

Spectroscopic Characterization by Up conversion of $\text{Ho}^{3+}/\text{Yb}^{3+}$ codoped CdF_2 Single Crystal

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Abstract

Single crystal of CdF_2 codoped with the couple $\text{Ho}^{3+}/\text{Yb}^{3+}$ with good optical quality were grown by a Bridgman technique after purification of the starting materials. Emission spectra are recorded at room temperature under UV and NIR excitation. The kinetics of the green and red emissions arising from both ($^5\text{F}_4$, $^5\text{S}_2$) and $^5\text{F}_5$ excited states of Ho^{3+} ions are analyzed in the frame of $\text{Ho}^{3+} \rightarrow \text{Ho}^{3+}$ and $\text{Yb}^{3+} \leftrightarrow \text{Ho}^{3+}$ energy transfers. The luminescence decays are parametrized using Inokuti-Hirayama model considering dipole-dipole interaction, in the case of UV excitation and also NIR excitation for the green emission, leading to a R_0 critical transfer distance of 9-11 Å. **The kinetics of the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ red upconverted emission is analyzed and discussed using a rate equation model.**

Keywords: cadmium fluoride, holmium and ytterbium, upconversion, kinetics, Inokuti-Hirayama, rate equation model

1. Introduction

In recent years visible and ultraviolet solid state lasers have attracted much attention due to the rapid growth of applications requiring tailored wavelength sources, such as full-color displays, optical data storage and biomedical instruments. Among various investigated systems, rare-earth-doped low phonon crystals or glasses have been reported as promising media for fiber and planar optical amplifiers and lasers [1]. Among the several investigated crystals, fluorides of the elements of group 2 of the periodic table are widely used as laser host material. The rare earth ions are usually applied as activators (dopants) for these fluorides. CdF_2 belongs to fluorite family of MF_2 ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{Hg}^{2+}$). The distinction of Cd belongs to the other M ions is the increase in nucleus charge comparatively to Sr by ten units, which gives rise to contraction of atom core. As result, the ionic size of Cd^{2+} is much less than that of Sr^{2+} . CdF_2 crystal can accommodate easily all trivalent rare-earth ions [2]. The substitutional RE^{3+} ions replace Cd^{2+} ions and the charge compensation is achieved at some distance by interstitial F_i^- ions. The presence of these ions increases the symmetry of the crystal field at the substituted trivalent ion site, making it remains mainly cubic in CdF_2 . In addition, the Raman spectrum of CdF_2 crystal at room temperature consists of a strong depolarized line peaking at 315 cm^{-1} [3].

Using the energy upconversion (UC) phenomenon from rare earth ions is an effective approach to obtain visible laser under IR pumping. UC luminescence materials have also received special attention because of their prospective use in solar NIR concentrators for photovoltaic exploitation, IR sensing and biological labelling [4, 5]. In several UC processes Yb^{3+} ion is chosen as a sensitizer because of its simple two level energy structure and its high absorption cross-section at 980 nm which matches with the commercially available high power diode lasers along with its effective energy transfer capability to codoped activator ions. On the other hand Ho^{3+} ions have very distinct characteristic emission transitions both in the visible and IR wavelength range [6]. **Yb^{3+} ion is used as sensitizer to augment the UC process since absorption cross-section of Yb^{3+} for NIR radiation is much higher than Ho^{3+} .** The synthesis and spectroscopic properties of CdF_2 codoped $\text{Ho}^{3+}/\text{Yb}^{3+}$ has already been reported [7]. However, the UC in this system was never reported. This is the subject of the present report where the emission of the Ho^{3+} ions *via* an NIR excitation provided by commercial 980 nm diode or by OPO pulsed laser for checking the dynamical processes ions and also in the UV wavelength range for comparison.

2. Sample properties and preparation

Cadmium difluoride (CdF_2) compound crystallizes in a face centered cubic structure, having the fluorite type and belonging to $Fm3m$ (225) space group with four unit formula and cell parameter of 5.3810 \AA . The crystallographic sites are Cd^{2+} (4a) and F^- (8c) with C_{4v} site symmetry for Cd^{2+} [8-10]. The ionic radius of Ho^{3+} , Yb^{3+} and Cd^{2+} is 89.4 pm, 85.8 pm and 95 pm, respectively. The crystal structure of CdF_2 is reported in Fig.1.

The CdF_2 single crystals are grown by use of the Bridgman technique from a vacuum furnace in fluorine atmosphere. The CdF_2 commercial powder, coming from Merck, is purified by repeated growth of simple crystals. After the purification step, the holmium and ytterbium doping ions are introduced in the form of trifluoride powders, HoF_3 and YbF_3 , with nominal concentration of 1% for both ion ones. The mixture is heated under vacuum for 2 h with progressive temperature increase until $400\text{ }^\circ\text{C}$. The pulled crystal has more than 8 mm in diameter and 10–25 mm in length. Checked in polarized light, it is exempt of makles and crackles. It could easily cut into laser bulk single crystal with high optical quality. The sample

used for optical measurements was cut and polished to flat and parallel faces with 4.81 mm thickness (see inset of Fig.1).

3. Experimental procedure

All the measurements were carried out at room temperature.

Luminescence emission spectra and decays were recorded using a pulsed Nd:YAG OPO Ekspla NT342A laser (210-2600 nm, 3–5 ns pulse duration, 10 Hz, 5 cm⁻¹ line width, 0.3 mJ-20 mJ in the UV and NIR range). The emitted photons were detected at right angle to the excitation and analyzed via an Edinburgh FLS980 spectrometer (Czerny-Turner monochromator, 300 mm focal length, 1200 grooves mm⁻¹ grating and minimum pass band of 0.1 nm) equipped with Hamamatsu R928P PMT (200–850 nm range). The CW-NIR excitation is provided by a 980 nm beam of CW- diode laser CNI Model FC-980nm-4W. The UC emitted photons by the crystal are detected at right angle from the excitation and analyzed through a Horiba/Jobin-Yvon monochromator (Triax 550) combined with a cryogenically cold charge coupled device (CCD) camera (Horiba/Jobin-Yvon Symphony LN2 series).

4. Results and discussion

4.1: Steady state luminescence

4.1.1: Pulsed excitation

The recorded emission spectra under OPO pulsed laser at room temperature are reported in Fig.2, under excitation at 360 nm which corresponds to the $^5I_8 \rightarrow ^5G_4$ absorption transition of Ho³⁺ and in Fig.3, under excitation at 980 nm which is resonant within the $^2F_{7/2} \rightarrow ^2F_{5/2}$ absorption transition of Yb³⁺.

The Stokes emission spectrum exhibits the emission bands peaking at 418, 486, 546, 580, 646 and 750 nm. On the basis of absorption spectrum reported in [7] and fluorescence spectra reported for LaF₃:Ho³⁺ [11] and CaF₂:Ho³⁺ [12] the five first emission bands correspond respectively to the transitions $^5G_5 \rightarrow ^5I_8$, $^5F_3 \rightarrow ^5I_8$, $(^5F_4, ^5S_2) \rightarrow ^5I_8$, $^5G_4 \rightarrow ^5I_6$, $^5F_5 \rightarrow ^5I_8$ (with possible overlap with the $^5F_3 \rightarrow ^5I_7$ [12]). The emission at 750 nm could be assigned to the $^5I_4 \rightarrow ^5I_8$ or to the $(^5F_4, ^5S_2) \rightarrow ^5I_7$ transitions or to the overlap of the two transitions, but the transition probability of the first one is very much smaller than that of the second [13]. On the other hand, the rise and decay of the luminescence at 750 nm, are similar with that measured for the time dependence of the 546 nm emission band (reported in the next section) which originates from the same $(^5F_4, ^5S_2)$ levels. This also supports the assignation of the 750 nm emission band to the $(^5F_4, ^5S_2) \rightarrow ^5I_7$ transitions. The UC emission spectrum exhibits mainly the $(^5F_4, ^5S_2) \rightarrow ^5I_8$, $^5F_5 \rightarrow ^5I_8$ and $(^5F_4, ^5S_2) \rightarrow ^5I_7$. However, the $^5F_3 \rightarrow ^5I_8$ emission is also recorded with very weak intensity as observed in the magnified part of the spectrum of Fig.3. For both spectra, the green emission related to the $(^5F_4, ^5S_2) \rightarrow ^5I_8$ transition is the most intense. The intensity ratio between green (546 nm) and red (646 nm) is ~ 3.8 under UV excitation and reaches ~ 13 under NIR pulsed excitation. Based on the above results, down conversion and up-conversion excitation and luminescence processes are proposed, as shown in Fig.4. The following mechanism is proposed for explaining the violet, blue, green and red emissions under excitation at 360 nm. Ho³⁺ absorbs UV photons to 5G_4 level, followed by nonradiative relaxations to 5G_5 , 5F_3 , 5F_2 and 3K_8 levels in turn via multiphonon relaxation. The 5F_2 state relaxes to the 5F_3 and $(^5F_4, ^5S_2)$ states in cascade, which emit the blue 486 nm ($^5F_3 \rightarrow ^5I_8$) and green 546 nm ($^5F_4, ^5S_2 \rightarrow ^5I_8$) radiations and also the red 750 nm ($^5F_4, ^5S_2 \rightarrow ^5I_7$)

emission. The partial population at 5G_5 level directly relax to 5I_8 states in cascade, which emit the violet 418 nm ($^5G_5 \rightarrow ^5I_8$) radiation. The populations at (5F_4 , 5S_2) levels can be followed by nonradiative relaxation to 5F_5 state from which the 646 nm ($^5F_5 \rightarrow ^5I_8$) red emission arises. The other possible channel for the feeding of the 5F_5 level is the resonant cross relaxation ($^5F_3 + ^5I_8 \rightarrow ^5F_5 + ^5I_7$) as reported for $YF_3: Ho^{3+}$ [14]. The band peaking at 580 nm is due to radiative relaxation for part of the population in 5G_4 to 5I_6 . In the case of NIR excitation, as reported in several works, the (5F_4 , 5S_2) excited state is mainly populated via the ($^2F_{5/2}$, 5I_6) \rightarrow ($^2F_{7/2}$, (5F_4 , 5S_2)) ETU process, followed by nonradiative relaxation to 5F_5 giving rise to green and red emissions at 546, 646 and 750 nm [15]. However, it seems that the mechanism responsible of for the $Ho^{3+}:^5F_5$ UC emission, as reported in $LiYF_4:Ho^{3+}$ [16], involves only Ho^{3+} ions, with no Yb^{3+} contribution. An alternative mechanism for the 5F_5 UC luminescence involving only Ho^{3+} ions is outlined below. The weak blue emission at 486 nm ($^5F_3 \rightarrow ^5I_8$) can also arise by two photon process, as observed in the case of $NaYF_4:Yb^{3+}, Ho^{3+}$ [15], instead of four photon process. No emissions were observed from the upper 5G_4 and 5G_5 , since in that case the UC process needs a simultaneous absorption of more than three NIR photons.

4.1.2: UC emission under CW excitation

In order to understand the UC mechanisms responsible for emerging the visible radiations, comparatively to pulsed excitation, a detailed discussion of the energy level diagram, as shown in Fig.4 has been considered. Fig.5 reports the measured (5a) and normalized (5b) emission spectra of $CdF_2:1\%Ho^{3+}, 1\%Yb^{3+}$ under CW excitation at 980 nm. Only the visible green and red UC emissions, related to the 5F_4 , $^5S_2 \rightarrow ^5I_8$ and $^5F_5 \rightarrow ^5I_8$ transitions of Ho^{3+} , are considered. However the intensity ratio $I(546)/I(646)$ between the green (5F_4 , 5S_2) $\rightarrow ^5I_8$ transition and the red $^5F_5 \rightarrow ^5I_8$ transition varies according to the pulsed and the CW excitation regimes, since on UC recorded spectra it reaches around ~ 4 and ~ 13 respectively. Moreover, this ratio is independent on the power pump of the NIR laser diode. Such difference indicates that the related dynamics between the green and red emission is different. Such difference will be discussed in the next section. In addition, usually, UC emission at 646 nm (red) occurs when the 5F_5 level is populated by non-radiative relaxation from the upper ($^5F_4 + ^5S_2$) excited state after it relaxes radiatively to the 5I_8 ground state by emitting red photons. Thus, the decrease in the intensity of the red emission, at 980 nm excitation, is an indication that the non-radiative relaxation from the ($^5F_4 + ^5S_2$) excited state to the lower 5F_5 level is weak. Another possibility is that a back transfer connecting the $Ho^{3+}: ^5F_5$ level with the $^2F_{5/2}$ level of Yb^{3+} can occurs, leading to the decrease of the intensity arising from this level. This means that the 5F_5 level is more depopulated during two successive laser pulses than it's feeding from the de-excitation of the (5F_4 , 5S_2) levels.

In Fig.6, we have plotted the power dependence of the intensity of the green emission under a 980 nm excitation. The power of the diode is just an indication and is not corrected to provide the effective density in ions excited by cm^3 . For an unsaturated up-conversion process, the number of photons which is responsible for the conversion mechanism can be calculated by [17]:

$$I_f \propto P^n \quad (1)$$

where I_f is the fluorescent intensity, P is the pump power, and n is the number of the diode laser photons required. Double logarithmic plot of the relationship between pump energy and up-conversion emission integral intensities of the samples gives the slope n .

The log-log plot of the results leads to slope close to 2 which imply that a quadratic dependence indicating the mechanism involved is two photon UC processes as reported in

several papers related to the UC in Yb³⁺-Ho³⁺ pairs embedded in glasses or crystals. Same result is obtained by considering the red emission peaking at 646 nm. Saturation is clearly observed when the power supply is fixed at value higher than ~ 260 mW/cm².

4.2: Luminescence decay analysis

Due to the limitation in emission detection of our experimental set-up, only the decays of Ho³⁺ in the visible range were recorded.

The decay of green emission, under UV excitation, is reported in Fig.7. It exhibits a rise time, as shown in the inset of this Fig.7, which corresponds to feeding of the (⁵F₄, ⁵S₂) excited state from the upper levels ones. This rise time is followed by non-exponential decaying indicating that an energy transfer occurs from this level. In first approximation, the decay is fitted by simple sum of exponential functions, one in the rise and two in the tail of decay, leading to the time constants of 6.6 μs in the rise and 67 and 250 μs in the long decaying part (Table 1). The average lifetime in case of a bi-exponential decay can be calculated using the equation [18]:

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

The derived τ_{av} from the fit is around ~ 202 μs (Table 1). All these values are lower than the estimated radiative lifetime reported for this excited state which is of 400 μs; value which is extracted from the analysis by Judd-Ofelt theory of the absorption spectrum of CdF₂:1% Ho³⁺, 1%Yb³⁺ [7]. The reducing of the lifetime and exhibiting non-exponential shape is clearly an indication that energy transfer occurs, between the Ho³⁺ ions, or from Ho³⁺ ions to Yb³⁺ ions, also present in the host, as reported in the case of CaSc₂O₄: Ho³⁺,Yb³⁺ [19]. To understand the donor–acceptor interactions in the present host, well established theoretical model like ‘Inokuti–Hirayama’ (I-H) for direct energy transfer [20] can be used. Such fitting have been applied on the decay profiles of Ho³⁺ ions in the presence of acceptor, Ho³⁺ or Yb³⁺ ions by considering the ion interactions are dipole–dipole in nature due to the low concentration of active ions in the crystal CdF₂. When the energy transfer process is the cross-relaxation within a system of identical ions, the acceptor concentration equals the total concentration of activators.

In CdF₂ crystal, the concentration of active ions is of 2.55x10²⁰ ions/cm³ [21], assuming the nominal doping level of 1% for both Ho³⁺ and Yb³⁺, which becomes 5.10x10²⁰ ions/cm³ when we consider that both ions can act as acceptors, since an Ho³⁺ → Yb³⁺ energy transfer exists [22, 23]. This is due to the fact that in addition of radiative decay, Ho³⁺ ions in (⁵F₄, ⁵S₂) level can also transfer their excitation energy to Yb³⁺ ions through the following cross-relaxation process:



For such purpose, the following equation where used to fit the decay of (⁵F₄, ⁵S₂) → ⁵I₈:

$$I(t) = I_0 \exp\left[-\frac{t}{\tau_0} - \frac{C_A}{C_0} \Gamma\left(1 - \frac{3}{s}\right) \left(\frac{t}{\tau_0}\right)^{\frac{3}{s}}\right] \quad (4)$$

where t=time; τ_0 =lifetime for low acceptor ion concentration; s= 6, 8, or 10 for dipole–dipole, dipole–quadrupole, or quadrupole–quadrupole interactions, respectively; and Γ is Euler’s gamma function : $\Gamma(1-3/s)$ =1.77, 1.43, and 1.30 for s = 6, 8, and 10, respectively. C_A is the concentration of acceptor ions, and C_0 is the critical concentration given by $C_0 = 3 / (4\pi R_0^3)$ (R_0

is the critical transfer distance defined as that separation at which the rate of energy transfer between a donor–acceptor pair is equal to the intrinsic decay rate τ_0^{-1}). The donor–acceptor energy transfer parameter C_{DA} is related to R_0 as $C_{DA} = R_0^s \tau_0^{-1}$. When we set $s = 6$ ($\Gamma(1-3/6) = 1.77$), and treat C_A/C_0 and τ_0 as adjustable parameters, the best fits of Eq. (4) to the experimental data are achieved (see Fig.7), which leads us to conclude that the interaction between $\text{Yb}^{3+}/\text{Ho}^{3+}$ ions ($\text{Ho}^{3+} \rightarrow \text{Ho}^{3+} \rightarrow \text{Yb}^{3+}$) occurs *via* a dipole–dipole interaction. The derived and calculated values are gathered in Table 2.

However, the derived τ_0 value is 631 μs , value which is quite larger than that estimated in [7] (400 μs). Indeed, the use of the estimated τ_0 value leads to unsatisfactory fitting. Since we don't have a weakly doped crystal with Ho^{3+} , we can refer to the value of the radiative lifetime measured in CaF_2 : 0.01% Ho^{3+} [24]. In this crystal, the green fluorescence related to the $(^5\text{F}_4, ^5\text{S}_2) \rightarrow ^5\text{I}_8$ emission of Ho^{3+} , at room temperature under pulsed excitation at 488 nm, is characterized by single exponential decay with time constant of 666 μs . This value is close to that we have derived from our fitting (631 μs), confirming that the use of I-H model reproduces well the luminescence decay mechanism of the green emission. Then, the results of the fits show clearly that the luminescence dynamics process is more related to direct energy transfer than energy migration followed by transfer to acceptor.

In Fig.8, we have reported the decay of the red emission peaking at 646 nm, under UV excitation at 360 nm, arising from the $^5\text{F}_5$ excited level of Ho^{3+} ions. The decay exhibits no rise time indicating fast feeding of this level under UV excitation. The time constants derived using bi-exponential fitting are of ~ 47 and ~ 103 μs (Table 1), values which are largely shorter than that reported for the green emission peaking at 546 nm (67 and 250 μs with $\tau_{av} = 202$ μs , Table 1). The obtained τ_{av} using Eq.2 is of ~ 85 μs . **It is not so far from that measured in LiYF_4 :2% Ho^{3+} , 2% Yb^{3+} where it reaches ~ 102 μs [16].** As in the case of the green emission, the decay was also fitted using I-H model. The derived and calculated values leading to the best fit are gathered in Table 1. The value of τ_0 which leads to this best fit is 125 μs . This value of pure radiative lifetime of the $^5\text{F}_5$ excited level is largely lower than that derived from J-O analysis of absorption spectra in several fluorides, crystals of glasses which is between 1.2 ms and 400 μs . Notably this value is estimated as ~ 549 μs in CdF_2 :1% Ho^{3+} , 1% Yb^{3+} [7]. Only few reports exist in the literature giving the direct measurement of this radiative lifetime, notably in weakly doped sample containing Ho^{3+} ions. The only value which is close to our derived estimation for this radiative lifetime is found for $\alpha\text{-NaYF}_4$: Ho^{3+} , Yb^{3+} [25] in which the decay of the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ emission at room temperature is fitted by a single exponential in the singly doped $\alpha\text{-NaYF}_4$: 0.5% Ho^{3+} with time constant of 117 μs , value which is close to our derived τ_0 radiative time constant of the $^5\text{F}_5$ excited level (125 μs). To prove that our fit is consistent with the experimental results, we need to grow singly doped Ho^{3+} crystal with very low concentration, less than 1%. However, comparing the values derived from the fits by I-H for both green and red emissions, we observe that the C_{DA} (energy transfer microparameter) and R_0 critical transfer distance are quite always the same, **around $\sim 10^{-39} \text{ cm}^6\text{s}^{-1}$ and ~ 9 Å and in the same order to that found in LiYF_4 : Ho^{3+} [26] ($1.2 \times 10^{-38} \text{ cm}^6/\text{s}$ and 14.2 Å for d-d interaction respectively)** and in several crystals or glasses activated by Ho^{3+} or Ho^{3+} - Yb^{3+} ion pairs [27]. This means that this value is a characteristic parameter which can be considered in the design of Ho^{3+} - Yb^{3+} pairs activated luminescent materials (optimum average distance between the active ions).

Fig.9 reports the decay of the UC green emission under excitation at 980 nm. As in the case of UV excitation the decay, in the first approximation, is fitted by exponential function in the rise and by bi-exponential function in the tail of the decay. The derived parameters from the fit are of 8.4 μs in the rise and 97 and 296 μs in the tail of the decay, leading to a τ_{av} of ~ 219 μs using Eq.2 (Table 1). The rise time and τ_{av} are in the same order than that measured under

UV excitation, 6.6 μs versus 8.4 μs , and 202 μs versus 219 μs respectively. Such observations seems to indicate that the feeding of the ($^5\text{F}_4$, $^5\text{S}_2$) level is quite similar under the UV or NIR excitations. Under UV excitation, the ($^5\text{F}_4$, $^5\text{S}_2$) level is filled by the relaxation from the upper states mainly $^5\text{G}_5$, $^5\text{F}_3$, levels from which an emission is observed as depicted in Fig.2. The feeding of the ($^5\text{F}_4$, $^5\text{S}_2$) level under NIR excitation needs in the first step a ground state absorption (GSA) in the Yb^{3+} ions followed by an $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer which promotes the Ho^{3+} from their ground state $^5\text{I}_8$ to the phonon excited side states of the $^5\text{I}_6$ excited level from which, an excited state absorption (ESA) occurs by the absorption of second photon provided by the de-excitation of Yb^{3+} ions. After the two step excitation, inside of the Ho^{3+} ions (cooperative sensitization mediated by the $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer), the ($^5\text{F}_4$, $^5\text{S}_2$) level is filled. This means that in that case, the rise time reflects more probably the decay time of the $^5\text{I}_6$ level which acts as reservoir for the second step and also perhaps that of the $^2\text{F}_{5/2}$ level of Yb^{3+} ions and that of the $^5\text{F}_3$ level, since $2 \times ^2\text{F}_{5/2} (\text{Yb}^{3+}) \rightarrow ^5\text{F}_3 (\text{Ho}^{3+}) \rightarrow (^5\text{F}_4, ^5\text{S}_2) (\text{Ho}^{3+})$ leads to the observation of the emission arising from the $^5\text{F}_3$, however with very weak intensity as observed on Fig.3. Nevertheless, the intrinsic radiative lifetime of the Yb^{3+} : $^2\text{F}_{5/2}$ level is expected to be long, as reported in the case of $\text{Ca}_{1-x}\text{Yb}_x\text{F}_{2+x}$, in which the measured value at $x=0.2$ is ~ 3 ms [28]. In addition, the derived absorption strength of the $^5\text{I}_8 \rightarrow ^5\text{I}_6$ transition of Ho^{3+} from absorption spectra of $\text{CdF}_2:\text{Ho}^{3+}$ is of $\sim 9.2 \times 10^{-20} \text{ cm}^{-2}$ [7] which is high and comparable to that of the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition of Yb^{3+} , measured around $\sim 1.9 \times 10^{-20} \text{ cm}^2$ [29]. Such considerations lead to suppose that the observed build-up on the decay of the green emission is more probably related to feeding from the $^5\text{I}_6$ metastable level by ETU process through the ($^2\text{F}_{5/2}$, $^5\text{I}_6$) \rightarrow ($^2\text{F}_{7/2}$, $^5\text{S}_2/^5\text{F}_4$), as suggested in [16] for $\text{LiYF}_4:\text{Yb}^{3+}$, Ho^{3+} , in addition of that from the $^5\text{F}_3$, which can perhaps explain why the rise is quite the same under both UV and NIR excitations.

On the same Fig.9, we have reported the fitting of the UC green emission using I-H model. In this case, we have considered that only the Ho^{3+} ions acts as acceptors, considering that $\text{Ho}^{3+} \rightarrow \text{Yb}^{3+}$ energy back transfer is expected to be weak. The derived and calculated parameters from the fit are reported in Table 2. As in the case of UV excitation, satisfactory fit is obtained using τ_0 value of 631 μs , derived from the UV excited green emission using I-H model, with reliability factor of 98.7%. This factor is notably enhanced when we use 590 μs as the τ_0 value, since this reliability factor reaches 99.8%. The two values of τ_0 lie in the same numerical range. In addition, the calculated R_0 critical transfer distance (~ 11 Å) is similar to that found under UV excitation, in agreement with our assessment that the decaying dynamics from the ($^5\text{F}_4$, $^5\text{S}_2$) excited level is independent on the excitation used, UV or NIR.

Fig.10 shows the luminescence decay of the red emission ($^5\text{F}_5 \rightarrow ^5\text{I}_8$) under NIR excitation at 980 nm. The experimental points are largely dispersed due to the weak luminescence intensity recorded under our setup with pulsed excitation laser. The decay consists of rise time followed by exponential decaying. The time constants derived from the fit are of 15 μs in the rise and 43 μs in the tail. These values diverge notably from that reported under NIR excitations in $\text{LiYF}_4:0.5\% \text{ Ho}^{3+}$, (27 μs and 105 μs respectively under excitation at 890 nm into the $^5\text{I}_5$ level) [30] and in $\text{LiYF}_4:2\% \text{ Yb}^{3+}$, 20% Ho^{3+} (20 μs and 770 μs respectively under excitation at 1150 nm into the $^5\text{I}_6$ level) [16], while for such compounds, direct excitation of the $^5\text{F}_5$ level lead to decays times of 105 μs [30] and 102 μs [16]. Surprisingly, it appears from these two works [16, 30] that the rise time of the UC red emission is quite similar despite that the lifetimes of the $^5\text{I}_6$ and $^5\text{I}_5$ excited states are notably different: 1.6 ms [12, 16] and 20 μs [12, 30] respectively. The situation is then different than that of the green emission for which the decays are quite similar under both UV and NIR excitations. Under UV excitation, the feeding of the $^5\text{I}_6$ level is provided by de-excitation from upper excited states, such as $^5\text{G}_4$, $^5\text{F}_3$, $^5\text{F}_5$, ($^5\text{F}_4$, $^5\text{S}_2$) [12]. Under NIR excitation, the Ho^{3+} ions are promoted in this

excited state by direct energy transfer from Yb^{3+} ions. Part of these Ho^{3+} ions in their $^5\text{I}_6$ excited state become not available for their feeding by the de-excitation from the upper levels. Such assumption is supported by the increase of τ_{av} of the green emission under NIR excitation (Table 1) since the non-radiative rate of this emission is decreased. Another consequence of the direct feeding of the $^5\text{I}_6$ level is the increase the cross-relaxation (CR) connecting the $^5\text{F}_5$ and $^5\text{I}_6$ levels ($^5\text{F}_5, ^5\text{I}_8 \rightarrow ^5\text{I}_6$) which provides de-excitation channel, leading to the decrease of the intensity of the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ emission under pulsed excitation since this CR is expected to be efficient occurring during low repetition-rate nanosecond pulse excitation (10 Hz, 5ns).

The shape of the decay of the red emission arising from the $^5\text{F}_5$ level under NIR excitation is clearly different from that recorded under UV excitation. Based on the luminescence processes proposed, as shown in Fig.4 and on the discussion made above; we can then consider that the UC process can be represented by a simple three level system where the intermediate state **at the present stage can be $^5\text{I}_7$ or $^5\text{I}_6$ even the $^5\text{I}_5$ without further distinctions.** The $^5\text{I}_7$ level is populated *via* cross relaxation from the $^5\text{I}_6$ level ($^5\text{I}_8, ^5\text{F}_5 \rightarrow ^5\text{I}_6, ^5\text{I}_7$) more probably than by non-radiative relaxation from the $^5\text{I}_6$ [12] **despite that this non-radiative relaxation seems to be not very efficient as suggested for $\text{LiYF}_4:\text{Yb}^{3+}, \text{Ho}^{3+}$ [16]. Moreover two Ho^{3+} ions in the $^5\text{I}_6$ excited state can interact *via* the $(^5\text{I}_6, ^5\text{I}_6) \rightarrow (^5\text{I}_7, ^5\text{I}_5)$ leading to the population of the $^5\text{I}_5$ level.** This means that mechanism of ion-ion interaction between Ho^{3+} ions is responsible for populating of $^5\text{F}_5$ level. The use of **one of these** levels as the intermediate state comes from the fact that the Log-Log plot of the red emission under CW-excitation versus the power of the NIR laser diode leads to quadratic dependence. In this simplified model (see inset of Fig.4), the time dependent populations of different energy states can be described by the following rate equations [31] valid in the case of ion-ion interaction between two identical ions [32]:

$$\frac{dN_1}{dt} = N_0 AI - W_1 N_1 - W_T N_1^2 \quad (5)$$

$$\frac{dN_2}{dt} = \frac{1}{2} W_T N_1^2 - W_2 N_2 \quad (6)$$

where N_0 , N_1 and N_2 stand for the population densities of the ground state $^5\text{I}_8$ and excited states **Is (Is for intermediate state)** and $^5\text{F}_5$ respectively. W_1 and W_2 are the decaying rate of the **Is** and $^5\text{F}_5$ levels. AI is the product of the absorption cross-section with the laser intensity and W_T is ETU rate. The system of these two equations has no analytical solution and can be solved through numerical simulations as reported for example in [33, 34]. However, in the low pumping regime the term $W_T N_1^2$ can be neglected in Eq.5 [32]. In these conditions, the integrated intensities $I_1(t)$ and $I_2(t)$ are directly proportional to the populations

$$I_1(t) = I_1(0)e^{-W_1 t} \quad (7)$$

$$I_2(t) = \frac{1}{2} \frac{W_T I_1^2(0)}{W_2 - 2W_1} (e^{-2W_1 t} - e^{-W_2 t}) \quad (8)$$

Eq.8 refers to the up converted emission and can be rewritten using $W_1 = 1/\tau_1$ and $W_2 = 1/\tau_2$

$$I_2(t) \propto \frac{\tau_1 \tau_2}{(\tau_1 - 2\tau_2)} \left(e^{-2t/\tau_1} - e^{-t/\tau_2} \right) \quad (9)$$

were τ_1 and τ_2 stand for the values of the kinetics of both $^5\text{I}_6$ intermediate level, and $^5\text{F}_5$ emitting state, obtained under direct laser excitations in the singly Ho^{3+} doped material, neglecting a possible de-excitations, by energy transfer to unwanted acceptors, or by cross-relaxations. The rise is always attributed to the level which exhibits more fast decay [32]. On Fig.10, we have reported the fitting of the decay of the UCL from $^5\text{F}_5$ level under NIR excitation using Eq.9. The values derived from the best fit are of 15 μs in the rise and 43 μs in the tail as reported above (Table 1). We have no information about the decay times of the $^5\text{I}_7$, $^5\text{I}_6$ and $^5\text{I}_5$ levels in $\text{CdF}_2:\text{Ho}^{3+}$. If we consider that $\tau_1 > 2\tau_2$ Eq.9 leads to lifetime nearly the half of that for the considered state under Stokes excitation. It seems that this situation is fulfilled considering the $^5\text{F}_5$ level since the estimated lifetime is 85 μs (Table 1), $\sim 100 \mu\text{s}$ in $\text{LiYF}_4:\text{Ho}^{3+}$ [30] and $\text{LiYF}_4:\text{Yb}^{3+}, \text{Ho}^{3+}$ [16] : $85 \mu\text{s}/2 \approx 43 \mu\text{s}$ as measured from Fig.10. In this frame, the recorded rise time is puzzling, since only the $^5\text{I}_5$ level with lifetime of 20 μs can satisfy Eq.9. Such rise time value is reported for $\text{LiYF}_4:0.5\%$ as discussed above [30]. The $^5\text{I}_7$ and $^5\text{I}_6$ are metastable states with long effective lifetime of the order of several milliseconds. In the case of $\text{LiYF}_4: 2\% \text{Ho}^{3+}, 20\% \text{Yb}^{3+}$ [16] the rise time measured for the UC red emission arising from the $^5\text{F}_5$ excited state (20 μs) is assumed to be related to the inverse of energy transfer rate through $(^5\text{I}_6, ^5\text{I}_6) \rightarrow (^5\text{I}_7, ^5\text{I}_5)$ energy transfer process (23 μs in the simulated decay). However, in this paper the time constant measured in the tail of the decay is of 770 μs (instead of 102 μs under direct excitation of the $^5\text{F}_5$ level), and can corresponds, perhaps to half of the lifetime of the $^5\text{I}_6$ level ($770 \mu\text{s} \approx 1.6 \text{ ms}/2$) assuming Eq.9. To provide support for the mechanism for the $^5\text{F}_5$ Ho^{3+} UC emission in $\text{CdF}_2: 1\% \text{Yb}^{3+}, 1\% \text{Ho}^{3+}$, several experiments must be performed, notably by recording the decays of the UC red emission under selective excitation in the $^5\text{I}_7$, $^5\text{I}_6$ and the $^5\text{I}_5$ levels.

5. Conclusion

We have studied down and upconversion luminescence mechanisms at room temperature in $\text{CdF}_2:1\% \text{Ho}^{3+}, 1\% \text{Yb}^{3+}$ single crystal. OPO pulsed laser in addition to CW -980 nm-laser diode were used to investigate the emission and luminescence decays arising from the main excited states of Ho^{3+} , namely ($^5\text{F}_4, ^5\text{S}_2$) and $^5\text{F}_5$ levels. Several cross-relaxations connect the excited states of Ho^{3+} under both UV and NIR excitations in addition of upconversion energy transfer (ETU), ground state absorption (GSA) and excited state absorption (ESA) involving the feeding of the $^5\text{I}_6$ and $^5\text{I}_7$ excited states of Ho^{3+} . They have been used to propose a diagram depicting the several exciting/decaying channels for the green and red emissions. The upconversion mechanism is a two-photon process as usually reported for such $\text{Yb}^{3+}/\text{Ho}^{3+}$ pair. The analyses of the kinetics are discussed considering that $\text{Ho}^{3+} \rightarrow \text{Ho}^{3+}$ and $\text{Yb}^{3+} \leftrightarrow \text{Ho}^{3+}$ energy transfer pathways exist in this system. The luminescence decays of the green ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$), and red $^5\text{F}_5 \rightarrow ^5\text{I}_8$ are discussed. The green emission decays are characterized by same dynamics shapes suggesting that the ($^5\text{F}_4, ^5\text{S}_2$) level is fed in rather similar way under either UV or NIR excitations. Such consideration is supported by the fact that the temporal decaying of this emission is well reproduced using I-H model, considering dipole-dipole electrical interaction between the active ions, leading to an R_0 critical transfer distance of 9-11 Å. The feeding of the $^5\text{F}_5$ depends on the excitation used. Under UV excitation, this excited

state presents no rise time indicating that its population is reached quickly, probably during the laser pulse duration, due to an effective fast cross relaxation or a non-radiative de-excitation from the (5F_4 , 5S_2) level. Under NIR excitation, the luminescence decay of the emission arising from the 5F_5 is parametrized using a rate equation system considering a simple three level system, where the intermediate level is not clearly attributed.

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Author Contributions

The manuscript was written through contributions of all authors.

CRediT authorship contribution statement

S. Bordj: Investigation, Data curation. H. Satha: Supervision, Validation, Visualization, Project administration, Writing - review & editing. A. Barros: Formal analysis, Data curation, Visualization. D. Zambon: Formal analysis, Data curation, Visualization. J.P. Jouart: Methodology, Formal analysis. M. Diaf: Supervision, Validation, Visualization, Project administration, Writing - review & editing. R. Mahiou: Conceptualization, Supervision, Validation, Visualization, Project administration, Writing – original draft, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure captions

Figure 1: Crystal structure of CdF_2 . The inset shows cut and polished crystal sample

Figure 2: Emission spectrum of $\text{CdF}_2:1\%\text{Ho}^{3+}, 1\%\text{Yb}^{3+}$ single crystal under pulsed excitation at 360 nm.

Figure 3: UC emission spectrum of $\text{CdF}_2:1\%\text{Ho}^{3+}, 1\%\text{Yb}^{3+}$ single crystal under pulsed excitation at 980 nm. The added picture shows bright green UC emission corresponding to the main emission ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$) under 980 nm excitation.

Figure 4: Energy transition diagram of $\text{Yb}^{3+}/\text{Ho}^{3+}$ ions in $\text{CdF}_2:1\%\text{Ho}^{3+}, 1\%\text{Yb}^{3+}$ under UV (360 nm) and NIR (980 nm) excitations. ETU is related to the $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer by upconversion, and B.T to the $\text{Ho}^{3+} \rightarrow \text{Yb}^{3+}$ energy back transfer. The inset shows the simple energy levels diagram used for the red UC emission.

Figure 5: Measured (5a) and Normalized (5b) UC emission spectra of $\text{CdF}_2:1\%\text{Ho}^{3+}, 1\%\text{Yb}^{3+}$ versus the power of the CW-980 nm laser diode.

Figure 6: Log of green UC emission at 546 nm versus the log power of the CW-980 nm laser diode. The solid line represents the linear fitting which leads to slope of 1.86.

Figure 7: Decay profile of green ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$) emission of Ho^{3+} ions under UV excitation at 360 nm. The red solid line represents the fitting obtained using bi-exponential decaying and the green solid line represents the fit obtained using I-H model as discussed in the text. The inset shows the fitting of the rise time recorded under UV excitation.

Figure 8: Decay profile of red $^5\text{F}_5 \rightarrow ^5\text{I}_8$ emission of Ho^{3+} ions under UV excitation at 360 nm. The red solid line represents the fitting obtained using bi-exponential decaying and the green solid line represents the fit obtained using I-H model as discussed in the text.

Figure 9: Decay profile of green ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$) emission of Ho^{3+} ions under NIR excitation at 980 nm. The red solid line represents the fitting obtained using bi-exponential decaying and the green solid line represents the fit obtained using I-H model as discussed in the text. The inset shows the fitting of the rise time recorded under NIR excitation.

Figure 10: Decay profile of red $^5\text{F}_5 \rightarrow ^5\text{I}_8$ emission of Ho^{3+} ions under NIR excitation at 980 nm. The solid line represents the fitting obtained using bi-exponential decaying (one in the rise and another in the tail of the decay) derived from the rate equation model as discussed in the text.

Figure 1

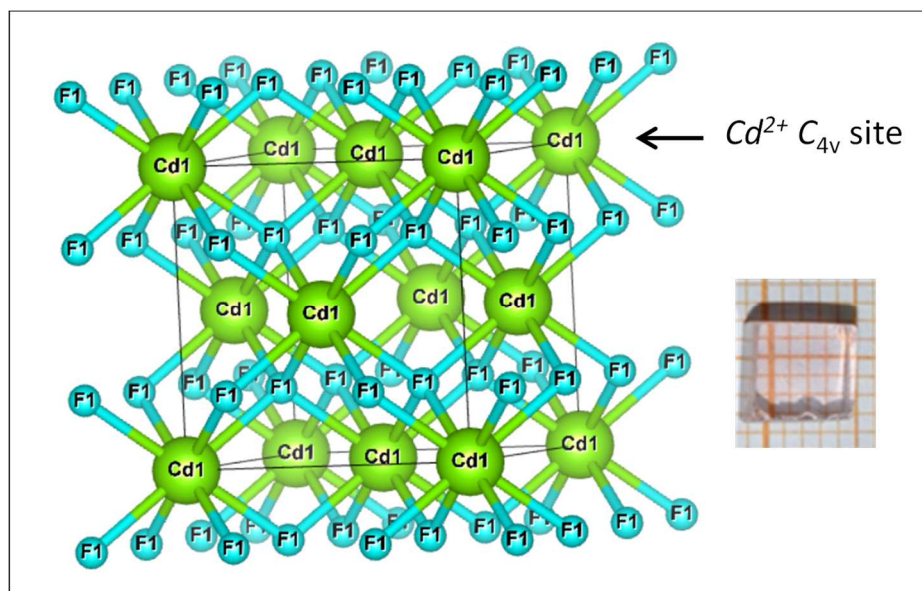


Figure 2

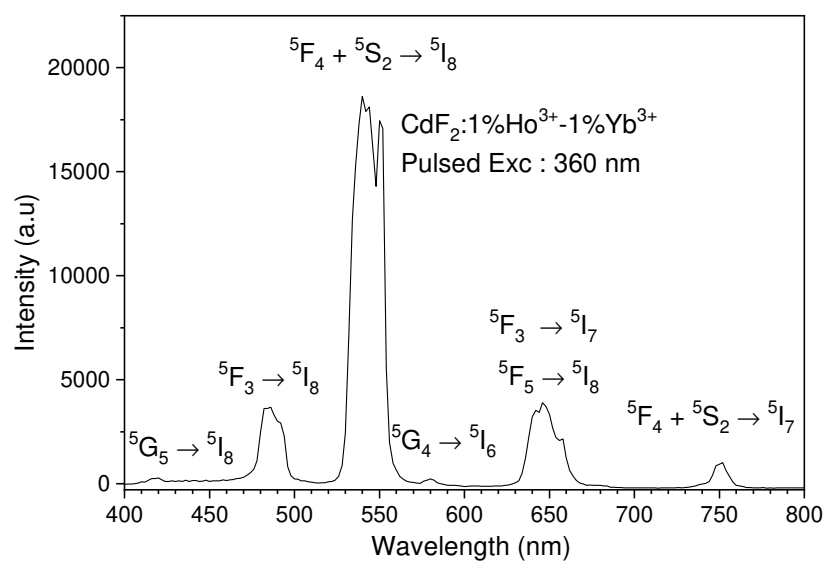


Figure 3

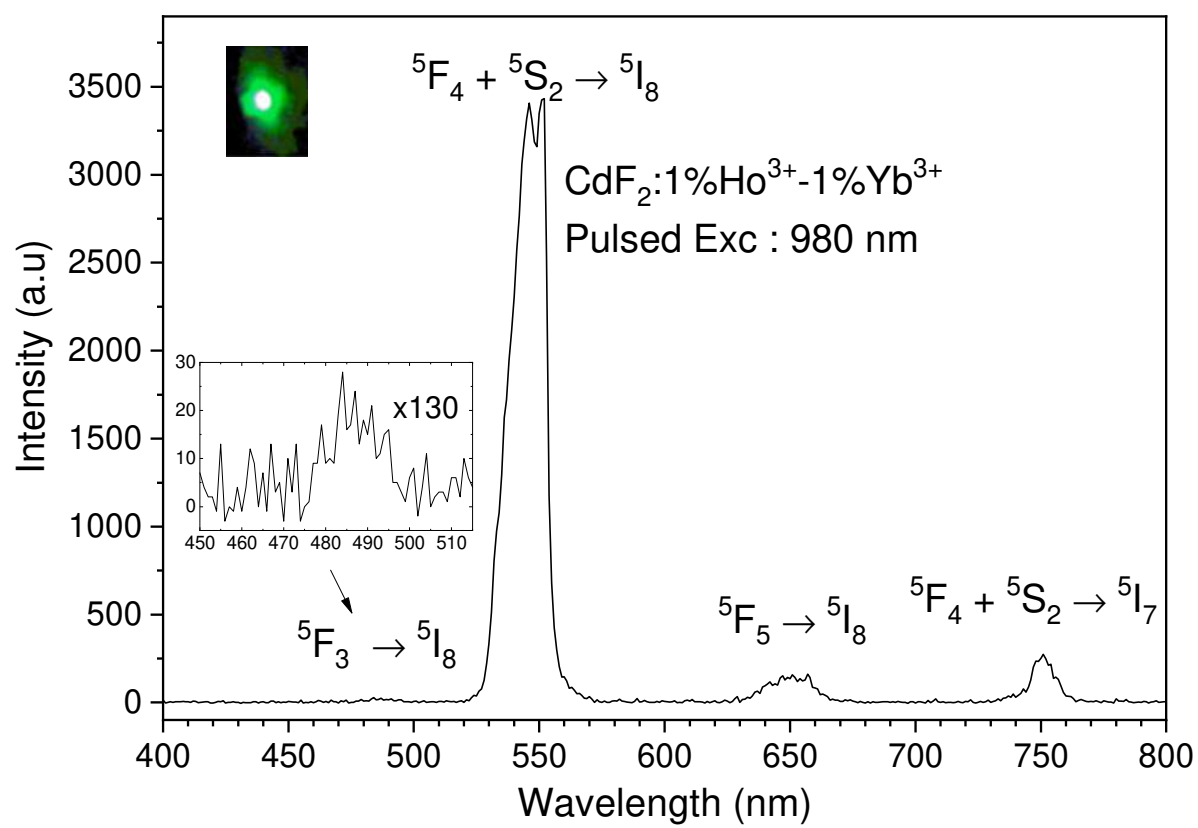


Figure 4

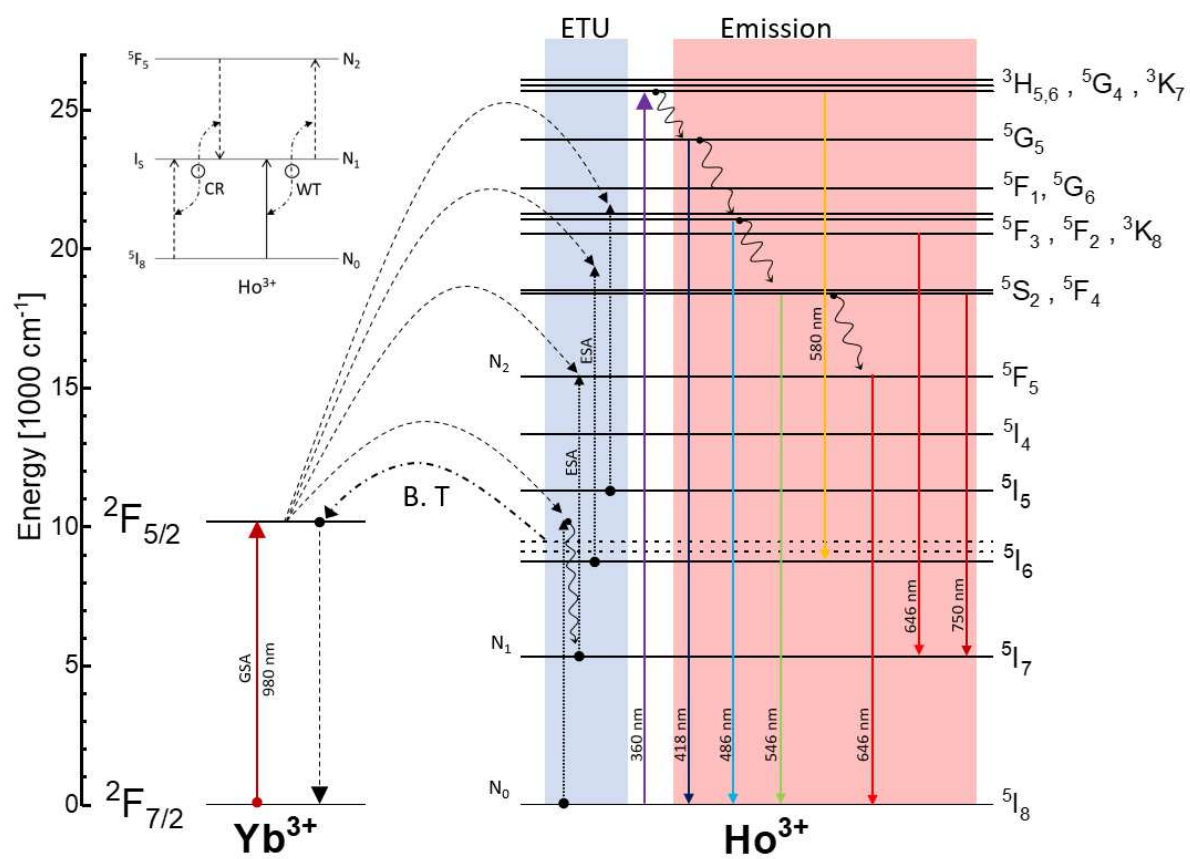


Figure 5

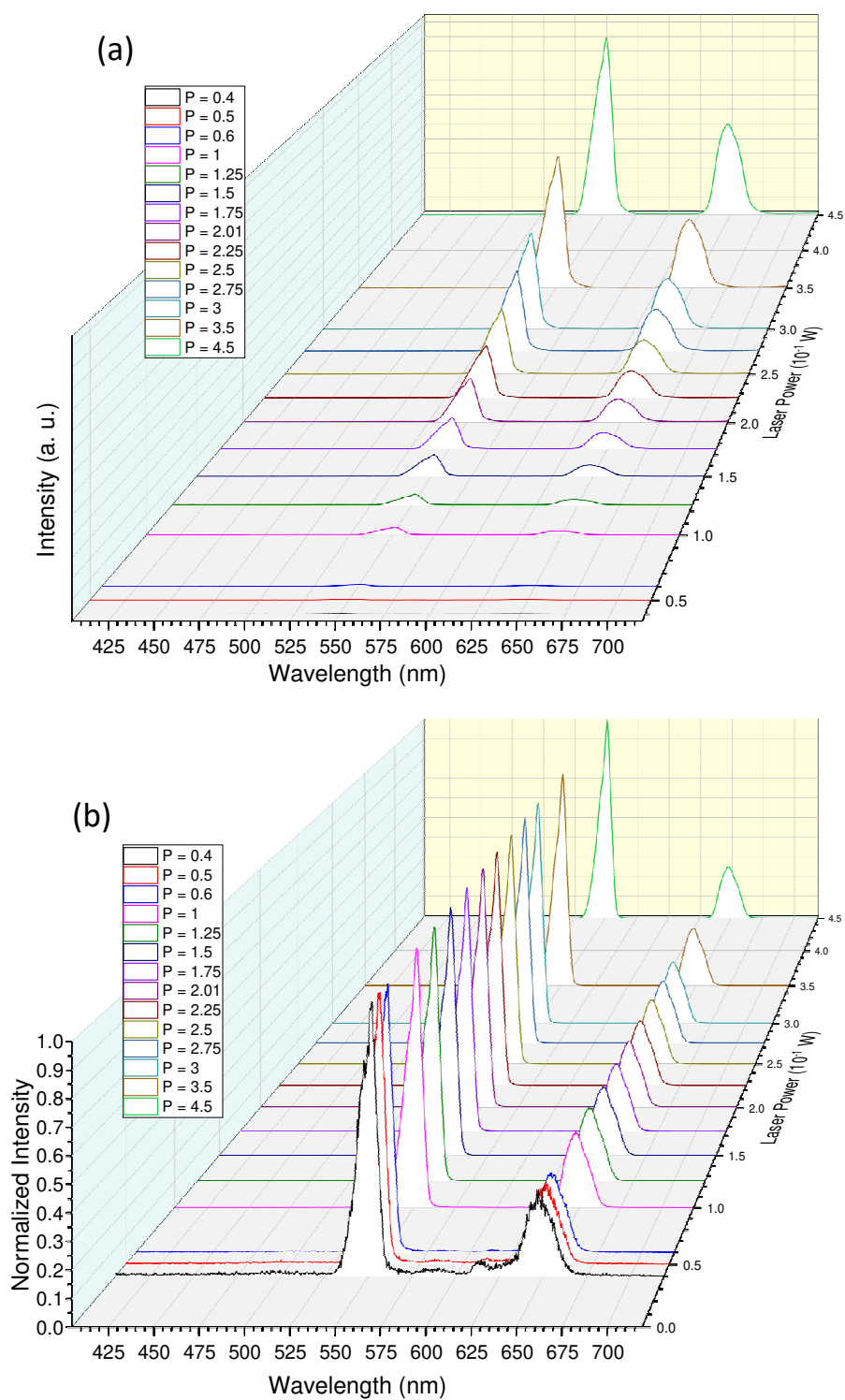


Figure 6

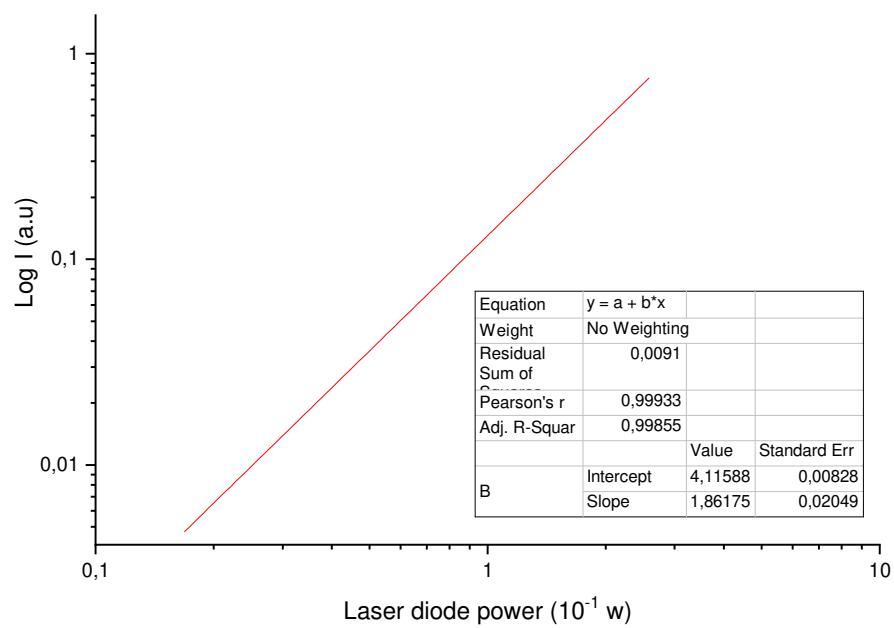


Figure 7

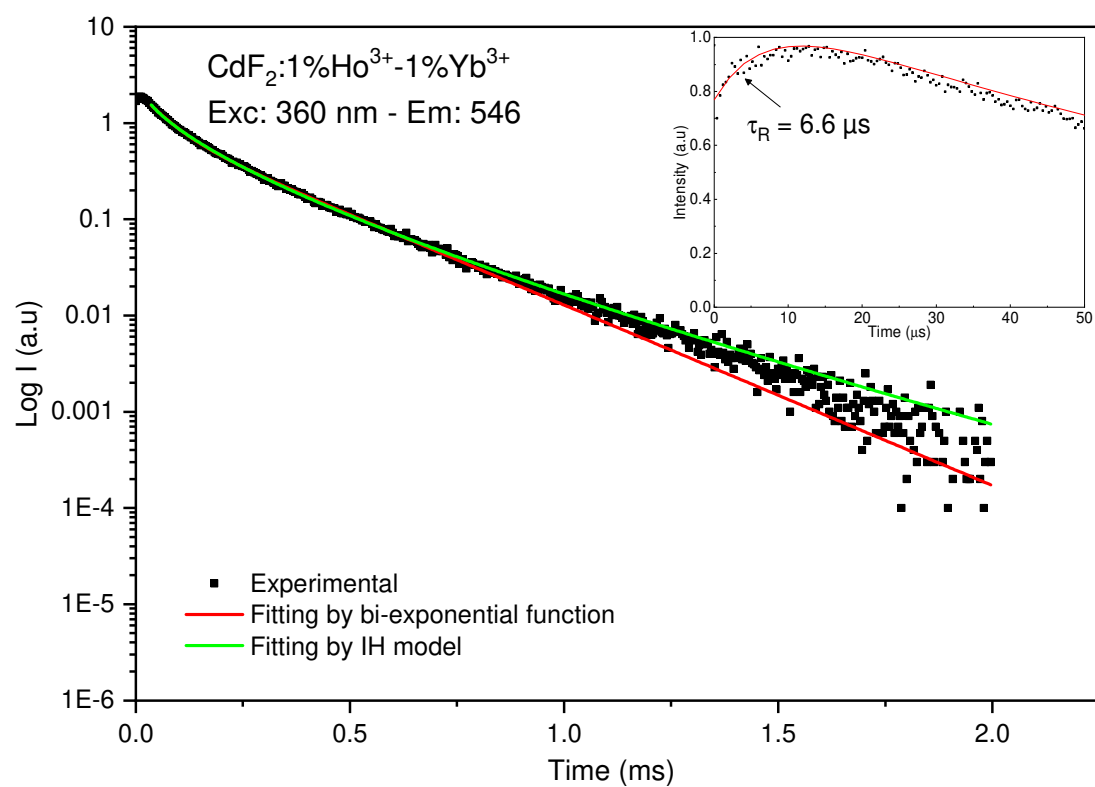


Figure 8

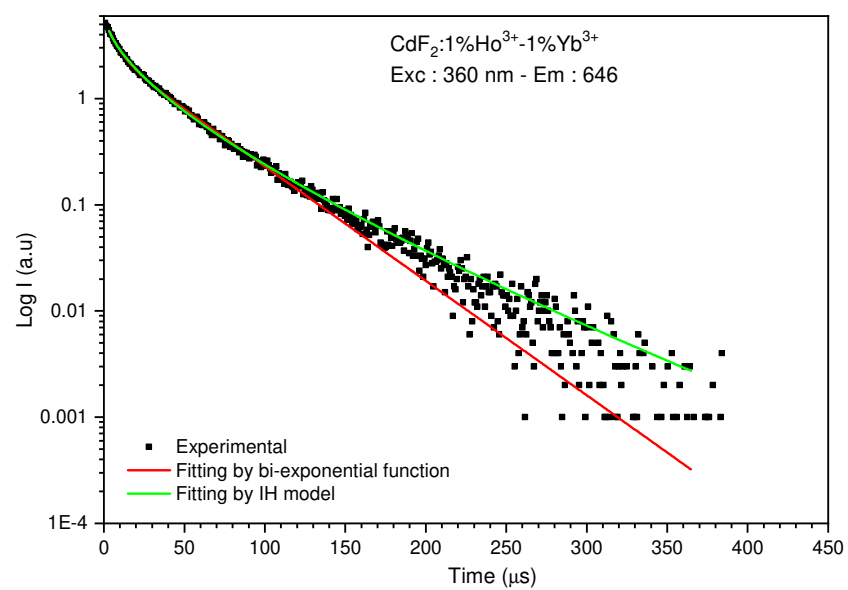


Figure 9

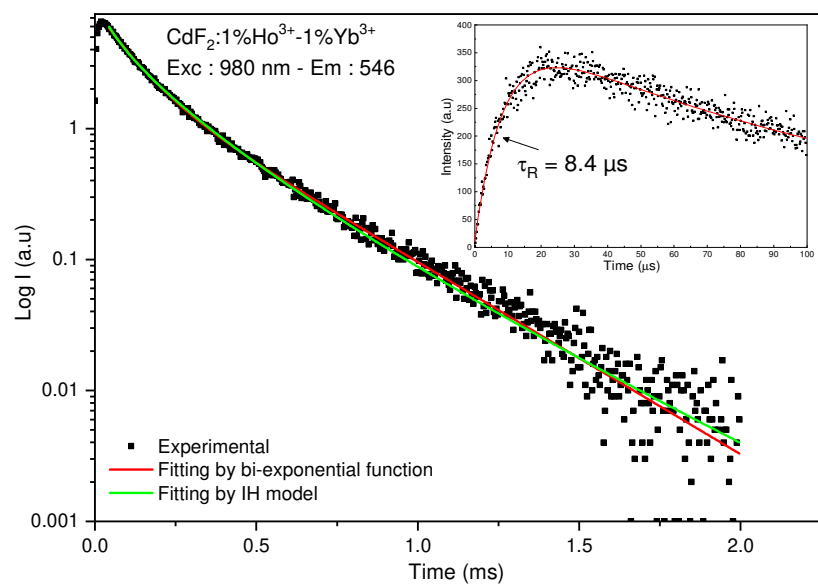
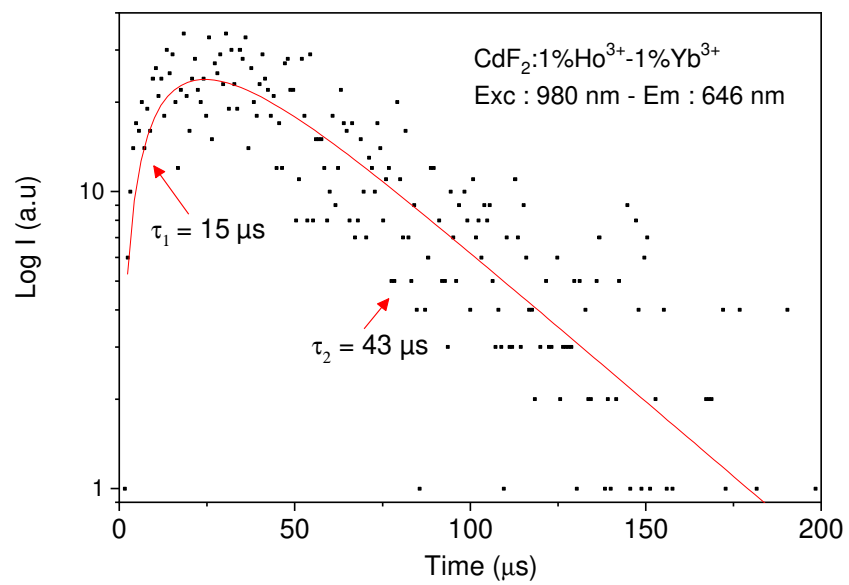


Figure 10



Table

Table 1: Experimental values of time constants (μs) derived from fitting by sum of exponential functions of the luminescence decays for green and red emissions of Ho^{3+} in CdF_2 under UV and NIR excitations.

Emission (Excitation)	τ_R	τ_1	τ_2	τ_{Av}
546 nm (360 nm)	6.6	67	250	202
646 nm (360 nm)	-	47	103	85
546 nm (980 nm)	8.4	97	296	219
646 nm (980 nm)	15	43	-	-

Table

Table 2: Experimental values of τ_0 , C_A/C_0 , critical concentration (C_0), energy transfer microparameter (C_{DA}), and critical distance (R_0) derived from fitting by I-H model for both green and red emissions of Ho^{3+} in CdF_2 .

Emission (Excitation)	τ_0 (μs)	C_A/C_0	C_A (10^{20} ions/ cm^3)	C_0 (10^{20} ions/ cm^3)	C_{DA} (10^{-39} cm^6s^{-1})	R_0 (\AA)
546 nm (360 nm)	631	1.7	5.1	3	1.1	9.3
646 nm (360 nm)	125	1.64	5.1	3.1	4.9	9.2
546 nm (980 nm)	590	1.36	2.55	1.9	2.8	10.8

Graphical Abstract

