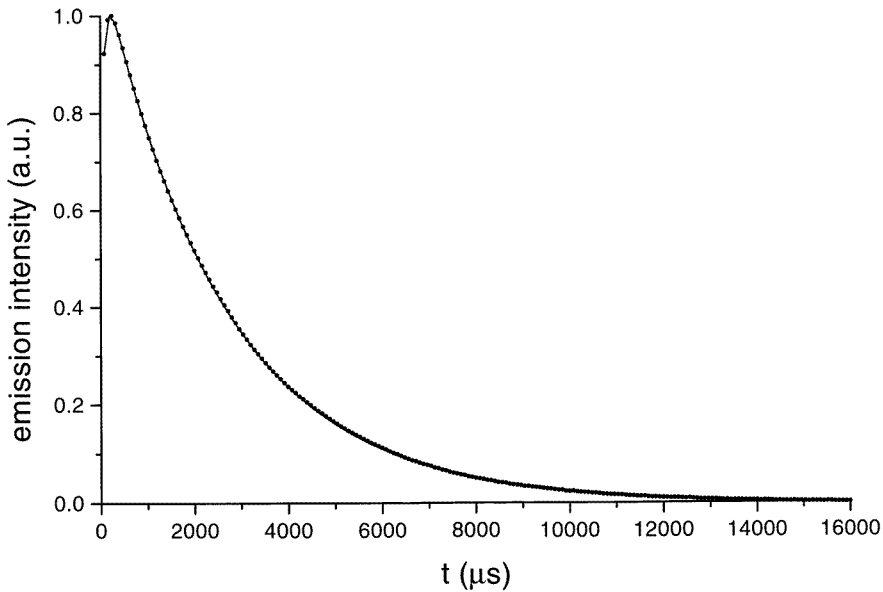
**Figure 4.** Room temperature  ${}^3\text{F}_4$  fluorescence decays in (curve (a))  $\text{YVO}_4:0.5\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$  and (curve (b))  $\text{YVO}_4:1\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$  after 690 nm excitation. The solid lines are fits to the Inokuti–Hirayama model for electric dipole–electric dipole interaction. For the sake of clarity, not all of the data points have been plotted.

In the case of the  $\text{YVO}_4:1\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$  crystal, the situation is similar to that for  $\text{YVO}_4:0.5\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$  (figure 4). There is no clear rise and an exponential fits the data very badly, giving  $\tau = 60 \mu\text{s}$ . The data can be reasonably fitted using an IH model for a dipole–dipole interaction in the absence of migration, yielding  $\tau_D = 95 \mu\text{s}$ . The decay is similar to that of  ${}^3\text{H}_4$  in the same crystal, suggesting that  ${}^3\text{H}_4$  is responsible for feeding  ${}^3\text{F}_4$ , and that the quenching of the latter state is fast.

The room temperature decay of  ${}^3\text{F}_4$  in  $\text{YVO}_4:0.5\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$ , after excitation of the  ${}^3\text{H}_5$  level, is fast and strongly non-exponential. An exponential fit is very bad, giving  $\tau = 38 \mu\text{s}$ . Clearly the cross-relaxation mechanism described above efficiently quenches the  ${}^3\text{F}_4$  state. A fit of the long-time exponential tail is good, giving  $k = 1.54 \times 10^4 \text{ s}^{-1}$ , corresponding to  $\tau = 65 \mu\text{s}$ . This indicates that the decay does not occur in a regime described by the IH model (fast transfer, slow migration), because we should expect to observe a long-time decay similar to that of the isolated donor ( $\tau = 1.29 \text{ ms}$ ). In fact, an attempt to fit the curve using the IH model ( $s = 6$ ) gives quite a bad fit, but more importantly the  $1/\tau_D$  value for the isolated donor is far too high to be meaningful in an IH model ( $1.4 \times 10^4 \text{ s}^{-1}$ ) as it should approach the decay constant of the isolated  ${}^3\text{F}_4$  state ( $775 \text{ s}^{-1}$ ; see above). This argument and the non-exponential shape of the curve indicate that the  $\text{Tm} \rightarrow \text{Tb}$  transfer occurs in the intermediate regime, in which the donor–acceptor transfer and the migration in the donor subset have comparable rates.

In the case of the  $\text{YVO}_4:1\% \text{Tm}^{3+}, 1\% \text{Tb}^{3+}$  crystal, the room temperature decay curve of  ${}^3\text{F}_4$ , after pumping in  ${}^3\text{H}_5$ , is even faster. An exponential fit is bad, giving  $\tau = 36 \mu\text{s}$ , whereas an exponential fit of the tail yields  $\tau = 49 \mu\text{s}$ . The IH model gives for the internal decay of the donor  $1/\tau_D = 1.61 \times 10^4 \text{ s}^{-1}$ , incompatible with the decay of the isolated  ${}^3\text{F}_4$  state. The transfer occurs in the intermediate regime (rate of the transfer  $\approx$  rate of the migration).

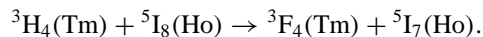




**Figure 5.** The room temperature  ${}^5\text{I}_7$  fluorescence rise and decay in  $\text{YVO}_4:1\% \text{Tm}^{3+}$ ,  $1\% \text{Ho}^{3+}$ , after 690 nm excitation. The solid line is a fit to the difference of two exponentials. For the sake of clarity, not all of the data points have been plotted.

#### 4.3. $\text{YVO}_4:\text{Tm}^{3+}$ , $\text{Ho}^{3+}$ crystals

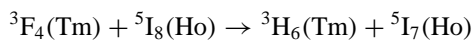
The decay curve of  ${}^3\text{H}_4$  in  $\text{YVO}_4:1\% \text{Tm}^{3+}$ ,  $1\% \text{Ho}^{3+}$ , obtained at room temperature by pulsed excitation at 690 nm, is non-exponential and slightly faster than for  $\text{YVO}_4:1\% \text{Tm}^{3+}$  (figure 3). An exponential fit gives  $\tau = 84 \mu\text{s}$ . The following  $\text{Tm} \rightarrow \text{Ho}$  energy-transfer mechanism can contribute to the decay:



However, this process requires a higher mismatch ( $1441 \text{ cm}^{-1}$ ) than the one required by the internal  $\text{Tm}^{3+}$  cross-relaxation ( $854 \text{ cm}^{-1}$ ); the  $1441 \text{ cm}^{-1}$  mismatch cannot be bridged by just one phonon, as the vibrational cut-off wavenumber is  $891 \text{ cm}^{-1}$ . On the basis of the small difference of the decay curves, it is reasonable to conclude that the internal cross-relaxation is more important in determining the decay, in agreement with the results obtained for YAG crystals doped with  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  [17]. The experimental decay appears to be well described by the IH model for a dipole–dipole interaction in the absence of migration. The fit is good and gives for the internal decay of the isolated  ${}^3\text{H}_4$  state  $1/\tau_{\text{D}} = 8.03 \times 10^3 \text{ s}^{-1}$ , i.e.  $\tau_{\text{D}} = 125 \mu\text{s}$ , and a critical distance (taking into account just the  $\text{Tm} \rightarrow \text{Tm}$  cross-relaxation) of  $R_0 = 7.8 \text{ \AA}$ . These values are similar to the ones reported above for the  $\text{YVO}_4:1\% \text{Tm}^{3+}$  crystal.

Pulsed excitation at 690 nm allows one to observe the decay of the  ${}^5\text{I}_7$  state of  $\text{Ho}^{3+}$  at  $2 \mu\text{m}$  in  $\text{YVO}_4:1\% \text{Tm}^{3+}$ ,  $1\% \text{Ho}^{3+}$  (figure 5). The time evolution of the luminescence shows an evident rise. The decay part of the curve is fitted with an exponential, yielding  $\tau = 2.60 \text{ ms}$ . A fit with the difference of two exponentials is good and gives  $\tau = 2.56 \text{ ms}$  (decay) and  $\tau = 81 \mu\text{s}$  (rise). The rise is similar to the decay of the  ${}^3\text{H}_4$  state in the same crystal, indicating that the  ${}^5\text{I}_7$  state is fed through  ${}^3\text{H}_4$ . This process can occur directly (see

above) or through a cross-relaxation  ${}^3H_4 \rightarrow {}^3F_4$ , followed by a fast transfer [17–19]:



for which the mismatch (taking into account the Stark components) is  $\Delta E = 388 \text{ cm}^{-1}$ . In fact, the  ${}^3F_4(Tm)$  and  ${}^5I_7(Ho)$  states have been shown to be thermalized in YAG [17]. The transfer probability could in this case be enhanced by migration in the  ${}^3F_4$  state.

## 5. Conclusions

In this work we have investigated the fluorescence dynamics of the  ${}^3H_4$  and  ${}^3F_4$  states of  $Tm^{3+}$  in  $YVO_4$  crystals singly doped and codoped with  $Tb^{3+}$  or  $Ho^{3+}$  ions. A cross-relaxation process leading to a weak depopulation of the  ${}^3H_4$  state is observed in the  $YVO_4:Tm^{3+}$  crystals. The presence of  $Tb^{3+}$  increases only slightly the quenching of the  ${}^3H_4$  state, but depopulates very efficiently the  ${}^3F_4$  state through energy-transfer processes. These results indicate that in codoped  $YVO_4:Tm^{3+}$ ,  $Tb^{3+}$  crystals the fluorescence lifetime of the terminal level of the  ${}^3H_4 \rightarrow {}^3F_4$  transition is strongly reduced, whilst the quenching of the  ${}^3H_4$  state is rather inefficient. For this reason,  $YVO_4:Tm^{3+}$ ,  $Tb^{3+}$  codoped crystals appear promising as laser crystals for the eye-safe spectral region around  $1.5 \mu\text{m}$ .

## Acknowledgment

We thank Thomson-BMD for their interest in this work and for financial support.

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