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Upconversion fluorescence of Ho^{3+} ions in a BaF_2 crystal

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Abstract

Efficient upconversion luminescence from the Ho^{3+} C_{3v} centre in a BaF_2 crystal is reported. The red-to-green and red-to-blue upconversion is observed upon pumping with a single cw red dye laser. The upconversion mechanism is assigned as a sequential two-photon excitation process in which the excitation wavelength is resonant with either ground state absorption (GSA) or excited state absorption transitions. The efficient green upconversion with excitation into GSA results from a double-resonant excitation between the $^5I_8 \rightarrow {}^5F_5$ and $^5I_7 \rightarrow {}^5F_3$ transitions.

1. Introduction

Owing to the relatively lower lattice phonon energy, fluoride crystals and glasses are good host materials for frequency upconversion when doped with rare earth ions such as Er^{3+}, Tm^{3+} and Ho^{3+} [1–6]. The BaF_2 has a fluorite-type structure with a crystal lattice parameter of 6.20 Å. As in other fluorite-type crystals, a charge compensator is necessary to maintain the electrical neutrality when the trivalent rare earth ions replace the divalent Ba^{2+} ions in the lattice. The most usual compensator is a fluorine interstitial ion (F_i^-). When F_i^- is placed at the nearest, next-nearest or in distance positions to the trivalent ions, a tetragonal C_{4V}, trigonal C_{3V} or a cubic O_h site is obtained, respectively. It has been found that as the ionic radius of the cation is increased through the series Cd → Ca → Sr → Ba, the C_{3V} site is preferably formed in the crystal [2]. Therefore, the predominant site should be the C_{3V} site at low concentrations in BaF_2.

The Ho^{3+} ion has a $4f^{10}$ electronic configuration. It gives rise to efficient green or blue upconversion in many host materials upon red or infrared laser excitation. Laser site selective upconversion fluorescence of Ho^{3+} doped CaF_2 and SrF_2 has recently been reported [5,6]. In this Letter, we present an upconversion study of an Ho^{3+} activated BaF_2 crystal upon red dye laser excitation between 620 and 670 nm at 77 K. The upconversion is considered as a two-step sequential excitation from either ground state absorption (GSA) or excited state absorption (ESA) transitions.

2. Experimental

The sample studied in this work is a BaF_2 monocrystal doped with 0.05 at% Ho^{3+}, which has been purchased from the Optovac company. The absorption spectrum obtained with a Perkin–Elmer Lambda-9 spectrophotometer shows several weak absorption lines corresponding to the Ho^{3+} 4f–4f transitions. An 8 W cw Spectra Physics (SP) 2000 Ar^+ ion laser pumped SP 375 tunable dye laser was

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used as the excitation source to study the upconversion. The working media is Kiton Red which permits the dye laser to be tuned from 620 to 670 nm with a maximum laser power of about 600 mW at 640 nm. Crystal samples were placed in a cryostat cooled to liquid nitrogen temperature (77 K). The laser beam was focused into the crystal with a 20 cm focal lens. The emission signal from the samples was dispersed by a Coderg T800 three-grating monochromator and detected by a water-cooled photomultiplier (EMI 9558 QB). Studies of the luminescence dynamics were performed with a Metrix oscillograph (OX 750-2). The laser beam was chopped by a Pockels cell and an on-line computer was used for analysing the rise and decay signals.

3. Results and discussion

Fig. 1a shows the green upconversion fluorescence spectrum with 100 mW red laser excitation at

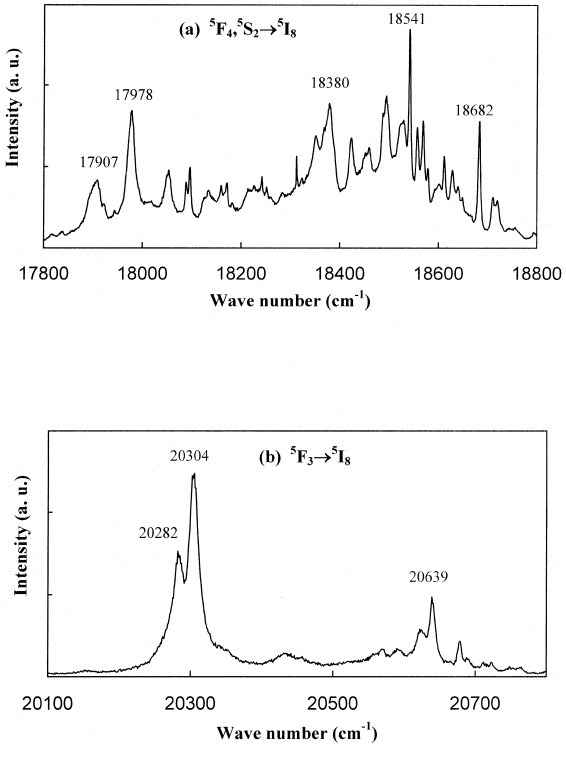

Fig. 1. Green (a) and blue (b) upconversion spectra of the Ho^{3+} C_{3V} centre in BaF_2 with excitation into the $^5I_8 \rightarrow ^5F_5$ (GSA) transition at 15766 cm^{-1} at 77 K.

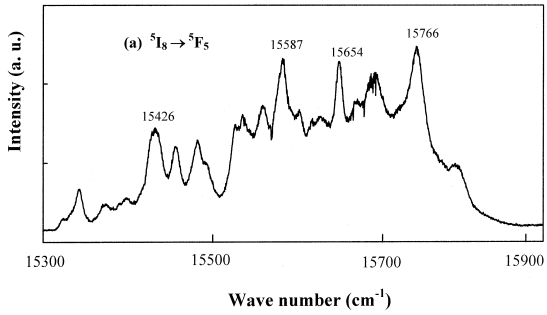

Fig. 2. 77 K excitation spectra of the Ho^{3+} C_{3V} centre from $^5I_8 \rightarrow ^5F_5$ (a) and $^5I_7 \rightarrow ^5F_2, ^3K_8$ (b) transitions, monitoring the green emission line at 18541 cm^{-1}.

15766 cm^{-1}. The observed spectrum is characterised by the $^5F_4, ^5S_2 \rightarrow ^5I_8$ transition of the Ho^{3+} ion. Unlike what has been observed in other fluorite-type crystals such as CaF_2 and SrF_2 [5,6], only one spectrum could be identified in 0.05 at.% Ho^{3+} doped BaF_2 crystal implying only one crystal-field site. The high-resolution spectrum shows several narrow emission lines on the higher energy side and several broad lines observed on the lower energy side. The most intense emission line is located at 18541 cm^{-1}, the same position as that observed for the C_{3v} centre in SrF_2:Ho^{3+} crystals [6].

The blue upconversion obtained for excitation of the 15766 cm^{-1} is depicted in Fig. 1b, with a laser power of 100 mW. Extending from 20100 to 20800 cm^{-1}, it can be ascribed to the $^5F_3 \rightarrow ^5I_8$ transition. The blue upconversion is much weaker than the green emission by a factor of 8.

Compared to the upconversion spectra observed in SrF_2:Ho^{3+} crystals [6], both green and blue emission spectra are similar to those observed for the C_{3V} centre in SrF_2:Ho^{3+}. This phenomenon indicates that these spectra arise from a similar centre in BaF_2, the C_{3V} centre in this case. The result is consistent with that predicted by the structural analysis [2].

The excitation spectrum obtained whilst monitoring the 18541 cm^{-1} green upconversion transition is shown in Fig. 2a,b. In addition to the lines arising from the ground state absorption from $^5I_8$ to the $^5F_5$ levels between 15450 and 15900 cm^{-1} (a), we observe a series of excitation lines between 16000 and 16400 cm^{-1} (b). These lines (in Fig. 2b) match exactly the energy gap between the $^5I_7$ and $^5F_2, ^3K_8$ multiplets. The average energy difference between

the GSA and ESA is about 400 cm^{-1}. This mismatch can be bridged readily by one or two lattice phonons (the phonon energy in BaF_2 is about 370 cm^{-1} [7]).

In contrast to the results for Er^{3+} in CaF_2 crystals [8], in BaF_2:Ho^{3+} we have found that it is more efficient to resonantly excite GSA transitions than the ESA transitions. When the GSA transitions are resonantly excited, phonon mediation is not needed because the second step $^5I_7 \rightarrow {}^5F_3$ is also resonant. The terminal level of the ESA transition ($^5F_2$, $^3K_8$) locates several hundreds cm^{-1} higher than that of the GSA transition ($^5F_3$) through a two-step excitation process. When the excitation wavelength was tuned to that of the ESA transitions, the energy mismatch between the $^5I_8 \rightarrow {}^5F_5$ and $^5I_7 \rightarrow {}^5F_2$, $^3K_8$ transitions must be bridged by phonon sideband absorption which limits the ESA transition probability.

The build-up and decay characteristics for the green upconversion have been studied under cw dye laser excitation at 15766 cm^{-1} which corresponds to a GSA transition. The rise and decay curves are shown in Fig. 3a,b. The rise curve is composed of two exponential components which is in accordance

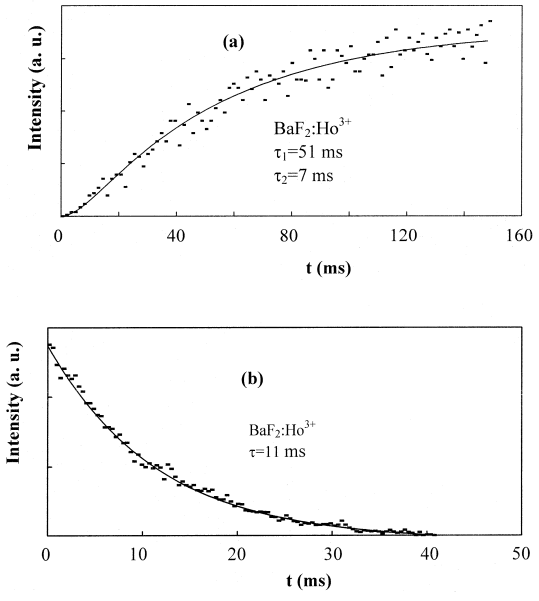

Fig. 3. Green upconversion rise (a) and decay (b) curves upon GSA excitation at 15766 cm^{-1} at 77 K.

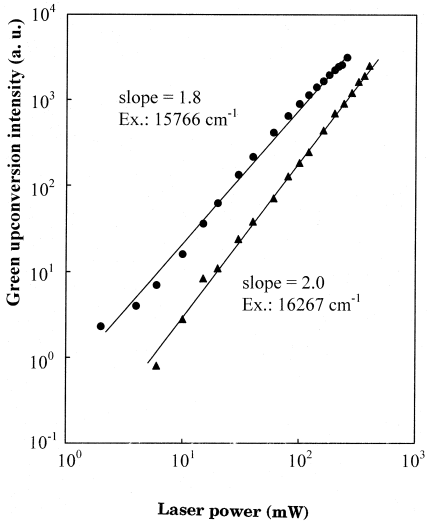

Fig. 4. Laser power-dependence of the green upconversion fluorescence of the Ho^{3+} C_{3V} centre upon GSA and ESA excitations.

with the two-step absorption character [9]. The curve can be fitted by the following equation:

$$I = I_0\left[1 - \frac{\tau_1}{\tau_1 - \tau_2}\exp\left(\frac{-t}{\tau_1}\right) + \frac{\tau_2}{\tau_1 - \tau_2}\exp\left(\frac{-t}{\tau_2}\right)\right] \quad (1)$$

where τ_1 is a time constant related to the lifetime of the intermediate level and the absorption probability of the ground state, while τ_2 is a constant associated with the lifetime of the emission level [9]. The real rise-time is therefore represented by τ_1 and the effect of τ_2 on the rise curve is reflected by a time delay at the beginning of the rise curve. In Fig. 3a, the solid line is the result fitted by Eq. (1) which gives a rise time τ_1 of 51 ms. The decay curve is exactly exponential with a time constant of 11 ms. These values are comparable to those observed with the C_{3V} centre in the SrF_2 crystal [6]. Under 16108 cm^{-1} excitation, the upconversion rise curve cannot be correctly registered due to the weak emission intensity.

A study of the Ho^{3+} green emission intensity upon the incident laser power has shown a quadratic dependence with a slope of 1.8 and 2.0 for excitation of the GSA transitions (15766 cm^{-1}) and the ESA transitions (16267 cm^{-1}) respectively (Fig. 4). Hence, we propose an upconversion mechanism of a

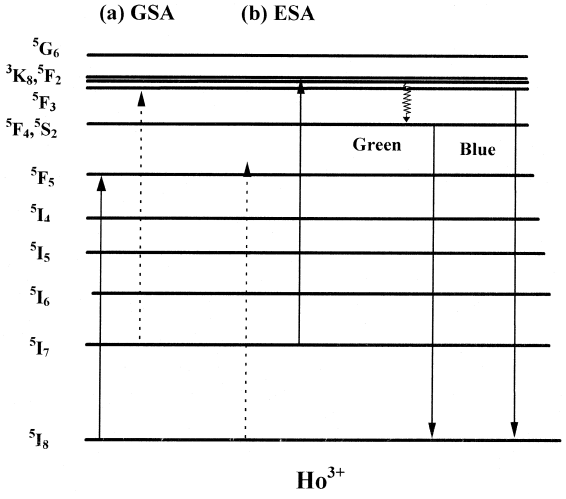

Fig. 5. Upconversion mechanisms for excitation into GSA (a) and ESA (b) transitions.

sequential two-phonon absorption process, with the laser resonant with both GSA and ESA transitions (Fig. 5).

4. Conclusion

The efficient red-to-green upconversion upon pumping with a red dye laser observed from the C_{3V} centre in Ho^{3+} doped BaF_2 crystal has been reported. Compared to the multi-site character observed in other fluorite-type crystals, the presence of a single C_{3V} symmetry site in BaF_2 could produce a single upconverted emission. The observation is probably further in favor of obtaining upconversion laser operation. The spectral and dynamic results indicate that a sequential two-photon excitation process is responsible for the observed upconversion with the laser excitation resonant with both the GSA and ESA transitions. The GSA excitation is much more efficient than the ESA owing to a double resonant characteristic.

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