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Site-selective upconversion in Ho^{3+} doped fluorite crystals MF_2 ($\text{M}=\text{Ca}, \text{Sr}, \text{Cd}$)

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ABSTRACT With tunable dye laser (620-660 nm) excitation, the site-selective upconversion properties of 0.1 mole% Ho^{3+} doped CaF_2 , SrF_2 and CdF_2 monocrystals were studied at 77K. Three distinct luminescence centres (C_{4v} , C_{3v} and cluster) were identified for both CaF_2 and SrF_2 crystals, whereas only one cluster centre was detected for CdF_2 . The upconversion mechanism for the isolated Ho^{3+} single site (C_{4v} or C_{3v}) is different from that for the cluster centre, with a two-step excitation process for the former and an energy transfer process for the latter.

1. INTRODUCTION

In fluorite-type crystals, the rare earth ions usually show three kinds of crystallographic sites of tetragonal (C_{4v}), trigonal (C_{3v}) and cubic (O_h) symmetry, corresponding to a fluoride ion compensation in a first-nearest-neighbour interstitial position, in a second-nearest-neighbour interstitial position and in a distant position, respectively[1]. At high dopant concentration, dimer pairs of ($\text{Re}^{3+}\text{-F}^-$) are formed. The multicentre characteristics make the rare earth doped fluorite-type crystals suited for the laser site-selective study. We show that the site-selective upconversion spectroscopy can be used as an efficient method in identifying different centres. In this paper, we briefly report the results obtained for 0.1% Ho^{3+} doped CaF_2 , SrF_2 and CdF_2 crystals.

2. EXPERIMENTAL

The $\text{CaF}_2:0.1\% \text{Ho}^{3+}$ and $\text{SrF}_2:0.1\% \text{Ho}^{3+}$ crystals used in this study were purchased from Optovac Inc.(USA). The $\text{CdF}_2:0.1\% \text{Ho}^{3+}$ was grown in our laboratory using the Bridgman technique. The optical absorption spectra were measured at room temperature using a Perkin-Elmer Lambda-9 spectrophotometer. A cw-Argon ion laser pumped dye laser (working on Kiton red) was used as excitation source. The laser beam can be continuously tuned from 620 to 660 nm ($15200\text{-}16200 \text{ cm}^{-1}$), with a maximum output of about 400 mw at 640 nm (15620 cm^{-1}), and is focused into the crystal. The fluorescence from the sample was dispersed by a Coderg three-grating monochromator, and detected by a cooled photomultiplier (EMI 9558 QB). For the dynamic study, the laser beam was cut-off by a Pockels cell. The rise and decay signals were recorded by a OX750-2 Metrix oscillograph, and analysed by a microcomputer. All the fluorescence measurements were performed at 77 K.

3. RESULTS AND DISCUSSION

The upconversion properties from three distinct centers (C_{4v} , C_{3v} and cluster) of $\text{CaF}_2:0.1\% \text{Ho}^{3+}$ crystal will be reported in detail soon by us. All these centres show upconversion fluorescence at blue ($^5\text{F}_3 \rightarrow ^5\text{I}_8$), green ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$) and near infrared at about 750 nm ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_7$) regions. Although the upconversion of the $\text{Ho}^{3+} \text{C}_{3v}$ centre was not detected in slightly doped (0.005 mole% Ho^{3+}) crystal[2], we have observed a green emission intensity similar to that of the other two centres. The blue emission, however, is dominated by the cluster centre.

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In $\text{SrF}_2:0.1\% \text{Ho}^{3+}$ crystal, we have also identified three luminescence centres. The most intense one has a tetragonal (C_{4v}) symmetry[2], which is also observed in $\text{CaF}_2:0.1\% \text{Ho}^{3+}$ crystal. Under red laser excitation, anti-Stokes fluorescence from $^5\text{F}_3$ and $^5\text{F}_4, ^5\text{S}_2$ levels have been detected (Fig.1). The second centre gives mainly a blue upconversion fluorescence (Fig.2b), and the green (Fig.2a) and infrared emissions are relatively weak. In addition, this centre shows very short fluorescence rise and decay times. These behaviours are parallel to those of the cluster centre in CaF_2 . Note that either the emission or excitation spectra for this centre are totally different from those of the cluster in CaF_2 . To our knowledge, the spectral properties for this centre was not reported before.

Fig.1 Green (a) and blue (b) upconversion spectra for the $\text{Ho}^{3+} \text{C}_{4v}$ centre in SrF_2 at 77K, $\text{Ex}=15642 \text{ cm}^{-1}$

Fig.2 Green (a) and blue (b) upconversion spectra for the Ho^{3+} cluster centre in SrF_2 at 77K, $\text{Ex}=15703 \text{ cm}^{-1}$

The remaining minority centre shows only weak green emission accompanied by several vibrational bands (Fig.3). No blue and infrared emission was observed under the same excitation condition. Compared with the emission spectra of the other two centres, the emission lines are narrow. The result obtained in this work generally agree with that of the C_{3v} centre reported under conventional excitation by Mujaji et al[2]. This centre is probably a C_{3v} centre with a fluoride interstitial in a next-nearest-neighbour. The typical

Fig.3 Green upconversion spectra for the $\text{Ho}^{3+} \text{C}_{3v}$ centre in SrF_2 at 77K, $\text{Ex}=15786 \text{ cm}^{-1}$

excitation spectra for the three centres are shown in Fig.4. Furthermore, for the third centre, we have detected many excitation lines located between 16000-16350 cm^{-1} (Fig.5 shows excitation spectrum up to 16250 cm^{-1}). These lines correspond to the magnetic dipole transition $^5\text{I}_7 \rightarrow ^3\text{K}_8$, whereas no excitation line can be observed for other centres in this region.

Fig.4 Excitation spectra of the green emission for the three centres observed at 77K. (a) C_{4v} (18192 cm^{-1}); (b) C_{3v} (18688 cm^{-1}); (c) cluster (18131 cm^{-1})

Fig.5 Excitation spectrum from the $^5\text{I}_7 \rightarrow ^3\text{K}_8$ ($^5\text{F}_2$) for C_{3v} centre (18688 cm^{-1})

In Ho^{3+} doped CdF_2 crystal, only one centre is detected, and both the emission and excitation spectra are much similar to those of the cluster in CaF_2 . Just as observed in CaF_2 , strong blue upconversion is obtained, which is more intense than the green emission. So, this centre is considered as a cluster centre.

The lifetimes of Ho^{3+} in different centres in CaF_2 are similar to the results reported before [2-3]. In SrF_2 , both the rise and decay times for Ho^{3+} different centres are longer than those in CaF_2 . The results are shown in Table 1. Table 1 also gives the lifetimes of infrared emission $>1.7 \mu\text{m}$. For this measurement, a optical filter which is transparent for all the infrared light longer than $1.7 \mu\text{m}$ is placed in front of the detector, and a decay time as long as 110 ms is observed for the C_{3v} centre. The long lifetimes of Ho^{3+} emission in SrF_2 correspond to the weak perturbation of the cubic site of the fluorite lattice.

Table 1 Experimental fluorescence rise and decay times (in ms) for the three Ho^{3+} centres in SrF_2 at 77K

		infrared $\lambda > 1.7 \mu\text{m}$	red	green	blue
C_{4v}	rise	25	0.42	16.4	6.8
	decay	32	0.44	1.7	0.47
C_{3v}	rise	91	0.53	68	
	decay	111	0.52	6.3	
cluster	rise	5.0	0.43	0.43	0.62
	decay	6.4	0.44	0.54	0.42

With changing the laser power, the dependence of upconversion fluorescence for all the Ho^{3+} centres, except C_{3v} in SrF_2 , show two features: quadratic dependence for lower power

and linear for higher power. For the C_{3v} centre of SrF_2 , only quadratic dependence is observed. It is clear that a two-photon process takes place for all the centres, and the linear dependence is well-known as a saturation effect[4]. In SrF_2 , the C_{3v} centre resembles a cubic centre, and the excited state absorption is not very efficient, thus no saturation appears under the experimental condition. The upconversion mechanism for the isolate centres (C_{4v} and C_{3v}) and for the cluster centres is different. Generally, the excitation spectra of upconversion fluorescence include both transition from ground state and transition from excited state for C_{4v} and C_{3v} centre, whereas only transition from the ground state is observed for that of the cluster centre. Therefore, a successive two-step excitation process is proposed for C_{4v} and C_{3v} centres, and an energy transfer process for the cluster centres, as shown in Fig.6.

Fig.6 Upconversion mechanisms for the Ho^{3+} different centres in MF_2 . (a) two-step excitation; (b) energy transfer, 1,2 show the two possible cross-relaxations.

4. CONCLUSION

Red dye laser induced upconversion of Ho^{3+} ions in CaF_2 , SrF_2 and CdF_2 monocrystals were investigated and compared at 77 K. Two single centres of C_{4v} and C_{3v} , and a cluster centre were identified in both CaF_2 and SrF_2 crystals. Only one cluster centre was detected in CdF_2 . The fluorescence rise and decay times for Ho^{3+} in SrF_2 are much longer than those in CaF_2 , reflecting the weak perturbation of the cubic site of the fluorite lattice of the former. For the upconversion mechanisms, a two-step excitation is suggested for those single centres C_{4v} and C_{3v} , and an energy transfer process for the clusters.

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