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EPR and photoluminescence study of irradiated anion-defective alumina single crystals

V.S. Kortov *, D.V. Ananchenko, S.F. Konev, V.A. Pustovarov

Ural Federal University, Ekaterinburg 620002, Russia

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ABSTRACT

Electron paramagnetic resonance (EPR) and photoluminescence (PL) spectra of anion-defective alumina single crystals were measured. Exposure to a dose 10 Gy–1 kGy causes isotropic EPR signal of a complex form, this signal contains narrow and broad components. At the same time, in the PL spectrum alongside with a band of F^+-centers (3.8 eV) an additional emission band with the maximum of 2.25 eV is registered. This band corresponds to aggregate F_2^{2+}-centers which were create under irradiation. By comparing measurements in EPR and PL spectra with further stepped annealing in the temperature range of 773–1473 K of the samples exposed to the same doses, we were able to conclude that a narrow component of isotropic EPR signal is associated with the formation of paramagnetic F_2^{2+}-centers under irradiation. A wide component can be caused by deep hole traps which are created by a complex defect ($V_{Al}^{2-} - F^+$) with a localized hole.

1. Introduction

Alumina (α-Al_2O_3) has a number of unique properties, which makes it widely used in industry. Due to the development of nuclear engineering and radiation technologies, there is a great interest in high radiation resistance of alumina. Thus, its electron structure, optical and luminescent properties, the changes of these properties under of ionizing radiation are intensively studied [1–10]. A great number of papers are devoted to the research of luminescent and dosimetric characteristics of non-stoichiometric alumina with high concentration of oxygen vacancies. Anion-defective alumina serves as the base for highly-sensitive detectors of ionizing radiation (TLD-500), these detectors are widely used for personal dosimetry and radiation monitoring of environment [11–13]. Studies in recent years show that due to high radiation resistance, TLD-500 detectors can be used for high-dose measurements including dosimetry of electron beams of accelerators [14,15].

The nature of luminescence centers in TLD-500 detectors is studied mainly with methods of optical and luminescent spectroscopies. It has been found that the main peak of thermoluminescence (TL) at 460 K is a superposition of two or three elementary peaks which are caused by different defects [16–20]. Measurements of photoluminescence spectra showed that there are centers created by both intrinsic defects (oxygen vacancies in different charge states) and impurities in anion-defective alumina. Indirect experimental evidences show that both electron traps and hole ones contribute to TL of the main dosimetric peak as well as to that of high-temperature peaks associated with deep traps. However, the nature of the defects that create the reported traps remains unidentified when only methods of optical and luminescent spectroscopies are used. Other methods sensitive to intrinsic radiation-induced defects and impurities in the material are necessary.

EPR is one of the effective tools to study defectiveness in solids including the ones exposed to ionizing radiation. There are investigations showing that this method is successfully used to research both hole and electron centers in alumina and other oxides. The formation of paramagnetic centers with $g_\perp = 2.012$ and $g = 2.008$ in α-Al_2O_3 after γ-irradiation was found [21]. The authors presented a complex, asymmetric EPR signal as superposition of three absorption lines associated with two types of defects: a hole localized on an anion adjacent to a cation site which is deficient in positive charge and an electron trapped at an anion vacancy. Further, hole centers in γ-irradiated oxidized alumina were studied with EPR method in [22]. Exposure of the samples caused formation of hole V^{2-} and V^- centers. A one-hole V^{2-} center (a center comprised of an O^- adjacent to an aluminum vacancy) was formed first under irradiation being a precursor of two-hole V^- centers (two O^- adjacent to an aluminum vacancy). V^- centers were annealed near 370 K and transformed into V^{2-} centers which exhibited $g_\perp = 2.013 \pm 0.004$ and a line width of about 50 G. The one-hole centers were thermally ionized at 500 K. In their later paper [23],

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

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these authors describe EPR study of non-oxidized Al_2O_3. A line of resonance absorption 45 G wide with $g_\perp = 2.011$ emerges in EPR spectrum after γ-irradiation of ^{137}Cs at room temperature. The authors believed that the found center was $V_{\overline{OH}}$: an OH^- ion adjacent to V^{2-}. When the sample was heated, the amplitude of the resonance absorption line of $V_{\overline{OH}}$ center dropped and disappeared at 400 K. Annealing at 1623 K caused disintegration of a paramagnetic center due to removal of OH^- ions from alumina during oxidation.

A broad EPR spectrum with 13 resolved absorption lines at g = 2.0029 in neutron irradiated alumina was registered [24]. The authors interpreted this spectrum as the hyperfine interaction of F^+ center's unpaired electron with two pairs of Al^{3+} nuclei.

Doping of Al_2O_3 with Mg^{2+} and Li^+ ions with the presence of Ti^{3+} ions (to intensify introduction of impurity ions) makes new defects appear [25]. EPR spectra of Al_2O_3:Mg,Ti, Al_2O_3:Li,Ti and oxidized Al_2O_3:Ti feature three slightly different lines of resonance absorption with S = 1/2 attributed to single holes trapped by negatively charged defects Mg^-_{Al} ($g_x = 2.030$), Li^{2-}_{Al} ($g_x = 2.023$), V^{3-}_{Al} ($g_x = 2.020$) respectively. When alumina is doped with chromium oxide, resonance absorption lines of isolated Cr^{3+} ions (g = 3.33, 2.34, 1.95, 1.49, 1.26) which predominate at low Cr_2O_3 concentration are registered in EPR spectrum [26]. Pairs of Cr^{3+} ions which were electronically coupled in non-irradiated samples of α-cromia-alumina solid solution were formed at the concentration of Cr_2O_3 above 1.5% (0.4% chromium ions) [27]. With such concentrations, two absorption lines with g = 1.99 ± 0.01 appeared in the EPR spectrum. At the same time, the intensity of the absorption lines associated with electronically isolated Cr^{3+} ions decreased in the spectrum.

The works mentioned above used as prepared or oxidized alumina samples. We have not found any publications devoted to EPR study in anion-defective alumina crystals with high concentrations of oxygen vacancies.

Our work presents the results of combined research of EPR and PL spectra of anion-defective alumina single crystals when an exposure dose is changed and annealing is performed.

2. Materials and methods

Anion-defective alumina single crystals (standard TLD-500 detectors) were studied. The samples with certain amount of oxygen vacancies formed via thermo chemical coloration were in the form of pellets 5 mm in diameter and 1 mm thick. Crystallographic axis C was perpendicular to the flat surface of the sample. The concentration of F-centers, which was calculated from the measurements of optical absorption by using Smacula formula, was about $1.3 \cdot 10^{17}$ cm^{-3}.

ELEXSYS 580 spectrometer (by Bruker, USA) with the resonance frequency of 9.27 GHz (wave number 0.31 cm^{-1}) was used to study EPR in the induction variation interval of constant magnetic field from 480 to 6000 G. Super High-Q rectangular resonator was employed to continuously collect spectral data. The sensitivity of the spectrometer was $1.2 \cdot 10^9$ spin/G. The following conditions of the records of EPR spectra were used: modulation frequency of the magnetic field was 100 kHz, amplification factor was 60 dB, the modulation magnitude of the magnetic field was 10 G, magnetic field scanning time was 46.2 s, the level of super-high frequency power was 4.74 mW.

Photoluminescence was excited with a 400 W discharge deuterium lamp on the automated unit based on two double DMR-4 monochromators with quartz prisms. PL spectrum was recorded with FEU-106 photomultiplier with the maximum sensitivity in the spectral region of 400–440 nm.

Before measuring EPR and PL, the samples were irradiated with a β-source ($^{90}Sr/^{90}Y$) with the 8 mGy/min dose rate or an industrial ^{60}Co-gun with the 1.36 Gy/min γ-dose rate.

To find the connection of EPR and PL spectra with the defects, the irradiated samples were annealed step-by-step in a muffle furnace in the air in the temperature interval of 700–1600 K with varying time of isochronal annealing.

3. Results and discussion

Fig. 1a shows EPR-spectra of the non-irradiated crystals and of the crystal after its exposure to β-irradiation with doses in the range of 10–400 Gy. The spectrum of the non-irradiated sample features narrow anisotropic signals (III) with g = 3.46 and 1.27, the positions of these signals after irradiation greatly depend on the crystal orientation in respect to the magnetic field. Exposure of the samples to a dose less than 1 Gy is not accompanied by emergence of additional resonance lines. Further increasing of the exposure dose causes formation of paramagnetic centers in the samples. A new signal of resonance absorption appears after β-irradiation with the dose higher than 10 Gy (Fig. 1b).

A narrow EPR signal (I) of low amplitude is observed in the spectrum, when induction of the magnetic field is 3500 G. An increasing dose up to 240 Gy causes formation of intensive complex signal (Fig. 1c) which is a superposition of two components: broad resonance absorption line (II) at the induction of the magnetic field 3240 G, and narrow line (I) at the magnetic field of 3500 G. When the exposure dose increases up to 400 Gy, the amplitude of resonance lines (I) and (II) changes slightly (Fig. 1d). The values of g-factors of absorption lines (I) and (II) for the irradiated detector are 2.008 and 2.11 respectively.

Let us first consider a possible interpretation of the nature of narrow anisotropic EPR signals. Such signals are recorded in non-irradiated crystals; their amplitude does not depend on an exposure dose. Annealing of the irradiated crystals in the 773–1423 K range also did not affect the amplitude and a number of anisotropic resonance lines. The reported facts allow concluding that impurity centers (more likely Cr^{3+}) are responsible for these resonances in alumina. Similar conclusion had been made earlier [26]. In the crystals under study, the concentration of the impurity centers of chromium ions did not exceed 0.001 wt.%. Therefore, we believe that narrow anisotropic EPR signals in anion-defective alumina are associated with electronically isolated Cr^{3+} ions.

The nature of a complex wide EPR signal is of special interest. The amplitude of this signal depends on the exposure dose and (as it will be shown below) on the annealing temperature. It is known that correct comparison of the intensity of EPR signals is possible only when the amplitude of resonance absorption line does not depend on the sample orientation respective to the static magnetic field (isotropic signal). Fig. 2 shows EPR spectra of γ-irradiated crystals (1 kGy) with a different angle between the magnetic field and crystalline axis C in the samples. The angle changed from 0° up to 180° in increment of 15°. It is seen that the intensity and position of EPR signal were invariant to the angle between the crystalline axis and magnetic field. Thus, the broad EPR signal which emerges after irradiation is isotropic.

It is known that when anion-defective alumina single crystals are irradiated and heated, transformation of defects occurs [28]. During this transformation, paramagnetic centers can emerge and disappear. By comparing the temperature intervals of the changing amplitude of EPR signal and thermal evolution of the defects, one can obtain useful data on the nature of paramagnetic centers. In this regard, we studied the effect of annealing in the temperature interval of 773–1473 K in the irradiated crystals on a wide (II) and narrow (I) components of the resonance lines of isotropic signal in the EPR spectrum.

When the samples were heated up to 800 K, there were no changes in the EPR spectrum. At 820 K, a decay of the amplitude