

# LUMINESCENCE AND SCINTILLATION PROPERTIES OF $Ce_xLa_{1-x}F_3$ MONOCRYSTALS

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In this communication we present our results concerning luminescence and scintillation properties of mixed cerium-lanthanum trifluoride monocrystals,  $Ce_xLa_{1-x}F_3$ . The luminescence, luminescence excitation spectra and decays are complex, indicating the presence of  $Ce^{3+}$  ions in regular and parasitic "perturbed" sites. The efficient energy transfer from regular  $Ce^{3+}$  ions (emitting at 286 and 303 nm) to "perturbed"  $Ce^{3+}$  ions (emitting at 340 nm) and the lack of the fast energy migration between  $Ce^{3+}$  ions are responsible for non-exponential decays of the short-wavelength emission and a relatively long rise-time of the long-wavelength emission. The short-wavelength emission decays are described by the Inokuti-Hirayama model of statistically distributed donors and acceptors. Our estimates of oscillator strengths, at  $13.1 \times 10^{-3}$  for  $Ce^{3+}$ , and  $13.5 \times 10^{-3}$  for  $Ce_{per}^{3+}$ , confirm that the  $d-f$  transition on the  $Ce^{3+}$  ion in a different site must be responsible for the long-wavelength emission. Calculations of the Ce-Ce and Ce- $Ce_{per}$  energy transfer rates give  $7.7 \times 10^5 s^{-1}$  and  $1.56 \times 10^9 s^{-1}$ . The concentration of "perturbers" in good  $CeF_3$  samples has been reduced down to about 0.11%. It is likely that the constant and significant progress made by crystal growers (Optovac Inc.) may eventually produce a superior material for applications in high energy and nuclear physics.

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## 1. Introduction

Efficient and fast decaying broadband emissions due to the parity allowed  $d-f$  transitions on the rare earth ions have recently attracted attention of scintillation detectors users [1]. The most spectacular of new applications is undoubtedly the proposed  $CeF_3$  calorimeter at CERN (130000 monocrystals, 60 m<sup>3</sup>) [2]. The  $CeF_3$  scintillator was discovered independently by Anderson [3], and Moses and Derenzo [4]. Initially there were some hopes that the ultra-fast component (2-5 ns) could be

used in high-rate applications [5], until it was demonstrated that it was due to the quenching of the Ce emission [6]. In low quality crystals the large part of the total emission shows up at longer wavelengths (LWL — long-wavelength luminescence) while the Ce emission is almost completely quenched with some residual intensity left in the ultra-fast component. The spectrum of this component corresponds exactly to the spectrum of the  $\text{Ce}^{3+}$  ion emission in better quality  $\text{CeF}_3$  crystals (SWL — short-wavelength luminescence) [6]. It was suggested that the LWL was due to  $\text{Ce}^{3+}$  ions in “perturbed” sites ( $\text{Ce}_{\text{per}}^{3+}$ ) [6]. The long rise time of the LWL pulse led to conclusion that  $\text{Ce}_{\text{per}}^{3+}$  ions were fed by a nonradiative energy transfer from regular  $\text{Ce}^{3+}$  ions [6, 7]. This conclusion is supported by more detailed studies of luminescence excitation spectra which show that except of the characteristic band at 270 nm, the spectra of  $\text{Ce}_{\text{per}}^{3+}$  are identical to those of  $\text{Ce}^{3+}$  [8, 9]. The presence of perturbed Ce ions is to be avoided, since it invariably produces changes in intensities, spectra and decay times along the crystal length in larger crystals required for applications in high energy and nuclear physics.

In this communication we present some results of our studies of  $\text{Ce}^{3+}$  ions in regular and “perturbed” sites of  $\text{Ce}_x\text{La}_{1-x}\text{F}_3$  crystals under optical and ionizing excitations. The experimental setup has been described in details elsewhere [10]. The full account of our work will be published later.

## 2. Materials and experimental results

$\text{LaF}_3$  and  $\text{CeF}_3$  crystals are characterized by the same space group,  $D_{3d}^4$ . There is only one La (Ce) site of the  $C_2$  symmetry and there are eleven  $\text{F}^-$  ions at distances between 2.42 and 2.99 Å in its first coordination sphere. The density of  $\text{Ce}_x\text{La}_{1-x}\text{F}_3$  is about 6.16 g/cm<sup>3</sup> and the number density of  $\text{La}^{3+}(\text{Ce}^{3+})$  ions is  $1.88 \times 10^{22}$  ions/cm<sup>3</sup>. The  $\text{Ce}_x\text{La}_{1-x}\text{F}_3$  refractive index  $n$  for composition  $x$  and wavelength  $\lambda$  can be calculated from the equation [9]

$$\frac{1}{n^2 - 1} = \frac{A}{\lambda^2} + B. \quad (1)$$

From the fit to the data from [9]:  $A = -5076 - 738.1x$  and  $B = 0.6552 - 0.01648x$ .

In Fig. 1 we present the room temperature, steady state luminescence spectra under optical (250 nm) excitation for three crystals of  $\text{Ce}_x\text{La}_{1-x}\text{F}_3$ . The spectra of  $\text{LaF}_3$ : Ce (0.01%) and the and the recently grown  $\text{CeF}_3$  (24 M) are similar, although the LWL band contribution is higher for  $\text{CeF}_3$ . Curiously, the  $\text{Ce}_{0.5}\text{La}_{0.5}\text{F}_3$  crystal shows much higher contribution of the LWL band. The two SWL bands, peaking at 286 nm and 303 nm, are due to transitions between the lowest state of the crystal field split  $d^1$ -configuration and the spin-orbit split  $^2F_{7/2}$  and  $^2F_{5/2}$  states of the  $f^1$ -configuration of the unperturbed  $\text{Ce}^{3+}$  ion. The LWL band, peaking at about 340 nm, was ascribed to the  $\text{Ce}^{3+}$  ions in perturbed sites [6]. In Fig. 2 we present selected luminescence and luminescence excitation spectra taken at 25 K which are free of distortions (see discussion in [8, 10]) and were decomposed to find Gaussian lineshapes, shown by dashed lines. In Fig. 3 we present pulses of the SWL and LWL under ionizing  $\gamma$  and  $\beta$  excitations. As noted before [11, 6], there is a striking difference between pulses of these two emissions. While

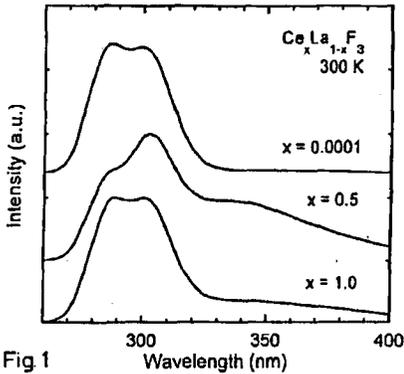


Fig 1

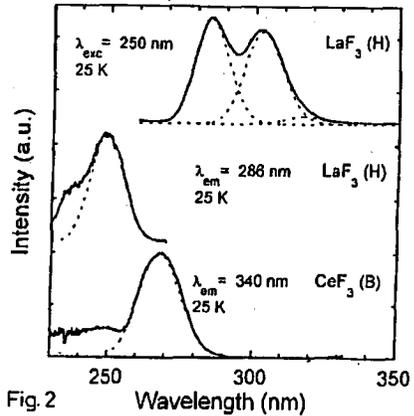


Fig.2

Fig. 1. Luminescence spectra of the mixed  $Ce_xLa_{1-x}F_3$  crystals excited by the 250 nm light from the Xe lamp at 300 K.

Fig. 2. Luminescence and luminescence excitation spectra of inadvertent Ce impurity in nominally pure  $LaF_3$  (designation H) and  $CeF_3$  (designation B) at 25 K. The luminescence of the  $LaF_3$  crystal was excited by the 250 nm Xe lamp light while the excitation spectrum was taken with the luminescence wavelength set at 286 nm. The lowest trace shows the LWL excitation spectrum of the  $CeF_3$  (B) with the luminescence wavelength set at 340 nm.

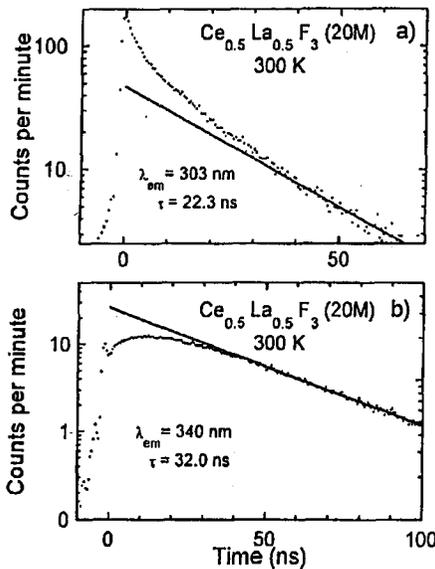


Fig. 3. Scintillation pulse shapes of the SWL (a) and LWL (b) emissions of the  $Ce_{0.5}La_{0.5}F_3$  (20 M) at 300 K. Straight lines indicate single exponential fits for longer delays, with decay times of 22.3 ns (303 nm) and 32.0 ns (340 ns).

the SWL pulse is characterized by an instantaneous rise and many component decay with characteristic times increasing with delay from about 2–5 ns (ultra-fast component) to 20–23 ns, the LWL pulse has a relatively long rise time (10–15 ns) and, after some delay, assumes a single exponential character with decay time of the order of 30–35 ns.

### 3. Discussion

The adequate theory to describe the transfer between  $\text{Ce}^{3+}$  and  $\text{Ce}_{\text{per}}^{3+}$  ions is that of Inokuti and Hirayama [12]. Since the radiative transitions on both  $\text{Ce}^{3+}$  and  $\text{Ce}_{\text{per}}^{3+}$  ions are electric-dipole allowed, the donor ( $\text{Ce}^{3+}$ )–acceptor ( $\text{Ce}_{\text{per}}^{3+}$ ) transfer rate  $W_{\text{da}} = \alpha_{\text{da}}/R^6$ , where  $\alpha_{\text{da}}$  stands for the transfer rate constant and  $R$  is the distance between donor and acceptor [12]. The decay of the  $\text{Ce}^{3+}$  emission is given by

$$I(t) = I_0 \exp \left[ -\frac{t}{\tau_r} - \frac{4}{3} \pi^{3/2} n_a (\alpha_{\text{da}} t)^{1/2} \right], \quad (2)$$

where  $\tau_r$  is the radiative lifetime of the donor emission and  $n_a$  is the concentration of the acceptors [12]. Equation (2) can be reduced to  $y = ax^2 + bx + c$ , where  $y = \log_e I(t)$ ,  $x = t^{1/2}$ ,  $a = -1/\tau_r$ , and  $b = -\left[\frac{4}{3} \pi^{3/2} n_a (W_{\text{da}} R^6)^{1/2}\right]$ . From the second-order polynomial fits, shown in Fig. 4, we find  $\tau_r$  for the sample 24M (23.8 ns) and B (38.1 ns). While 24M designates a recently grown good sample,

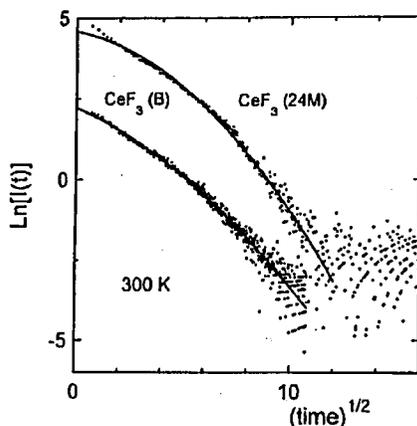


Fig. 4. Decays of the SWL emission for two different samples of  $\text{CeF}_3$ . Natural logarithm of intensity vs. square root of time is shown. Points represent experimental data, solid lines indicate fits to the Inokuti–Hirayama theory of a nonradiative energy transfer.

the sample B is an older one, showing distortions in SWL (indicative of radiation trapping) and higher contribution of the LWL. We assume, therefore, that the radiative lifetime of the  $\text{Ce}^{3+}$  emission is 23.8 ns, in agreement with decays. To find concentrations of  $\text{Ce}_{\text{per}}^{3+}$  ions we need an estimate of  $W_{\text{da}}$

$$W_{\text{da}} = \left[ \frac{1}{4\pi\epsilon_0} \right]^2 \frac{3\pi\hbar e^4}{n^4 m^2 \omega^2} \frac{1}{R^6} f_d f_a \int g_d(E) g_a(E) dE, \quad (3)$$

where  $m$  and  $e$  are the electron mass and charge,  $\omega$  is an average angular frequency of transitions involved,  $f_d$  and  $f_a$  are oscillator strengths of the  $Ce^{3+}$   $d-f$  transition (emission) and  $Ce_{per}^{3+}$   $f-d$  transition (absorption),  $R$  is the distance between donor and acceptor, and  $g_d(E)$ ,  $g_a(E)$  are normalized lineshape functions of the relevant transitions [12]. The oscillator strength  $f_d$  is related to the Einstein coefficient  $A_{tot}$  of a transition connecting two sets of states  $i$  and  $j$

$$A_{tot} = \sum'_i \sum_j \frac{1}{4\pi\epsilon_0} \frac{2\omega_{ij}^2 e^2}{mc^3} \left[ \frac{E_{loc}}{E} \right]^2 n f_{ij}, \quad (4)$$

where primed sum indicates summing and thermal averaging over the initial states, the second sum includes all the final states,  $\omega_{ij}$  and  $f_{ij}$  are the angular frequencies and oscillator strengths of transitions connecting two states  $i$  and  $j$ ,  $(E_{loc}/E)^2 = (n^2 + 2)^2/9$  is the local field correction and  $n$  is the refractive index [12]. In our case the luminescence transition connects one Kramers' doublet of the  $d^1$ -configuration ( $i = 1$ ) with seven Kramers' doublets of the  $f^1$ -configuration. By converting frequency to wavelength, using the expression for the local field correction and inserting numerical constants we have

$$f_d = \sum_{j=1}^7 f_{1j} = A_{tot} \left[ \frac{n(n^2 + 2)^2}{1.35 \times 10^5 \lambda^2} \right]^{-1}. \quad (5)$$

Putting  $A_{tot} = 1/\tau_r = 4.2 \times 10^7 \text{ s}^{-1}$ ,  $\lambda = 295 \times 10^{-9} \text{ m}$ ,  $n = 1.66$  we find  $f_d = 13.1 \times 10^{-3}$ . Since the absorption transition on the  $Ce_{per}^{3+}$  ion connects only two Kramers' doublets we can estimate  $f_a$  using (6) if we assume that all seven ground state doublets contribute equally. Taking the Einstein coefficient for the LWL as  $A_{tot} = 1/32 \text{ ns} = 3.13 \times 10^7 \text{ s}^{-1}$ , the refractive index at  $\lambda = 340 \times 10^{-9} \text{ m}$ ,  $n = 1.64$ , we calculate  $f_a = 13.5 \times 10^{-3}/7 = 1.93 \times 10^{-3}$ . To find overlap integrals we use Gaussian functions shown in Fig. 3. The overlap integrals are  $8.54 \times 10^{13} \text{ J}^{-1}$  and  $1.64 \times 10^{18} \text{ J}^{-1}$ , the angular frequencies and refractive indices at maxima of overlaps are  $6.98 \times 10^{15} \text{ s}^{-1}$ ,  $6.75 \times 10^{15} \text{ s}^{-1}$  and 1.670, 1.665 and transfer rates are  $7.7 \times 10^5 \text{ s}^{-1}$  and  $1.56 \times 10^9 \text{ s}^{-1}$ , for Ce-Ce and Ce- $Ce_{per}$  4.1 Å apart. It is important to point out that, in comparison to the radiative transition rate, the value of the Ce-Ce energy transfer rate is very low. This excludes the possibility of the fast Ce-Ce energy migration in the  $CeF_3$ .

Having Ce- $Ce_{per}$  transfer rate we calculate concentrations of perturbed Ce ions which are  $2.2 \times 10^{20} \text{ cm}^{-3}$  or 1.2% (sample 24M) and  $4.6 \times 10^{20} \text{ cm}^{-3}$  or 2.5% (sample B). The probability  $P$  that the Ce site is not perturbed is, therefore, 0.988 for 24M and 0.975 for B. If we assume that perturbors substitute for  $F^-$  (e.g. oxygen or fluorine vacancies) and since there are eleven  $F^-$  ions around each Ce ion,  $P = (1-x)^{11}$ , where  $x$  stands for the probability of  $F^-$  site being occupied by the perturber. For the sample 24M we find  $x = 1.1 \times 10^{-3}$  (0.11%, 1100 ppm or  $6.2 \times 10^{19}$  perturbors/cm<sup>3</sup>) and for the sample B,  $x = 2.3 \times 10^{-3}$  (0.23%, 2300 ppm or  $1.3 \times 10^{20}$  perturbors/cm<sup>3</sup>).

#### 4. Conclusions

In this communication we have presented initial results of our studies of  $Ce_xLa_{1-x}F_3$  monocrystals. The most important conclusion is that *all detrimental*

effects observed in these materials are not due to the high concentration of Ce but to the presence of perturbed cationic sites. In particular, there is no presence of perturbed cationic sites fast energy migration between regular Ce ions. The red shift of the  $Ce_{per}$  absorption band is responsible for much higher overlaps and very fast Ce- $Ce_{per}$  energy transfer which is responsible for the generation of the ultra-fast component in Ce-emission decays. Also radiation trapping observed in some samples is due to the reabsorption of the Ce-emission by  $Ce_{per}$ . We have shown that concentrations of perturbed sites have been significantly reduced in the  $CeF_3$  crystals grown recently by Optovac Inc. Our estimates of concentrations of perturbers exclude inadvertent impurities like eationic impurities or oxygen and point to fluorine vacancies. Further improvements in the quality of the  $CeF_3$  crystals may require more strict control of the material stoichiometry.

### 5. Acknowledgments

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### References

- [1] P. Lecoq, in: *Conference Record of the 1992 IEEE Nuclear Science Symposium and Medical Imaging Conference*, Orlando (USA) 1992.
- [2] D. Ferrere, M. Lebeau, M. Schneegans, M. Vivargent, P. Lecoq, *Nucl. Instrum. Methods Phys. Res. A* **315**, 332 (1992); P. Lecoq, M. Schussler, M. Schneegans, *Nucl. Instrum. Methods Phys. Res. A* **315**, 337 (1992).
- [3] D.F. Anderson, *IEEE Trans. Nucl. Sci.* **NS-36**, 137 (1989).
- [4] W.W. Moses, S.E. Derenzo, *IEEE Trans. Nucl. Sci.* **NS-36**, 173 (1989).
- [5] D.F. Anderson, *Nucl. Instrum. Methods. Phys. Res. A* **287**, 606 (1990).
- [6] A.J. Wojtowicz, E. Berman, Cz. Koepke, A. Lempicki, in: *Conference Record of the 1991 IEEE Nuclear Science Symposium and Medical Imaging Conference, Santa Fe (USA) 1991*, Vol. 1, p. 153; A.J. Wojtowicz, E. Berman, Cz. Koepke, A. Lempicki, *IEEE Trans. Nucl. Sci.* **NS-39**, 494 (1992).
- [7] C. Pedrini, B. Moine, J.C. Gacon, B. Jacquier, *J. Phys., Condens. Matter* **4**, 5461 (1992).
- [8] E. Berman, Ph.D. Thesis, Boston University, Boston 1992.
- [9] R. Laiho, M. Lakkisto, *Philos. Mag. B* **48**, 203 (1983).
- [10] A.J. Wojtowicz, E. Berman, A. Lempicki, *IEEE Trans. Nucl. Sci.* **NS-39**, 1542 (1992).
- [11] W.W. Moses, S.E. Derenzo, *Nucl. Instrum. Methods Phys. Res. A* **299**, 51 (1990).
- [12] B. Henderson, G.F. Imbusch, *Optical Spectroscopy of Inorganic Solids*, Clarendon Press, Oxford 1989, p. 445.