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# FLUORESCENCE PROCESSES AND SCINTILLATION OF $\text{CeF}_3$ CRYSTALS EXCITED BY UV AND X-RAY SYNCHROTRON RADIATION\*

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Photoluminescence properties of  $\text{CeF}_3$  have been investigated. Two kinds of emitting centers have been identified: regular  $\text{Ce}^{3+}$  sites exhibiting two close emission bands (285 and 300 nm) and a fast fluorescence (20 ns) and several physically different perturbed  $\text{Ce}^{3+}$  sites giving rise to a broad emission band near 340 nm and a longer fluorescence (30–40 ns) the decay time of which varies with wavelength. An energy transfer occurs between these two kinds of centers. Scintillation properties have been studied under UV and X-ray excitation. The additional fast decay always observed at short time under ionizing radiation is interpreted by a temperature dependent luminescence quenching phenomenon due to high excitation density.

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## 1. Introduction

The search of new and better scintillators for radiation detection is very active. Today scintillating materials play a prominent role in many fields of basic research. They have also found many applications elsewhere, e.g. in nuclear medicine, in geological surveys (well logging), in airport security systems.

Cerium fluoride crystal is a very good candidate for applications in high energy physics [2]. It is a fast scintillator, dense enough to exhibit short radiation length and hard to ionizing radiation. Its relatively low light yield, however, is not a serious drawback for using in high rate calorimetry.

The scintillation properties of  $\text{CeF}_3$  have been studied extensively and excellent reviews have been compiled very recently [2, 3] containing many references. New contributions can be also found in this special issue [4] and in [5].

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\*This work was performed as part of the "Crystal Clear" collaboration, CERN Research and Development project RD-18 [1].

The aim of the present paper is to summarize and interpret the photoluminescence properties of  $\text{CeF}_3$  and to propose a model to explain the decay behaviour of the scintillation which is still not understood.

The single crystals studied in this paper were all obtained from OPTOVAC and grown by the Bridgman technique. Two kinds of samples were used: (i)  $\text{CeF}_3$  of a first generation grown long time ago for different users and (ii)  $\text{CeF}_3$  of a second generation specially prepared for us and consisting of a series of single crystals of increasing quality made during one year.

## 2. Photoluminescence

$\text{CeF}_3$  exhibits five absorption bands in near UV range between 180 and 260 nm assigned to  $4f-5d$  parity allowed transitions, the degeneracy of the  $d$  level being completely left due to the very low local symmetry ( $C_2$ ).

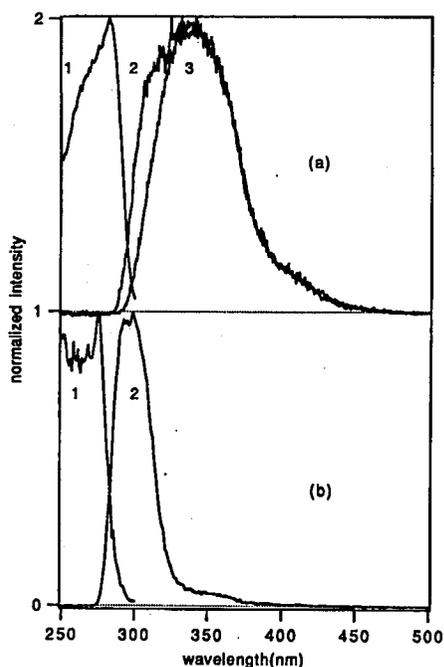


Fig. 1. Emission spectra of  $\text{CeF}_3$  at room temperature. (a) Sample of first generation ("with defects"): 1 — excitation spectrum (em: 360 nm), 2 — emission spectrum (exc: 220 nm), 3 — emission spectrum (exc: 280 nm). (b) Latest sample of second generation ("pure"): 1 — excitation spectrum (em: 360 nm), 2 — emission spectrum (exc: 200 nm).

Emission spectra strongly depend on the quality of the samples and on the photoexcitation energy. In the case of sample of the first generation, there are observed under 220 nm excitation an emission band peaking near 310 nm and a broader one at 340 nm (Fig. 1a). The latter is the only band under 280 nm

excitation. In addition, the excitation spectrum is extended up to 300 nm when the emission at long wavelength is considered.

In the case of the latest sample of the second generation (Fig. 1b), the band at 340 nm is very weak and two main peaks are observed near 285 and 300 nm (much better resolved at low temperature) as a result of transitions from the lowest  $d$  level to the two components  $^2F_{5/2}$  and  $^2F_{7/2}$  of the ground state split by the spin-orbit coupling and separated by roughly  $2000\text{ cm}^{-1}$ .

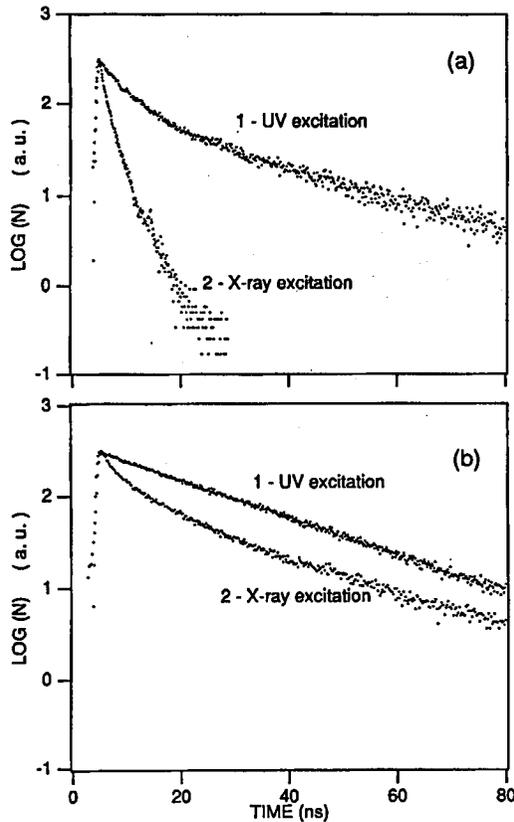


Fig. 2. Decay curves of the high energy luminescence band for two different  $CeF_3$  crystals ((a) — “with defects”, (b) — “pure”) measured under X-ray and UV excitations at 300 K.

This latter fluorescence is therefore interpreted as due to cerium ions occupying regular lattice sites while the broad emission band is assigned to perturbed  $Ce^{3+}$  sites. The most effective perturbations are probably due to  $F^-$  vacancies or  $F^-$  ion in an interstitial position or to the presence of some impurity ions like  $O^{2-}$ . The large variety of perturbations due to the nine non-equivalent ligands [6] leads to an important inhomogeneous broadening of the emission band. The perturbed  $Ce^{3+}$  sites are absorbing in the region of the emission of regular  $Ce^{3+}$  sites, an

efficient energy transfer between these centers is expected. This is confirmed by the strong nonexponentiality of the fluorescence decay of the donors in the case of the sample of the first generation (Fig. 2a, curve 1) which is supposed to contain a relatively large amount of perturbed  $\text{Ce}^{3+}$  sites. The latest sample of the second generation exhibits an exponential fluorescence decay with a time constant around 20 ns (Fig. 2b, curve 1) [7]. The 340 nm emission exhibits a variation of decay time with wavelength which confirms evidence for the existence of several physically different perturbed  $\text{Ce}^{3+}$  sites. Note that the decay of acceptors is preceded by a short rise which reflects the energy transfer more efficient at short time where donor-acceptor pair interactions are involved.

### 3. Scintillation

In Fig. 2 the high energy (300 nm) fluorescence decays measured under UV and X-ray excitations are pictured. It is clear that for the two samples "with defects" and "pure" an additional fast decay component is observed after excitation by ionizing radiation, as already often reported not only for  $\text{CeF}_3$  but also for  $\text{Ce}^{3+}$  in several other crystals and glasses (see [3] and references herein).

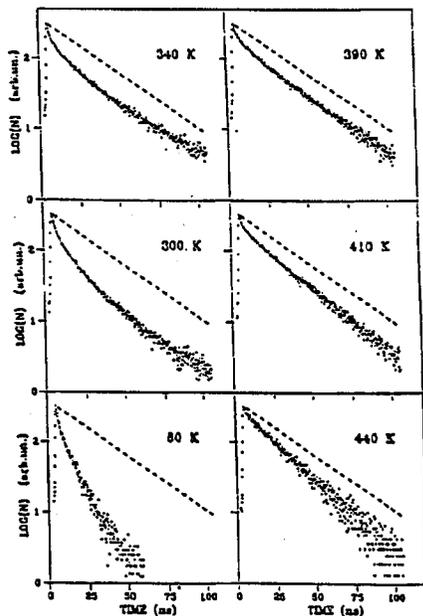


Fig. 3. Temperature dependence of the luminescence decay curves of "pure"  $\text{CeF}_3$ . For comparison, exponentials with  $t = 28$  ns are given (dashed lines).

The cause and the mechanism of quenching under high energy excitation remain unresolved. We think that the acceleration of the decay at short time can be caused by quenchers created in the vicinity of the emitting center by the same photon of high energy which excites the emitting center. In case of high excitation density and because both 4*f*-hole and 5*d*-electron in ( $Ce^{3+}$ ) are highly localized (one can expect low mobility of such exciton-like excitation), there exists a large probability to create two adjacent excited cerium ions and a kind of up-conversion process can occur leading to the quenching



Such mechanism can start to act at energies of incident photons higher than the threshold of multiplication of electronic excitations which is at about 17 eV in  $CeF_3$ .

Because the mobility of the exciton is involved, we should observe a temperature dependence of the quenching. Figure 3 clearly shows that the region of quenching becomes narrower as the temperature increases and completely vanishes at  $T = 440$  K. Accordingly, the emission intensity increases up to 330 K and then decreases due to the thermal quenching. This latter induces a net shortening of the decay above 390 K which is also observed in Fig. 3.

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