Fast 20 ns 5d–4f luminescence and radiation trapping in BaF$_2$:Ce

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Abstract

Parity-allowed UV 5d–4f transitions characterized by a high oscillator strength make trivalent cerium an interesting activator for fast and efficient scintillator crystals. Indeed, several materials are known, in which the radiative lifetime of the Ce$^{3+}$ ions is shorter than 20 ns (e.g. LuAlO$_3$:Ce and YAlO$_3$:Ce). For the case of BaF$_2$:Ce, however, the value of 27 ns is known from literature. In this communication we show that the 5d–4f luminescence in BaF$_2$:Ce is in fact faster. Having analyzed several series of time profiles recorded at various temperatures between 25 and 350 K, we conclude that the true radiative lifetime of the Ce$^{3+}$ ions in BaF$_2$ is close to 20 ns and it is the radiation trapping caused by the temperature-dependent reabsorption of cerium emission which prolongs the effective decay time.

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1. Introduction

Radiation trapping is a phenomenon, in which a photon once emitted by a luminescence center is absorbed by another center of the same kind. Such a process is possible if the emission and absorption bands of the center overlap. As photons “trapped” in this way are usually emitted again, the basic consequence of radiation trapping is rather not a reduction of light yield, but a prolongation of the emission decay time. Considering that reabsorption and reemission acts are repeated many times before a photon leaves the crystal, one can expect serious changes in luminescence time profiles.

Several examples of radiation trapping can be found in literature. Sakai et al. [1] proposed a method of deconvolution of nonexponential time profiles due to reabsorption of emitted light. As an example they examined fluorescence decays of two dye solutions. Visser et al. [2] observed that the decay time constant of the 5d–4f emission in BaF$_2$:Ce depended on both cerium concentration and sample thickness. The shortest decay time of $\tau = 27$ ns was found for the lowest concentration of the Ce$^{3+}$ ions (0.0012%). For BaF$_2$:0.17%Ce $\tau = 30$ ns (powder) or even $\tau = 37$ ns (1.9 mm thick sample). Note that these values concern room temperature. Wojtowicz et al. [3] explained with radiation trapping the...
conversion of short-wavelength (SWL) to long-wavelength (LWL) luminescence in Ce$_x$La$_{1-x}$F$_3$. This effect was much stronger at higher temperatures due to a larger overlap between the SWL emission and LWL absorption bands.

In this paper we discuss the results of systematic studies on the Ce$^{3+}$ 5d–4f luminescence time profiles as a function of temperature in the BaF$_2$ host. We show that the thermal broadening of the cerium absorption bands enhances the radiation trapping and as a result prolongs the observed decay times. Hence the decay time constant of about 27 ns [2] is no longer true at temperatures distinct from 293 K. At temperatures close to liquid helium we find a value of about 20 ns, which we take as the radiative lifetime of the Ce$^{3+}$ ions in BaF$_2$.

2. Materials and experiment

The BaF$_2$:0.05%Ce and BaF$_2$:0.2%Ce crystals were grown by Optovac Inc., North Brookfield, USA, using the Bridgman method. The cerium concentrations are that added to the melt (in mole %). No contamination by oxygen was observed and the samples were not subjected to any chemical reducing procedure. The spectra of synchrotron radiation excited luminescence and time profiles were recorded at the Superluminescence station of Hasylab (Hamburg, Germany). A detailed description of this setup was given by Zimmerer [4].

3. Results and conclusions

The interconfigurational 5d–4f emission of the Ce$^{3+}$ ions in the BaF$_2$ host forms two close bands with maxima at about 305 and 320 nm due to the spin–orbit split $^2$F$_{5/2}$ and $^2$F$_{7/2}$ levels of the 4f configuration (Fig. 1a). The excitation spectra of this emission are presented in Fig. 1b. They are dominated by two 4f–5d absorption bands around 200 and 290 nm, accompanied by some bands in the VUV region (50–150 nm). The thermal broadening of the 4f–5d bands is evident: the FWHM is over 10 nm wider at room than at low temperature.

Although the shape of the 5d–4f band is the same regardless of the excitation wavelength (Fig. 1a), differences occur in the luminescence time profiles. At direct excitation into the 5d levels (200 nm), as well as at the most energetic excitation (60 nm), the cerium emission is fast at any temperature, while at 75 and 90 nm excitation slower components appear above 200 K. However, as these peculiarities have already been explained in the frame of a trap model [5], for the purposes of the present work we limit our attention to profiles not affected by any traps.

In Fig. 2a we compare two representative time profiles of the 5d–4f luminescence, excited at 200 nm at two different temperatures: 25 and 303 K. Solid lines imposed on the experimental points have been obtained from a fit to the following formula:

$$I = I_0 + A_1 \exp\left(-\frac{(t - t_0)}{\tau_1}\right) - A_2 \exp\left(-\frac{(t - t_0)}{\tau_2}\right),$$

(1)
where \( I \) is the luminescence intensity, \( A_i \) the amplitudes, \( \tau_1 \) the decay time constant, \( \tau_g \) the rise time constant, \( I_0 \) and \( t_0 \) the two additional parameters responsible for vertical and horizontal shifts of the experimental curve, respectively. Note that the decay at low temperature is faster. Indeed, \( \tau_1 = 25.3 \) ns at 25 K, while at 303 K \( \tau_1 = 30.1 \) ns. The other values of \( \tau_1 \) within this series (Fig. 3) increase almost linearly with temperature between 25 and 350 K.

Two representative time profiles of the cerium emission excited at 60 nm are presented in Fig. 2b. Similar to Fig. 2a, one observes a faster decay at 25 K than at 303 K. Moreover, a comparison of the decay time constants derived from various series of fits (Fig. 3) indicates that at any temperature the 5d–4f luminescence is faster at 60 nm excitation than at 200 or 290 nm. We shall discuss this fact later on.

A summary of decay time constants that covers seven independent series of time profiles is shown in Fig. 3. It is clear that the higher the temperature the longer is the emission decay time. Assuming that

\[
\tau_1 = \tau_{1,0} + cT,
\]

we obtain \( c = (0.039 \pm 0.003) \) ns/K and \( \tau_{1,0} = (20.23 \pm 0.61) \) ns. This means that the 5d–4f luminescence decay time is close to 20 ns at liquid helium temperatures, but it is about 0.04 ns longer per every Kelvin when the temperature increases.

We stress that this is a new result, placing the BaF\(_2\) host on the same level as YAlO\(_3\) and LuAlO\(_3\) in respect of the speed of the cerium emission. Unfortunately, this is true only at very low temperatures.

To explain the observed thermal prolongation of the decay time constant we focus our attention on the phenomenon of radiation trapping, occurring in BaF\(_2\):Ce due to the large overlap between the cerium emission and absorption bands. Suppose that at a certain moment excited cerium ions (characterized by a mean lifetime \( \tau_{1,0} \)) emit \( n \) photons, of which \( n_1 \) leave the crystal and \( n'_1 = n - n_1 = an \) (\( a \)—reabsorption ratio) are absorbed by Ce\(^{3+}\) ions in the ground state. Although some of the absorbed photons, \( n_p' = \eta n \) (\( \eta \)—probability of photon reemission) are emitted again, they are delayed to these \( n_1 \) that have left the crystal first. Moreover, a fraction of the delayed photons may
be absorbed once more, then in part reemitted, reabsorbed, and so on. As a result we get a prolonged decay time $\tau_1$, which can be approximated [2] by the expression

$$\tau_1 = \frac{\tau_{1,0}}{1 - \eta a}. \quad (3)$$

Although Eq. (3) clearly shows that $\tau_1 > \tau_{1,0}$, it provides no explicit relation between the observed decay time and the temperature. Therefore, we clarify that the dependence of $\tau_1$ upon $T$ is hidden in the coefficient $a$. At low temperatures the 4f–5d absorption bands are much narrower (Fig. 1b), so the overlap between the emission and absorption bands is not large. This decreases the number of reabsorbed photons, giving a lower value of $a$ and consequently a shorter decay time $\tau_1$. Fig. 4 presents three $\tau_1 = \tau_1(a(T))$ curves computed using different photon reemission probabilities ($\eta = 1, 0.75, 0.5$). Note that the higher the probability $\eta$, the stronger is the influence on the decay time constant $\tau_1$.

The (non)linearity of the $\tau_1 = \tau_1(T)$ curves is also worth discussing. The $\tau_1 = \tau_1(a(T))$ curves defined by Eq. (3) are, of course, nonlinear, however, our results have suggested a linear relation between $\tau_1$ and $T$ (Fig. 3), and a linear function (Eq. (2)) has been fitted. This contradiction can be reconciled if we consider the quasilinear parts of the curves in Fig. 4. Indeed, for low values of the $\eta a$ product we get a linear approximation $\tau_1 \approx \tau_{1,0} (1 + \eta a)$. Between 0 and 293 K the decay time constant varies from $\tau_{1,0} \approx 20$ ns to $\tau_{1,293} \approx 31$ ns. From Eq. (3) we find $a_{293} = 0.35, 0.47, 0.71$ for $\eta = 1, 0.75, 0.5$, respectively. Although the high-quantum efficiency of the cerium emission suggests a high reemission probability, it is still difficult to decide, which of the $(\eta, a_{293})$ pairs is appropriate for the case of BaF$_2$:Ce. However, ranging from 0 to $a_{293}$ the $\tau_1 = \tau_1(a)$ curves are nearly linear regardless of the value of $\eta$, i.e. what supports the radiation trapping as the main reason of the decay time prolongation.

Now we remind that at any temperature the cerium luminescence at the high-energy excitation is faster than at the direct 4f–5d excitation. This can also be interpreted in the frame of the radiation trapping process. The 200 or 290 nm photons penetrate the material much deeper than the 60 nm ones. In this way the 60 nm excited luminescence, as coming out from close-to-surface layers of the crystal, is much less affected by the radiation trapping.

Concluding, the decay time constant of the Ce$^{3+}$ 5d–4f uminescence in the BaF$_2$ host is close to 20 ns at liquid helium temperatures. Longer decay times at higher temperatures are due to the radiation trapping. Thus we conclude that the true radiative lifetime of the Ce$^{3+}$ ions in BaF$_2$ does not exceed 20 ns. Such a value indicates that the oscillator strength for the 5d–4f transitions in BaF$_2$:Ce is very high. Using the following formula [6]

$$f = 1.5 \times 10^4 \frac{9 \lambda_{emi}^2}{\tau_{rad} N (N^2 + 2)^2}, \quad (4)$$

where $f$ is the oscillator strength, $\lambda_{emi}$ the emission wavelength, $\tau_{rad}$ the radiative lifetime of the emitting ion, and $N$ the refractive index, for $N = 1.5, \lambda_{emi} = 320$ nm, and $\tau_{rad} = 20$ ns, we find $f = 2.6 \times 10^{-2}$. This number confirms the Loh’s estimation [7] for CaF$_2$:Ce ($f \sim 10^{-2}$). For a comparison, in LaF$_3$:Ce $f = 3.2 \times 10^{-3}$ [8], over 8 times less than that in BaF$_2$:Ce.

Undoubtedly for scintillator applications the effect of radiation trapping should be somehow reduced. The lowering of the cerium concentration seems to be the most promising idea, however, no
differences between the BaF2:0.05%Ce and BaF2:0.2%Ce crystals have been observed. Much lower amounts of cerium make no sense, as the emission intensity would fall down. Therefore, it is possible that the radiation trapping is an irremovable fault of BaF2:Ce.

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References