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Photoluminescence of anion-defective alumina single crystals exposed to high-dose gamma-radiation

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ABSTRACT

The method of UV and VUV spectroscopy with synchrotron radiation was used to measure photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra in anion-defective alumina single crystals exposed to high doses of gamma-radiation. A change in the intensity of the excitation band of F-centers near the fundamental absorption edge (8.8 eV) was found to depend on doses and temperatures. New wide bands with μs–ms decay kinetics of emission were registered in the PL spectra at excitations with VUV and UV photons. The obtained results show that high-dose irradiations of the crystals under study lead to appearance of F_2-type aggregate centers in different charged states. These centers are additional traps of charge carriers. Emission bands of other aggregate and impurity centers, which form an experimental PL spectrum in the crystals exposed to high doses, were also identified. The evolution of the centers, produced by oxygen vacancies and impurities, creates the features of dose responses of dosimetric α-Al_2O_3:C single crystals exposed to high doses of radiations.

1. Introduction

Luminescent and optical properties of anion-defective single crystals of aluminum oxide have been extensively studied for many years now [1–5]. Grown in highly reduced media at the presence of carbon, such crystals (α-Al_2O_3:C) contain oxygen vacancies with one or two trapped electrons. These vacancies form F^+ and F-centers which are involved in generating and trapping free charge carriers as well as in luminescence at the further thermal (TL) or optical stimulations (OSL). The TL and OSL yields are proportional to an absorbed dose in the range of 10^{-7}–10 Gy. The α-Al_2O_3:C crystals are used for design and development of highly sensitive detectors for personal dosimetry and environmental radiation monitoring. For low doses, other commercial luminescent detectors of radiation are also used [6]. The saturation of TL yield at doses over 10–20 Gy of these detectors is a common feature, which is related to the limited capacity of the traps responsible for the main dosimetric TL peak [7]. Saturation of the TL yield does not allow registration of high doses. Thus, properties of highly sensitive detectors in the range of high doses of irradiations have not been the focus of many studies.

However, there is a growing need in high-dose measurements due to advances in radiation technologies, necessity in dosimetric control of nuclear power plant equipment, radiation monitoring in spent-fuel storages and testing radiation resistance of materials and devices. Obvious advantages of luminescent dosimetry over non-luminescent methods (OA, ESR, calorimetry, chemical reaction) have generated a considerable research interest in behavior of dosimetric phosphors exposed to high doses of radiation. Such studies were carried out, e.g. for a highly-sensitive LiF:Mg,Cu,P detector, by Polish researchers [8]. The main dosimetric peak at 220 °C in the mentioned detectors was found to transform after high-dose irradiations with electron beams from an accelerator. Its shape changed and the amplitude decreased. Simultaneously, a new TL peak started forming at 450 °C. The TL yield of the peak increased linearly in the range of 50–500 kGy. Additional emission bands were found in the PL spectrum, which is an evidence of appearance of new trapping, and recombination centers, whose nature is not defined yet [9]. In α-Al_2O_3:C crystals the TL yield was measured in the main dosimetric TL peak at 460 K in a wide dose range from 20 Gy to 1000 kGy. The TL yield of the peak remained saturated up to 80 kGy, and then it increased sublinearly up to 800 kGy [5]. This result was another evidence of the formation of new trapping centers in the crystals exposed to high doses of irradiations. The centers are responsible for a growing TL yield in the given dose range. The emergence of the new centers was proved by the changes observed in the PL spectrum of the crystals exposed to high doses.

The purpose of this work was to study the photoluminescence and nature of the new luminescent centers in single crystals of anion-defective aluminum oxide (α-Al_2O_3:C) exposed to high doses of gamma-radiation.

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2. Material and methods

Aluminum oxide is a wide-band gap insulator (E_g=9.2–9.4 eV) [10]. The absorption band of F-centers (6.1 eV) is near the border of the vacuum ultraviolet (VUV) range [11], and the decay time of the emission of F^+-centers does not exceed 2 ns [12]. In this connection, the PL and PLE spectra under selective photoexcitations with synchrotron radiation (SR) were measured by using the time-resolved VUV spectroscopy method at the SUPERLUMI station (HASYLAB, DESY, Hamburg) [13]. The measurements were performed using a helium-flow cryostat providing vacuum of $5 \cdot 10^{-8}$ Pa. To selectively excite the PL in the 3.7–12 eV energy range, a 2 m vacuum monochromator with spectral resolution of 0.32 nm, equipped with a diffraction grating with Al-coating, was used. The PL excitation spectra are normalized to an equal number of photons, incident on the sample, by using sodium salicylate. To register the PL bands, the ARC Spectra Pro-308i monochromator and photomultiplier tube R6358P (Hamamatsu) operating in the time correlated single photon counting mode were used. Some PL spectra in red-infrared regions were measured using a cooled CCD-camera. The time-resolved PL spectra were recorded within time windows of the Δt=3 ns length correlated with the arrival of exciting SR-pulse delayed t=0.5 ns.

In all the measurements the Pl spectra were recorded when the sample was placed in front-scattering geometry respect to the excitation beam.

The 400 W deuterium discharge lamp with the continuous UV emission spectrum and the primary prismatic DMR-4 monochromator were used to measure the PL and PLE spectra in the low-energy range of about 2.4–5.5 eV in our laboratory. The PLE spectra were normalized to an equal number of photons, acting on the sample, by using yellow lumogen with an independent energy quantum yield over the studied spectral range.

The samples under study were cylindrical 1 mm thick by 5 mm in diameter. These were made of α-Al_2O_3:C single crystals grown in highly reducing atmosphere with the presence of carbon. According to the optical absorption data, the concentration of oxygen vacancies in single crystals was $1.3 \cdot 10^{17}$ cm^{-3}. The content of the main impurities in the crystals, measured by the arc atomic emission spectrometry using a PDS-2-MAEC spectrometer, is shown in Table 1.

The samples were exposed to high doses of gamma-radiation by using an industrial ^{60}Co-gun with the dose rate of 1.36 Gy/h.

3. Results and discussion

One should recall that PL spectra depend much on the energy E_{exc} of the exciting photons. Intracenter transitions in F- and F^+-centers play a defining role in forming PL spectra of α-Al_2O_3:C single crystals. These emission transitions are observed in intracenter excitations or in interactions of the centers with free charge carriers in accordance with the well-known following reactions:

$$e^- + F^+ \rightarrow F^* \rightarrow F + h\nu\ (3.0\ \text{eV}) \quad \text{and} \quad h^+ + F \rightarrow F^{+*}$$
$$\rightarrow F^+ + h\nu\ (3.8\ \text{eV}).$$

As the luminescence decay of F^+-centers occurs within several nanoseconds, a emission band associated with F-centers dominates in the experimental PL and PLE spectra measured without a time resolution. Fig. 1 shows the PLE spectra of the crystals under study exposed to various doses of gamma-radiation. The spectra are measured at SR excitation for the emission band at 3.0 eV. The PLE spectrum is composed of two intensive bands. The band at 6.1 eV is associated with the intracenter transition in F-centers. The band at 8.8 eV is in the region of the fundamental absorption edge of α-Al_2O_3. This band is connected with excitation of the excitons near F-centers or the exciton energy transfer to F-centers [14]. As can be seen, the intensity of the high-energy band decreases significantly when the exposure dose increases. This suggests that with the increasing dose, the concentration of new color centers different from F-centers grows as compared with the non-irradiated sample. Trapping excitons by such centers forms a competing channel of their relaxation, which leads to a drop of the PL yield of F-centers at excitation of this spectral region.

Formation of new trapping centers after high-dose irradiations of the crystals under study is also proved by the data in Fig. 2. It shows PLE spectra of F-centers which were measured in the sample exposed to 72.8 kGy at different temperatures. For comparison with PLE spectrum of unirradiated samples one can use Fig. 1 (curve 1). At a low temperature the PL intensity of F-centers under excitation in the region of the fundamental

Table 1
The content of main impurities in α-Al_2O_3:C single crystals.

Impurities	Cr	Ti	Mg	Fe
Mass fraction, %	$< 1 \cdot 10^{-3}$	$(5–8) \cdot 10^{-3}$	$(2–9) \cdot 10^{-3}$	$(7–12) \cdot 10^{-3}$

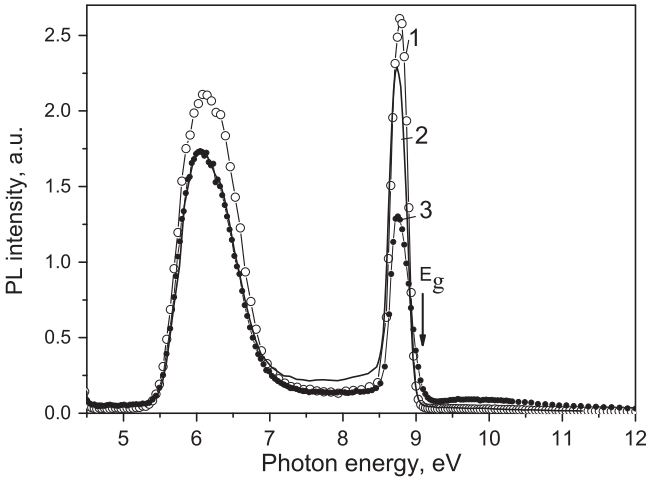

Fig. 1. PLE spectra of F-centers of the initial and exposed to different doses α-Al_2O_3:C crystals at a room temperature: (1) – initial; (2) – 10 Gy; (3) – 72.8 kGy.

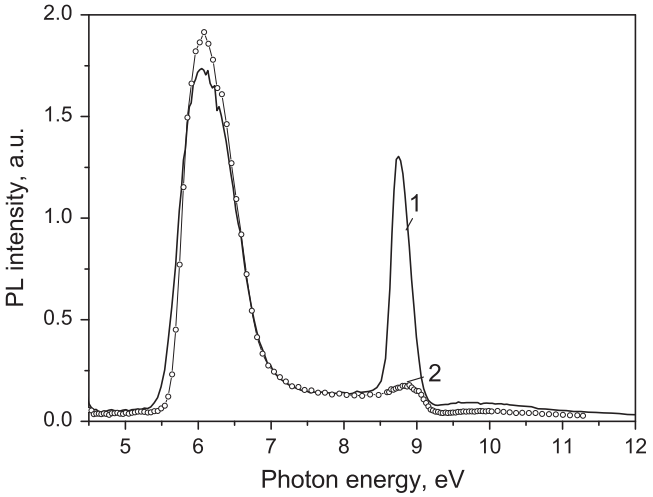

Fig. 2. PLE spectra of F-centers at T=300 K (1) and T=8 K (2) measured in α-Al_2O_3:C exposed to a gamma-radiation dose of 72.8 kGy.