Journal of Alloys and Compounds 275–277 (1998) 345–348

Upconversion dynamics in Yb^{3+}–Ho^{3+} doped fluoroindate glasses

I.R. Martín*, V.D. Rodríguez, V. Lavín, U.R. Rodríguez-Mendoza

Dpto. Física Fundamental y Experimental, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain

---

Abstract

The mechanisms and dynamics of the upconversion emissions in Yb^{3+}–Ho^{3+}-doped fluoroindate glasses by exciting at 975 nm have been analysed. The upconversion efficiencies have been measured as a function of temperature in the range from 12 to 295 K. The temporal evolution of the 545- and 650-nm upconversion emissions obtained under flash excitation at 975 nm in codoped samples with 2.25 mol.% of Yb^{3+} and 0.75 mol.% of Ho^{3+} cannot be described using the energy migration model. This indicates that at this concentration of Yb^{3+} the rapid migration regimen between these ions has not been reached. A model is proposed in order to explain the temporal evolution of these emissions taking into account energy migration between donors and backtransfer processes.

Keywords: Upconversion dynamics; Fluoroindate glasses; Yb^{3+}–Ho^{3+}

---

1. Introduction

The Yb^{3+}–Ho^{3+} system is especially interesting because it allows to obtain a compact green laser that can be pumped with a commercial 975 nm laser diode by using the energy transfer from Yb^{3+} to Ho^{3+} [1]. However, recent studies in different fluorides have demonstrated that Ho^{3+} to Yb^{3+} backtransfer plays an important role in quenching the green upconversion at room temperature [2]. In this way, although a Yb^{3+}-sensitised Ho^{3+} green upconversion laser has been obtained at 77 K in BaY_2F_8 crystal [3], no such lasing has been achieved at room temperature because backtransfer efficiency increases with temperature [4].

The upconversion dynamics with backtransfer has been analysed by the energy migration model [5]. This model assumes an infinite rate constant for energy migration and then it is only valid in the regime of rapid energy migration. In the present work, a more precise analysis of upconversion processes with migration and backtransfer is developed in order to describe experimental results in fluoroindate glasses codoped with Yb^{3+} and Ho^{3+}.

2. Experimental

The samples used in this study were prepared with the following composition in mol.%: (40-x-y) InF_3, $20ZnF_2$, $20SrF_2$, $20BaF_2$, $xYbF_3$ and $yHoF_3$, with x and y in the range 0–2.25.

Emission spectra were obtained by exciting the samples with light from a 300-W Xe arc lamp passed through a 0.25-m double monochromator. Fluorescence was detected through a 0.25-m monochromator with a photomultiplier. The emission spectra were corrected by the system spectral response. For upconversion measurements, a calibrated pyroelectric detector has been utilised to analyse the incident power radiation.

The measurements of emission temporal evolution were carried out with a tunable jet dye laser as excitation source. This laser was pumped by the 532 nm pulsed light from a doubled Nd–YAG laser. The fluorescence was recorded using a digital storage oscilloscope controlled by a personal computer.

For low temperature measurements, a helium continuous-flow cryostat was utilised in the range from 12 to 295 K.

3. Results and discussion

The energy level diagram of Yb^{3+} and Ho^{3+} ions obtained in fluoroindate glasses is presented in Fig. 1. Different upconversion mechanisms giving visible emissions are possible with this diagram. By exciting at 975 nm (Yb^{3+}:${}^2F_{7/2}\rightarrow{}^2F_{5/2}$) a fluoroindate glass doped with 2.25 mol.% of Yb^{3+} and 0.75 mol.% of Ho^{3+}, the upconversion spectrum showed in Fig. 2 is observed. This figure also

---

*Corresponding author.

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00336-3

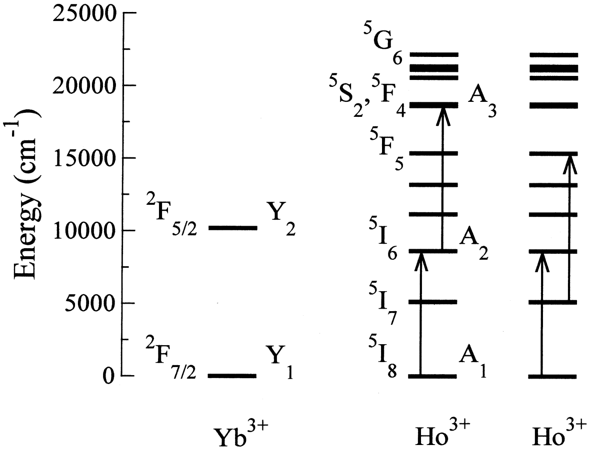

Fig. 1. Energy level diagram of Yb^{3+} and Ho^{3+} ions in fluoroindate glasses. Upconversion excitation mechanisms are indicated.

included, for comparison, the spectrum obtained by direct excitation at 450.5 nm (Ho^{3+}:$^5I_8 \rightarrow ^5G_6$). The two spectra coincide except in the relative intensity of the 650 nm band, which is enhanced in the upconversion spectrum.

All the upconversion emissions show a quadratic dependence on excitation intensity and Yb^{3+} concentration. Taking into account these results, it would be concluded that the processes for the green (545 nm) and the infrared (750 nm) emissions under infrared excitation are based on two successive transfers from Yb^{3+} ions. In the first transfer, a Ho^{3+} ion is excited to the $^5I_6$ level and the energy excess (about 1600 cm^{-1}) is given to the matrix. Finally, a second transfer from other Yb^{3+} ion excites the same Ho^{3+} ion from the $^5I_6$ level to the $^5S_2(^5F_4)$ thermalized emitting levels and the energy excess (about 260 cm^{-1}) is again given to the matrix.

The red upconversion emission (650 nm) can be obtained by populating the $^5F_5$ level from the $^5S_2(^5F_4)$ levels. However, this process does not explain the enhancement in this emission observed in Fig. 2. In this way, an extra upconversion mechanism has been proposed in another matrix which populates the $^5F_5$ level from the $^5I_7$ level, previously populated from $^5I_6$ by multiphonon emission [6,7].

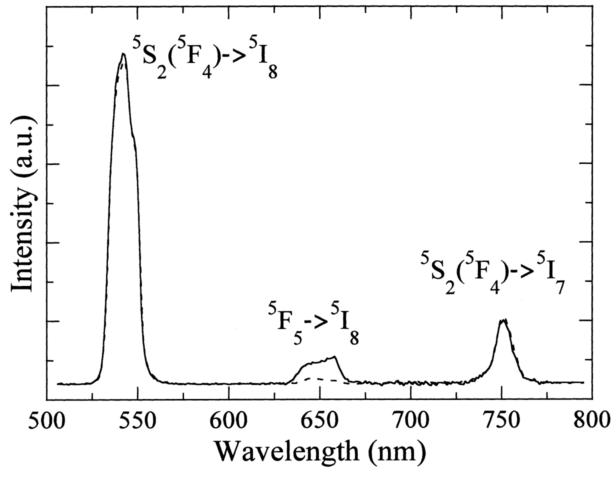

Fig. 2. Upconversion emission spectrum by exciting at 975 nm (solid line) and emission spectrum by exciting at 450.5 nm (dashed line) in fluoroindate glass doped with 2.25 mol.% of Yb^{3+} and 0.75 mol.% of Ho^{3+}.

The temperature dependences of the upconversion efficiency for the different upconversion emissions obtained with an excitation intensity of 81 mW cm^{-2} are presented in Fig. 3. As can be observed in this figure, the upconversion efficiency of the emission at 545 nm presents a maximum about 125 K. This result could be explained based on the temperature dependence of the energy transfer parameter from Yb^{3+} ions obtained from kinetic models, and the multiphonon emission from the $^5S_2(^5F_4)$ levels [8]. Moreover, as was indicated, upconversion efficiency of this emission in the BaY$_2$F$_8$ crystal [4] depends on the backtransfer processes from the $^5S_2(^5F_4)$ levels of Ho^{3+} to Yb^{3+} ions. In order to analyse the importance of these energy transfer processes in fluoroindate glasses, the green emission decay curves have been measured after direct pulsed excitation at 532 nm of the $^5S_2(^5F_4)$ levels in different codoped samples. When the Yb^{3+} concentration is increased the decay curves are faster. These decay curves can be analysed by the Inokuty–Hirayama formula [9], assuming an interaction of dipole–dipole character and the notation indicated in Fig. 1, then

$$A_3(t) = A_3(0)\exp\left[-\frac{1}{\tau_3}t - \frac{4\pi^{3/2}}{3}Y_1\sqrt{C_{AD}t}\right] \qquad (1)$$

where $A_3(t)$ is the population of Ho^{3+} ions in the excited state $^5S_2(^5F_4)$, τ_3 is the lifetime of this state, Y_1 is the Yb^{3+} concentration and C_{AD} is the energy backtransfer parameter for the channel

$$^5S_2(^5F_4)(\mathrm{Ho}^{3+}),\ ^2F_{7/2}(\mathrm{Yb}^{3+}) \rightarrow\ ^5I_6(\mathrm{Ho}^{3+}),\ ^2F_{5/2}(\mathrm{Yb}^{3+})$$

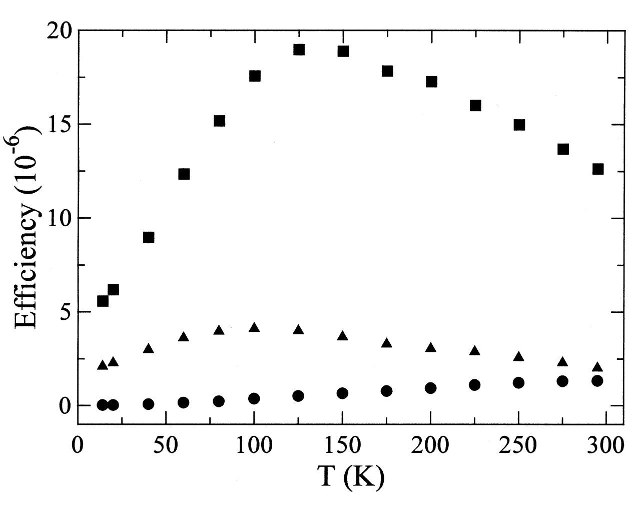

Fig. 3. Temperature dependence of the upconversion efficiency for the different emissions: 545 (■), 650 (●) and 750 nm (▲).

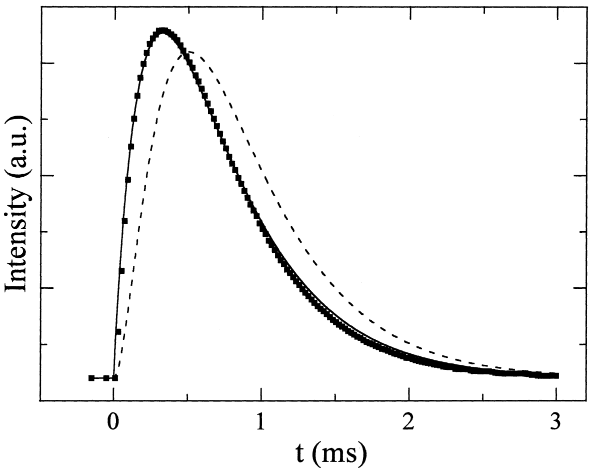

Fig. 4. Temporal evolution of the green luminescence (545 nm) when pumping at 975 nm a fluoroindate glass codoped with 2.25 mol.% of Yb^{3+} and 0.75 mol.% of Ho^{3+}. The dashed and solid lines correspond to the fits to the energy migration model and to the proposed model, respectively.

Considering a value of 310 μs for τ_3, obtained from decay luminescent measurements [8], the emission decays are well fitted by Eq. (1). From these fits a mean value of 3.2×10^{-40} cm^6 s^{-1} for the C_{AD} parameter has been obtained, which does not depend appreciably on Yb^{3+} concentration.

The dynamics of the green luminescence, when pumping a codoped sample with Yb^{3+} and Ho^{3+} ions at 975 nm, contains a rise and a decay part, as can be seen in Fig. 4. The temporal analysis of the upconversion emissions can be analysed by the energy migration model [5]. In this model, a set of rate equations describes the populations of the states involved in the upconversion process. A rapid migration between ions is assumed in these equations. As can be seen in Fig. 4, this model does not fit the experimental data for glasses with 2.25 mol.% of Yb^{3+} ions. This result suggests that the rapid migration regimen between Yb^{3+} ions has not been reached at this concentration of ions. In order to revise the rate equations of the energy migration model, the temporal evolution of the excited Yb^{3+} ions can be expressed by the Yokota and Tanimoto diffusion model [10] or by the more simple equation of Parent et al. [11], i.e.

$$Y_2(t) = Y_2(0)\exp\left[-\frac{1}{\tau_D}t - \frac{4\pi^{3/2}}{3}A_1\sqrt{C_{DA1}t} - Wt\right] \tag{2}$$

where $Y_2(t)$ is the population of excited Yb^{3+} ions, τ_D is the lifetime of the Yb^{3+} ions, A_1 is the Ho^{3+} concentration, C_{DA1} is the energy transfer parameter for the first transfer $Yb^{3+}\rightarrow Ho^{3+}$ and W depends on energy migration between Yb^{3+} ions [11]. Therefore, the rate equation for $Y_2(t)$ after pulsed excitation can be expressed by

$$\frac{dY_2(t)}{dt} = -\frac{1}{\tau_D}Y_2(t) - \left[\frac{\frac{2\pi^{3/2}}{3}A_1\sqrt{C_{DA1}}}{\sqrt{t}} + W\right]Y_2(t) \tag{3}$$

The expression in brackets in Eq. (3) indicates the desexcitation rate of Yb^{3+} ions towards Ho^{3+} acceptor ions. Therefore, the rate equation for population can be expressed by

$$\frac{dA_2(t)}{dt} = -\frac{1}{\tau_2}A_2(t) + \left[\frac{2\frac{\pi^{3/2}}{3}A_1\sqrt{C_{DA1}}}{\sqrt{t}} + W\right]Y_2(t) \tag{4}$$

where τ_2 is the lifetime of the A_2 level.

Finally, the rate equation for A_3 population can be expressed as

$$\begin{aligned}\frac{dA_3(t)}{dt} = &-\frac{1}{\tau_3}A_3(t)\\ &-\left[\frac{\frac{2\pi^{3/2}}{3}\left(A_1\sqrt{C_{CR}} + Y_1\sqrt{C_{AD}}\right)}{\sqrt{t}}\right]A_3(t)\\ &+F_{UP}(t)Y_2(t)\end{aligned} \tag{5}$$

where C_{CR} is the energy transfer parameter for the cross relaxation processes from the A_3 level and $F_{UP}(t)$ is the upconversion probability. Taking into account the analytic form of the expression for the energy transfer rate, the following expression for $F_{UP}(t)$ is proposed

$$F_{UP}(t) = \frac{\frac{2\pi^{3/2}}{3}A_2(t)\sqrt{C_{DA2}}}{\sqrt{t}} \tag{6}$$

where C_{DA2} is the energy transfer parameter for the second transfer $Yb^{3+}\rightarrow Ho^{3+}$.

The lifetimes and energy transfer parameters that appear in Eqs. (3)–(5), except C_{DA2}, have been obtained analysing the emission decays in different single or codoped samples. The obtained values are presented in Table 1. With these parameters, the temporal evolution of the green upconversion emission can be described by numerically solving these coupled differential equations. A very good

Table 1
Values for the parameters that appear in Eqs. (3)–(5) obtained in fluoroindate glasses doped with 2.25 mol.% of Yb^{3+} and/or 0.75 mol.% of Ho^{3+}

τ_D (ms)	τ_2 (ms)	τ_3 (ms)	W (s^{-1})	C_{DA1} (cm^6 s^{-1})	C_{CR} (cm^6 s^{-1})	C_{AD} (cm^6 s^{-1})	Y_1 (cm^{-3})	A_1 (cm^{-3})
2.13	3.79	0.31	929	2.1×10^{-40}	1.1×10^{-39}	3.2×10^{-40}	4.6×10^{20}	1.5×10^{20}

fit to the experimental data is obtained (see Fig. 4). However, this fit does not depend appreciably on C_{DA2}, so it has not been possible to obtain this parameter.

In the decay of A_3 population, the relative weigh of the backtransfer processes versus cross-relaxation is given by

$$Y_1 \sqrt{C_{AD}}/A_1 \sqrt{C_{CR}}$$

from Eq. (5). A value of 1.7 for this ratio is obtained with data in Table 1. This indicates that, in the quenching of the green upconversion, the backtransfer is more important that cross-relaxation.

The temporal evolution of the upconversion emission at 650 nm after pulsed excitation at 975 nm is also well described by the proposed equations, considering now a second additional mechanism in which A_2 corresponds to the $^5I_7$ level and A_3 to the $^5F_5$ level. The experimental data and the fit are presented in Fig. 5. The relative weights for the two upconversion mechanisms that populate the $^5F_5$ level are indicated in the figure.

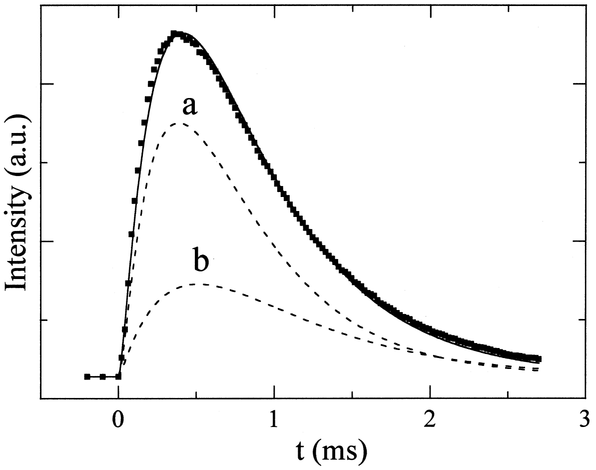

Fig. 5. Temporal evolution of the red luminescence (650 nm) when pumping, at 975 nm, a fluoroindate glass codoped with 2.25 mol.% of Yb^{3+} and 0.75 mol.% of Ho^{3+}. The dashed lines correspond to the two mechanisms which populate the $^5F_5$ level: (a) from the $^5S_2(^5F_4)$ levels and (b) from the $^5I_7$ level. The solid line corresponds to the addition of (a) and (b).

4. Conclusions

The upconversion dynamics in doped glasses can be analysed by rate equations that consider migration and backtransfer. A very good agreement with experimental results is obtained in fluoroindate glasses codoped with Yb^{3+} and Ho^{3+}. The dynamics of the upconversion emissions at 545 and 650 nm after pulsed excitation are well described by the proposed model. It should be noted that lifetimes and energy transfer parameters were fixed in the fits to previously calculated values.

An appreciable temperature dependence of the upconversion efficiencies is observed, which can be understood considering the variation of the energy transfer parameters from Yb^{3+} ions and the multiphonon emission from the emitting levels.

References

[1] J.Y. Allain, M. Monerie, H. Poignant, Electron. Lett. 26 (1990) 261.
[2] X.X. Zhang, P. Hong, M. Bass, R.E. Peale, H. Weidner, B.H.T. Chai, J. Luminesc. 60–61 (1994) 878.
[3] L.F. Johnson, H.J. Guggenheim, Appl. Phys. Lett. 19 (1971) 44.
[4] X.X. Zhang, P. Hong, M. Bass, B.H.T. Chai, Appl. Phys. Lett. 63 (1993) 2606.
[5] M.P. Hehlen, G. Frei, H.U. Gudel, Phys. Rev. B 50 (1994) 16264.
[6] D.G. Ettinger, T.M. Niemczyk, J. Chem. Phys. 68 (1978) 872.
[7] M.A. Chamarro, R. Cases, J. Luminesc. 42 (1988) 267.
[8] I.R. Martín, V.D. Rodríguez, M. Morales, U.R. Rodríguez-Mendoza, V. Lavín, J. Appl. Spect. 62 (1995) 78.
[9] M. Inokuti, F. Hirayama, J. Chem. Phys. 43 (1965) 1978.
[10] M. Yokota, O. Tanimoto, J. Phys. Soc. Jpn. 22 (1967) 779.
[11] C. Parent, C. Lurin, G. Le Flem, P. Hagenmuller, J. Luminesc. 36 (1986) 49.