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Luminescence and radiation-induced color centers in anion-defective alumina crystals after high-dose irradiation

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HIGHLIGHTS

- PL and PLE spectra of the alumina crystals exposed to high doses were measured.
- Aggregate F_2-type centers are responsible for an additional PL band.
- The PL of aggregate centers is accompanied by a decreasing intensity of F^+- band.
- F^+-centers cause formation of charged aggregate color centers.
- F-centers are not engaged in creation of aggregate centers.

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ABSTRACT

A method of UV spectroscopy was used to measure photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra in anion-defective alumina crystals exposed to high doses of gamma-radiation. An additional emission band in the range of 1.6–2.75 eV appears in the exposed crystals. Aggregate F_2-type centers in different charge states are responsible for this band. It was found that growing intensity of PL aggregate centers occurs at doses corresponding to saturation of dose response and is accompanied by a sharp drop in the intensity of F^+-band in the PL spectrum resulting from combination of F^+-centers into aggregates. Uncharged F_2-centers are formed when electrons are trapped by F_2^+ and F_2^{2+}-centers. The main role of F^+-centers in radiation-induced transformations of color centers under high-dose irradiation of anion-defective alumina crystals was indicated.

1. Introduction

Dosimetric phosphors on the base of anion-defective alumina single crystals were developed 25 years ago (Akselrod et al., 1990). Unlike other materials which are used in radiation dosimetry, luminescence centers in non-stoichiometric alumina are created not by dopants, but by intrinsic defects of the crystalline lattice, namely by oxygen vacancies. The vacancies trapping two or one electron form F and F^+-centers which are responsible for luminescence. The presence of carbon when the crystals are grown makes the reaction of alumina reduction effective and increases the concentrations of oxygen vacancies.

The new phosphor possessed a number of competitive advantages. It was highly sensitive (0.1 μGy) when X-ray and gamma-radiations were registered, had an isolated dosimetric thermoluminescence (TL) peak, a wide range of linear measurement of dose response (up to 1 Gy), and low fading. Therefore, commercial TLD-500 detectors were developed on the base of the phosphor. They are widely used at present for TL and OSL personal dosimetry and radiation environment monitoring.

Practical applications of anion-defective alumina crystals are ahead of studies of the nature of dosimetric traps, processes of their formation and transformations under irradiation. The structure of complex defects including F, F^+-centers and impurities is little studied. Such defects are responsible for trapping and storing charge carriers under exposure and for electron–hole recombinations at thermo- or photostimulation. Experimental studies showed that charge states of single oxygen vacancies, which are the main luminescence centers in the crystals under discussion, changed both at the stage of irradiation and at further stimulation (Solov'ev et al., 2013). Conversion of F ↔ F^+- centers allows the concentration ratio of F/F^+-centers to be kept within a constant

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value (Yukihara et al., 2003), which makes the material highly sensitive on the linear region of dose response. However, the saturation of luminescence yield with a further growing dose illustrates disbalance in the concentration of F and F^+-centers. One of the possible reasons for this effect is connected with radiation-induced formation of aggregate F_2-type centers in different charge states. Such aggregate centers were found experimentally in alumina irradiated with electrons having the energy of 10 MeV (Surdo et al., 1985), as well as with high-energy fluxes of fast neutrons (Izerrouken and Benyahioa, 2010).

Formation of aggregate defects is accompanied by creation of additional traps of charge carriers responsible for the effect of high-dose sensitization, which was found when the crystals under study were exposed to gamma-rays and nanosecond electron pulses (Kortov et al., 2015). The performed experiments are the primary stage of research of radiation-induced evolution of color centers, which significantly affects luminescent properties of dosimetric phosphors. Direct experimental evidences are necessary, which will prove participation of F and F^+-centers in the process of formation of aggregate centers. Detecting dose range in which aggregate centers form is required. Transformation processes of luminescent centers in the studied crystals in the dose range beyond linear changes of dose response are of special interest.

In the present paper the results of research into effects of radiation-induced color centers on photoluminescence in anion-defective alumina crystals.

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. The photomultiplier tube R6358P (Hamamatsu) was used to register PL spectra. The PL spectra were recorded with a resolution of about 10 nm and were corrected taking into account spectral sensitivity of the registration channels (spectrometer and detector). All the emission spectra were measured at T = 300 K. Deconvolution of PL spectra into Gaussians were carried out following a standard technique using the Origin software (version 8.5.1). The samples were exposed to gamma-radiation by using a ^{60}Co-gun with the dose rate of 1.36 kGy/h and medical ^{60}Co-gun with the dose rate of 3.1 Gy/min.

3. Results and discussion

It is known that only two emission bands centered at 3.0 eV and 3.8 eV are registered in the PL spectrum of non-irradiated alumina crystals. F and F^+-centers created by single oxygen vacancies are responsible for these emission bands (Evans, 1995; Izerrouken and Benyahioa, 2010). Fig. 1 shows PL spectrum of the crystals under study after gamma-exposure to a dose of 72.8 kGy at excitation into a band of F^+-centers (4.8 eV). The PL spectrum features an intensive emission band of F^+-enters, a weak band of F-centers and an additional wide emission band in the range of 1.6–2.75 eV centered at 2.3 eV. Emergence of an additional band in the PL spectrum is an evidence of formation of new emission centers under high-dose exposure.

To understand their nature, the PLE spectrum was measured for E_{em} = 2.3 eV, which corresponds to the intensity maximum of an additional emission band. The PLE spectrum is shown in Fig. 2. The

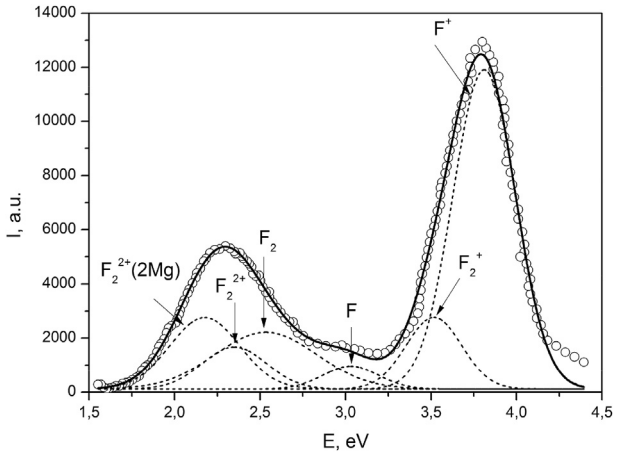

Fig. 1. PL spectrum of anion-defective alumina crystals (E_{exc} = 4.8 eV) to a 72.8 kGy dose: the light dots are experiments; the solid line is a calculation after deconvolution into Gaussians.

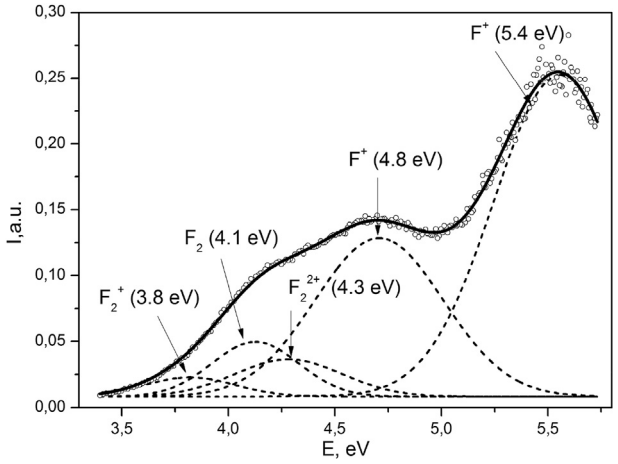

Fig. 2. PLE spectrum (E_{emis} = 2.3 eV) in alumina crystals exposed to a dose 72.8 kGy: light dots are experimentally, a solid line is calculation after deconvolution into Gaussians.

spectrum is a wide band in the range of 3.5–5.7 eV. In this band one can distinguish the bands centered at 4.8 eV and 5.4 eV belonging to F^+-centers. A long-wave region of the PLE spectrum is a curve with indistinct bends, which is typical for superposition of several bands. These bands were singled out when the spectrum was deconvoluted into Gaussians. The analysis of the deconvolution results indicates that the PLE spectrum, except for the bands of F^+-centers, features emission bands of aggregate F_2-type centers in different charge states (F_2, F_2^+, F_2^{2+}). The experimental PLE spectrum and the one calculated as a superposition of elementary bands are in good agreement.

Aggregate F_2, F_2^+ and F_2^{2+}-centers are oxygen divacancies which trap four, three or two electrons, respectively. Their excitation and emission bands are well-known (Izerrouken and Benyahioa, 2010; Solov'ev et al., 2013). They have the maximums at 2.3 eV (F_2^{2+}), 2.5 eV (F_2), 3.5 eV (F_2^+). Taking into account the reported data, the PL spectrum in Fig. 1 was deconvoluted into Gaussians. The results of deconvolution show that aggregate F_2 and F_2^{2+}-centers make the main contribution to an additional emission band in the exposed crystals. The bands of the centers overlay each other. An emission band of an F_2^+-center also overlays with an F^+-band, which causes its broadening in the experimental spectrum of the irradiated