Energy transfer upconversion in Ho^{3+} and Ho^{3+}, Yb^{3+} doped CdF_2 crystals

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Abstract. A comparative spectroscopic study for Ho^{3+} and Ho^{3+}, Yb^{3+} doped CdF$_2$ crystals has been realised at liquid nitrogen temperature. The Ho^{3+} single-doped sample shows principally blue emission corresponding to the $^5F_3 \rightarrow {}^5I_8$ transition, whereas the Ho^{3+}, Yb^{3+} codoped sample gives rise to a very efficient green emission which is ascribed to the $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ transition. The total integrated upconversion emission intensity (including blue and green emissions) for the codoped crystal is three times more intense than that of the Ho^{3+} doped one, while the ratio for green emission rises to 27. The green emission in the codoped sample results mainly from the Ho^{3+}–Yb^{3+} mixed centre, whereas the blue emission is essentially due to the Ho^{3+}–Ho^{3+} pair. Two energy transfer upconversion mechanisms have been proposed and are discussed in the paper.

1. Introduction

Cadmium fluoride (CdF$_2$) has a fluorite-type (CaF$_2$) crystal structure with a lattice parameter of about 5.39 Å [1]. When introduced into the CdF$_2$ crystal lattice, the rare earth ions replace the original Cd^{2+} positions, and therefore, a charge compensator is required to attain electric neutrality. Unlike the case in other fluorite-type crystals such as CaF$_2$ and SrF$_2$, the single Ln^{3+} ions in CdF$_2$ do not preferentially associate with a nearby interstitial fluoride ion (F$_i^-$), and thus the C$_{4v}$ and C$_{3v}$ sites are less important in this crystal [2–5]. It has been found that for most of the rare earth ions, there are two kinds of principal crystal site in the doped CdF$_2$ crystal: an Ln^{3+} ion with cubic symmetry where the fluoride interstitial compensates the La^{3+} ion distantly and a dimer site (or pair) formed by two adjacent Ln^{3+} ions accompanied by two F$_i^-$ ions [2, 3]. The cubic site generally plays an important role in the crystals at low impurity concentration until the formation of clusters. In heavily doped crystals, in contrast, the Ln^{3+}–Ln^{3+} cluster configuration is the dominant site.

The infrared to green and blue upconversion induced by energy transfer from the Yb^{3+} ion to the Ln^{3+} ions (Er^{3+}, Ho^{3+}, Tm^{3+}) has been investigated extensively in various host materials since the 1960s [6–14]. Among them, the first upconversion laser operation has been realized [12]. In several cases, the Yb^{3+} ion can be also employed as a 'bridge' of excitation energy: Yb^{3+} functions both as an energy acceptor and an energy donor, and the absorbed energy was transferred from one activator ion (such as Ho^{3+}) to another through

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Yb^{3+} ions. As a result, one can obtain upconversion luminescence from the levels which cannot be reached without Yb^{3+}, or one can greatly enhance the upconversion intensity from the same level as the Ln^{3+} single-doped crystal [13, 14]. In this paper, we have studied the Ho^{3+} upconversion luminescence properties and the role played by Yb^{3+} in the Ho^{3+} green upconversion in CdF_2 crystals.

The crystals studied are CdF_2:2 mol% Ho^{3+} and CdF_2:2 mol% Ho^{3+}, 2 mol% Yb^{3+}. Since the concentrations for both rare earth ions are relatively high, the principal sites are paired Ho^{3+}, Ho^{3+} and Ho^{3+}, Yb^{3+} mixed centres. Actually, we have identified only one kind of emission and excitation spectrum in both crystals. It has been found that in the codoped crystal the Yb^{3+} ion serves as a very efficient energy bridge which converts the original Ho^{3+} red emission ($^5F_5 \rightarrow {}^5I_8$) into the green emission ($^5F_4$, $^5S_2 \rightarrow {}^5I_8$) when the dye laser is tuned on the Ho^{3+} $^5I_8 \rightarrow {}^5F_5$ excitation transition. The result of this conversion is that the Ho^{3+} green emission is multiplied by more than 27 times, which implies a preference to form Ho^{3+}–Yb^{3+} mixed centres in this crystal.

2. Experiment

The Ho^{3+} and Yb^{3+} doped crystals were grown in our laboratory by the well known Bridgman technique [15]. For both crystals, the Ho^{3+} and Yb^{3+} ions were introduced in the form of Ho_2O_3 and Yb_2O_3 with a concentration of 1 mol% for both rare earth oxides. The crystal growth was realized under a fluoride atmosphere, and the oxygen-free crystals were obtained [15].

For upconversion study, the emission and excitation spectra were obtained by exciting the crystals with an Ar^+ laser (Spectra Physics 2000) pumped tuneable dye laser (Spectra Physics 375). The working media is Kiton red to permit the dye laser to be tuned from 620 to 670 nm with a maximum at about 640 nm. The crystal was placed in a cryostat cooled to liquid nitrogen temperature (77 K). The laser beam was focused into the crystal with a lens of 20 cm focal length. Emission signal from the sample was dispersed by a Coderg T800 three-grating monochromator and detected by a water-cooled photomultiplier (EMI 9558 QB). Dynamic study of the luminescence was performed with a Metrix oscillograph (OX 750-2). The laser beam was chopped by a Pockels cell. The rise and decay signals were analysed by a micro-computer.

3. Experimental results and discussion

Under red dye laser excitation, Ho^{3+} single-doped crystals show principally blue upconversion extending from 21 000 cm¹ to 21 800 cm¹, corresponding to the $^5F_3 \rightarrow {}^5I_8$ transition. The green upconversion intensity of $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ transition is relatively weak compared to that of the blue emission. The excitation spectra of the blue, green and red emissions show similar structure, indicating that the upconversion probably results from the energy transfer between paired Ho^{3+} ions, whereas the successive absorption is less important. This phenomenon was also observed for the Ho^{3+} dimer centres in CaF_2 and SrF_2 [16, 17]. By comparing with the results observed in Ho^{3+} doped CaF_2 and SrF_2 crystals, no single Ho^{3+} C_{3v}, C_{4v} sites were recognized. Therefore, the sites present in the CdF_2 crystal are essentially some kinds of cluster centres.

The crystal codoped with the Yb^{3+} and Ho^{3+} ions shows a very bright green upconversion upon the same excitation. The excitation spectra of the green emission from two crystals doped with Ho^{3+} and Ho^{3+}, Yb^{3+}, respectively, are shown in figure 1. It is
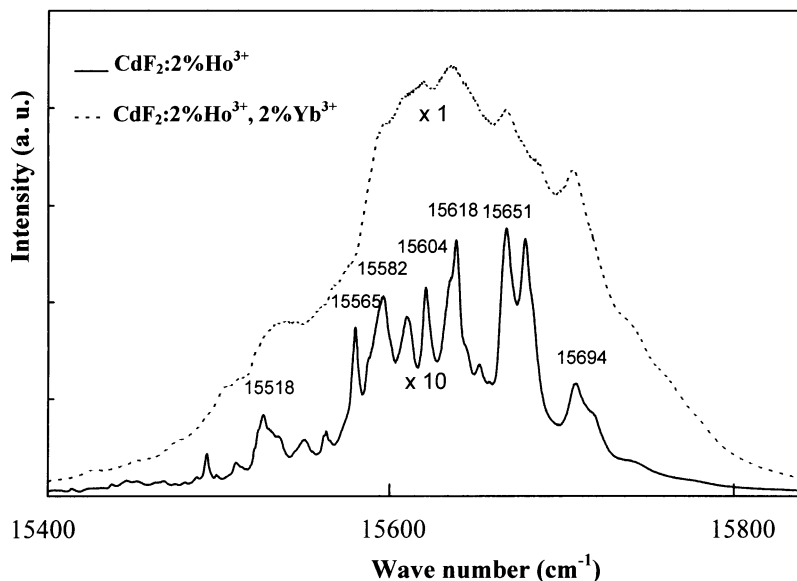
Figure 1. Red laser excitation spectra for the green upconversion at 18 118 cm⁻¹ of the Ho³⁺ ions in CdF₂:2% Ho³⁺ and CdF₂:2% Ho³⁺, 2% Yb³⁺ at 77 K.

evident that the codopant Yb^{3+} changes both the shape and the relative intensities of the Ho^{3+} excitation spectrum. First, an inhomogeneous broadening due to the modification of the Ho^{3+} crystal environment can be clearly observed. Second, compared with the single-doped sample, the structureless spectrum of the codoped sample probably results from the diversification of the sites caused by Yb^{3+}, and the resulting spectrum is a contribution of many centres with slightly different crystal environments. Similar results have been observed for the emission spectra (see figures 2 to 4). The green and blue upconversion luminescence spectra are given in figures 2 and 3. It can be found from figure 2 that the integrated emission intensity of the green emission increases greatly in the codoped crystal by 27 times with respect to that of the single-doped crystal. Notice that the Ho^{3+} concentration is the same (2 mol%) in both samples.

Concerning the blue emission, the integrated emission intensity decreases twofold in the codoped sample, as shown in figure 3. This implies that the enhancement of green emission cannot be a result of the decrease of the blue emission intensity. The red Stokes emissions of the two crystals studied are given in figure 4, which shows that the integrated red emission intensity for $CdF_2:Ho^{3+}$, Yb^{3+} is five times weaker than that for $CdF_2:Ho^{3+}$. Note that the integrated intensity of red emission is stronger than that of the total upconversion emissions (green + blue) in $CdF_2:Ho^{3+}$, while weaker than the green upconversion intensity in $CdF_2:Ho^{3+}$, Yb^{3+}. There must be some relationship between the changes in the two emission intensities. A possible explanation is that the energy transfer to Yb^{3+} depopulates the $^5F_5$ level and finally populates the $^5F_4$, $^5S_2$ level of the Ho^{3+} ion.

The luminescence lifetimes of the Ho^{3+} green and blue upconversions and the red Stokes emission were measured in both crystals. Surprisingly, the lifetime of Ho^{3+} green emission from the $^5F_4$, $^5S_2$ level is very much shorter in $CdF_2:Ho^{3+}$ (29 μs) than in $CdF_2:Ho^{3+}$, Yb^{3+} (230 μs), as shown in figure 5. The short lifetime in Ho^{3+} single-doped crystal can be interpreted by an efficient energy transfer process involving two paired Ho^{3+} ions
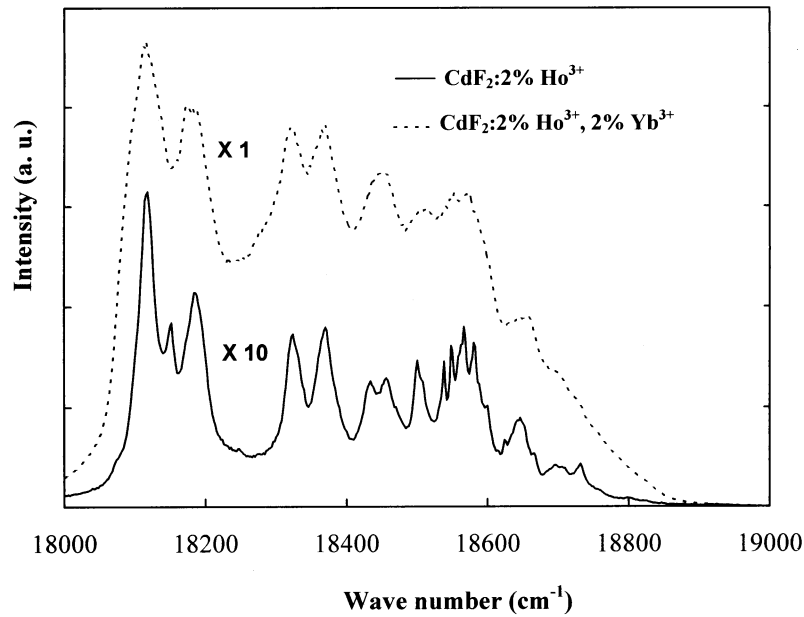
Figure 2. Green upconversion spectra of the Ho^{3+} ions in CdF_2:2% Ho^{3+} and CdF_2:2% Ho^{3+}, 2% Yb^{3+} at 77 K with red laser excitation at 15 612 cm^{-1}.
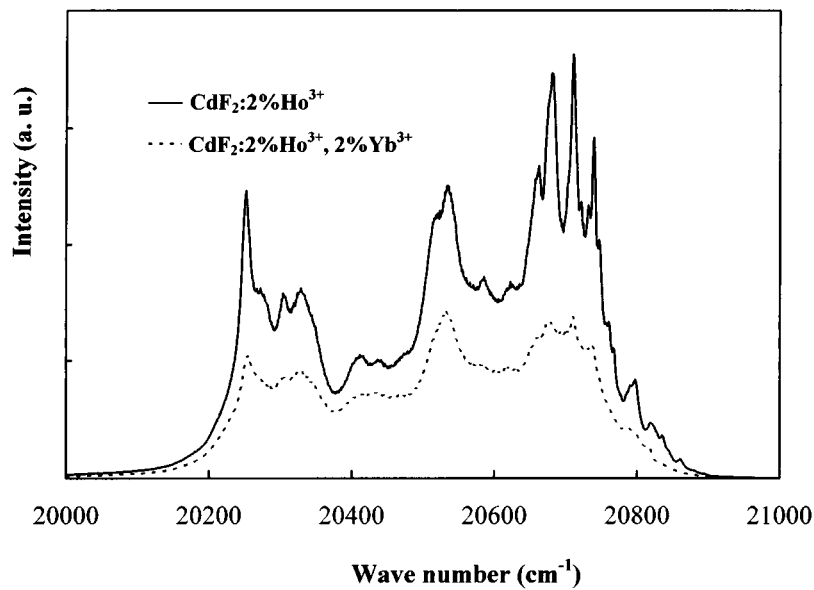

Figure 3. Blue upconversion spectra of the Ho^{3+} ions in CdF_2:2% Ho^{3+} and CdF_2:2% Ho^{3+}, 2% Yb^{3+} at 77 K with red laser excitation at 15 612 cm^{-1}.

excited in the $^5F_4$, $^5S_2$ state, because the energy interval between $^5F_4$, $^5S_2$ and $^5I_4$ levels has a good coincidence with that between $^5F_4$, $^5S_2$ and $^5G_5$ levels. Furthermore, owing to this energy transfer, the $^5F_3$ level is repopulated by the non-radiative relaxation from upper-lying
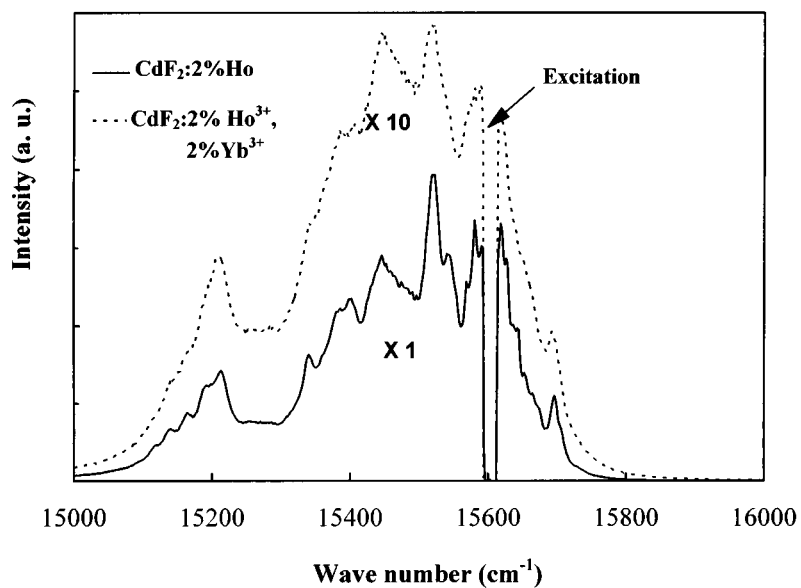
Figure 4. Red emission spectra of the Ho³⁺ ions in CdF₂:2% Ho³⁺ and CdF₂:2% Ho³⁺, 2% Yb³⁺ at 77 K with red laser excitation at 15 612 cm⁻¹.
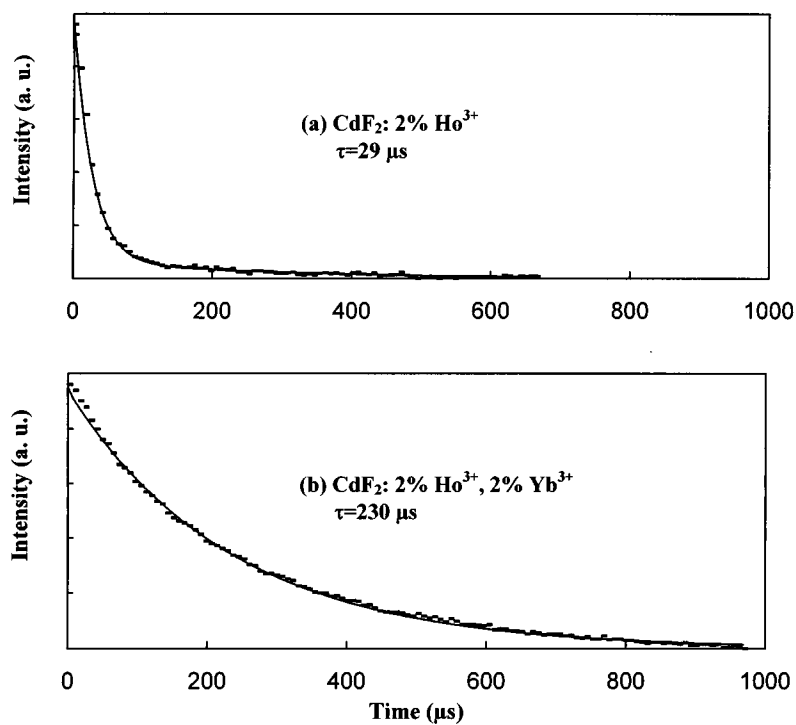
Figure 5. Fluorescence decay curves for the Ho³⁺ green emission in CdF₂:2% Ho³⁺ (a) and CdF₂:2% Ho³⁺, 2% Yb³⁺ (b) at 77 K.
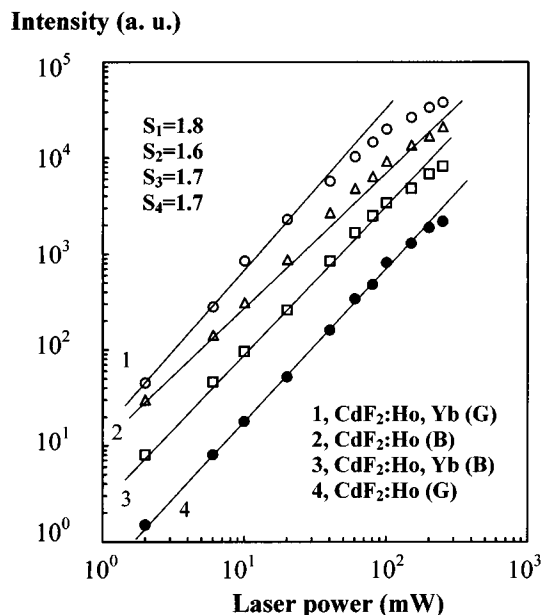
Figure 6. Laser power dependence of the Ho^{3+} blue and green upconversion intensities in CdF_2:2% Ho^{3+} and CdF_2:2% Ho^{3+}, 2% Yb^{3+} at 77 K.

levels. As a result, the blue upconversion is enhanced and the green emission is quenched. The decay time of the Ho^{3+} red emission in the codoped sample is about 55 μs, which is shorter than that for the Ho^{3+} single-doped sample (68 μs). This observation confirms the assumption for the enhancement of the green emission.

A study of the Ho^{3+} green and blue emission intensities on the incident laser power has shown a quadratic dependence in both crystals. The results are presented in figure 6. In spite of their similar power dependence character, the excitation mechanisms for green and blue upconversions are different. The two proposed mechanisms are depicted in figure 7(a) and (b). In the CdF_2:Ho^{3+} crystal, the energy transfer between two adjacent Ho^{3+} ions in the $^5F_5$ level excites one ion into the high-lying $^5G_4$ level, and the $^5F_3$ level is then populated through a non-radiative or radiative relaxation process. The Ho^{3+} green emission level ($^5F_4$, $^5S_2$) is first populated by the non-radiative relaxation from the upper-lying $^5F_3$ level, and then a cross-relaxation process between two excited Ho^{3+} ions depopulates the $^5F_4$, $^5S_2$ in favouring the $^5F_3$ level:

$$^5F_4,^5S_2 +^5F_4,^5S_2 \rightarrow {}^5G_5 +^5I_4.$$
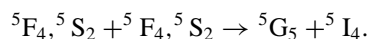
As to the CdF_2:Ho^{3+}, Yb^{3+} crystal, since the essential blue emission arises from the Ho^{3+} pairs, the populating process for the blue upconversion is the same as that in CdF_2:Ho^{3+}. For the green emission, however, the Yb^{3+} ion plays a very important role. The excitation energy absorbed by the Ho^{3+} $^5F_5$ level at first transfers to the nearby Yb^{3+} ions with the energy transfer:

$$^5F_5 +^2F_{7/2} \rightarrow {}^5I_7 +^2F_{5/2} \text{ (process 1)}$$
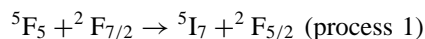
and then a back energy transfer to another excited Ho^{3+} populates the $^5F_4$, $^5S_2$ level:

$$^5I_6 +^2F_{5/2} \rightarrow {}^5F_4,^5S_2 +^2F_{7/2} \text{ (process 2)}.$$
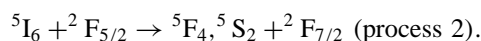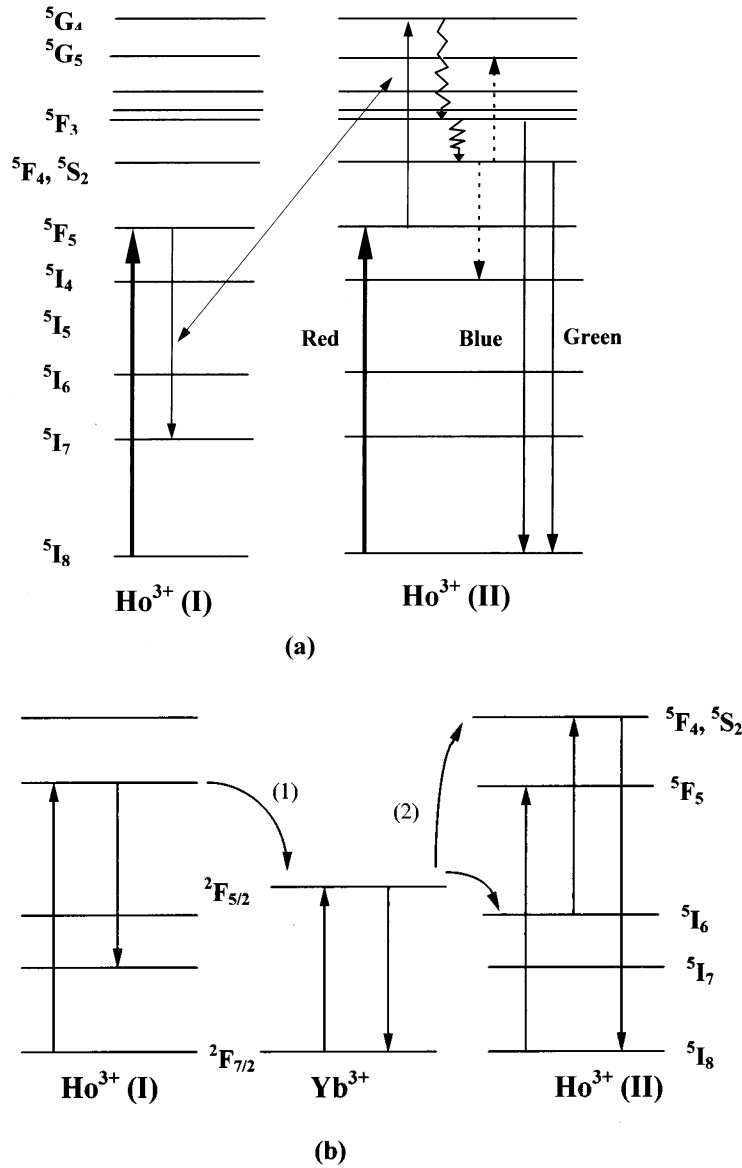
Figure 7. Energy level diagram for the proposed upconversion mechanisms. (a) Energy transfer process for Ho^{3+}–Ho^{3+} pair. (b) Energy transfer process for Ho^{3+}–Yb^{3+}–Ho^{3+} mixed centres.

In this mechanism, the Yb^{3+} ion serves as an energy bridge to convert the red emission into green emission, and excitation energy is transferred through Yb^{3+} from one Ho^{3+} ion to another. On the other hand, the presence of Yb^{3+} between two Ho^{3+} ions prevents the interaction between the excited Ho^{3+} ions. This mechanism can explain the results that the green upconversion is greatly enhanced but the blue emission is quenched in codoped sample. Similar process has been also found in the Er^{3+} and Tm^{3+} codoped system upon 1.5 μm excitation [18].

4. Conclusion

At 77 K, Ho^{3+} single-doped CdF_2 crystal shows a blue upconversion, whereas the Ho^{3+} and Yb^{3+} codoped sample exhibits a very intense green emission under red dye laser excitation. Both upconversion emissions present mainly a quadratic laser power dependence, indicating a two-step process. However, these mechanisms are different. The blue emission is mainly from the energy transfer between the Ho^{3+}–Ho^{3+} centres and the green emission is essentially from the Ho^{3+}, Yb^{3+} mixed centres. In the later case, Yb^{3+} ion plays a role of both an energy bridge to convert the red emission to the green upconversion and an energy barrier to prevent the interaction between the excited Ho^{3+} ions. The efficient upconversion reported in this paper shows that the Ho^{3+} and Yb^{3+} codoped crystal could be a prospective candidate in searching for infrared or red to green upconversion lasers.

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