Nuclear Instruments and Methods in Physics Research B 353 (2015) 42–45

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Radiation-induced transformations of luminescence centers in anion-defective alumina crystals under high-dose irradiations

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

Ural Federal University, Ekaterinburg 620002, Russia

ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form 13 April 2015
Accepted 17 April 2015
Available online 29 April 2015

Keywords:
Alumina
High-dose irradiation
Oxygen vacancies
Aggregated centers
Photoluminescence

ABSTRACT

Luminescent spectroscopy is used to show formation of new trapping centers of charge carriers in anion-defective alumina crystals at radiation-induced transformations of F and F^+-centers created by oxygen vacancies when exposed to high-dose gamma-radiation. A new wide band in the range 440–700 nm was registered in the photoluminescence spectrum at excitations with UV photons. High-dose irradiation of the crystals leads to appearance of F_2-type aggregate centers in different charged states. These centers are additional traps of charge carriers. The new traps increase a luminescent yield at high-dose irradiation with gamma-rays and an electron beam.

1. Introduction

Anion-defective alumina crystals were suggested as dosimetric phosphors [1]. They are highly sensitive to ionizing radiation, which is caused by oxygen vacancies. The vacancies emerge when the crystals are grown in a highly reducing medium. They form the traps of one or two electrons giving rise to F^+ and F-centers correspondingly. These centers take part in the creation of dosimetric traps which capture free electrons resulting from irradiation. Thermal or optical ionization of such traps with the following recombination of delocalized electrons causes the luminescence according to the following reactions: $F + h \rightarrow (F^+)^* \rightarrow F^+ + h\nu$ (330 nm) and $F^+ + e \rightarrow F^* \rightarrow F + h\nu$ (420 nm). The luminescence intensity is proportional to the dose of X-ray, gamma- and beta radiation in the range of 10^{-7}–10 Gy [2]. The high-sensitive detectors TLD-500 are developed on the basis of alumina anion-defective single crystals. The detectors are widely used for personal dosimetry, radiation environmental monitoring, and in medicine, i.e. in measurements of low doses.

With the dose increase higher than 10 Gy, the luminescence intensity is saturated due to a limited capacity of the dosimetric traps [3]. This does not allow using the anion-defective alumina crystals for high dose measurements. Therefore, luminescent and dosimetric properties of these crystals at high dose irradiation have not been studied until recently. However, there is a growing need in high-dose measurements due to advances in usage of electron accelerators for 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 behaviour of dosimetric phosphors exposed to high doses of radiation. Such studies were carried out for highly sensitive thermoluminescent detectors, namely, LiF:Mg, Cu, P [4–6] and Al_2O_3:C [7,8]. Additional emission bands in irradiated detectors were found in the photoluminescence spectra, which is an evidence of appearance of new trapping and recombination centers, whose nature is not defined yet [9,10].

In this paper we report the results of the studies of luminescence center transformations and the changes in luminescent properties of anion-defective alumina crystals exposed to gamma-radiation and an electron beam with the dose up to 10–10^6 Gy.

2. Material and methods

The samples under study were disks 5 mm in diameter and 1 mm thick. These 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 oxygen vacancies in single crystals was 1.3×10^{17} cm^{-3}.

* Corresponding author. Tel.: +7 343 3754443; fax: +7 343 3754415.
E-mail addresses: vskortov@mail.ru (V.S. Kortov), vpustovarov@bk.ru (V.A. Pustovarov), t.v.shtang@gmail.com (T.V. Shtang).

http://dx.doi.org/10.1016/j.nimb.2015.04.039
0168-583X/

A 400 W deuterium discharge lamp with a continuous UV emission spectrum and a primarily prismatic DMR-4 monochromator were used to measure photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra in the spectral range of about 2.4–5.5 eV. The PLE spectra were normalized to the equal number of photons acting on the sample using yellow lumogen with the independent energy quantum yield over the studied spectral range. A photomultiplier tube R6358P (Hamamatsu) was used to register PL and PLE spectra. The thermoluminescence (TL) of the exposed crystals was measured at a heating rate of 2 K/s.

To irradiate the crystals, the radiation sources of two types were employed. We used an industrial ^{60}Co-gun with dose rate of 1.36 kGy/h. Another source of high-dose radiation was a pulse electron accelerator with the following parameters: pulse length is 2 ns, medium electron energy is 130 keV, and current density is 60 A/cm^2. The absorbed dose from one accelerator pulse was preliminary calculated and then experimentally proved by the optical absorption method with the use of film dosimeters SORD (F) R-5/50. The medium absorbed dose (in water) was found to be 1.5 kGy/pulse at 10 mm distance [11]. In this case the temperature change of the sample does not exceed 1–2 K. The due irradiation dose can be obtained by increasing a pulse number.

3. Results and discussion

Fig. 1 shows the PL spectra of the crystals under study exposed to various doses of gamma-radiation at the excitation to the absorption band of F^+-centers (4.8 eV). The PL spectrum in the samples exposed to the doses of 10 and 100 Gy features an intensive emission band of F^+-centers (330 nm) and a weaker band of F-centers (420 nm). This implies that PL at the reported doses appears due to the excitation in the centers formed by single vacancies in a corresponding charge state.

As the exposure dose increases, an additional wide band with the maximum near 540 nm starts forming in the range of 450–700 nm in the PL spectrum. This suggests that new emission centers emerge in the crystals under study at high-dose irradiations. The centers with intensive emission in the yellow-green spectral region were observed in the samples of stoichiometric alumina after irradiation with an electron beam with the energy of 15 MeV [12], and by fast neutrons [13]. High-energy particles knock oxygen and aluminum atoms out of their sites in the lattice. At the same time F and F^+-centers as well as luminescence centers associated with the interstitial Al_i^+ ions are created. When the samples are irradiated with fast neutrons some oxygen vacancies combine and form aggregate F_2-centers. Such centers are divacancies with four trapped electrons. In anion-defective alumina crystals, F_2-type centers can emerge at thermal- and photo-induced transformations [14]. When the alumina crystals were exposed to gamma-radiation, the formation of aggregate centers was not studied.

We assume that the new wide PL band in the crystals under study is also caused by the formation of divacancies in different charge states. High concentration of oxygen vacancies and their increasing diffusion mobility are necessary for the centers to emerge. Both requirements are met in the reported samples. High concentration of oxygen vacancies (10^{17} cm^{-3}) which form F-centers was obtained when the crystals were grown in highly reducing conditions. Their enhanced diffusion mobility was induced by high-dose gamma-irradiation.

High-dose irradiation causes multistage transformations of luminescence centers. First, aggregate centers with different charges: $2F \leftrightarrow F_2$; $2F^+ \leftrightarrow F_2^{2+}$ and $F + F^+ \leftrightarrow F_2^+$ are formed. Other transformations are associated with the interactions between the resulting F_2-types centers and free charge carriers which emerge when the crystal is irradiated, e.g. $h + F_2 \rightarrow (F_2^+)^* \rightarrow F_2^+ + h\nu$ (380 nm); $F_2^+ + e \rightarrow F_2^* \rightarrow F_2 + h\nu$ (500 nm); $2\,h + F_2 \rightarrow (F_2^{2+})^* \rightarrow F_2^{2+} + h\nu$ (550 nm), etc. Moreover, the charged F_2-type centers can appear at ionization while the crystals are being exposed. The abovementioned luminescence bands of the aggregate F_2, F_2^+ and F_2^{2+}-type centers were found experimentally.

To identify emission centers in the new broad band in the PL spectrum of the crystals exposed to a high dose, PLE spectrum was measured for λ_{emis} = 540 nm. The spectrum is given in Fig. 2. It features bands at 4.8 eV and 5.4 eV associated with F^+-centers [15]. In addition, the spectrum includes indistinct maximums and bends, which are typical for superposition of several overlapping bands. The PLE spectrum was deconvoluted into elementary bands (Gaussians), a number of which corresponded to a number of presumably existing PL centers in the exposed samples. As can be seen, the experimental PLE spectrum and the one calculated as a superposition of elementary bands are in good agreement.

Alongside with the F^+-center bands PLE spectrum contains the bands centered at 4.1 eV, 4.3 eV and 3.8 eV. The appearance of

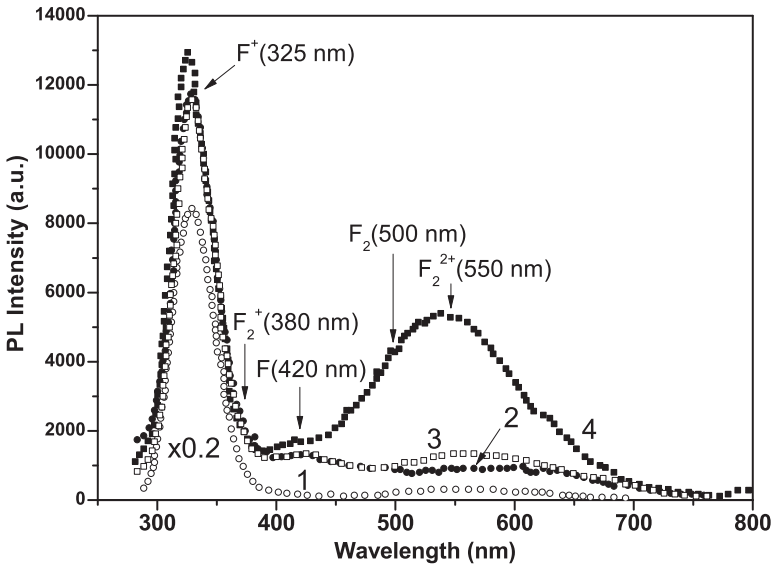

Fig. 1. PL spectra (E_{exc} = 4.8 eV, T = 300 K) in anion-defective alumina single crystal after gamma-rays irradiation with various doses: 1-10 Gy; 2-100 Gy; 3-1 kGy; 4-72.8 kGy.