

FLUORESCENCE DECAY CHARACTERISTICS OF THE GREEN EMISSION FROM $\text{CaF}_2:\text{Ho}^{3+}$

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Variations in the decay times of the characteristic green emissions at 522.7, 551.3, 549.6, 547.6, 542.2, 540.2, 535.9 and 533.5 nm from $\text{CaF}_2:\text{Ho}^{3+}$ with concentration are studied at RT and LNT. A pulsed N_2 laser beam of power density 1.5 MW cm^{-2} is used for the excitation. Temperature dependent concentration quenching of the decay times are observed for all the emission bands. But an increase in the decay time due to the reabsorption process is also observed for a few of the above bands.

1. INTRODUCTION

THE DEVELOPMENT of solid state lasers has generated wide spread interest in the spectroscopy of ions in crystals. Extensive research on the properties of doped rare earth ions in crystals with particular reference to concentration and temperature quenching of fluorescence has been reported [1]. Most of the studies are on Nd^{3+} doped crystals and they showed strong quenching of fluorescence decay times with concentration and temperature for most of the upper levels of Nd^{3+} [2, 3]. To the authors' knowledge such studies are not reported for $\text{CaF}_2:\text{Ho}^{3+}$ and we report here the variations of decay times of the characteristic green emission of $\text{CaF}_2:\text{Ho}^{3+}$ for different concentrations of Ho^{3+} at RT and LNT. The emission spectra of these crystals along with the variations in the intensities of the bands have been reported by the authors earlier [4].

2. EXPERIMENTAL

$\text{CaF}_2:\text{Ho}^{3+}$ crystals with three different Ho^{3+} concentrations (0.2, 0.4 and 1%) obtained from Optovac Inc. and having the same dimensions (10 mm x 4 mm) were irradiated with an N_2 laser ($\sim 1.5 \text{ MW cm}^{-2}$). The emission spectra were recorded at RT and LNT using a 0.5M Jarrell Ash monochromator, and EMI model 9683 KQB photomultiplier and an Ominiscribe $x-t$ recorder. The grating used was the one blazed at 500 nm. The exit and entrance slit widths of the monochromator were kept at $600 \mu\text{m}$ so that a resolution of nearly 0.48 nm was achieved. The fluorescence spectra of $\text{CaF}_2:\text{Ho}^{3+}$ when excited by the nitrogen laser gave several distinct emission peaks in the region 530 nm. The fluorescence decay times of the emission bands were detected with the help of a PMT, a box car averager (EG & G PARC Model 162) and Ominiscribe model 3000 $x-y$ recorder. The details of the experimental setup are discussed elsewhere [5].

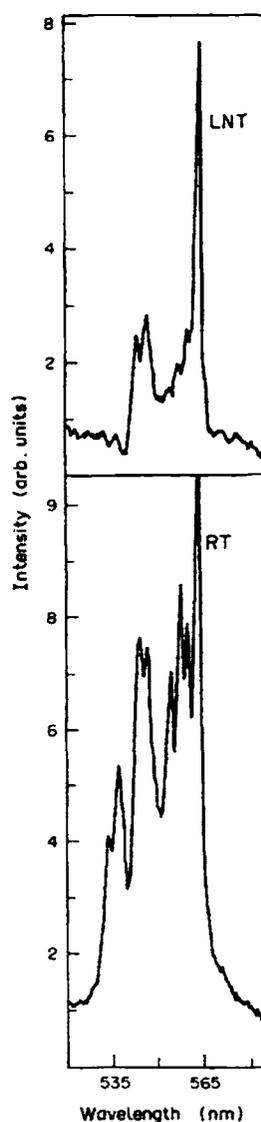


Fig. 1. Fluorescence spectra of $\text{CaF}_2:\text{Ho}^{3+}$ (0.2%) around 530 nm.

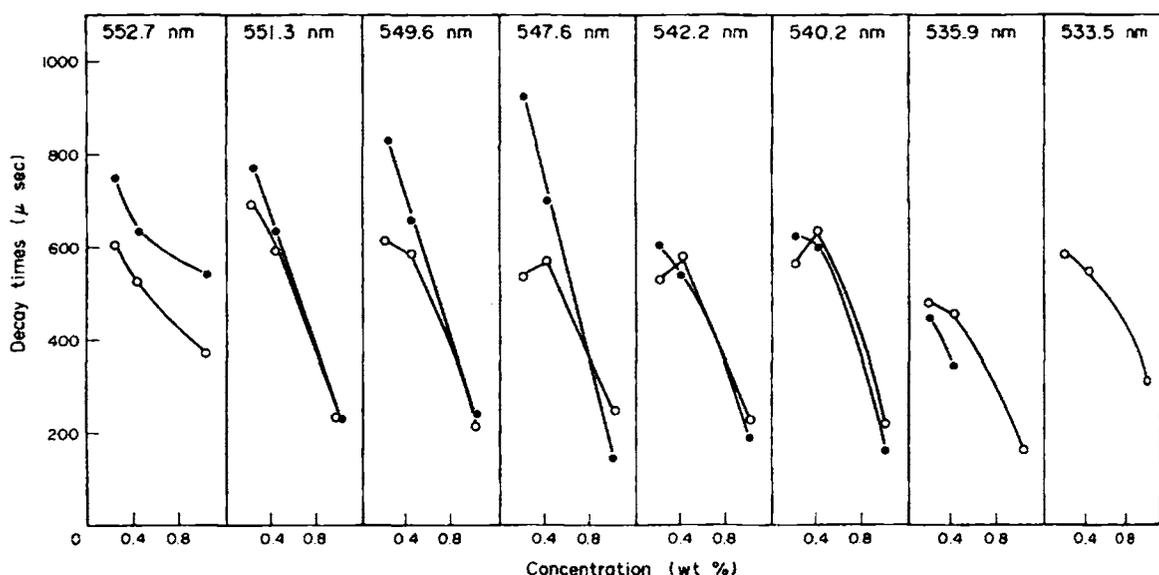


Fig. 2. Variation of decay times with Ho^{3+} concentration and temperature ○-○ at RT, ●-● at LNT.

3. RESULTS AND DISCUSSIONS

The nitrogen laser induced fluorescence emission of Ho^{3+} around 530 nm consists of eight well defined narrow bands (Fig. 1) at 552.7, 551.3, 549.6, 547.6, 542.2, 540.5, 535.9 and 533.5 nm. These green emissions are attributed to the $5F_4 \rightarrow 5I_4$ and $5S_2 \rightarrow 5I_4$ transitions of Ho^{3+} [6] while the line structure is due to transitions among the various Stark levels. The total fluorescence intensity of this green band is found to decrease considerably at LNT. Two of the fluorescence lines at 533.5 and 535.9 nm even vanish at LNT. It is also clear from the spectra that the changes in the intensity ratios with temperature are not the same for all the bands.

The variations in the decay times with Ho^{3+} concentration for all the eight transitions at RT and LNT are shown in Fig. 2. A sharp decline in the decay time with the concentration is observed at both RT and LNT. In fact, the effect is more pronounced at the lower temperature. Also for some of the emissions the decay time at LNT is less than that at RT. The strong quenching of decay time with concentration indicates that there is a large contribution from concentration dependent relaxation processes (CDRP). A similar dependence of decay time on concentration has been reported by Asawa and Robinson for Nd^{3+} in LaF_3 [3]. The CDRP can be due to ion-ion interaction and energy migration leading to resonant and non-resonant ion-pair transitions. It may also be concluded that the CDRP contribution is different for different emission bands.

The decay time is found to decrease rapidly with concentration for the emissions at 551.3, 549.6 and 547.6 nm. Of these the 551.3 and 549.6 nm lines have almost the same decay time ($\sim 223 \mu\text{s}$) at RT and LNT

for 1% Ho^{3+} concentration. This indicates that the decrease in decay time at LNT due to CDRP is nearly equal to the decrease in decay time due to multi-phonon transitions at RT.

The contribution from the CDRP is found to be much less at RT than at LNT for the bands at 542.2, 540.2 and 535.9 nm which have decay times higher at RT than at LNT. This contrasting behaviour of decay time quenching at LNT may be due to the accidental matching of transitions. A close examination of energy levels of Ho^{3+} in CaF_2 [7] shows that cross relaxation are possible between many pairs of lines.

An increase in decay time is noted for the intermediate concentration for the bands at 547.6, 542.2 and 540.5 nm. For these bands at low concentrations the processes of reabsorption and ion-ion interaction are negligible. But with the increase in Ho^{3+} concentration, the reabsorption process may become dominant so that the decay times will increase with increasing concentration. As the concentration is further increased ion-ion interaction becomes a more dominant process resulting in a decrease in the decay time. The band at 552.7 nm shows a concentration and temperature dependence with the decay time at RT being less at low concentrations compared to the decay time at LNT. For the band at 533.5 nm the studies are reported only for RT because of the low intensity at LNT.

In general, it may be concluded from the present study that the CDRP contribution is different for different emission bands. A contrasting behaviour of decay time quenching is observed for some of the bands due to cross relaxations possible in the system. In addition, reabsorption processes are also taking place.

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