Luminescence of LaBr₃:Ce,Hf scintillation crystals under UV-VUV and X-ray excitation

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Abstract. The present study was carried out by means of the low temperature time–resolved luminescence UV–VUV spectroscopy as well as the optical and thermally activation spectroscopy. The Ce³⁺ centers in regular lattice sites and located in the vicinity of the point defects of crystal structure were observed. Spectral and kinetic characteristics of the luminescence of these centers were defined. A photoluminescence of new point defects of the crystal structure are also manifested. We evaluated the energy of the interband transitions as $E_g \approx 6.2$ eV in LaBr₃. At the excitation energies $E_{exc}>13$ eV (higher than $2E_g$) the effect of the electronic excitations multiplication was detected.

1. Introduction

The LaBr₃:Ce scintillator manufactured by the company Saint–Gobain, in fact, is very attractive for both spectrometric applications and for medical imaging. Nowadays a mechanism of the scintillation pulse’s formation in these crystals is well known due to the investigations of luminescence under different kinds of excitations as well as to research of the electron excitation energy transfer to Ce³⁺ impurity center [1–3]. Photoluminescence (PL) studies of d→f emission in Ce³⁺ ions and self–trapped excitons (STE) under excitation by photons in ultraviolet (UV) and vacuum ultraviolet (VUV) ranges in LaBr₃:Ce was reported in Ref. [1, 2] only. In these studies the values of the fundamental absorption edge and the interband transition energy $E_g$ were determined approximately ($E_g = 5.9$ eV at $T=10$ K). In the later works the results presented in Ref. [1, 2] are quoted, however further similar investigations of LaBr₃ in VUV range were not carried out and this result seems to be ambiguous.

In our previous report [4] we investigated a nonlinearity of response light yield in LaBr₃:Ce in extremely ultraviolet (XUV) region (45–290 eV). Our first results of LaBr₃:Ce PL investigations under VUV excitation are presented in Ref. [5]. LaBr₃:Ce crystals are hygroscopic, therefore the method of growth of LaBr₃:Ce single crystals doped with hafnium was developed in Russia [6]. These LaBr₃:Ce,Hf crystals have low hygroscopicity and they are more suitable for practical applications. The main goal of present work is the studies of luminescence of the LaBr₃:Ce,Hf crystals produced in Russia. The present study was carried out by means of the time-resolved luminescence UV-VUV spectroscopy as well as the optical absorption spectroscopy.

2. Experiment

2.1. Methods

Time–resolved and time–integrated PL spectra (1.5–5.0 eV), time–resolved PL excitation spectra (3.7–32.0 eV) and PL decay kinetics were measured using SR at the SUPERLUMI station (beam line I, HASYLAB at DESY, Hamburg). The primary monochromator with Al or Pt gratings had a spectral resolution of 3.2 Å. The PL spectra were measured using a 0.3m monochromator model ARC Spectra Pro-308i and an R6358P photomultiplier tube (Hamamatsu) in two time windows $\Delta t_1 = 11$ ns (fast component) and $\Delta t_2 = 30$ ns (slow component), which were delayed relative to the start of the SR-excitation pulse by $\delta t_1 = 3.0$ ns and $\delta t_2 = 36$ ns respectively. The PL excitation spectra were normalized to the same number of SR–exciting photons using sodium salicylate. The time resolution of the whole detection system was 0.8 ns (FWHM). The temporal interval between SR pulses equaled 96 ns. The
400W deuterium discharge lamp and the prismatic DMR–4 monochromator were used to measure the PL excitation spectra in the low-energy range of 2.4–5.8 eV in Ural Federal University. The spectra of the X–rays induced luminescence (XRL) were studied by means of a BSV2–Cu X–ray tube (30 kV, 10 mA), a MDR–23 monochromator and a FEU–106 photomultiplier tube. The experimental details for XUV excitation are presented in Ref. [4].

2.2. Samples preparation
The examined single crystal with high optical quality (5 wt.% of cerium and 0.05–0.5 wt.% of hafnium in charge) have been grown using Bridgman process in the Russian company Stark Ltd [6]. The synthesized single crystals were certificated by a XRD and mass–spectrometry method with inductive–bound plasma, both the chemical and X-ray fluorescence analysis were also used. The introduction of hafnium into the melt reduces the hygroscopicity of grown crystals [9]. Because of the hygroscopic nature of LaBr3, any contact with the atmospheric air leads to degradation of the sample surface that becomes cloudy due to the formation of crystalline hydrates. In all our experiments the samples (5x5x1 mm3) were cleaved from crystal boule in an atmosphere of a dry hot air and immediately mounted in a cryostat with a fast vacuum pumping.

3. Experimental results
The luminescence spectra of LaBr3:Ce,Hf crystals under X–ray and XUV excitations are very similar to those of LaBr3:Ce crystals presented in Ref. [4]. The XRL spectra of LaBr3:Ce,Hf crystals measured at different temperatures are shown in figure 1. These spectra contain emission bands at 356 and 382 nm. The time–resolved luminescence spectra are formed by the typical radiative d → f transitions in Ce3+ ions [2]. An additional broad band at 450 nm with microsecond PL decay kinetics appears at low temperatures. According to data [2], this band can be formed by self-trapped exciton (STE) emission. The PL spectra depend on the excitation energy (Eexc) significantly. The PL spectra of LaBr3:Ce at T=8K under excitation by photons in the fundamental absorption region (Eexc=6.9 eV) corresponds well to the luminescence spectra under X–ray or XUV excitation. On the contrary, the PL spectra of LaBr3:Ce,Hf shift to long wave region and contain narrow bands at 384 and 412 nm, as well as a broad band in the region of 500–600 nm with a microsecond PL decay kinetics (figure 2). The PL kinetics measured for the bands at 384 and 412 nm under excitation by photons with Eexc=3.7–5.0 eV have a single exponential decay with τ = 20 ± 1 ns. The value of the PL decay time is less than that in LaBr3:Ce crystals (τ = 23–25 ns depending on Eexc, see Ref. [5]).

Figure 1. Luminescence spectra of LaBr3:Ce,Hf crystals under X–ray excitation measured at 90 and 295 K.

Figure 2. Time–resolved PL spectra of LaBr3:Ce (solid lines) and LaBr3:Ce,Hf (mugs–lines) under Eexc= 6.9 eV: time–integrated (1), fast (2) and slow (3) components, T=8 K.
Figure 3 shows the PL excitation spectra measured for 384 nm emission band and absorption spectrum of LaBr\(_3\):Ce,Hf (5%). The absorption spectrum of LaBr\(_3\):Ce (0.5%) calculated from transmission spectrum presented in Ref. [7] is also shown. The optical density in the region of 3.5–5.5 eV depends on the concentration of Ce\(^{3+}\) ions and its value increases dramatically at energies above 5.5 eV. The PL excitation spectra measured for 412 and 550 nm emission bands are represented in figure 4. Separate bands with maxima at 3.6 and 5.05 eV are observed.

![Figure 3](image1.png)

**Figure 3.** PL excitation spectra measured for 384 nm emission band (1, 2) in LaBr\(_3\):Ce,Hf (5% of Ce), absorption spectra (T=295 K) of LaBr\(_3\):Ce,Hf (5% of Ce) (3) and LaBr\(_3\):Ce (0.5%) (4) from Ref. [7], (5) – linear fit. The energy positions of the d–states of Ce\(^{3+}\) ions in LaBr\(_3\):Ce from Ref. [1] are shown.

Figure 4. PL excitation spectra of LaBr\(_3\):Ce,Hf measured for 412 (1), 540 or 600 nm (2) emissions.

![Figure 4](image2.png)

Figure 5. (a) – Time–resolved PL excitation spectra of 384 nm Ce\(^{3+}\) emission band in LaBr\(_3\):Ce,Hf, T=295K: time–integrated (1), fast (2) and slow (3) components. Spectrum (1) was measured using the Al and Pt gratings. (b) – 3D image of PL excitation spectrum and PL decay kinetics.

![Figure 5](image3.png)

4. Discussion

The analysis of presented spectra shows that Ce\(^{3+}\) ions in regular lattice sites (marked as the A–centers) and Ce\(^{3+}\) ions located in the vicinity of the defects of crystal structure (marked as the B–centers) are observed in LaBr\(_3\):Ce,Hf. PL of the B–centers under intracenter excitation has a decay time of 20 ± 1 ns. PL spectrum is shifted to lower energies. Stokes shift does not change practically. PL was efficiently excited by 3.6 eV photons, however, f → d electronic transitions in the absorption
spectrum do not appear in this spectral region. This fact indicates that the concentration of such B–
centers is relatively low. Accordingly, in the XRL spectra only the A–centers appear.

New defects of the crystal structure were found in addition to the B centers in LaBr3:Ce,Hf. The PL
spectrum at T = 8 K has a broad band with maximum at 550 nm (2.25 eV, FWHM = 0.8 eV). The PL
yield has its maximum at $E_{\text{exc}} = 5.05$ eV (Stokes shift is 2.8 eV) and it falls under excitation in the
fundamental absorption edge and region of interband transitions. From this it follows that the intra-
center PL is observed, and that the efficiency of the energy transfer to these centers by excitons or
band charge carriers is low. The structure of such defects is not clear.

The sharp increase of optical density at energies above 5.7 eV indicates the beginning of the
fundamental absorption in these crystals. Linear fit shown in figure 3, allows us to estimate the energy
of the edge of the interband transitions at $E_{\text{fa}} = 5.5$ eV. Slow microsecond components in the PL decay
kinetics appear at PL excitation in this energy region (figure 5, curve 3). These facts indicate the
participation of the band charge carriers in the formation of Ce$^{3+}$ emission. Based on these data
it is possible to estimate the energy of inter band transitions $E_g \approx 6.2$ eV in LaBr$_3$. It should be noted that
our values $E_{\text{fa}}$ and $E_g$ differ from the data presented in Refs. [2, 5]. Apparently, the measurement of
Urbach tail absorption in LaBr$_3$ crystals will determine a more precise value of $E_g$.

The efficiency of Ce$^{3+}$ PL excitation drops in the fundamental absorption edge and region of
interband transitions. The competition of capture of the band carriers on Ce$^{3+}$ centers and on crystal
structure defects, the formation of STE, and predominantly non–radiative annihilation of the band
carriers on the crystal surface determines to this PL yield decrease. The PL yield stabilizes with a
further increase of the kinetic energy of the band carriers. The PL yield increases monotonically at
energies $E_{\text{exc}} > 13$ eV. Based on the studies of the luminescence excitation spectra in XUV region
presented in figure 5–a (see in details Ref. [4]) we believe that at energies $E_{\text{exc}} > 13$ eV (higher than 2$E_g$) the effect of electronic excitations multiplication is observed. This effect is an attribute of
effective scintillation process. In crystals with a narrow valence band ($E_v$) of $p$-type the threshold
energy for this effect should lie just in the region of (2–3)$E_g$ [8]. We can reasonably assume that $E_v < E_g$ in LaBr$_3$ crystals, so the generation of secondary electron–hole pairs is due to the inelastic
scattering of photoelectrons.

5. Conclusions
The present study was carried out by means of time–resolved luminescence UV–VUV spectroscopy
as well as optical spectroscopy. Both Ce$^{3+}$ centers in regular lattice sites and located in the vicinity of
the point defects of crystal structure were observed. A PL of new point defects of the crystal structure
was observed. We evaluated the energy of interband transitions as $E_g \approx 6.2$ eV in LaBr$_3$. At the
energies $E_{\text{exc}} > 13$ eV (higher than 2$E_g$) the effect of electronic excitations multiplication was detected.

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