Phonon-assisted cooperative sensitization of Tb³⁺ in SrCl₂:Yb, Tb

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Abstract

Excitation into the Yb³⁺ ²F_{5/2} excited states leads to visible-by-eye green luminescence spanning the spectral region from 490 to 790 nm, with a quadratic power dependence. Optical absorption, luminescence, and excitation spectroscopy as well as pulsed measurements on single-crystal SrCl₂:Yb(1%), Tb(1%) are used to determine the upconversion (UC) properties of this system. The upconverted luminescence is easily detectable by eye from RT to 100 K, at which point the intensity drops significantly and a change in colour from green to blue is observed. Pulsed measurements coupled with excitation spectroscopy lead to the unambiguous assignment of a phononassisted cooperative sensitization mechanism as the dominant UC process for T > 50 K with $\frac{VIS}{NIR}$ photon ratios on the order of 10^{-2} % for a laser power of 56 W mm⁻². Below 50 K, the dominant UC emission becomes the wellknown Yb–Yb cooperative luminescence around 500 nm, with a consequential reduction of Tb³⁺ emission by more than three orders of magnitude from RT to 10 K.

1. Introduction

The upconversion (UC) of low-energy photons to high-energy photons is a well-studied phenomenon which now has use in many applications. These include solid-state lasers, phosphor materials, optical data storage, IR counters, among other devices which have the advantage of cheap and readily available excitation sources, namely IR diodes, as well as consisting of all solid-state components [1]. The key to synthesizing new and improved UC devices relies on the fundamental understanding of the principles which govern the UC process. The Yb³⁺-sensitized UC luminescence of Tb³⁺ ions has been studied for many years and has

even been proposed by previous authors as a system which could potentially produce laser action [2, 3]. Using Yb³⁺ as a sensitizer ion is attractive because of the relatively strong oscillator strength of the Yb³⁺ ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transitions, which are in the near-infrared (NIR) range of inexpensive efficient solid-state diode lasers. In addition, the ${}^{2}F_{5/2}$ state has a quantum efficiency near to 1 in ionic lattices. Additionally, the Tb³⁺ ion is attractive as the active emitting ion because of its broad emission range, allowing tunability in the visible, and its tendency to relax radiatively instead of through non-radiative channels, such as cross-relaxation or multiphonon decay, which would reduce the quantum efficiency away from the theoretical limit of 50% for UC processes. Although the Yb:Tb UC system was introduced in 1969, there is still some debate as to what is the dominant process which converts low-energy photons into higher-energy visible photons [2,4,5]. Therefore the focus of this paper is on gaining a better understanding of the Yb:Tb system and determining the dominant UC mechanism.

The confusion about UC in the Yb:Tb system arises because it can not be explained with the 'normal' UC mechanisms for heterogeneous systems, i.e. systems which involve two different ions. The reason is that Yb³⁺ has only one excited state, ${}^{2}F_{5/2}$ around 10 000 cm⁻¹, and Tb³⁺ does not have any excited states in this spectral range. The two mechanisms proposed by previous authors to describe the UC are cooperative sensitization and the so-called GSA/ESA (ground-state absorption/excited-state absorption). The former involves energy transfer from two excited Yb³⁺ ions, called the sensitizer, simultaneously to the Tb³⁺ ion, called the activator. The GSA/ESA process involves a ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ ground-state absorption of the Yb³⁺ ion followed by an excited-state absorption from the Yb³⁺ meta-stable level to the Tb³⁺ meta-stable level. These two processes, which will be discussed in greater detail later, have the same characteristics as the well-known GSA/ETU (ground-state absorption/energy transfer UC) and GSA/ESA, respectively, which describe homogeneous systems involving only one chromophore. To distinguish between GSA/ETU and GSA/ESA, two standard techniques are generally used, namely short-pulse measurements and excitation spectroscopy [6]. We apply these two techniques to the Yb:Tb system to determine the dominant UC mechanism.

We have chosen $SrCl_2:Yb(1\%)$, Tb(1%) for this study because of the tendency of rareearth (RE) ions to group together due to the charge mismatch of substituting a trivalent ion for a divalent host ion [7]. This grouping of ions can be advantageous for UC involving energy transfer, since this process requires interactions between the active ions and is therefore dependent upon their distance [8].

It is important to note that energy conservation dictates for cooperative sensitization that the energy of the relevant activator ion level, $Tb^{3+5}D_4$, must be less than or equal to twice the sensitizer energy level, $Yb^{3+2}F_{5/2}$. This requirement is often not satisfied in Yb:Tb compounds, including the title compound. The small energy gap between these levels, however, can be bridged by phonons, and therefore the UC luminescence in this system is strongly dependent on the temperature of the crystal, as will be discussed in section 4.3.2.

We present results of pulsed and CW spectroscopy performed on SrCl₂:Yb, Tb which lead to the clear assignment of a phonon-assisted cooperative sensitization mechanism responsible for Tb³⁺ luminescence under Yb³⁺ excitation above 50 K. The UC luminescence temperature dependence is presented to determine the activation energy of the process. An activation energy of 150 cm⁻¹ is found which is equal to the energy difference between the lowest Tb³⁺ ⁵D₄ crystal-field level and two times the lowest crystal-field level of Yb³⁺ $^{2}F_{5/2}$. The rate constant associated with the energy transfer is determined by pulsed measurement with 1×10^{7} W mm⁻² at 10 190 cm⁻¹ and analysis through rate equations to be 2000 s⁻¹ at 100 K. It is discussed in terms of dynamical considerations as well as the efficiency of the UC process. We also show and briefly discuss the two dominant crystal-field sites for Yb³⁺ in this lattice which both contribute to the Tb³⁺ UC luminescence at high temperatures.

2. Experimental techniques

2.1. Synthesis of SrCl₂:Yb, Tb

Stoichiometric amounts of SrCl₂, TbCl₃, and YbCl₃ precursors were mixed, fired to 890 °C, and single crystals were grown via the Bridgman technique. The TbCl₃ and YbCl₃ starting materials were prepared from Tb₄O₇ (99.9999%), Yb₂O₃ (99.9999%), NH₄Cl (>99.9%), and HCl (47%) by the ammonium halide method [9, 10]. The SrCl₂ was prepared from SrCO₃ (99.994%) by dissolving in HCl and adding NH₄Cl. The product was dried and decomposed under heating in vacuum in analogy with the ammonium halide method. At all stages of growth and handling, the samples were kept in an inert atmosphere of either vacuum, He, or N₂, to prevent the adsorption of water. Absorption measurements were performed on a 0.4 cm long clear crystal, which was cut, polished, and sealed in a copper cell with optical windows filled with He gas. Since SrCl₂ is cubic, a random orientation and unpolarized light could be used. Samples for luminescence measurements were sealed in quartz ampoules with a low-pressure atmosphere of He gas. The concentration of dopant ions is nominally 1% for both, and from the strength of absorption transitions the actual concentration is estimated to be close to this for both Yb³⁺ and Tb³⁺ [11].

2.2. Spectroscopy

The absorption spectra were recorded on a Cary 5e spectrophotometer coupled with a closedcycle cryogenic refrigerator (Varian) for cooling. Cooling for luminescence measurements was achieved via quartz He gas flow-tubes. Luminescence of the sample was excited via an Ar⁺-ion laser (Spectra Physics 2060-10 SA) or with a Ti:sapphire laser (Spectra Physics 3900S), pumped by the same Ar⁺-ion laser, for Tb³⁺ luminescence and Yb/UC luminescence, respectively. The emission was dispersed through a 0.85 m double monochromator (Spex 1402) with 500 nm blazed 1200 groves mm⁻¹ gratings and detected with a cooled red-sensitive photomultiplier tube (Hamamatsu 3310-01). A Stanford Research SR-400 photon counter was used with a PC for data collection. The excitation laser beam was focused using an f = 53 mm lens. All spectra are presented as photons s⁻¹ versus cm⁻¹ and are corrected for the throughput of the detection system, the detector response, and for the index of refraction of air.

Kinetic measurements were performed with either the same excitation sources as described above coupled through an acousto-optical modulator (Coherent 305, Stanford Research DS 345 function generator) or the Raman-shifted (Quanta Ray, RS-1, H₂, 340 p.s.i.) output of a dye laser (Lambda Physik FL 3002, pyridine 1 in methanol) pumped with the second harmonic of a Nd: YAG laser (Quanta Ray DCR 3). The luminescence was dispersed through a 0.75 m single monochromator (Spex 1702) with a 750 nm blazed 600 grooves mm⁻¹ grating and detected with the same PMTs as above, coupled with a multichannel scaler (Stanford Research SR 430).

3. Results

The survey absorption, (a), and emission spectra, (b), are presented in figure 1. Sharp lines in the low-energy range of the absorption spectrum below 6000 cm⁻¹ are transitions within the Tb³⁺ ⁷F_J manifold, and the lines located around 10 000 cm⁻¹ are due to ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transitions of Yb³⁺. The Tb³⁺ ⁷F₆ $\rightarrow {}^{5}D_{4}$ transition is expanded by a factor of 100 and is located around 20 500 cm⁻¹. At higher energy, f–d transitions of an Yb²⁺ impurity are observed [12]. Both emission spectra (upside down) are excited with 10 626 cm⁻¹ (56 W mm⁻²) light at T = 100 K. The emission around 10 000 cm⁻¹ is due to the Yb³⁺ ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition



Figure 1. (a) The survey absorption spectrum of SrCl₂:Yb, Tb at 10 K. The Tb³⁺ $^{7}F_{6} \rightarrow ^{5}D_{4}$ absorption has been scaled up by 10². (b) The luminescence spectrum at 100 K under an excitation energy of 10 626 cm⁻¹ plotted upside down. The Tb³⁺ $^{5}D_{4} \rightarrow ^{7}F_{6}$ luminescence has been scaled up by 10⁴.



Figure 2. Absorption spectra for $Yb^{3+} {}^2F_{7/2} \rightarrow {}^2F_{5/2}$, (a), and $Tb^{3+} {}^7F_6 \rightarrow {}^5D_4$, (b), transitions at 15 K. Transitions for different Yb^{3+} sites are labelled. Note the broken energy axis between (a) and (b).

and is 1×10^4 times stronger than the total of the five Tb³⁺ ${}^5D_4 \rightarrow {}^7F_J$ emissions between 14 000 and 20 500 cm⁻¹ under the same excitation conditions.

High-resolution absorption spectra are presented in figure 2 for $Yb^{3+} {}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transitions, (a), and for $Tb^{3+} {}^{7}F_6 \rightarrow {}^{5}D_4$ transitions (b). The spectra were taken with a 0.4 cm thick sample at 15 K. Absorption lines corresponding to two different Yb^{3+} sites are labelled A and B.

Yb³⁺ IR emission spectra with excitation at 10138 cm⁻¹ (site A in figure 2) and 10192 cm⁻¹ (site B in figure 2), at T = 10 K, are shown in figures 3(a) and (b) respectively. The spectrum in (a) represents emission from only site A, while the spectrum in (b) shows emission from both sites.

The Yb³⁺ and Tb³⁺ luminescence decays at T = 100 K are plotted in a semi-log plot in figure 4. Square-wave pulses at 10 626 cm⁻¹ were used for Yb³⁺ while detecting luminescence at 10 192 cm⁻¹ (site B). 10 138 cm⁻¹ light was used for excitation into Yb³⁺ site A (not shown) while detecting luminescence around 10 000 cm⁻¹. Tb³⁺ luminescence was excited directly (20 486 cm⁻¹, solid) and by UC (10 626 cm⁻¹, dashed). The excitation power was



Figure 3. High-resolution luminescence spectra of Yb^{3+} at 10 K with excitation energies of 10 138 and 10 192 cm⁻¹ for (a) and (b), respectively.

 Table 1. Lifetimes of different levels. The values are calculated using the decay rate constants determined from figure 4.

Level		τ (ms) $\pm 1\%$	300 K
	10 K	100 K	
$\overline{{}^2F_{5/2}}$, site A	0.46	0.48	0.47
$^{2}F_{5/2}$, site B	0.53	0.50	0.47
⁵ D ₄	2.5	2.5	2.5
$^{5}D_{4}{}^{a}$	2.2	2.1	1.9

^a Lifetime determined under UC excitation conditions.

 $0.56 \text{ W} \text{ mm}^{-2}$ for direct and 56 W mm⁻² for UC. All the decays are single exponential, and the lifetimes derived from these experiments are presented in table 1.

Figure 5 displays the temperature-dependent Tb³⁺ luminescence spectra under two different excitation energies, $\tilde{v}_{exc} = 10\,626 \text{ cm}^{-1}$ and $\tilde{v}_{exc} = 20\,486 \text{ cm}^{-1}$, for (a) and (b) respectively. All spectra are independently normalized. The temperature dependence of the intensities will be presented in figure 8.

The UC excitation spectrum (a) and the square of the Yb³⁺ absorption spectrum (b) for T = 100 K are plotted in figure 6. The excitation spectrum is obtained by scanning the Ti:sapphire laser through the Yb³⁺ absorption region while monitoring the UC luminescence intensity at 18 360 cm⁻¹. The GSA spectrum presented in (b) has been squared due to the quadratic dependence of the UC luminescence on the excitation power. (c) and (d) display the power dependence of the Yb³⁺ and Tb³⁺ UC luminescence for excitation at 10 626 cm⁻¹ (site B) and detecting at 10 000 and 18 360 cm⁻¹ respectively. The Yb³⁺ luminescence power dependence, (c), is found to have a slope of 1.0, while the line through the points in (d) is a linear regression with a slope close to 2, representing the two-photon nature of the UC process.

Figure 7 displays the UC luminescence ($\tilde{v}_{det} = 18360 \text{ cm}^{-1}$) temporal response for 8 ns pulsed excitations into the Yb³⁺ ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ absorption at 10 192 cm⁻¹ (site B) at T = 100 K, for a peak power estimated to be $1 \times 10^{7} \text{ W mm}^{-2}$. There is a clear rise of the UC luminescence which can be better seen in the inset (b). Part (c) is a semi-logarithmic plot which highlights the single-exponential nature of the decay part of the transient.

Temperature-dependent UC luminescence spectra are plotted in figure 8(a) where each curve is corrected for the square of the absorption cross-section at the excitation wavelength,



Figure 4. Responses of Tb³⁺ and Yb³⁺ luminescence intensities at 100 K under square-wave excitation energies of 20 486 and 10 626 cm⁻¹, respectively, in a semi-logarithmic representation. The dashed data represent the Tb³⁺ luminescence decay after square-wave UC excitation at 10 626 cm⁻¹. The lifetimes of Tb³⁺ and the two Yb³⁺ sites can be found in table 1.



Figure 5. Luminescence spectra of SrCl₂:Yb, Tb at three temperatures produced by: (a) UC excitation at 10 626 cm⁻¹ and (b) direct excitation at 20 486 cm⁻¹. The spectra are not on the same *y*-axis scale.

 $\tilde{\nu}_{exc} = 10\,626 \text{ cm}^{-1}$ (site B) (56 W mm⁻²). The laser power and energy are kept constant for all the spectra. The correction is made because the UC process is a two-photon process—see figure 6(d)—and thus it is dependent upon the square of the absorbed photons. From 10 K to RT the UC intensity increases by more than three orders of magnitude, as shown in figure 8(b).

4. Discussion and analysis

4.1. SrCl₂ and trivalent dopant ions

 $SrCl_2$ crystallizes in the space group O_h with the fluorite structure. The Sr^{2+} ions are surrounded by eight Cl^- ions with cubic coordination [13]. The introduction of trivalent RE ions into this structure, substituting for divalent Sr ions, has been studied and it has been determined that, in addition to the many possible single-ion sites due to different local and distant charge compensation possibilities, these dopant ions tend to form clusters [7]. And these clusters form at lower concentrations than in other fluorite crystals. Wietfeldt and Wright [13] determine that



Figure 6. The 100 K UC luminescence excitation spectrum, monitoring 18 360 cm⁻¹ luminescence, is plotted in (a). The square of the ground-state absorption spectrum of Yb³⁺ at 100 K is plotted in (b) for comparison. (c) and (d) are log–log intensity versus power representations at 100 K of the Yb³⁺ emission at 10 000 cm⁻¹ and the Tb³⁺ UC emission at 18 360 cm⁻¹, respectively. The excitation energy is 10 626 cm⁻¹ for both. The lines through the data points are linear regression fits with slopes of 1.0 (\pm 0.05) and 1.9 (\pm 0.1) respectively.



Figure 7. UC luminescence transient response, monitored at 18360 cm⁻¹, after 8 ns pulsed excitation at 10192 cm⁻¹ for T = 100 K (dashed data). The inset (b) shows the same data on an expanded *x*-axis. Inset (c) shows the same data in a log–linear representation. The solid curves in all plots are simulations using equations (1a)–(1d) with parameter values found in table 2.

for a Eu³⁺ dopant concentration of 3×10^{-3} mol% the cluster sites are already the dominant sites with two of the six identified sites being dominant at higher concentrations. It was also shown that the energy transfer between ions was greatly enhanced due to this clustering of ions. These conditions are ideal for UC processes involving interactions between different ions such as for Tb³⁺ and Yb³⁺.

This clustering of ions manifests itself in the optical spectra as inhomogeneously broadened absorption and emission bands [14]. There are four broad ($\sim 10-40 \text{ cm}^{-1}$) Yb³⁺ absorption features, for T = 15 K, observed at 10 138, 10 192, 10 270, and 10 626 cm⁻¹ (figure 2(a)). The two low-energy lines are assigned to the ${}^{2}F_{7/2}(0) \rightarrow {}^{2}F_{5/2}(0')$ transitions for two different sites labelled A and B respectively. Due to the width of the higher-lying bands and the fact that they



Figure 8. (a) The UC luminescence spectra for temperatures of 30, 100, and 300 K. Each spectrum has been divided by the corresponding square of the absorption cross-section at the excitation energy of 10 626 cm⁻¹. (b) An Arrhenius plot of the natural logarithm of the normalized total UC luminescence intensity versus the inverse of the temperature times 1000. The solid line is a fit using equation (3) described in the text.

overlap in energy, it is not possible to define clearly the crystal-field splitting of the ${}^{2}F_{5/2}$ level for each site. From the absorption spectrum we estimate that 14% of the ions are located on site A while 86% are located on site B. This estimate assumes equal oscillator strengths for the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition at each site, which is reasonable considering the similar lifetimes of the levels; see table 1. Wietfeldt and Wright [13] found that in SrCl₂:Eu two defect sites were dominant at high concentrations in agreement with our results. The emission spectrum of site A is shown in figure 3(a). Excitation into site B, (b), leads to emission from both site A and site B due to partial energy transfer from B to A. Again it is difficult to determine the crystal-field splitting of the ${}^{2}F_{7/2}$ ground states with any accuracy, but there are clear differences between the two spectra. The broad band located at 10 010 cm⁻¹ is associated with site A while the two bands located around 9750 and 9880 cm⁻¹ are clearly associated with transitions involving Yb³⁺ on site B. The energetic positions of these luminescence peaks correspond roughly to crystal-field levels of Yb³⁺ in Cs₂NaYbCl₆ [15–17].

The Tb³⁺ absorption spectrum, figure 2(b), is also broad and difficult to assign accurately. Relatively sharp transitions are observed in the region spanning 20 460 to 20 700 cm⁻¹ which are assigned to ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ ground-state absorption transitions. For our study we are interested in the lowest-energy transition located at 20 468 cm⁻¹, which will be important in section 4.3.2 when discussing the temperature dependence of the UC luminescence. The energetic position of the four lowest peaks in the Tb³⁺ absorption spectrum of figure 2(b) is similar to energies found in Cs₂NaTbCl₆ [15–17].

Decay time measurements for both Tb^{3+ 5}D₄ and Yb^{3+ 2}F_{5/2} levels are presented in figure 4, for 100 K. The Tb^{3+ 5}D₄ lifetime stays constant between 10 and 300 K—see table 1—and we conclude that it is radiative. The same is true for the Yb³⁺ site A luminescence lifetime. The Yb³⁺ site B lifetime, on the other hand, changes with temperature and depends on the excitation and detection energy. At 10 K, $\tau_A = 0.46 (\pm 0.01)$ ms, while the lifetime of site B is longer, with $\tau_B = 0.53 (\pm 0.01)$ ms. As the temperature is raised, τ_B decreases and reaches a value which is comparable to that for site A. This reduction in lifetime with temperature is due to increasing energy transfer from B to A as the transfer process becomes more probable at higher temperatures. This energy transfer is also evident in figure 3 where excitation into site B leads to emission which contains features of both sites. From this spectrum we estimate that 40%



Figure 9. A diagram representing the cooperative sensitization of Tb^{3+} luminescence by two excited Yb^{3+} ions. The solid arrows represent radiative transitions and the dashed arrows represent non-radiative transitions involving energy transfer. The parameters in the diagram are described in the text and correspond to the parameters used in equation (1).

of the excitation into site B is transferred to site A at 10 K. Efficient energy transfer between Yb^{3+} ions was also found in previous studies [13, 18].

4.2. Upconversion mechanism

4.2.1. General considerations. The typical UC process, of heterogeneous systems, involves first an excitation of one ion, called the sensitizer. The energy is then transferred from the sensitizer to the second ion, called the activator, via a resonant or non-resonant energy transfer process. The activator is then further excited to a higher meta-stable state through a second energy transfer from a sensitizer. This process can be very efficient and some UC laser systems have been built on this principle using Yb³⁺ as the sensitizer ion [1]. It is clear from the Yb³⁺ and Tb³⁺ energy levels that this process cannot be responsible for the UC observed after excitation to the Yb³⁺ ion [19]. The excited meta-stable state of Yb³⁺ lies around 10 000 cm⁻¹ whereas the Tb³⁺ levels closest in energy to this are at 6000 and 20 000 cm⁻¹. Energy transfer to the 6000 cm⁻¹ level of Tb³⁺, in addition to being highly off-resonant and therefore unlikely, cannot lead to UC as the second quantum of Yb³⁺ ${}^2F_{7/2} \rightarrow {}^2F_{7/2}$ excitation will then not be sufficient in energy to excite the Tb³⁺ to the higher meta-stable level, 20 000 cm⁻¹.

Due to the failure to explain the UC in Yb:Tb via standard processes, Ovsyankin and Feofilov [20] proposed the cooperative sensitization process. The cooperative sensitization mechanism involves the absorption of two NIR photons by two Yb³⁺ ions and subsequently the simultaneous energy transfer from the Yb³⁺ ions to a close Tb³⁺ ion:

$$2 \times Yb^{3+}({}^{2}F_{5/2}):Tb^{3+}({}^{7}F_{6}) \Rightarrow 2 \times Yb^{3+}({}^{2}F_{7/2}):Tb^{3+}({}^{5}D_{4}).$$

A model of this process for the Yb:Tb system is presented in figure 9. This process was considered to be the dominant mechanism in the first study of Yb:Tb UC by Livanova *et al* [4]. The study was performed on doped CaF₂, and SrF₂ crystals, and assignment of the UC mechanism was based on the efficiency of the process. Later papers made similar assignments with different evidence such as the rise in UC intensity after a short excitation pulse into the Yb³⁺ excited states [2, 21–26]. The rise after a short pulse is a well-known fingerprint

of an energy transfer process which needs no light to proceed and therefore continues after the laser pulse. Besides the short-pulse experiment, excitation spectroscopy can be used to assign a GSA/ETU mechanism. An excitation spectrum of UC luminescence governed by a GSA/ETU-type mechanism should resemble the square of the ground-state absorption to the intermediate level. This can be understood by considering the model in figure 9 and noting that the solid upward-pointing arrows, which represent absorption transitions which lead to UC luminescence, only concern transitions to the intermediate level. Since it takes two of these transitions for the UC to proceed, the excitation spectrum follows the square of the ground-state absorption of the sensitizer ion.

Other reports in the literature have assigned the UC mechanism to a GSA/ESA-type mechanism [2, 27]. This process proceeds through a sequence of two cooperative absorption steps:

$$\begin{split} Yb^{3+}(^{2}F_{7/2}): Tb^{3+}(^{7}F_{6}) + photon \Rightarrow Yb^{3+}(^{2}F_{5/2}): Tb^{3+}(^{7}F_{6}) + photon \\ \Rightarrow Yb^{3+}(^{2}F_{7/2}): Tb^{3+}(^{5}D_{4}). \end{split}$$

The fingerprints for this type of process are:

- (1) immediate decay upon short-pulse excitation since the termination of the light also terminates the UC;
- (2) transitions observed in the UC excitation spectra which do not match GSA transitions, i.e. ESA transitions.

The GSA/ESA mechanism has been well studied in many single-ion UC systems [6]. However, until recently no reports have conclusively shown an UC system where the GSA transition occurs on one ion followed by an ESA transition to a different ion [28,29]. Valiente *et al* report on Yb–Mn pairs where the UC luminescence is attributed to GSA/ESA transitions within a single chromophore, namely an Yb–Mn dimer. This assignment was made on the basis of pulsed measurements which showed only decay, i.e. no rise, immediately following the excitation pulse into an Yb^{3+ 2}F_{5/2} level. Excited-state excitation spectroscopy further verified this assignment. Our study will focus on similar experiments to establish the UC mechanism in SrCl₂:Yb, Tb

4.2.2. *CW spectroscopy.* Excitation into the Tb³⁺ ⁷F₆ \rightarrow ⁵D₄ or the Yb³⁺ ²F_{7/2} \rightarrow ²F_{5/2} absorption regions, figures 1 and 2, leads to visible-by-eye green Tb³⁺ luminescence with the same spectral features for T = 100 K and greater; see figure 5. The UC luminescence can therefore be readily assigned to Tb³⁺ ⁵D₄ \rightarrow ⁷F_J transitions. For temperatures below T = 100 K the UC emission changes colour from green to blue with strongly decreasing intensity. The UC luminescence spectrum changes accordingly with the Tb³⁺ luminescence decreasing in intensity by orders of magnitude (see figure 8), and a remaining very weak UC luminescence band located around 20 000 cm⁻¹ (see figure 5). The broad emission around 20 000 cm⁻¹ is readily assigned to the well-known Yb–Yb pair emission [30]. Additional features are observed at 18 000 and 15 000 cm⁻¹ which we assign to ⁴S_{3/2} \rightarrow ⁴I_{15/2} and ⁴F_{9/2} \rightarrow ⁴I_{15/2} transitions, respectively, of trace Er³⁺ impurities present in the compound. Despite the use of 6N purity starting materials, trace amounts of Er³⁺ ions are present and appear in the UC emission spectrum due to the high efficiency of Yb³⁺-sensitized Er³⁺ UC luminescence [1,31]. Many papers in the past have mistakenly reported Er³⁺ luminescence as Tb³⁺-ion or some other RE-ion luminescence under UC conditions. The Yb–Yb pair luminescence is also observed in the T = 100 K plot in figure 5 but has the dominant Tb³⁺ luminescence superimposed—see figure 8—at higher temperatures.

One possible explanation for the UC mechanism is the absorption of Yb–Yb luminescence by the ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ transition of Tb³⁺. However, the Yb–Yb pair luminescence has an observed $\frac{\text{VIS}}{\text{NIR}}$ ratio of 10⁻⁶ in SrCl₂ and in many other hosts [31]. The Tb³⁺ UC luminescence is found to have a $\frac{\text{VIS}}{\text{NIR}}$ ratio starting below 10⁻⁸ at 10 K and increasing to 1 × 10⁻⁴ (figure 1) at 100 K and finally 5 × 10⁻⁴ at 300 K. Since these high-temperature values are significantly larger than for the Yb–Yb pair luminescence, this process can be eliminated. The following discussion of the cooperative UC mechanism in SrCl₂:Tb, Yb will focus on temperatures at and above 100 K.

The excitation spectrum of Tb^{3+} UC luminescence at 100 K in figure 6 closely resembles the square of the $Yb^{3+} {}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition (GSA²). This is what is expected from an ETU mechanism—section 4.2.1—where the absorption which leads to UC only occurs to the intermediate meta-stable level. Also, since two excitations to the intermediate level are needed for bringing one Tb^{3+} ion to the excited state, we find a power-dependent slope of 2 (figure 6(d)). More importantly, there are no extra transitions observed in the excitation spectrum which can be ascribed to an ESA step. If a GSA/ESA mechanism were the active UC process, there would be more than just the ground-state absorption transitions in the excitation spectrum.

4.2.3. Dynamics. To investigate this system further, we performed pulsed measurements. Time-dependent measurements also allow the distinction between a GSA/ESA mechanism, i.e. immediate decay, and a GSA/ETU process, i.e. rise from zero followed by decay; see section 4.2.1 [6]. The dynamic behaviour of cooperative sensitization corresponds to that of the ETU mechanism for more simple systems and can be treated in a similar manner. In particular, the cooperative sensitization relies on energy transfer from the two sensitizer ions to the activator and this process is relatively slow. Also, this process does not require the presence of light and therefore will continue after the pulse is terminated. For the Yb:Tb system the rise is expected to be related to half the Yb³⁺ lifetime and the decay should be related to the Tb³⁺ lifetime.

The UC luminescence temporal response for our system at 100 K after a short, 8 ns, pulse is given in figure 7. The luminescence intensity starts at zero, and this is followed by a rise and a decay. The rise is indicative of an energy transfer process and thus eliminates the possibility of a mechanism which involves an ESA step. The rise, shown in detail in figure 7(b), has a time constant of ~150 μ s and is thus shorter than the decay time, $\tau = 0.5$ ms, of the Yb³⁺ ion; see table 1. Figure 7(c) displays the single-exponential behaviour of the UC luminescence decay which has a time constant of 2.1 ms which is slightly shorter than the lifetime, $\tau = 2.6$ ms, of the Tb³⁺ under direct excitation; see table 1. The rise and decay will be discussed in more detail in section 4.2.4. This experiment, coupled with the excitation spectroscopy, allows the conclusive assignment of Yb:Tb UC luminescence at T = 100 K in SrCl₂:Yb, Tb to the cooperative sensitization mechanism.

4.2.4. Model. The transient data can be simulated by considering the cooperative sensitization mechanism shown schematically in figure 9. Using this diagram we can write down the four coupled differential rate equations describing the populations of each level, N_i :

$$\frac{\mathrm{d}N_0}{\mathrm{d}t} = -GN_0 + k_1 N_1 + 2w_{CS}(N_1)^2 N_2,\tag{1a}$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = GN_0 - k_1 N_1 - 2w_{CS}(N_1)^2 N_2,\tag{1b}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = k_3 N_3 - w_{CS} (N_1)^2 N_2, \tag{1c}$$

$$\frac{\mathrm{d}N_3}{\mathrm{d}t} = -k_3 N_3 + w_{CS} (N_1)^2 N_2. \tag{1d}$$

Table 2. Decay rate constants of Yb³⁺ and Tb³⁺ at 100 K determined by square excitation (figure 4). The UC power-dependent rate constant was determined by fitting equations (1a)–(1d) to the experimental data in figure 7.

Transition		Decay rate constant (s^{-1})
${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$	k_1	2020 (±50)
${}^{5}\mathrm{D}_{4} \rightarrow {}^{7}\mathrm{F}_{6}$	k_3	400 (±5)
$^{5}\mathrm{D}_{4} ightarrow ^{7}\mathrm{F_{6}}^{a}$	k_3^*	470 (±5)
UC power-dependent rate constant ^b	$w_{CS}N_1N_2$	2000 (±500)

^a Decay rate determined under UC excitation conditions.

^b Peak power 1×10^7 W mm⁻².

 k_1 represents the Yb³⁺ ²F_{5/2} decay rate constant, k_3 the Tb³⁺ ⁵D₄ decay rate constant, *G* the power-dependent ground-state absorption rate constant, and w_{CS} is the cooperative sensitization rate parameter. All the parameters in the figure and equations (1*a*)–(1*d*) are listed in table 2 and were determined from independent measurements—section 4.1—except for the energy transfer rate constant $w_{CS}N_1N_2$.

We use equations (1a)-(1d) to simulate the transient response of the UC luminescence after short-pulsed excitation into an Yb³⁺ level. This simulation is plotted on top of the experimental data as a solid curve in figure 7. In this figure, and the insets, the simulation matches the experimental data with good agreement. In general the rise of the transient corresponds to the level possessing the shortest lifetime while the decay is related to the level with the longest lifetime. From table 1 we know that the $Yb^{3+2}F_{5/2}$ lifetime is shorter than the $Tb^{3+5}D_4$ lifetime and thus we expect the rise to be determined at least in part by the $Yb^{3+2}F_{5/2}$ lifetime. The decay is single exponential—figure 7(c)—and is of the order of the Tb³⁺ ${}^{5}D_{4}$ lifetime. However, upon modelling the data, if one takes the value for k_3 determined in the direct excitation measurements, one finds that the simulation has values that are too high at the later times. For this reason we use the k_3^* -value determined from the square-wave UC decay transients-table 2-which has a 20% larger value than with direct excitation, i.e. a shorter lifetime. This difference is due to the selective nature of the UC measurement. UC excitation preferentially excites those Tb³⁺ ions which are located near two Yb³⁺ ions, whereas the direct excitation into the $Tb^{3+5}D_4$ level excites all Tb^{3+} ions. The difference in lifetimes is due to the different local environments of the two sets of Tb³⁺ ions. Under UC excitation we observe only the highly UC-active ions which are a small subset of the bulk of the impurity ions. This effect is often seen in doped systems where the UC-active subset of ions differs from the bulk ions [32]. Previous authors have also attributed this difference to an extra decay channel for the Tb³⁺ ions near two Yb³⁺ ions, namely cross-relaxation from one Tb³⁺ to two Yb³⁺ ions [21, 22, 25, 33].

From the rate equations it can be seen that the rise derives from the Yb³⁺ lifetime and the power-dependent energy transfer UC rate constant $w_{CS}N_1N_2$. We report on the powerdependent rate constant instead of the power-independent parameter w_{CS} , because of the difficulties of measuring the initial number of excited Yb³⁺ ions, N_1 . We use the values from table 2 for the decay rate constants and vary the value of $w_{CS}N_1N_2$ to allow for the best simulation of the data. From this procedure we obtain a value of 2000 s^{-1} for $w_{CS}N_1N_2$, with excitation at 10 192 cm⁻¹ and 1×10^7 W mm⁻². This will be discussed in more detail in the next section.

4.3. Upconversion efficiency and temperature dependence

4.3.1. *Efficiency.* To discuss the quantum efficiency, $\eta = \frac{\text{VIS}_{out}}{\text{NIR}_{abs}}$, of this process we consider the ratio of VIS photons out to NIR photons out. As Yb³⁺ has a quantum efficiency of 1,

we use the Yb³⁺ luminescence to estimate the number of NIR photons absorbed. Thus, the quantum efficiency is approximated by the photon ratio $\frac{\text{VIS}_{out}}{\text{NIR}_{out}}$. For 100 K and CW excitation at 10 626 cm⁻¹ with 56 W mm⁻², we find a photon ratio of 1×10^{-4} . This photon ratio increases to 5×10^{-4} at RT.

From this $\frac{\text{VIS}}{\text{NIR}}$ ratio at 100 K and equation (1*d*), one can estimate the $w_{CS}N_1N_2$ rate constant for a CW experiment:

$$\frac{w_{CS}N_1N_2}{k_1} = \frac{k_3N_3}{k_1N_1} = \frac{\text{VIS}}{\text{NIR}}.$$
(2)

Using these values we derive a value of $w_{CS}N_1N_2$ of 0.2 s⁻¹. This value determined for CW excitation is four orders of magnitude smaller than that found under pulsed excitation; see section 4.2.4. To account for this discrepancy in the estimated value of $w_{CS}N_1N_2$, we consider the differences between the two experiments used to estimate this value. In the pulsed experiment the peak power density is ~5 orders of magnitude greater than in the CW measurement. Since the UC rate constant contains the number of ions excited during the NIR pulse, N_1 , or written explicitly $N_1 = GN_0$, it is a power-dependent parameter. Thus, the UC rate constant, $w_{CS}N_1N_2$, increases with increasing power and is thus expected to be ~1 × 10⁵ times greater for the pulsed measurements. This value can be reduced from saturation effects. From our measurements we derive values differing by four orders of magnitude, in very good agreement with the theoretical expectations.

4.3.2. Temperature dependence. So far we have not discussed the energies of the levels involved in the CS process and what is required for UC to proceed. It is clear from the energies of the lowest excited states of both site A, 10 138 cm⁻¹, and B, 10 190 cm⁻¹, of Yb³⁺ (figure 2(a)) that cooperative sensitization from two of these cannot populate the Tb^{3+ 5}D₄ level, 20 468 cm⁻¹ (figure 2(b)), at 10 K. There is a gap in energy of 192 and 88 cm⁻¹, for A and B respectively. And this is the main reason for the observed dramatic temperature dependence of the UC luminescence intensity.

The Tb^{3+ 5}D₄ emission intensity shows a very strong dependence on temperature especially in the region between 10 and 100 K, where it increases by more than two orders of magnitude with increasing temperature; figure 8(a). This strong temperature dependence has been quantified by analysing the integrated number of emitted photons as a function of inverse temperature; figure 8(b). The line drawn through the data is a linear regression using the Arrhenius equation (3):

$$\ln\left(\frac{I}{I_0}\right) = \frac{-\Delta E}{k_B T} \tag{3}$$

where *I* represents the integrated emitted photons of Tb³⁺, ΔE is the activation energy, k_B is Boltzmann's constant, and *T* is the temperature. The data are all normalized to the highest value of $I_0 = I(300 \text{ K})$, and are corrected by the square of the absorption cross-section at $\tilde{\nu}_{exc} = 10\,626 \text{ cm}^{-1}$, at each temperature, as described in section 3. Analysis of these data yields a slope of $\Delta E = 150 \pm 12 \text{ cm}^{-1}$ for the activation energy of the UC luminescence intensity. This value is close to the energy mismatch between the lowest level of Tb³⁺ ⁵D₄ at 20 468 cm⁻¹ and twice the lowest Yb³⁺ ²F_{5/2} level for both site A and site B. From this analysis it is clear that the cooperative sensitization process is facilitated only at higher temperatures, where host phonons can contribute to the energy of the UC-active ions. At higher temperatures, vibronic ²F_{5/2} levels of the Yb³⁺ ions are thermally populated, from which the energy transfer can occur. Thus, from the temperature-dependent data, the excitation spectroscopy, and the dynamic measurements, the full assignment of phonon-assisted cooperative sensitization can be made for the mechanism of UC in this crystal.

5. Conclusions

The UC properties of Yb³⁺-sensitized Tb³⁺ luminescence has been investigated for many years. Despite this, many papers have been published concerning the UC mechanism of the Yb:Tb system with little agreement. We present results in this report where, for the first time, both standard techniques for determining UC mechanisms, namely excitation spectroscopy and time-resolved spectroscopy, have been coupled with temperature-dependent measurements to conclusively show a phonon-assisted cooperative sensitization mechanism governing the UC of Yb:Tb between 100 and 300 K. Many of the systems which are studied concerning Yb:Tb UC are similar to the SrCl₂ host. In this sense our result on SrCl₂ is a more general result applying to many crystals. The high efficiency of some Yb:Tb UC systems is also a sign that they are dominated by a cooperative sensitization process as opposed to a GSA/ESA process which is expected to be weaker, and is found to be of the order of the Yb-Yb pair luminescence in Yb^{3+} -doped Cs₃Tb₂Br₉ [5,34]. For the system of SrCl₂:Yb, Tb the cooperative sensitization is quenched at low temperatures due to the lack of spectral overlap between twice the Yb3+ emission and the ${}^{5}D_{4}$ absorption at low temperatures. We have investigated the temperature dependence of the UC luminescence and determined the thermal activation energy of the cooperative sensitization. At temperatures where the cooperative sensitization is active, we have investigated the temporal behaviour by modelling the transient measurements with one adjustable parameter. The room temperature $\frac{VIS}{NIR}$ ratio of this system was found to be of the order of 10^{-4} , but could be enhanced by an appropriate choice of dopant concentrations. However, enhancements by orders of magnitude are needed for an UC system which will yield efficient laser action. This paper, while specific to SrCl₂, suggests that the cooperative sensitization mechanism is the process most likely to be operative in efficient Yb:Tb systems.

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References

- [1] Lenth W and Macfarlane R M 1992 Opt. Photon. News 3 8
- [2] Noginov M A, Venkateswarlu P and Mahdi M 1996 J. Opt. Soc. Am. B 13 735
- [3] Qiu J, Shojiza M, Kawamoto Y and Kadono K 2000 J. Lumin. 86 23-31
- [4] Livanova L D, Saitkulov I G and Stolov A L 1969 Sov. Phys.-Solid State 11 750
- [5] Salley G M, Valiente R and Güdel H U 2001 J. Lumin. 94–5 305
- [6] Gamelin D R and Güdel H U 2001 Top. Curr. Chem. 214 1
- [7] Tallant D R, Moore D S and Wright J C 1977 J. Chem. Phys. 67 2897
- [8] Kushida T 1973 J. Phys. Soc. Japan 34 1334
- [9] Reed J B, Hopkins B S and Audrieth L F 1936 Inorg. Synth. 1 28
- [10] Meyer G 1989 Inorg. Synth. 25 146
- [11] Carnall W T, Fields P R and Rajnak K 1968 J. Chem. Phys. 49 4412
- [12] Piper T S, Brown J P and McClure D S 1967 J. Chem. Phys. 46 1353
- [13] Wietfeldt J R and Wright J C 1987 J. Chem. Phys. 86 400
- [14] Jones G D and Murdoch K M 1994 J. Lumin. 60-1 131
- [15] Tanner P A, Ravi Kanth Kumar V V, Jayasankar C K and Reid M F 1994 J. Alloys Compounds 215 349
- [16] Richardson F S, Reid M F, Dallara J J and Smith R D 1985 J. Chem. Phys. 83 3813
- [17] Schwartz R W, Brittain H G, Riehl J P, Zeakel W and Richardson F S 1977 Mol. Phys. 34 361
- [18] Voron'ko Yu K, Osiko V V and Shcherbakov I A 1969 Sov. Phys.-JETP 29 86

- [19] Dieke G H 1968 Spectra and Energy Levels of Rare Earth Ions in Crystals (New York: Interscience)
- [20] Ovsyankin V V and Feofilov P P 1966 JETP Lett. 3 317
- [21] Ostermayer F W and van Uitert L G 1970 Phys. Rev. B 1 4208
- [22] Antipenko B M, Dmitryuk A V, Karapetyan G O, Zubkova U S, Kosyakov V I, Mak A A and Mishailova N V 1973 Opt. Spectrosc. 35 315
- [23] Brown R S, Brocklesby W S, Barnes W L and Townsend J E 1995 J. Lumin. 63 1
- [24] Adam J L, Duhamel-Henry N and Allain J Y 1997 J. Non-Cryst. Solids 213-14 245
- [25] Strek W, Deren P and Bednarkiewicz A 2000 J. Lumin. 87-9 999
- [26] Martín I R, Yáñes A C, Mendez-Ramos J, Torres M E and Rodriguez V D 2001 J. Appl. Phys. 89 2520
- [27] Bilak V I, Zverev G M, Karapetyan G O and Onischenko A M 1971 JETP Lett. 14 199
- [28] Valiente R, Wenger O S and Güdel H U 2001 Phys. Rev. B 63 165102-1
- [29] Valiente R, Wenger O S and Güdel H U 2000 Chem. Phys. Lett. 320 639
- [30] Nakazawa and Shiyonoya 1970 Phys. Rev. Lett. 25 1710
- [31] Goldner Ph, Pellé F, Meichenin D and Auzel F 1997 J. Lumin. 71 137
- [32] Gamelin D R and Güdel H U 1999 Inorg. Chem. 38 5154
- [33] Strek W, Bednarkiewicz A and Deren P J 2001 J. Lumin. 92 229
- [34] Salley G M and Güdel H U 2002 Phys. Rev. B at press