VUV-excited luminescence time profiles of Ce- and Pr-doped BaF_2: the contribution from V_K centers

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Studies on energy transfer and charge trapping processes are necessary to establish the scintillation mechanism in any scintillator material. Although thermoluminescence (TL) is widely regarded as the basic experimental technique providing information on traps that are likely to interfere with the process of scintillation production, it is also possible to find the trap parameters in other ways. In this report we show how we find the activation energy E and the frequency factor s of the V_K center [1], which is the prominent hole trap occurring in barium fluoride, the fastest known inorganic scintillator. To do this we analyze several series of VUV-excited luminescence time profiles of BaF_2:Ce and BaF_2:Pr recorded in years 1998-2000 at the SUPERLUMI station at the beam I of the DORIS storage ring. The samples of BaF_2:Ce and BaF_2:Pr (some of them with 0.2% addition of Na) were grown by Optovac Inc., North Brookfield, USA, using the Bridgman method.

It was shown earlier [2] that photoluminescence time profiles of BaF_2:Ce excited at, say, 70-100 nm, emulate well its radioluminescence time profiles. When this material is excited by ionizing radiation, some of the generated electron-hole pairs promptly reach the luminescence centers, i.e. the Ce^{3+} ions, producing emission of VUV light decaying with the centers' radiative lifetime τ_r. A fraction of holes, however, self-traps forming more or less stable trap centers, the mean lifetime of any of which can be expressed as $\tau = [s \cdot \exp(-E / k_B T)]^{-1}$, where s, E, k_B, and T denote the frequency factor, activation energy, Boltzmann constant, and temperature, respectively. After activation, these holes also recombine with electrons at the luminescence centers. The evidence of such „trap-mediated" radioluminescence mechanism is the prolongation of the decay (or rise) times at temperatures, at which the trap lifetimes come near the radiative one. From among a few traps detected in BaF_2:Ce [2], only the V_K center can affect the time profiles in the thermal range of our experiment (10-350 K). Although a very precise analysis [3] shows that both modes of the V_K center movement activation, reported much earlier by Beaumont *et al.* [4], can be observed via time profiles, here we focus on the basic mode, modifying their decaying parts.

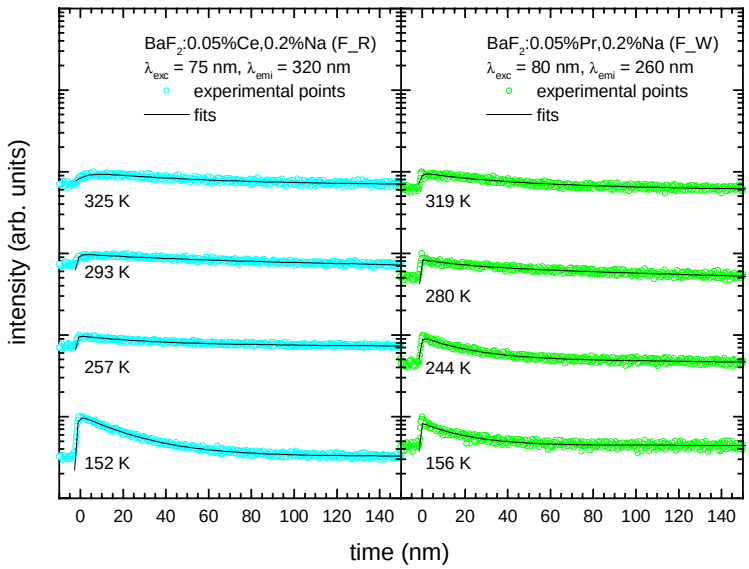
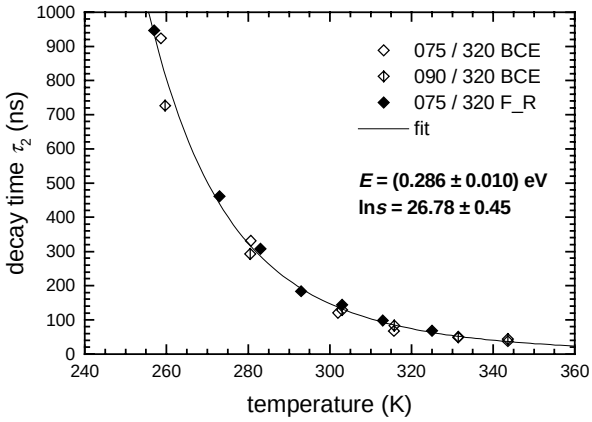


Figure 1: Representative time profiles of VUV-excited Ce^{3+} and Pr^{3+} luminescence at various temperatures. Samples: BaF_2:0.05%Ce,0.2%Na and BaF_2:0.05%Pr,0.2%Na. Fitting formulas: $I(t) \propto A_1 \cdot \exp(-t/\tau_r) - A_2 \cdot \exp(-t/\tau_g)$ for $T < 240$ K, $I(t) \propto A_1 \cdot \exp(-t/\tau_r) + A_2 \cdot (\exp(-t/\tau_2) - \exp(-t/\tau_g))$ for $T \geq 240$ K.

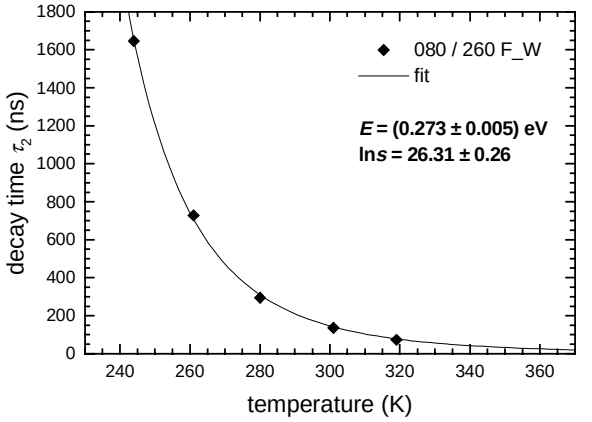
The time profiles of BaF_2:Ce were recorded at various excitation wavelengths (60, 75, 90, 200, and 290 nm), each at up to 18 temperature points ranging from 10 to 350 K. No effect associated with different Ce concentrations or addition of Na was observed. In case of direct $4f \rightarrow 5d$ excitation of the Ce^{3+} ions (200 and 290 nm) the decays are single-exponential with decay time constants of about 30 ns (radiative lifetime τ_r of the ions), slightly increasing with temperature. At 60 nm excitation the time profiles look the same (for explanation see refs. [2,5]). More complex profiles appear at 75 and 90 nm excitation (selected experimental curves and fits are shown in Fig. 1). From 10 to 240 K they resemble those excited at 60 nm, while above 240 K the decay time constants are longer (up to 130 ns). Then a better representation of the profiles is provided by a double-exponential function $I(t) \propto A_1 \cdot \exp(-t/\tau_r) + A_2 \cdot \exp(-t/\tau_2)$, where I, t, A_i, τ_r, and τ_2 stand for the luminescence intensity, time, amplitudes, radiative lifetime (fixed), and decay time constant of the second component, respectively. The values of τ_2 derived from the fits are presented in Fig. 2. Associating τ_2 directly with the V_K center lifetimes, we get the following parameters: E = 0.286 eV, ln$s$ = 26.78. They are in a satisfactory agreement with those received from TL and ITD experiments (E = 0.276 eV, ln$s$ = 26.77 [2]). This fact, particularly the almost identity of the frequency factors, confirms the sense of using thermally dependent time profiles to estimate trap parameters.

Figure 2: Thermal dependence of the decay time constants of the „trap-mediated" component in BaF_2:Ce. Samples: BaF_2:0.2%Ce (BCE) and BaF_2:0.05%Ce,0.2%Na (F_R); excitation: 75 or 90 nm; emission: 320 nm. Fitting formula: $\tau_2 = [s \cdot \exp(-E / k_B T)]^{-1}$.



Similar measurements were performed on BaF_2:Pr, with the excitation wavelength set to 60, 80 or 163 nm. As in case of BaF_2:Ce, no concentration effect (Pr, Na) was detected. The Pr^{3+} radiative lifetime $\tau_r \approx 22$ ns was found to be constant in the whole experimental range (10-350 K), both at direct $4f^2 \rightarrow 4f5d$ (163 nm) and VUV (60 nm) excitation. The participation of the V_K centers was observed again as prolongation of decay times above 240 K at 80 nm excitation (Fig. 1). Double-exponential fits provide the values of τ_2 shown in Fig. 3, which yield the following V_K center parameters: E = 0.273 eV, ln$s$ = 26.31. As they are close to those in BaF_2:Ce, we conclude that the nature of the „trap-mediated" energy transfer from the electron-hole pairs to the Ce^{3+} and Pr^{3+} must be the same.

Figure 3: Thermal dependence of the decay time constants of the „trap-mediated" component in BaF_2:Pr. Sample: BaF_2:0.05%Pr,0.2%Na (F_W); excitation: 80 nm; emission: 260 nm. Fitting formula: $\tau_2 = [s \cdot \exp(-E / k_B T)]^{-1}$.



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