Time-Resolved Photoluminescence of LaBr₃:Ce Scintillation Crystals under Ultrasoft X-Ray Excitation

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Abstract—Time-resolved X-ray-induced photoluminescence (PL) of LaBr₃:Ce scintillation spectrometer crystals excited by synchrotron radiation with photon energies within 45−290 eV has been studied at 7.5 and 295 K. It is established that the PL response is essentially nonproportional to the exciting photon energy in the regions of photoionization of the Br $3d$ and La $4d$ levels and especially in the vicinity of the giant resonance. The PL decay kinetics in the spectral region corresponding to the $d \rightarrow f$ luminescence of Ce^{3+} ions is nonexponential. The decay time is smaller than 15 ns and depends on the exciting photon energy and radiation wavelength. The influence of the products of interaction of these hygroscopic crystals with atmosphere on the spectral and kinetic characteristics of X-ray-induced PL has been determined.

Cerium-doped lanthanum bromide (LaBr₃:Ce) is a modern inorganic scintillator material for spectrometric detectors of photons. In particular, LaBr₃:Ce detectors available from Saint-Gobain Crystals Co. are characterized by high luminescent yields (~60 000 photons/MeV), small luminescence decay times (<25 ns), and high stability of parameters in a broad temperature range. Due to high energy resolution and good resistance to radiation, these detectors have good prospects for use in spectrometry and various medical applications [1−3]. In this context, it is a topical task to study the excitation-energy-nonproportional yield of photoluminescence (PL) from LaBr₃:Ce crystals, especially for excitation in the X-ray spectral range. Recently, Khodyuk and Dorenbos [4] measured the nonproportional response of these scintillators excited by synchrotron radiation in an X-ray photon energy range of 1.4−100 keV.

In the present work, we have studied the range of lower excitation energies, 45−290 eV, which covers the regions of photoionization of some electron shells in crystal-forming atoms and the region of the giant resonance. The main aim of this investigation was to establish specific features of radiative relaxation processes in LaBr₃:Ce crystals excited in the soft X-ray energy range.

The samples were studied by the method of time-resolved PL spectroscopy with excitation on the BW3 beam line at HASYLAB (DESY, Hamburg) [5]. The exciting beam extracted from an undulator was passed via a Zeiss SX700 monochromator. The spectra of X-ray-induced PL and the PL decay kinetics were measured using a 0.4-m monochromator and a Hamamatsu MCP 1645 microchannel plate detector. In addition to measuring the usual time-integrated PL spectra, we have also recorded the time-resolved spectra in two Δt-wide temporal windows delayed by δt relative to the excitation pulse front. The fast PL component was determined at $\delta t_1 = 2.0$ ns for $\Delta t_1 = 14.6$ ns, while the slow component was measured at $\delta t_1 = 28$ ns for $\Delta t_1 = 48$ ns. The temporal resolution of the detection system was about 250 ps. The interval between excitation pulses was 96 ns. The PL spectra were normalized to equal numbers of incident exciting photons with the aid of an AVUX-100 photodiode. The spectra presented in Fig. 1b were measured using a URS-55F instrument with a Cu anode operating at 30 kV and 10 mA, an MDR-23 monochromator, and an FEU-106 electron multiplier with a multialkaline photocathode.

LaBr₃:Ce crystals of optical quality (STARK Co., Obninsk) were grown by the Bridgman method in quartz ampules at a rate of 1 mm/h. The samples were characterized by methods of X-ray diffraction (XRD) and chemical analysis [6]. The PL measurements were performed on LaBr₃:Ce crystals (5 wt % C^{3+}) with dimensions of $10 \times 8 \times 1$ mm, which were freshly cleaved in dry atmosphere. The period of time between the cleavage of a sample and its introduction into an ultra-high-vacuum cryostat (with a residual gas pressure of ~1×10^{-8} mbar) was minimized.

The main experimental results are presented in Figs. 1−3. The spectra of X-ray-induced PL at $T = 295$ K exhibit a nonelementary emission band that is formed by typical $d \rightarrow f$ radiative transitions from an
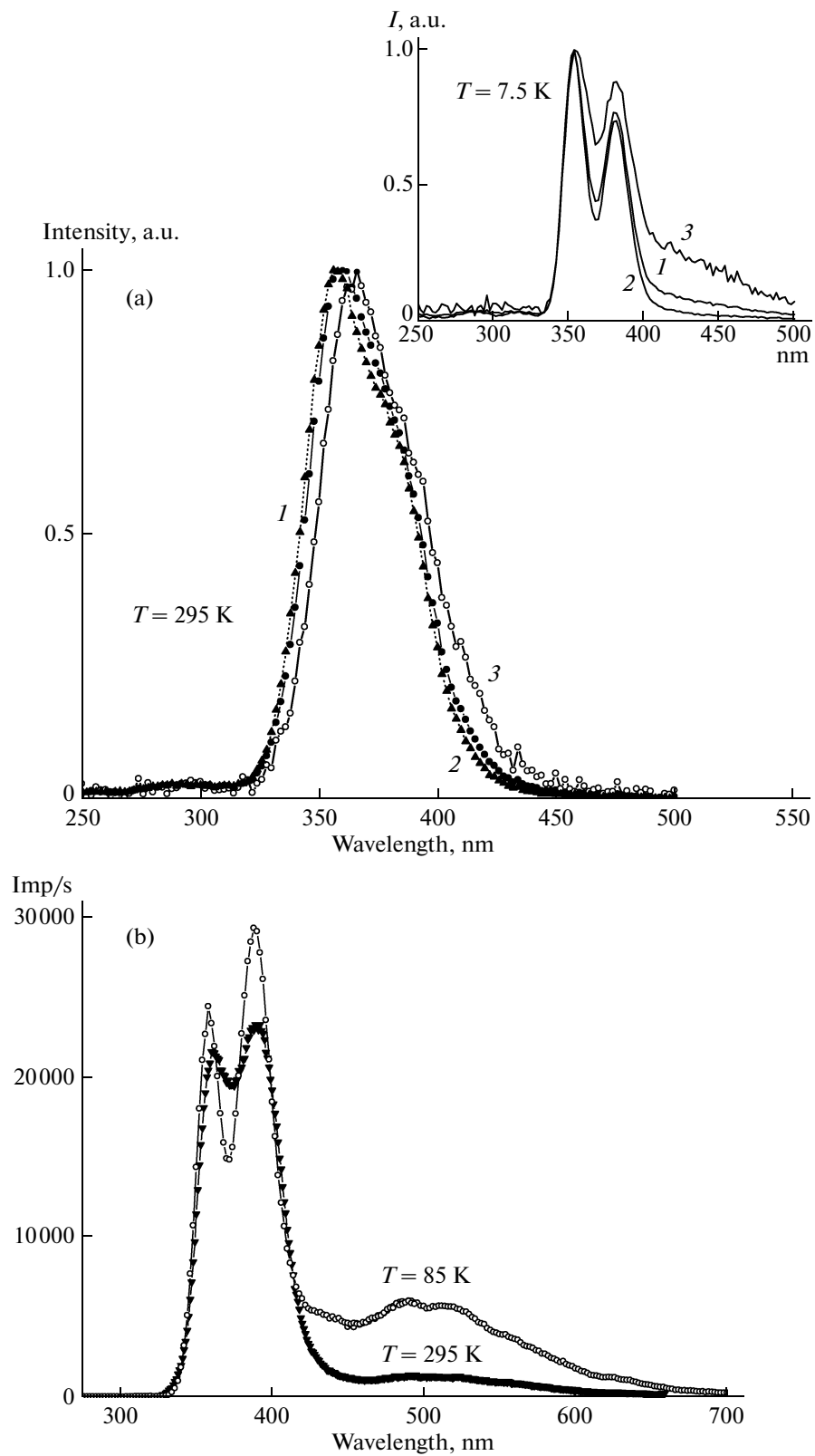
Fig. 1. (a) Time-resolved PL spectra of a LaB$_3$:Ce crystal excited at E_{exc} = 7.1 eV, showing (*1*) time-integrated response and its (*2*) fast and (*3*) slow components; (b) PL spectra measured when keeping the crystal in a rough vacuum for 24 h at room temperature.
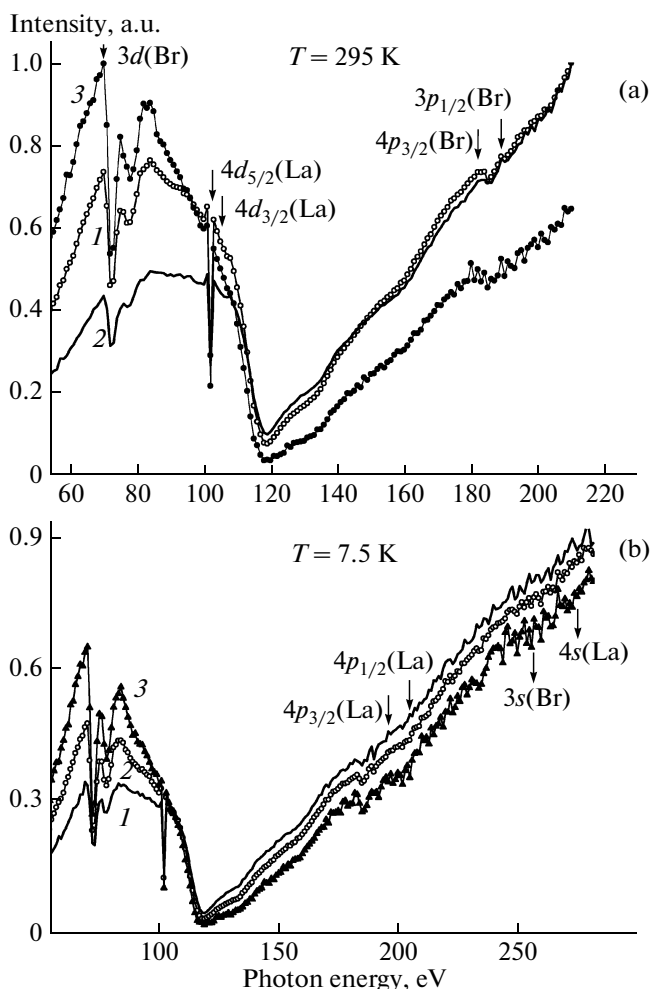
Fig. 2. Time-resolved PL excitation spectra of a LaB$_3$:Ce crystal at $\lambda_{emission} = 360$ nm, showing (*1*) time-integrated response and its (*2*) fast and (*3*) slow components measured at (a) $T = 295$ K and (b) $T = 7.5$ K. Arrows indicate the energies of photoionization of crystal-forming elements. The spectral resolution in the vicinity of $E_{exc} = 100$ eV is 0.1 eV.

Fig. 3. Decay kinetics of PL from a LaB$_3$:Ce crystal measured at $\lambda_{emission} = 405$ (*1, 2*) and 360 nm (*3–6*): (a) $T = 295$ K, $E_{exc} = 130$ (*1, 3*), 118 (*2, 5*), and 500 eV (*6*); (b) $T = 7.5$ K, $E_{exc} = 72$ (*1*), 102 (*2, 4*), 95 (*3*), 119 (*5*), and 285 eV (*6*). Horizontal bars indicate temporal windows corresponding to the fast and slow components of time-resolved PL spectra.

excited state to the ground state (F$_{5/2}$, F$_{7/2}$) split by a crystal field in Ce^{3+} ion (Fig. 1). This splitting is more pronounced at low temperatures (see inset to Fig. 1a). In the spectra measured with temporal resolution, the peak of a slow component is shifted toward longer wavelengths. This shift is related to the fact that the PL decay kinetics at fixed excitation energy E_{exc} depends on emission wavelength $\lambda_{emission}$.

Figure 3a shows the kinetics of PL decay at $T = 295$ K measured for two values of $\lambda_{emission}$. At $\lambda_{emission} = 405$ nm, the kinetics contains a pronounced slow (microsecond scale) component, which forms a pedestal of the PL decay curve. A shift of the slow component is more pronounced at low temperatures (see inset to Fig. 1a). In order to establish factors that take into account the observed shape of time-resolved PL spectra, we have
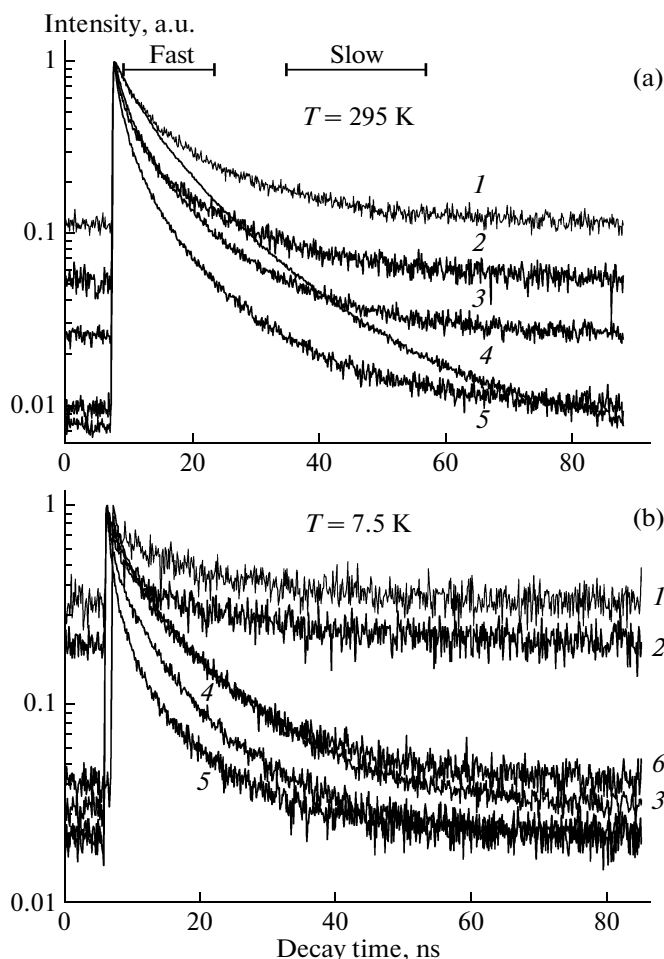
measured the PL spectra upon storage of the crystal at room temperature for 24 h in a rough vacuum. As can be seen from Fig. 1b, a long-wavelength band appears in the spectrum recorded upon storage, the intensity of which increases at a lower temperature. This fact points to the relation of this emission to a low-temperature glow of the oxidation products formed as a result of interaction of the surface of hygroscopic LaB$_3$:Ce crystals with residual atmospheric gases during storage in a rough vacuum.

It is also not excluded that the shape of the PL spectrum and the dependence of the PL decay kinetics on the emission wavelength can be influenced by the presence of point defects and/or macroscopic defects formed in the crystal during growth. However, even if this takes place, the obtained results show that it is

expedient to cut off a long-wavelength part of the PL spectrum ($\lambda_{emission}$ > 400 nm) with appropriate optical filters.

The PL excitation spectra have complicated shapes and reveal a difference between the time-integrated response and time-resolved components (Fig. 2). There are narrow dips and a broad deep minimum in the region of 118 eV against the background of monotonic growth in the PL intensity with the energy of exciting photons (E_{exc}). The energy positions of narrow dips correspond to the well-known ionization potentials of crystal-forming atoms. These positions and the corresponding states are indicated by the arrows in Fig. 2. The most significant features are observed in the regions of photoionization of the Br $3d$ and La $4d$ levels. For the excitation of Br $3p$ (deeper) levels, these features are much less pronounced. The mechanism of scintillations in LaB$_3$:Ce crystals, which has been studied in [1, 3], consists in a sequential radiative electron–hole recombination on Ce^{3+} centers. In this context, narrow dips in the PL excitation spectrum should be related to electron transitions from the corresponding core levels to the conduction band. The broad and deep minimum in the region of 118 eV in the PL excitation spectrum agrees well with the absorption spectrum of a La film [7], since these spectra exhibit fully antiphase variations. As is known, the optical absorption of lanthanoids in this energy range is a manifestation of the giant resonance [8]. In this region of fundamental absorption, the extinction coefficient is very large (~10^5–10^6 cm^{-1}) and, hence, only a very thin surface layer of the crystal is involved in excitation by photons at the indicated energies. The growth of absorption in the region of photoionization potentials and giant resonance leads to an increase in nonradiative recombination of charge carriers at the surface. Thus, competition between the radiative recombination of carriers on Ce^{3+} centers and their nonradiative recombination at the surface accounts for the observed shape of the PL excitation spectrum.

The observed PL decay kinetics is nonexponential and strongly depends on E_{exc} (Fig. 3). The shape of the $I(t)$ curve is satisfactorily approximated by a sum of two exponents as

$$I(t) = A_1 \exp[-(t - t_0)/\tau_1] + A_2 \exp[-(t - t_0)/\tau_2] + I_0,$$

where the term I_0 takes into account the contribution of slow (microsecond scale) components. Parameters of the PL decay kinetics for some characteristic E_{exc} values are given in the table.

Decay time constants τ_1 and τ_2 decrease at the energies of exciting photons that correspond to the narrow dips and giant resonance in the PL excitation spectrum (with a calculation error within 5%). This is also related to the aforementioned competition between the radiative recombination of carriers on

Parameters of PL decay kinetics in LaBr$_3$:Ce

E_{exc}, eV	$\lambda_{emission}$ = 360 nm			$\lambda_{emission}$ = 405 nm		
	τ_1, ns	τ_2, ns	I_0	τ_1, ns	τ_2, ns	I_0
T = 295 K						
118	1.3	8.0	0.011	2.9	15.0	0.055
130	2.1	10.2	0.026	3.0	14.2	0.11
500	5.9	16.0	0.007			
T = 7.5 K						
95	1.9	10.5	0.032			
102	1.1	9.8	0.021	13.3	126	0.21
119	1.0	9.2	0.022			
286	2.2	12.8	0.04			

Ce^{3+} centers and their nonradiative recombination in a thin near-surface layer.

For the samples cooled to T = 7.5 K, the PL excitation spectrum (Fig. 2b) exhibits the same features as those observed at room temperature. In the regions of excitation of the deeper (Br $3s$, Br $3p$, La $4s$, La $4p$) core levels, the structure in the PL excitation spectrum measured at 7.5 K is almost as indistinguishable as that at 295 K. The difference in the time-resolved spectra is related to the fact that the PL decay kinetics also depends on the energy of exciting photons. In the regions of narrow dips and at the giant resonance, the PL decay time constants exhibit a decrease. It should be noted that, at T = 7.5 K, the contribution of slow (microsecond scale) components for $\lambda_{emission}$ = 360 nm does not exceed 2–4% of the peak intensity (see Fig. 3b and table). In addition to a weak temperature dependence of the PL yield in the 90–400 K interval [9], this fact points to the possibility of using LaBr$_3$:Ce crystals as fast scintillators in a broad temperature range.

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SPELL: 1. scintillator