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Energy Transfer in Er:CeF$_3$ Crystals *

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Two Er:CeF$_3$ crystals doped with 1.0 and 1.2 wt.% Er$_2$O$_3$ and one pure CeF$_3$ crystal were grown, their absorption and fluorescence spectra at room temperature were measured. Compared with pure crystal,the emission intensity of Ce^{3+} in Er : CeF$_3$ decreased obviously, it is the sign of energy transfer from 5d state of lattice Ce^{3+} to 4f state of Er^{3+} ions which improves the stimulation emission efficiency of Er^{3+} ions.

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The fluorescence properties of Ce^{3+} compounds and Ce^{3+} doped materials are intensively studied[1-3] because some of them turned out to be good candidates for sintillation detectors. One of the very promising materials— CeF$_3$ crystal has already been investigated in scintillation and laser regime[4,5] and compared with other materials. Gao *et al.*[6] reported fluorescence properties of Nd: CeF$_3$ crystals. The purpose of our work is twofold: first, to find effects of doping ions on scintillation properties; second, to improve the laser efficiency of CeF$_3$-based crystals.

We have been undertaking the growth of CeF$_3$ crystals and have already obtained large high-quality crystals. Based on the growth techniques of CeF$_3$ crystals, we grew two CeF$_3$ crystals doped with different concentrations of Er^{3+}. The purities of CeF$_3$ and ErF$_3$ powders are 99.9 and 99.99%, respectively. The crystals are grown by Bridgeman method in a high vacuum furnace and the descending rate is 2 mm/h. The concentrations of Er^{3+} in CeF$_3$ crystals are 1.0 and 1.2 wt.%, respectively. Er^{3+} ions distribute in the crystals homogeneously.

CeF$_3$ has a hexagonal crystal structure ($C6/mcm$), the ionic radius of Ce^{3+} is 1.10 Å, isomorphic substitution of Er^{3+} is easily effected without charge compensation.

The absorption spectra of crystals were measured by a Shimadzu UV-2501 spectrophotometer. Figure 1 illustrates the comparison of absorption spectra of three crystals at room temperature. The absorption edge of pure CeF$_3$ is at 300 nm, the crystals with Er^{3+} dopants have very strong absorption at about 326 nm, in fact, their absorption edge is still at 300 nm, several peaks of Er^{3+} transitions from ground state to upper levels can be observed. The ground state of Ce^{3+} contains one $4f$ electron shielded by $5s^2 5p^6$ shells. The energy levels of Ce^{3+} are shown in Fig. 2, one $f-f$ transition occurs at 2000 cm^{-1} and $f-d$ transitions start at 31000 cm^{-1}.

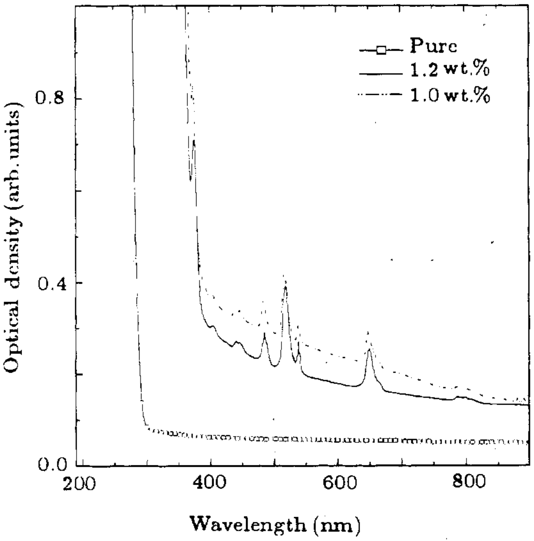

Fig. 1. Absorption spectra of CeF$_3$ crystals with and without Er^{3+} dopants.

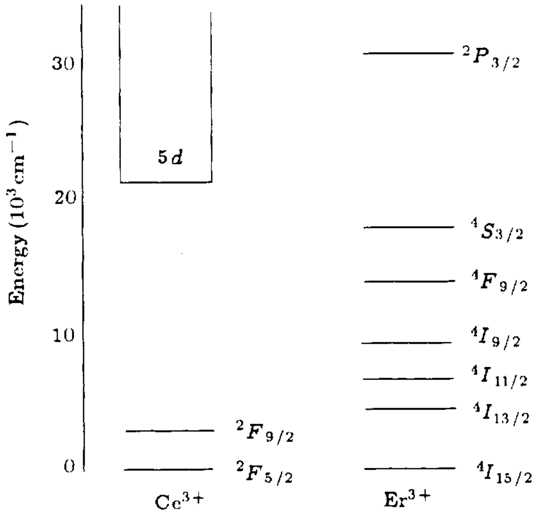

Fig. 2. Energy levels of Ce^{3+} and Er^{3+} ions.

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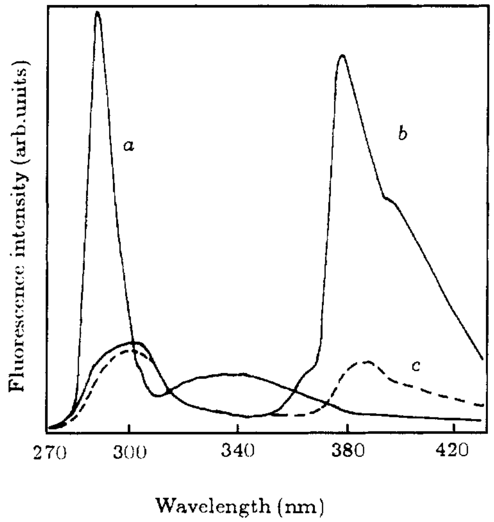

Fig. 3. Fluorescence spectra of CeF_3 crystals, curve *a*: pure, curve *b*: with 1.2 wt.% Er^{3+}, and curve *c*: with 1.0 wt.% Er^{3+}.

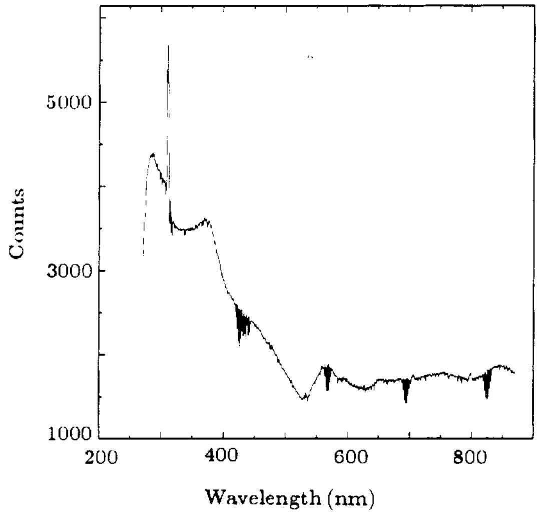

Fig. 4. Fluorescence spectra of pure CeF_3 crystal pumped by 266 nm.

There are two ways of energy transfer in crystals, one is from doping ions to other doping ions, another is direct energy transfer from lattice to doping ions. In latter case, donors have much more concentrations than those in the first case and result in greater transfer efficiency. The energy levels of CeF_3:Er^{3+} are shown in Fig. 2, it can be seen that the $5d$ state of Ce^{3+} is close to $4f$ excited state of Er^{3+}, so that the $5d-4f$ energy transfer is possible.

The peak of excitation spectrum of pure CeF_3 crystal is at 250 nm, which is in the absorption edge of CeF_3 crystals, so it can be absorbed by the lattice completely. The fluorescence measurements are performed by LS-50B spectrophotometer, the slit width is 10 nm, Fig. 3 is emission spectra of three crystals (excitation wavelength of 250 nm). In pure crystal there are two peaks, one is at 340 nm, which is trap emission of Ce^{3+}, another is at 292 nm, which in fact is superposition of two peaks (285 and 305 nm, respectively), as can be seen from the emission spectra of crystals pumped by the fourth harmonic of Nd:YAG laser (266 nm, ARC Spectrapro 275), shown in Fig. 4. In CeF_3:Er^{3+} crystals, the peak at 395 nm is the emission of Er^{3+} originated from $^2P_{3/2} \rightarrow {}^4I_{13/2}$ transition, compared with pure CeF_3 crystal, it is easily seen that the intensity of the 292 nm peak is decreased obviously, the 340 nm peak disappears, and the intensity of the 395 nm peak is increased with increasing Er^{3+} concentration. On the other hand, when excitation wavelength is 350 nm, the emission intensity of Er^{3+} at 395 nm is much lower than that pumped by 250 nm. It means that when Ce^{3+} cannot be excited effectively, the emission of Er^{3+} is weak. It can be concluded that there is energy transfer from Ce^{3+} to Er^{3+}.

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