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Luminescence upconversion mechanisms in Yb^{3+} – Tb^{3+} systems

G.M. Salley^a, R. Valiente^b, H.U. Guedel^{a,*}^a *Department für Chemie and Biochemie, Universität Bern, Freistrasse 3, CH-3000 Bern 9, Switzerland*^b *DCITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain*

Abstract

$\text{Tb}^{3+}({}^5\text{D}_4 \rightarrow {}^7\text{F}_J)$ luminescence has been observed in single crystals of $\text{SrCl}_2 : \text{Tb}^{3+}(1\%) : \text{Yb}^{3+}(1\%)$ and $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}(1\%)$ under excitation energies in the region of Yb^{3+} absorption. Previous reports of similar systems have postulated two possible upconversion mechanisms: (1) cooperative sensitization and (2) a sequence of two cooperative absorption steps, or GSA/ESA. We present results of emission, excitation and kinetic measurements at low and high temperatures. These measurements allow assignment of the mechanism responsible for upconversion in these systems. For temperatures greater than $T = 100$ K process (1) is the dominant mechanism, in agreement with previous assignments. However, for $T < 100$ K in $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}(1\%)$, the upconversion occurs through a GSA/ESA sequence, which is shown here in a clear manner for the first time. The efficiency of the Yb^{3+} – Tb^{3+} upconversion process for $\text{SrCl}_2 : \text{Tb}^{3+}(1\%) : \text{Yb}^{3+}(1\%)$, at room temperature, under $2.4(10)^4 \text{W}/\text{cm}^2$, is on the order of 10^{-4} and decreases with decreasing temperature by four orders of magnitude. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Upconversion; Tb^{3+} ; Yb^{3+}

1. Introduction

Green Tb^{3+} emission under NIR Yb^{3+} excitation was first observed by Livanova et al. in CaF_2 and SrF_2 doped with Yb^{3+} and Tb^{3+} [1]. The explanation of this process was based on the cooperative sensitisation of Tb^{3+} by two Yb^{3+} ions, i.e. $2*\text{Yb}^{3+}({}^2\text{F}_{5/2}) : \text{Tb}^{3+}({}^7\text{F}_6) \rightarrow 2*\text{Yb}^{3+}({}^2\text{F}_{7/2}) : \text{Tb}^{3+}({}^5\text{D}_4)$, shown schematically in Fig. 1(a) [2]. Near infrared (NIR) photons are absorbed by the Yb^{3+} ions after which two excited Yb^{3+} ions, which are near a Tb^{3+} ion, non-

radiatively transfer their energy to the Tb^{3+} ion. Most authors, investigating the Yb^{3+} – Tb^{3+} system, have agreed with Livanova's assignment [3–9]. However, at least two reports have proposed a process involving a ground state absorption (GSA) step followed by an excited state absorption (ESA) step within an Yb^{3+} – Tb^{3+} dimer [7,10].

Bilak et al. proposed that the upconversion (UC) process occurred by a sequence of two cooperative absorption steps [10], i.e. $\text{Yb}^{3+}({}^2\text{F}_{7/2}) : \text{Tb}^{3+}({}^7\text{F}_6) + \text{photon} \rightarrow \text{Yb}^{3+}({}^2\text{F}_{5/2}) : \text{Tb}^{3+}({}^7\text{F}_6) + \text{photon} \rightarrow \text{Yb}^{3+}({}^2\text{F}_{7/2}) : \text{Tb}^{3+}({}^5\text{D}_4)$. This assignment was based on UC kinetic measurements where the luminescence showed an immediate decay after a short excitation pulse, which is a finger print of a GSA/ESA process [11]. In another report by Noginov et al., extra absorption lines in

*Corresponding author. Tel.: +41-31-631-4249; fax: +41-31-631-4399.

E-mail address: hans-ulrich.guedel@iac.unibe.ch (H.U. Guedel).

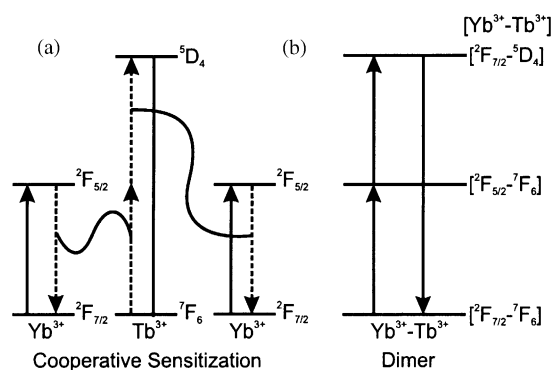


Fig. 1. Schematic of possible upconversion mechanisms for $\text{Yb}^{3+}\text{--Tb}^{3+}$, the cooperative sensitisation process, (a), and a weakly coupled dimer, model (b). Dashed arrows represent non-radiative transitions while the solid arrows represent radiative transitions.

the UC excitation spectrum were reported which were claimed to be an indication of an ESA step [7]. In a cooperative sensitisation mechanism, the excitation spectrum should replicate the squared GSA spectrum to the intermediate level, whereas the excitation spectrum of a process driven by the GSA/ESA mechanism should be the product of the two absorption spectra [11].

Recently, a GSA/ESA mechanism was proposed for the unusual upconversion luminescence observed in $\text{RbMnCl}_3 : \text{Yb}^{3+}$ [12,13]. Pulsed measurements, detecting Mn^{2+} emission while exciting Yb^{3+} ions, showed no rise time, only decay, leading to the assignment of a GSA/ESA mechanism responsible for the observed UC luminescence. This was further verified by two-colour excitation experiments revealing the spectrum of the ESA step, which matched the absorption of Mn^{2+} . These results lead to the assignment of a $\text{Yb}^{3+}\text{--Mn}^{2+}$ exchange coupled pair with an energy level diagram similar to the one in Fig. 1(b), shown here for the case of $\text{Yb}^{3+}\text{--Tb}^{3+}$.

In this paper we consider the two mechanisms shown in Fig. 1, which represent (a) cooperative sensitisation and (b) a GSA/ESA sequence in a weakly coupled pair, as possibilities for the UC luminescence in the following two systems, $\text{SrCl}_2 :$

$\text{Tb}^{3+}(1\%) : \text{Yb}^{3+}(1\%)$ and $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}(1\%)$. Previous experiments of $\text{Yb}^{3+}\text{--Tb}^{3+}$ UC systems have mostly been performed at room temperature (RT). In doing so, these studies avoided the question of energy conservation within the step from two excited Yb^{3+} ions to one excited Tb^{3+} ion. In most host lattices the lowest excited level of the Yb^{3+} ion is around $10,200\text{ cm}^{-1}$, and the emitting level of Tb^{3+} is about $10,450\text{ cm}^{-1}$. Thus, from simple energy conservation arguments UC by an energy transfer process should be quenched at low temperatures. This is essentially what we find below about 100 K. However, some weak UC features persist down to 10 K in $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}(1\%)$.

2. Experimental

Single crystals of $\text{SrCl}_2 : \text{Tb}^{3+}(1\%) : \text{Yb}^{3+}(1\%)$ and $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}(1\%)$ were grown by the Bridgman technique. Luminescence and excitation spectra were obtained via Ar^+ laser excitation ($20,486\text{ cm}^{-1}$) for Tb^{3+} luminescence and a Ti : sapphire laser for UC and Yb^{3+} luminescence. A Nd : YAG pumped dye laser coupled through a single pass Raman shifter was used for excitation in kinetic measurements. The luminescence was dispersed through a single 0.75 m, or double 0.8 m, Spex monochromator equipped with a cooled red-sensitive PMT. Cooling of the sample was achieved in a quartz flow tube.

SrCl_2 has the CaF_2 structure with a high tendency to form clusters of trivalent dopant ions [14]. Many papers have been written on the charge compensation of these trivalent ions replacing divalent ions in crystals with this structure, and we will not go into detail on this subject [15,16]. It is sufficient to say that the RE^{3+} ions have a tendency to form pairs, even clusters, which is advantageous for energy transfer and UC processes.

$\text{Cs}_3\text{Tb}_2\text{Br}_9$ belongs to the trigonal space group $\text{R}\bar{3}\text{c}$, which contains $\text{Tb}_2\text{Br}_9^{3-}$ face sharing dimers with D_{3h} symmetry. The site symmetry for the Tb^{3+} ion and consequently the Yb^{3+} dopant ion is C_{3v} [17].

3. Results and discussions

The Tb^{3+} luminescence spectra are presented in Fig. 2 for the $\text{SrCl}_2 : \text{Tb}^{3+}(1\%) : \text{Yb}^{3+}(1\%)$ crystal. Each spectrum has been normalized to the peak emission and comparisons can only be made between spectral positions and relative intensities within one spectrum. Fig. 2(a) plots the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ luminescence for $20,486 \text{ cm}^{-1}$ $^7\text{F}_6 \rightarrow ^5\text{D}_4$ excitation at $T = 10 \text{ K}$. The assignment of the multiplets as given at the top is straightforward. The next spectrum, (b) shows the UC spectra at $T = 10 \text{ K}$ with an excitation energy of $10,626 \text{ cm}^{-1}$ (170 mW). This spectrum looks drastically different than the previous spectrum, and practically no Tb^{3+} emission is observed. The broad peak around $20,000 \text{ cm}^{-1}$ is due to the well known cooperative emission of two Yb^{3+} ions. The peaks located at $18,000$ and $15,000 \text{ cm}^{-1}$, have been assigned to Tb^{3+} emission by other authors [18]. However, it is clear from this presentation that this cannot be Tb^{3+} emission and is assigned to a trace impurity, such as Er^{3+} , which exhibits Yb^{3+} sensitised UC luminescence with greater efficiency than Tb^{3+} at this temperature.

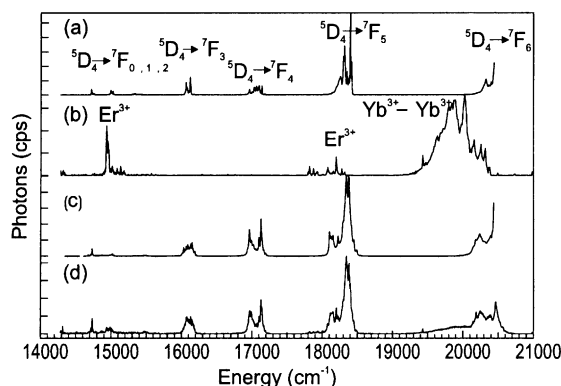


Fig. 2. Visible luminescence of $\text{SrCl}_2 : \text{Yb}^{3+}(1\%) : \text{Tb}^{3+}(\%)$. (a) and (b) are recorded at $T = 10 \text{ K}$, (c) and (d) at $T = 100 \text{ K}$. (a) and (c), were excited with light of energy $20,486 \text{ cm}^{-1}$ at a power of 11 mW. The UC spectra, (b) and (d) were excited with light of energy $10,626 \text{ cm}^{-1}$ and a power of 100 mW. In all spectra the exciting light was focused with a 53 mm focal length lens.

The unwanted trace impurities become irrelevant as the temperature is increased. Figs. 2(c) and (d) represent Tb^{3+} luminescence at $T = 100 \text{ K}$ after $20,486$ and $10,626 \text{ cm}^{-1}$ excitation, respectively. The spectra are almost identical and the assignment of the multiplets to the same $\text{Tb}^{3+}5\text{D}_4 \rightarrow ^7\text{F}_J$ transitions as in Fig. 2(a) can be confidently made. The broad peak in Fig. 2(d) around $20,000 \text{ cm}^{-1}$ is again $\text{Yb}^{3+}-\text{Yb}^{3+}$ cooperative emission. The temperature dependence of the total Tb^{3+} UC luminescence intensity follows a Boltzmann distribution with ΔE on the order of the energy difference between $2*\text{Yb}^{3+}2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ electronic origin and the origin of the $\text{Tb}^{3+}7\text{F}_6 \rightarrow ^5\text{D}_4$ absorption. This temperature dependence points towards a phonon assisted UC mechanism. The UC efficiency, defined as $(\text{VIS}_{\text{out}}/\text{NIR}_{\text{out}})$, changes from a lower limit of $10^{-6}\%$ at 10 K to $10^{-2}\%$ at 100 K .

To investigate the UC mechanism we performed pulsed measurements. Fig. 3 represents the time response of $\text{SrCl}_2 : \text{Tb}^{3+}(1\%) : \text{Yb}^{3+}(1\%)$ after a 10 ns pulse at $10,187 \text{ cm}^{-1}$, while detecting the $18,360 \text{ cm}^{-1}$ luminescence at $T = 100 \text{ K}$. The important result here is that the intensity of the Tb^{3+} luminescence rises from zero counts immediately after the pulse (see inset for higher resolution). Had there been an ESA step there should be some luminescence immediately after

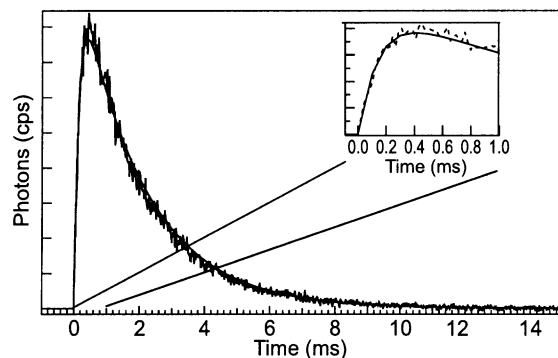


Fig. 3. Dynamic response of Tb^{3+} upconverted luminescence monitored at $18,360 \text{ cm}^{-1}$. The sample was kept at $T = 100 \text{ K}$ and excited with a 10 ns pulse of light with energy of $10,187 \text{ cm}^{-1}$. The inset shows the short time response with better resolution. The solid line in both plots represent the fits using Eq. (1).

the pulse. We conclude that an energy transfer step is involved in the UC process, and the most likely one is the cooperative sensitisation mechanism shown in Fig. 1(a) in which two excited Yb^{3+} ions simultaneously transfer their energy to Tb^{3+} . We have modelled the time dependence in Fig. 3 with the following equation:

$$I(t) = A[e^{-Bt} - e^{-Ct}]. \quad (1)$$

The best fit in Fig. 3 corresponds to $B = 526$ and $C = 6923 \text{ s}^{-1}$. B and C represent the decay and rise parts of the transient, respectively. We can roughly associate the rise part with the life time of the intermediate $^2\text{F}_{5/2}$ level and the decay part with the $^5\text{D}_4$ lifetime of Tb^{3+} at $T = 100 \text{ K}$. The occurrence of a cooperative sensitisation UC process is greatly facilitated if the Yb^{3+} excitations are mobile in the lattice. Based on earlier work we expect this to be the case for a chloride crystal with 1% Yb^{3+} doping [19]. However, we also note that clustering of trivalent ions in the divalent lattice has been suggested for concentrations above 0.1% [14]. As our concentrations of 1% are nominal ones and may well lie above 0.1%, we cannot exclude this possibility.

At $T = 10 \text{ K}$ in this crystal the UC efficiency is reduced by four orders of magnitude compared to $T = 100 \text{ K}$, and due to the presence of cooperative Yb^{3+} pair emission around $20,000 \text{ cm}^{-1}$ and Er^{3+} impurity emissions at lower energies, it was not possible to characterize this remaining UC luminescence at $T = 10 \text{ K}$.

However, we found in the $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}$ (1%) crystal, even at temperatures down to $T = 10 \text{ K}$, only emission from Tb^{3+} ions and Yb^{3+} – Yb^{3+} pairs. No trace impurity emission was observed. This system behaves very similar to $\text{SrCl}_2 : \text{Tb}^{3+}$ (1%) : Yb^{3+} (1%) at $T = 100 \text{ K}$, and upon cooling to $T = 10 \text{ K}$ the total UC intensity also drops by four orders of magnitude. But in this case we can characterise the $T = 10 \text{ K}$ UC mechanism. Fig. 4 compares the UC excitation spectrum at $T = 10 \text{ K}$, Fig. 4(a), with the corresponding NIR excitation spectrum squared, Fig. 4(b). The two are evidently very different. Besides a dominant feature around $10,590 \text{ cm}^{-1}$, corresponding to the $^2\text{F}_{7/2}(0) \rightarrow ^2\text{F}_{5/2}(2')$ GSA of Yb^{3+} , there are a large number of lines

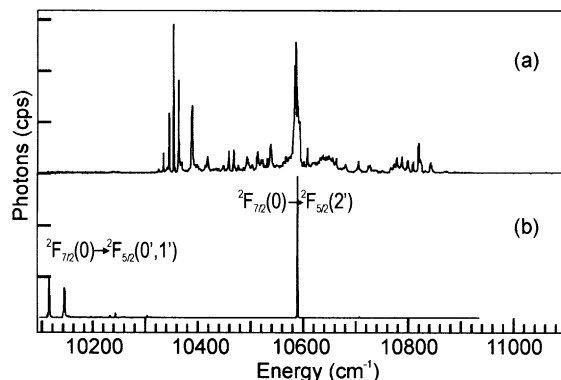


Fig. 4. Excitation spectra of $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}$ (1%) at $T = 10 \text{ K}$. (a) and (b) represent the excitation spectra observed while monitoring $\text{Tb}^{3+} 5\text{D}_4 \rightarrow 7\text{F}_5$ luminescence at $18,360 \text{ cm}^{-1}$ and the excitation spectrum squared of $\text{Yb}^{3+} 2\text{F}_{5/2} \rightarrow 2\text{F}_{7/2}$ luminescence at $10,000 \text{ cm}^{-1}$, respectively.

covering the energy range of $10,320$ – $10,850 \text{ cm}^{-1}$ in Fig. 4(a). A detailed analysis of these extra lines reveals that they are due to $[^2\text{F}_{5/2} - ^7\text{F}_6] \rightarrow [^2\text{F}_{7/2} - ^5\text{D}_4]$ ESA transitions according to the dimer picture in Fig. 1(b). They reflect the crystal-field splitting in both the $\text{Yb}^{3+} 2\text{F}_{7/2}$ ground state and the $\text{Tb}^{3+} 5\text{D}_4$ excited state. This excitation spectrum is the first clear evidence of a GSA/ESA sequence in an Yb^{3+} – Tb^{3+} system. It is a very weak effect with an efficiency of app. $10^{-6}\%$. The dimer picture is very appropriate in $\text{Cs}_3\text{Tb}_2\text{Br}_9 : \text{Yb}^{3+}$ (1%), because the lattice contains discrete $\text{Tb}^{3+}\text{Br}_9^{3-}$ dimers with a short Tb^{3+} – Tb^{3+} separation of 3.9 \AA . Thus, in the doped crystal we create Yb^{3+} – Tb^{3+} dimers with a relatively strong coupling, which enable the cooperative ESA transitions. In analogous Yb^{3+} – Mn^{2+} systems we have attributed the resulting upconversion to an exchange effect. This may also be true here, but with much lower efficiency.

In summary, we have shown that the dominant UC mechanism for Yb^{3+} – Tb^{3+} at temperatures 100 K or greater is the phonon assisted cooperative sensitisation of Tb^{3+} by two excited Yb^{3+} ions. In addition to this process, Tb^{3+} UC luminescence also arises by a sequences of GSA/ESA steps within a weakly coupled Yb^{3+} – Tb^{3+} dimer which can be observed only at temperatures low enough to quench the cooperative sensitisation process.

Acknowledgements

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