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

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Abstract

Tb$^{3+}$($^5D_4\rightarrow^7F_1$) luminescence has been observed in single crystals of SrCl$_2$:Tb$^{3+}$(1%) : Yb$^{3+}$(1%) and Cs$_3$Tb$_2$Br$_9$: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 Cs$_3$Tb$_2$Br$_9$: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 SrCl$_2$:Tb$^{3+}$(1%):Yb$^{3+}$(1%) at room temperature, under $2.4 \times 10^4$ W/cm$^2$, is on the order of $10^{-4}$ and decreases with decreasing temperature by four orders of magnitude.

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. $2*Yb^{3+}(^2F_{7/2})$:Tb$^{3+}(^7F_6)$→$2*Yb^{3+}(^2F_{5/2})$:Tb$^{3+}(^5D_4)$, 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. $Yb^{3+}(^2F_{7/2})$:Tb$^{3+}(^7F_6)$ + photon→$Yb^{3+}(^2F_{5/2})$:Tb$^{3+}(^7F_6)$ + photon→$Yb^{3+}(^2F_{5/2})$:Tb$^{3+}(^5D_4)$. This assignment was based on UC kinetic measurements where the luminescence showed an immediate decay after a short excitation pulse, which is a fingerprint of a GSA/ESA process [11]. In another report by Noginov et al., extra absorption lines in...
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 RbMnCl₃:Yb³⁺ [12,13]. Pulsed measurements, detecting Mn²⁺ emission while exciting Yb³⁺ 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 Mn²⁺. These results lead to the assignment of a Yb³⁺–Mn²⁺ exchange coupled pair with an energy level diagram similar to the one in Fig. 1(b), shown here for the case of Yb³⁺–Tb³⁺.

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, SrCl₂ : Tb³⁺(1%) : Yb³⁺(1%) and Cs₃Tb₂Br₉ : Yb³⁺(1%).

2. Experimental

Single crystals of SrCl₂ : Tb³⁺(1%) : Yb³⁺(1%) and Cs₃Tb₂Br₉ : Yb³⁺(1%) were grown by the Bridgeman technique. Luminescence and excitation spectra were obtained via Ar⁺ laser excitation (20,486 cm⁻¹) for Tb³⁺ luminescence and a Ti : sapphire laser for UC and Yb³⁺ 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.

SrCl₂ has the CaF₂ 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 RE³⁺ ions have a tendency to form pairs, even clusters, which is advantageous for energy transfer and UC processes.

Cs₃Tb₂Br₉ belongs to the trigonal space group R₃c, which contains Tb₂Br₉⁻ face sharing dimers with D₃h symmetry. The site symmetry for the Tb³⁺ ion and consequently the Yb³⁺ dopant ion is C₃v [17].
3. Results and discussions

The Tb\(^{3+}\) luminescence spectra are presented in Fig. 2 for the SrCl\(_2\) : Tb\(^{3+}\)(1%) : 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 \(5D_4 \rightarrow 7F_J\) luminescence for 20, 486 cm\(^{-1}\) excitation at \(T = 10\) K. The assignment of the multiplets as given at the top is straightforward. The next spectrum, (b) shows the UC spectra at \(T = 10\) K with an excitation energy of 10, 626 cm\(^{-1}\) and a power of 100 mW. This spectrum looks drastically different than the previous spectrum, and practically no Tb\(^{3+}\) emission is observed. The broad peak around 20,000 cm\(^{-1}\) is due to the well known cooperative emission of two Yb\(^{3+}\) ions. The peaks located at 18,000 and 15,000 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 SrCl\(_2\) : Yb\(^{3+}\)(1%) : Tb\(^{3+}\)(1%). (a) and (b) are recorded at \(T = 10\) K, (c) and (d) at \(T = 100\) K. (a) and (c), were excited with light of energy 20,486 cm\(^{-1}\) at a power of 11 mW. The UC spectra, (b) and (d) were excited with light of energy 10,626 cm\(^{-1}\) and a power of 100 mW. In all spectra the exciting light was focused with a 53 mm focal length lens.](image1)

The unwanted trace impurities become irrelevant as the temperature is increased. Figs. 2(c) and (d) represent Tb\(^{3+}\) luminescence at \(T = 100\) K after 20,486 and 10,626 cm\(^{-1}\) excitation, respectively. The spectra are almost identical and the assignment of the multiplets to the same Tb\(^{3+}\) \(5D_4 \rightarrow 7F_J\) transitions as in Fig. 2(a) can be confidently made. The broad peak in Fig. 2(d) around 20,000 cm\(^{-1}\) is again Yb\(^{3+}\)–Yb\(^{3+}\) cooperative emission. The temperature dependence of the total Tb\(^{3+}\) UC luminescence intensity follows a Boltzmann distribution with \(\Delta E\) on the order of the energy difference between \(2^2Yb^{3+}F_{7/2} \rightarrow 2^2F_{5/2}\) electronic origin and the origin of the Tb\(^{3+}\) \(7F_6 \rightarrow 5D_4\) 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 SrCl\(_2\) : Tb\(^{3+}\)(1%) : Yb\(^{3+}\)(1%) after a 10 ns pulse at 10,187 cm\(^{-1}\), while detecting the 18,360 cm\(^{-1}\) luminescence at \(T = 100\) 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 cm\(^{-1}\). The sample was kept at \(T = 100\) K and excited with a 10 ns pulse of light with energy of 10,187 cm\(^{-1}\). The inset shows the short time response with better resolution. The solid line in both plots represent the fits using Eq. (1).](image2)
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:

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

The best fit in Fig. 3 corresponds to \(B = 526\) and
\(C = 6923\) 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 \(2F_{5/2}\) level and the decay part
with the \(3D_4\) lifetime of Tb\(^{3+}\) at \(T = 100\) 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 \(T = 10\) K in this crystal the UC efficiency is
reduced by four orders of magnitude compared to
\(T = 100\) K, and due to the presence of cooperative
Yb\(^{3+}\) pair emission around 20,000 cm\(^{-1}\) and Er\(^{3+}\)
impurity emissions at lower energies, it was not
possible to characterize this remaining UC luminescence at \(T = 10\) K.

However, we found in the Cs\(_3\)Tb\(_2\)Br\(_9\) : Yb\(^{3+}\)
(1\%) crystal, even at temperatures down to
\(T = 10\) 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
SrCl\(_2\) : Tb\(^{3+}\)(1\%) : Yb\(^{3+}\)(1\%) at \(T = 100\) K, and
upon cooling to \(T = 10\) K the total UC intensity
also drops by four orders of magnitude. But in this
case we can characterise the \(T = 10\) K UC
mechanism. Fig. 4 compares the UC excitation
spectrum at \(T = 10\) K, Fig. 4(a), with the corre-
sponding NIR excitation spectrum squared, Fig. 4(b). The two are evidently very different.
Besides a dominant feature around 10,590 cm\(^{-1}\),
corresponding to the \(2F_{7/2}(0)\rightarrow 2F_{5/2}(2)\) GSA
of Yb\(^{3+}\), there are a large number of lines
covering the energy range of 10,320–10,850 cm\(^{-1}\)
in Fig. 4(a). A detailed analysis of these extra lines
reveals that they are due to \([F_{5/2}^1F_{4}]\rightarrow[F_{7/2}^2–
3D_4]\) ESA transitions according to the dimer picture in Fig. 1(b). They reflect the crystal-field
splitting in both the Yb\(^{3+}\)2F\(_{7/2}\) ground state and
the Tb\(^{3+}\)5D\(_4\) 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 Cs\(_3\)Tb\(_2\)Br\(_9\) :
Yb\(^{3+}\)(1\%), because the lattice contains discrete
Tb\(^{2+}\)Br\(_9\)\(_2\) dimers with a short Tb\(^{3+}\)-Tb\(^{3+}\)
separation of 3.9 A. 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 ex-
change 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 coopera-
tive 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 sensitisa-
tion process.
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References