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New Type of Near-Infrared to Visible Photon Upconversion in Tm^{2+}-Doped $CsCaI_3$

Eva Beurer, Judith Grimm, Pascal Gerner, and Hans U. Güdel*

Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

Received October 4, 2005; E-mail: hans-ulrich.guedel@iac.unibe.ch

Light-emitting inorganic materials, so-called phosphors, are widely used in lighting, display, and imaging applications. We are systematically investigating new materials which can be induced to emit visible (VIS) light by near-infrared (NIR) excitation in a so-called upconversion (UC) process.[1−4] Despite its intrinsic nonlinear character, this excitation mode is promising for future technologies because light-emitting diodes with extremely high energy efficiencies are now available as pump sources. Here we report the discovery of a new type of UC process involving 4f−5d excited states in a new family of Tm^{2+}-doped crystalline halides. The large absorption cross-sections of the relevant transitions make these systems very attractive UC materials.

As described in refs 5 and 6, the ease of synthesis and stability of Tm^{2+}-doped halides increases toward the heavier ones. Single crystals of $CsCaI_3$ doped with Tm^{2+} were grown by the Bridgman technique as described in ref 5. From the absorption and emission spectra, we can conclude that our samples contain no Tm^{3+}. Due to the hygroscopic nature of the materials, the handling occurred under inert atmosphere at all times, and the crystals of the title compound were sealed in an air-tight cell. The ternary halides $CsCaX_3$ ($X = Cl^-, Br^-, I^-$) crystallize in a perovskite structure with octahedral Ca^{2+} coordination. Whereas the chloride and bromide are cubic at room temperature and undergo phase transitions to slightly distorted structures at cryogenic temperatures, $CsCaI_3$ is orthorhombic already at room temperature.[5,7] The resulting distortion of the Ca^{2+} is not relevant for the data reported here, and Tm^{2+} will be considered octahedral in the following. Figure 1 shows part of the absorption spectrum and the luminescence spectrum excited in the NIR at 10 K of $CsCaI_3$ doped with 1% Tm^{2+}. The crystal absorption spectrum was measured on a Cary 6000i, and sample cooling was achieved with a He gas flow technique. The emission spectrum was measured with an experimental setup described in ref 8. The sharp absorption features around 8800 cm^{-1} are readily assigned to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions within the $(4f)^{13}$ electron configuration. The broad and intense absorptions above 12 000 cm^{-1} are due to 4f−5d transitions. These are parity allowed, and they are broad because of the different chemical bonding in the $(4f)^{12}(5d)^1$ electron configuration. The 5d orbitals are more extended in space than the shielded 4f orbitals. Therefore, the promotion of an electron from the 4f to the 5d orbitals leads to an increase in the metal−ligand bond length. From the observed bandwidths and Stokes shifts, we estimate Huang−Rhys factors of roughly 2.5 for these 4f−5d transitions. Excitation at 12 350 cm^{-1} into the lowest tail of the 4f−5d absorptions (see arrow in Figure 1), which corresponds to a "spin-forbidden" transition (see ref 5), leads to intense 5d−4f luminescences. Besides the "normal" Stokes-shifted band B centered at 11 400 cm^{-1}, there is a most unusual band D at 18 400 cm^{-1} which, for a power density of 4.26 kW/cm^2, carries about 11% of the emitted photons and appears as a very bright green light emission to the eye. Whereas band B depends linearly on the power of the excitation laser, the dependence of band D is quadratic. This nonlinear dependence of the emission intensity on power is a typical fingerprint of a nonlinear process such as UC.[1] As shown in Figure 2, pulsed NIR excitation leads to an immediate exponential decay of band D with no rise and a decay time of 5.5 μs at 10 K. The emissions B and D can also be induced by exciting into the strong absorption bands above 19 000 cm^{-1}. In this case, band D dominates band B by a factor of 20 at 10 K. Similar observations were made for Tm^{2+} doped into the isostructural $CsCaCl_3$ and $CsCaBr_3$ lattices.[5]

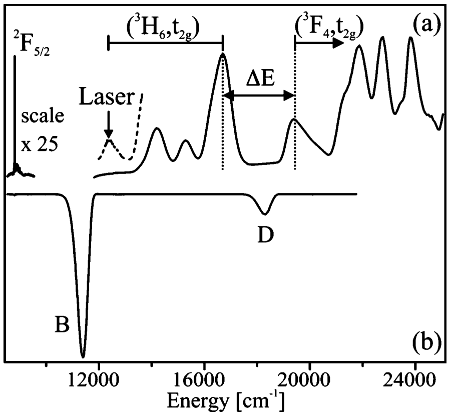

Figure 1. (a) Single-crystal absorption spectrum at 10 K of $CsCaI_3$:1% Tm^{2+} and (b) upconversion emission spectrum at 10 K excited at 12 350 cm^{-1} with an excitation power density of 4.26 kW/cm^2 (see arrow in a). The dashed line in (a) is the onset of the UC excitation spectrum. The labels and ΔE are explained in the text.

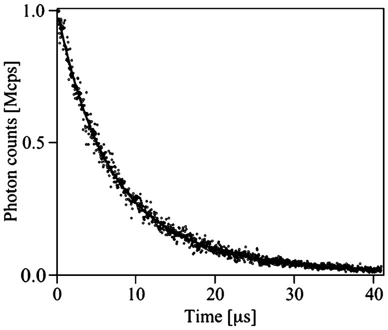

Figure 2. Time dependence of the upconversion band B at 10 K after a 10 ns excitation pulse at 14 350 cm^{-1}. The line is an exponential fit with a decay time of 5.5 μs.

These experimental findings clearly show the existence of an efficient upconversion process in the title compound, as illustrated in Figure 3. Besides the lowest-energy 4f−5d state in the NIR, there is a higher metastable 4f−5d state capable of light emission. It can be reached by one or both of two mechanisms: a sequence of ground-state absorption (GSA) and excited-state absorption (ESA) steps (GSA/ESA) or by two GSA steps on adjacent Tm^{2+} ions followed by an energy-transfer step (GSA/ETU). The immedi-

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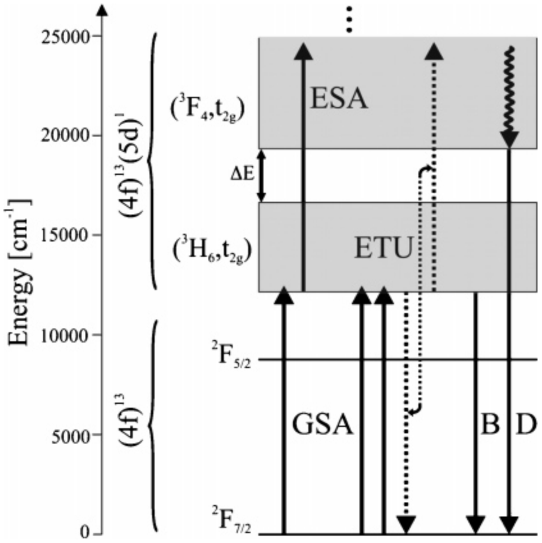

Figure 3. Energy diagram of Tm^{2+} in $CsCaI_3$ with the relevant excitation and relaxation processes. Straight arrows represent radiative processes, dotted and curly arrows are nonradiative processes. The arrows B and D correspond to the emission bands in Figure 1. GSA, ESA, and ETU stand for ground-state absorption, excited-state absorption, and energy-transfer upconversion, respectively.

ate decay of the UC emission after pulsed excitation shown in Figure 2 clearly demonstrates a dominant contribution from a GSA/ESA sequence. Such UC processes are widespread and well understood within the 4f−4f energy levels of trivalent lanthanides,[9] but it is most unusual and without precedent to find emission from a higher 4f−5d state which can be efficiently excited by UC.

Little work has been reported so far on the 4f−5d excited states and light emission from these states in Tm^{2+},[5,10−12] but this ion, doped into heavy halide lattices, has a number of extremely favorable properties, which enable the upconversion phenomenon. The 4f−5d states lie in a spectroscopically easily accessible region, in contrast to the trivalent lanthanides, where they are usually situated in the vacuum UV. Tm^{2+} has only one 4f−4f excited state, $^2F_{5/2}$, situated around 8800 cm^{-1}. Compared to oxides and fluorides, the vibrational energies of $CsCaX_3$ ($X = Cl^-, Br^-, I^-$) are significantly reduced. $CsCaI_3$ has an estimated highest phonon energy of $\hbar\omega_{max} \simeq 170$ cm^{-1}. This essentially determines whether a higher excited state is metastable and thus emissive. In the absorption spectrum in Figure 1a, we observe an energy gap, ΔE, between the highest absorption of the group of bands labeled $(^3H_6,t_{2g})$ and the lowest band of the $(^3F_4,t_{2g})$ absorptions; see also Figure 3. About 16 quanta of the highest-energy vibration are required to bridge this $\Delta E \simeq 2700$ cm^{-1} in $CsCaI_3{:}Tm^{2+}$. In $CsCaCl_3{:}Tm^{2+}$ and $CsCaBr_3{:}Tm^{2+}$, the corresponding numbers of $\Delta E/\hbar\omega_{max}$ are 9 and 12 quanta, respectively. The rate constant for nonradiative relaxation across a gap decreases exponentially with $\Delta E/\hbar\omega_{max}$, and in the title compound, the radiative green transition D in Figure 3 is highly competitive up to about 250 K. Above this temperature, the green emission decreases rapidly, not due a decrease in the UC efficiency but an increase in the nonradiative relaxation across ΔE; however, it remains visible by eye up to room temperature.

Numerous states arise from the $(4f)^{12}(5d)^1$ electron configuration. The octahedral crystal field splits the 5d orbitals into t_{2g} and e_g sets, separated by $10Dq \simeq 8500$ cm^{-1} in the title compound. All the absorption bands below 22 000 cm^{-1} thus belong to the $(4f)^{12}(t_{2g})^1$ electron configuration. The splitting within the $(4f)^{12}$ electron configuration resulting from Coulomb repulsion and spin−orbit coupling corresponds to the known splitting of the 4f levels in Tm^{3+}. We can thus assign the first multiplet of absorption bands in Figure 1 to $(^3H_6,t_{2g})$. This is separated by $\Delta E \simeq 2700$ cm^{-1} from the next higher multiplet, which is assigned to $(^3F_4,t_{2g})$. At higher energies, there is increasing overlap of the multiplets, and there exists no energy gap as large as ΔE. The energy splittings within a multiplet, such as $(^3H_6,t_{2g})$, arise from the Coulomb repulsion of the 4f and 5d electrons and the spin−orbit coupling of the 5d electron. The action of the Coulomb repulsion is most apparent in the $(^3H_6,t_{2g})$ as it splits the multiplet into a set of high-spin $S = {}^3/_2$ and a set of low-spin $S = {}^1/_2$ states. Emission B corresponds to the spin-forbidden emission from $(^3H_6,t_{2g})$ $S = {}^3/_2$ to the $^2F_{7/2}$ ground state. In the higher energy multiplet $(^3F_4,t_{2g})$, a distinction between spin-forbidden and spin-allowed transitions is no longer possible.[5]

Efficient UC in the title compound is enabled by ground- and excited-state absorption processes with high cross-sections at the excitation energy of 12 350 cm^{-1} and the presence of two long-lived 4f−5d excited states. The existence and longevity of the higher excited state is the real key, and it is due to the low phonon energies of the material. At room temperature, the green UC emission is significantly quenched, and no immediate application of this particular material is likely. However, the present study demonstrates that UC processes are not restricted to 4f−4f transitions in lanthanides. In recent years, we have significantly broadened the class of materials in which UC can be induced.[1−4,13] Besides d−d transitions in some selected transition metal systems, the combination of d and f elements in the same compound was shown to lead to new types of UC. We consider the present study as a first step to explore the field of UC using 4f−5d excited states in lanthanides.

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