THE DYNAMICS PROPERTIES ON LUMINESCENCE OF CeF$_3$ CRYSTALS

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This paper presents temperature dependence of emission spectra (290 nm and 340 nm bands), excitation spectra (250–3000 Å), luminescence decay time as well as their excitation effect for CeF$_3$ crystals. The results indicate that energy transfer from Ce$^{3+}$ to defect centers in the CeF$_3$ crystals was very efficient as temperature increased. The 340 nm emission band may originate from some defects near Ce$^{3+}$, rather than Ce$^{3+}$ perturbed defects.

1. Introduction

Luminescence properties of CeF$_3$ crystals have been extensively studied in the past few years.\textsuperscript{1–4} This is due to their good scintillation character, especially fast luminescence decay time (< 50 ns), higher luminescence efficiency. Compared with other scintillators, the CeF$_3$ crystal is a very good candidate as an electromagnetic calorimeter (ECAL) material used for the Large Hadron Collider (LHC), except that its density (6.16 g/cm$^3$) is lower than that of PbWO$_4$.\textsuperscript{5} It is also a scintillator used for nuclear medical imaging. However, its luminescence mechanism, especially luminescence center, is still under discussion. According to the high energy excitation process in the CeF$_3$ crystals, its light yield can reach to 7000–12000 photons/MeV, but its experimental value is only 1500–4500 photons/MeV,\textsuperscript{4} which indicated some nonradiative decay processes existing in the crystal. In our previous work,\textsuperscript{6} cascade energy transfer in the CeF$_3$ crystals was found. The path of the cascade transfer is as follows: Ce$^{3+} \rightarrow$ Ce$^{3+}$ perturbed by defect $\rightarrow$ defects centers $\rightarrow$ quenching centers. To understand this process further, the dynamics properties of CeF$_3$ luminescence, especially temperature dependence (5–350 K) of fluorescence emission and their excitation spectra as well as decay time, were studied in detail.

2. Experimental

The CeF$_3$ crystals were grown by Bridgman method in high vacuum ($10^{-5}$–$10^{-6}$ Torr). The original material was CeF$_3$ powder of purity 99.99% or more. The samples with dimensions $10 \times 10 \times 1$ mm$^3$ were polished on both sides. The emissions, excitation spectra and luminescence decay time were measured at the SUPERLUMI experiment station in HASYLAB, DESY, Germany. The resolution of the primary monochromator (2 m McPherson) and the secondary monochromator is 0.3 nm and 6.4 nm respectively. The full width at half maximum (FWHM) of the synchrotron radiation pulse for

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excitation is 130 ps. The detector is a photomultiplier (XP2020Q). The temperature of the sample can be varied from 5 K to 350 K. The details of the setup can be found elsewhere.\(^7\)

### 3. Main Results

The emission spectra of the CeF\(_3\) crystals at 5 K under VUV (61, 157, 191 nm) excitation consist of a strong band with double peaks at 286 and 304 nm, which is caused by the “spin–orbit” splitting of the 4f ground states (\(^2F_5/2, ^2F_7/2\)) in the transition of Ce\(^{3+}\); 5d \(\rightarrow\) 4f. As the temperature increase, however, the double peaks decrease and combine into one peak at 290 nm. Under UV 270 nm excitation at 5 K, there was only one emission band peaked at 342 nm, which may be luminescence from some defect centers near Ce\(^{3+}\).

As shown in Fig. 1, the excitation spectra of 340 nm emission at 5 K include a strong band centered at 266 nm and two weak bands peaked at 56 nm and 120 nm, the weak bands corresponding to the intrinsic excitation of core levels in the CeF\(_3\), while the excitation spectra of Ce\(^{3+}\) 290 nm emission at 5 K have a broad band of 4f \(\rightarrow\) 5d transition from 175 nm to 260 nm, which includes several subbands caused by crystal field splitting.\(^8\) The excitation spectra of 290 nm and 340 nm emission only overlap around 260 nm at 5 K. But the two spectra are similar in the range of 150–260 nm at 350 K. The fact indicates that the energy transfer from 290 nm emitted by Ce\(^{3+}\) to 340 nm emitted by some defect centers is quite efficient as the temperature increases.

The energy transfer from the 290 nm band to the 340 nm band was also further confirmed by luminescence decay time (\(\tau\)) at different temperatures. The decay times of the 290 nm and 340 nm emission bands excited by 61 nm (i.e. \(\tau_{290}, \tau_{340}\)) at RT were about 4 ns (fast component) and 30 ns, respectively. However, \(\tau_{340}\) was postponed from about 20 ns to 40 ns with rising temperature from 5 K to 350 K (Fig. 2). But no noticeable variation was found for the \(\tau_{290}\), as shown in Fig. 3.

The decay curves of 340 nm emission obviously depend on the excitation wavelength, as shown in Fig. 4. Under 190 and 270 nm excitation at 350 K, the first part of the decay curves was to go up to the maximum in about 20 ns, then decay. But under 61 nm excitation corresponding to core electron energy, the decay curve has no rising part.
Ce$^{3+}$ band in CeF$_3$ energy transfer from the 290 nm band to the 340 nm emission. It is a fundamental condition of partly with the excitation spectra (in 250–300 nm) of 340 nm emission. The energy transfer can be through reabsorption or resonance between two kinds of luminescence centers. The energy transfer has been proved by temperature dependence of the excitation spectra and decay time of 290 nm and 340 nm emission. The energy transfer probability increases with increasing temperature. It is due to the increasing overlap integral between the 290 nm emission band and the excitation spectrum of 340 nm emission as the temperature increases. In general, the decay time of energy donors (Ce$^{3+}$) should be shorter in the energy transfer and that of energy acceptors (defect luminescence centers) should be postponed, which has been shown in Fig. 3. But the decay time $\tau_{290}$ of Ce$^{3+}$ luminescence was not obviously changed. The reason may be that the radiation transition probability $P_r(\text{Ce})$ of Ce$^{3+}$ 5d $\rightarrow$ 4f (allowed transition about $\sim 10^9$/s) is much larger than energy transfer probability $P_{et}$ from Ce$^{3+}$ (290 nm emission) to some defect center (emitting 340 nm) and nonradiative transfer probability $P_{nr}$, i.e.

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\tau(\text{Ce}) = \frac{1}{P_r(\text{Ce})} = \left[ P_r(\text{Ce}) + P_{et} + P_{nr} \right]^{-1}
$$

$$
\approx \frac{1}{P_r(\text{Ce})},
$$

when $P_r \gg P_{et} + P_{nr}$, where $P_r(\text{Ce})$ is total transition probability of Ce$^{3+}$.

The energy transfer mentioned above was also confirmed by dependence of the decay curve on the excitation wavelength for 340 nm emission. In the decay curves under 270 and 190 nm excitation, there are the first rising region in about 20 ns. The 270 and 190 nm excitations correspond to 4f $\rightarrow$ 5d of Ce$^{3+}$, and there is direct energy transfer from Ce$^{3+}$ 5d states to 340 nm luminescence centers in about 20 ns. Thus, luminescence intensity was increased at the first part, and transfer time was about 20 ns, which is just the same order of magnitude as the decay time of Ce$^{3+}$ emission (slower component).

A popular point of view is that the 340 nm emission band originates from Ce$^{3+}$ perturbed by defects, but here we suggest that it may be from some defect centers near Ce$^{3+}$. The reason is as follows. The 340 nm emission band and its excitation spectra at low temperature have no characteristic of Ce$^{3+}$ except for fast decay time with several ten of nanoseconds. If the 340 nm band really is from Ce$^{3+}$ perturbed by defects, its spectral shape should show double peak structures at 5 K even though the relative intensity and positions of the peaks are different from regular Ce$^{3+}$, because splitting of Ce$^{3+}$ 4f ground states ($^2F_{5/2}, ^2F_{7/2}$) is about 2000 cm$^{-1}$, which is much larger than that of crystal field reaction (usually several ten to several hundred cm$^{-1}$) caused by some defects. At 5 K, there was no trace of Ce$^{3+}$ emission structure for the 340 nm emission band. On the other words, the 340 nm luminescence centers could be quite different from Ce$^{3+}$, but they should locate near Ce$^{3+}$ for efficient energy transfer from Ce$^{3+}$ to themselves with rising temperature.

4. Discussions

The 290 nm emission band from Ce$^{3+}$ overlaps partly with the excitation spectra (in 250–300 nm) of 340 nm emission. It is a fundamental condition of energy transfer from the 290 nm band to the 340 nm band in CeF$_3$ crystals. The transfer can be through reabsorption or resonance between two kinds of luminescence centers. The energy transfer has been proved by temperature dependence of the excitation spectra and decay time of 290 nm and 340 nm emission. The energy transfer probability increases with increasing temperature. It is due to the increasing overlap integral between the 290 nm emission band and the excitation spectrum of 340 nm emission as the temperature increases. In general, the decay time of energy donors (Ce$^{3+}$) should be shorter in the energy transfer and that of energy acceptors (defect luminescence centers) should be postponed, which has been shown in Fig. 3. But the decay time $\tau_{290}$ of Ce$^{3+}$ luminescence was not obviously changed. The reason may be that the radiation transition probability $P_r(\text{Ce})$ of Ce$^{3+}$ 5d $\rightarrow$ 4f (allowed transition about $\sim 10^9$/s) is much larger than energy transfer probability $P_{et}$ from Ce$^{3+}$ (290 nm emission) to some defect center (emitting 340 nm) and nonradiative transfer probability $P_{nr}$, i.e.

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5. Conclusion

According to experiment results on temperature dependence of emission spectra, excitation spectra and luminescence decay time of CeF$_3$ crystals, the energy transfer from the 290 nm band from Ce$^{3+}$ to the 340 nm band (emitted by some defects) was further confirmed. The energy transfer probability was increased with rising temperature. The origin of the 340 nm emission band may be some defect centers near Ce$^{3+}$ rather than Ce$^{3+}$ perturbed by defects.

### References