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Defect evolution and photoluminescence in anion-defective alumina single crystals exposed to high doses of gamma-rays

V.S. Kortov*, V.A. Pustovarov, T.V. Shtang

Ural Federal University, Yekaterinburg 620002, Russia

HIGHLIGHTS

- PL of alumina exposed to high doses was measured under UV and VUV excitations.
- The emission of F^+ and F-centers decreases with a growing dose.
- New wide emission bands appear in the PL spectrum after irradiation.
- Oxygen divacancies are formed under high-dose irradiation of alumina crystals.
- High-dose exposure intensifies PL in the red–NIR spectral region.

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ABSTRACT

A method of luminescent UV and VUV spectroscopy was used to study the evolution of color centers in anion-defective alumina single crystals exposed to high doses of gamma-radiation. A sharp drop in the intensity of the emission bands and, therefore, the concentration of F^+ and F-centers associated with the formation of aggregate F_2-type centers was found. The aggregate centers create an additional emission band in the range of (1.8–2.8) eV. When the crystals are exposed to middle and high doses, the photoluminescence (PL) intensity is the highest in the emission band of F_2^{2+}-centers, which indicates a high concentration of the aggregates from singly charged oxygen vacancies (of F^+-centers). When PL of the crystals exposed to high doses is excited with synchrotron radiation of the VUV range, a wide emission band in the red and near infrared (NIR) regions is registered. The centers related presumably to impurity defects, their aggregates and clusters consisting of several oxygen vacancies are responsible for this emission band.

1. Introduction

Recently the development and use of luminescent detectors for high-dose measurements of ionizing radiation have been arousing more and more interest. Luminescent detectors have a wider range of dose response, are capable of measuring radiations with different linear energy transfer (LET) and can be used in automated readers in comparison with known non-luminescent techniques of registering high doses (OA, EPR, calorimetry, etc). A growing need in high-dose measurements is caused by development of new radiation technologies. Such measurements are necessary for dosimetric control of the equipment at nuclear power plants, radiation monitoring of spent-fuel storage facilities, and testing radiation resistance of materials and devices. Measurements of doses from several kGy up to several hundreds of kGy are required in the reported cases.

Several materials for detecting high-dose radiations have been found by now. Such materials should be radiation-resistant. Several natural minerals (topaz, quartz and etc.) which have a linear dose response up to (1–3) kGy are among them (Souza et al., 2002; Khory et al., 2007; Teixera et al., 2011). Disordered and amorphous materials (ceramics, glasses) (Kortov et al., 1995; Farah et al., 2010) as well as nanostructured phosphors (Kortov, 2010; Salah, 2011) are promising for high-dose measurements. Their dose response is extended towards high doses up to (10–30) kGy.

In spite of successful experiments, there are no high-dose luminescent detectors with steady metrological characteristics. Thus, the studies of behavior under high-dose irradiation of commercial detectors for low-dose radiations are of special interest.

* Corresponding author.
E-mail address: vskortov@mail.ru (V.S. Kortov).

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Such detectors are used now for personal dosimetry and radiation environmental monitoring (McKeever at al., 1995; Kortov, 2007). A technology of production has been developed to manufacture batches of detectors with small parameters spread. However, the range of linearity in the dose response in these detectors is limited to doses of (10–20) Gy. With a further growing dose, saturation occurs. Therefore, the behavior of highly sensitive detectors of radiations at high-dose exposure had not been the focus of extensive studies before.

The situation changed when the results of the studies of luminescent and dosimetric properties of highly sensitive LiF:Mg, Cu, P and TLD-500 (Al_2O_3:C) detectors under high-dose irradiations were reported. It was shown that when LiF:Mg, Cu, P-detectors are exposed to intensive fluxes of gamma-rays, electrons, protons, neutrons alpha-particles, the main dosimetric thermoluminescent (TL) peak at 493 K broadens, and its intensity decreases with an increasing dose. With this a new temperature TL peak emerges at 723 K. The dose response of this peak grows linearly up to 1 MGy (Bilski et al., 2010). A detailed list of works on the reported issues can be found in (Obryk et al., 2013).

Different results are obtained when TLD-500 detectors are irradiated with high doses by a pulsed electron beam. The main dosimetric TL peak of the detector hardly changes its shape and temperature position (460 K). Its intensity is in saturation up to 80 kGy, then the TL yield increases with a growing dose to 800 kGy (Kortov et al., 2014). High doses can also be registered using TLD-500 detectors when the TL yield of high-temperature peaks associated with deep traps is measured. For example, a linear dose response in the range of (1.5–80) kGy was observed for the TL peak at 700 K (Kortov and Ustyantsev, 2013). The TL yield of the peak at 830 K showed a sublinear dependence in the range from 1.5 kGy to 1 MGy (Nikiforov and Kortov, 2014).

Positive results of the experiments with highly sensitive TL detectors triggered the study of the mechanisms of the processes which occur in them under high-dose irradiations. The measurements of PL spectra showed that 7–8 additional bands caused by emergence of new traps and recombination centers were observed in LiF:Mg, Cu, P-detectors (Mandowska et al., 2010). A considerable increase in intensity in the emission band of the aggregate centers created by oxygen vacancies found in PL spectra of the TLD-500 detectors exposed to high doses. These centers are also additional traps of charge carriers (Kortov et al., 2014).

In the present work the processes of formation and evolution of luminescence centers in anion-defective alumina crystals (Al_2O_3:C) exposed to high doses of gamma-radiation were studied using photoluminescent VUV and UV spectroscopy.

2. Material and methods

The samples under study were disks of 5 mm in diameter and 1 mm thick. They were made of alumina single crystals grown in highly reducing atmosphere with the presence of carbon. According to the optical absorption data, the concentration of F-centers in single crystals was 1.3×10^{17} cm^{-3}.

A 400 W deuterium discharge lamp with a continuous UV emission spectrum and a primarily prismatic DMR-4 monochromator were used to measure PL spectra in the spectral range of about 2.4–5.5 eV. A photomultiplier tube R6358P (Hamamatsu) was used to register PL spectra.

The PL spectra under selective VUV photo-excitations with synchrotron radiation (SR) were measured at the SUPERLUMI station (HASYLAB, DESY, Hamburg) (Zimmerer, 2007). 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. To register PL bands, the ARC Spectra Pro-308i monochromator and photomultiplier tube R6358P (Hamamatsu) operating in the time correlated single photon counting mode were used. PL spectra in red-infrared regions were measured using a cooled CCD-camera.

Spectral resolution when PL spectra were measured in the experiments on synchrotron was 5.4 nm. The PL spectra when excited with a deuterium lamp were recorded with a resolution of about 10 nm. PL spectra were corrected taking into account spectral sensitivity of the registration channels (spectrometer and detector).

All the emission spectra were measured at 300 K.

Deconvolution of PL spectra into single Gaussians was carried out following a standard technique using the Origin software (version 8.5.1).

The samples were exposed to high doses of gamma-radiation by using an industrial ^{60}Co-gun with the dose rate of 1.36 kGy/h. They were classified as three groups depending on the exposure dose:

- middle doses (0.2–5) kGy;
- high doses (10–100) kGy;
- ultra-high doses (200–1000) kGy.

3. Results and discussion

Anion-defective dosimetric alumina single crystals (Al_2O_3:C) are known to have a relatively high concentration of oxygen vacancies before exposure. The vacancies form F and F^+-centers. The concentration of F-centers is in the range of 10^{17}–5×10^{17} cm^{-3}, and that of F^+-centers is by an order of magnitude lower (Solov'ev et al., 2012). The proportion of F/F^+ concentrations remains roughly constant due to conversion of the centers under low-dose irradiation in the (10^{-6}–10) Gy linear range in the dose response. The conversion appears at irradiations as a result of the interactions of the centers and free charge carriers in terms of the following reactions: $h + F \rightarrow (F^+)^* \rightarrow F^+ + h\nu$ (320 nm) and $e + F^+ \rightarrow F^* \rightarrow F + h\nu$ (420 nm), where $(F^+)^*$ and F^* are excited states of the mentioned centers. The traps of a complex dosimetric luminescence centers containing F and F^+-centers are completely filled when the dose response is saturated (Chen et al., 2006). As the concentration of the free charge carriers rises with the further dose increase, new processes leading to transformation of color centers should occur. One can expect that these processes affect the concentration of the F and F^+-centers under high-dose exposure and change the intensity of the emission bands of the centers in PL spectra. The measurements of the PL spectra with varying exposure doses confirmed this suggestion.

Fig. 1 shows PL spectra in the emission band of F^+-centers in the samples before and after exposure to a gamma-dose of 300 Gy. The spectra were measured at UV excitation into the absorption band of F^+-centers (4.8 eV). As can be seen, in the range of middle doses (300 Gy) the intensity of the emission band of F^+-centers with the maximum at 3.8 eV (325 nm) drops drastically in comparison with the unirradiated crystal. Fig. 2 shows that this trend remains in the range of high and ultra-high doses (5–600) kGy.

A similar dependence of the emission intensity on irradiation dose was observed when the studied crystals were excited with a photon energy of 5.8 eV which is near the maximum of the absorption band of F-centers (6.1 eV) (Evans, 1995). The emission intensity of F-centers also decreases with growing dose; however it does not occur so dramatically as in case with F^+-centers. We estimated the rate of changing emission intensity as a ratio of a value ΔI to a dose increase ΔD in the range (1–300) Gy. An average rate of the emission intensity drop in the band of F-centers was approximately 3.6 times as low as in case of F^+-centers. Decreasing emission of F and F^+-centers, and thus a decrease in their