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Luminescent and dosimetric properties of ultrafine alumina ceramics with anion defects

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Abstract. Ultrafine oxygen-deficient alumina ceramics was obtained by high-temperature annealing of nanopowder compacts in a vacuum in a strong reducing medium. The spectra of pulsed cathodoluminescence, photoluminescence, electron paramagnetic resonance and thermoluminescence of the synthesized ceramics and anion-defective Al_2O_3 single crystals were measured. Dose dependences of the thermoluminescence intensity on a dose of β-radiation were found.

Introduction

Alumina is now a high-demand functional material in laser technology, optics, nuclear power, radiation dosimetry. Alumina dosimetric properties are a function of concentration of oxygen vacancies, which are formed in the bulk of material, for example, during a single crystal growth in a reducing medium. Thermoluminescent detectors of ionizing radiation based on oxygen-deficient alumina are highly sensitive, have low fading and a wide range of registered doses (0.5 μGy - 10 Gy) [1]. These detectors are used in personal dosimetry of ionizing radiation and environmental radiation monitoring. At the same time, there is a necessity to register higher radiation doses for the purposes of emergency dosimetry and radiation technologies.

Using nanostructured and ultrafine phosphors with enhanced radiation resistance is a promising trend in the development of materials for registration of ionizing radiation in high dose dosimetry. Such materials can be used to measure doses of radiation in the range of 100 Gy - 10 kGy [2]. The aim of this work was to study luminescent and dosimetric properties of oxygen-deficient alumina ultrafine ceramics in comparison with Al_2O_3 single crystals containing defects in anion sublattice.

Experimental

Ultrafine oxygen-deficient alumina ceramics were synthesized from the commercial high-purity α-Al_2O_3 (99.997%) nanopowder with the particle size of 50-70 nm produced by alcoholate method. The powder was pressed into compacts 5 mm in diameter and 1.3 mm thick by cold uniaxial pressing under 1000 kg/cm^2 using "Specac" hydraulic press. To create oxygen deficiency in the ceramic, it was annealed at high temperatures in the vacuum strongly reducing environment with the presence of carbon rod which was placed 5 mm from the samples in the vacuum chamber of the furnace. The annealing temperature was varied from 1500 to 1700ºC, the time of annealing ranged between 30 and 300 minutes. Alumina single crystals were grown from the melt (Stepanov's method) in highly reducing atmosphere with the presence of carbon. The crystalline samples were 5 mm in diameter and 1 mm thick. According to the optical absorption data, the concentration of oxygen vacancies in single crystals was $1.3 \cdot 10^{17}$ cm^{-3} [1].

The surface structure of the obtained ceramics was studied with a SIGMAVP scanning electron microscope (SEM) and a secondary electron detector (In-lens) in high vacuum with a 5 kV accelerating voltage. Analysis of the SEM images showed that average particle size in the ceramic samples synthesized at T = 1500˚C for 180 minutes was 173 nm.

The photoluminescence (PL) spectra were obtained using a luminescent LS-55 spectrometer (Perkin Elmer, USA) in the range of 200-800 nm. The comparative analysis of impurity ions and intrinsic defects present in the ultrafine ceramics and anion-defective alumina single crystals was carried out with the spectra of pulsed cathodoluminescence (PCL). The PCL was excited with an electron beam with the pulse duration of 2 ns, electron energy of 130 keV, current density of 60 A/cm^2, and was measured in the spectral region 300-700 nm. The standard method was used to perform TL measurements with a FEU-142 photomultiplier at the linear temperature change from 30 to 800˚C at the rate of 2˚C/s. The ceramic samples had been preliminarily exposed to the doses of 0.32-2000 Gy from the ^{90}Y/^{90}Sr β-source with the dose rate of 32 mGy/min.

ELEXSYS 580 (Bruker, USA) spectrometer with the resonance frequency 9.27 GHz (wave number 0.31 cm^{-1}) was used to study electron paramagnetic resonance (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 is $1.2 \cdot 10^9$ 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, 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.

Results and discussion

Creation of anionic defects in the ultrafine Al_2O_3 ceramic samples during high-temperature annealing in a reducing medium was confirmed by PCL spectra measuring. Fig. 1 shows PCL spectrum of alumina single crystal and ceramics synthesized at T = 1500˚C, 180 min. One can see that emission in the band of 400-450 nm, which results from triplet-singlet transitions $^3P \rightarrow {}^1S_0$ in F-center (oxygen vacancy with two trapped electrons), is observed in a single crystal and ceramics [4]. Decreasing in the intensity of ceramics compared to the single crystal is attributed to a lower concentration of oxygen vacancies in ceramics. Growing alumina single crystal from the melt (T_m = 2047˚C) in the presence of carbon provides conditions for a more efficient creation of oxygen non-stoichiometry in the oxide's sublattice.

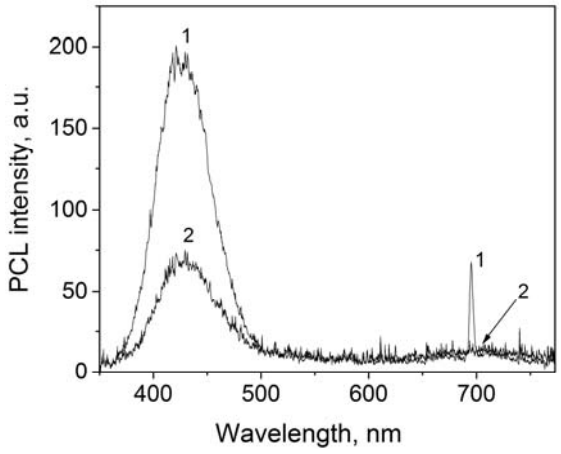

Figure 1. PCL spectra of oxygen-deficient alumina single crystal (1) and ceramics (2)

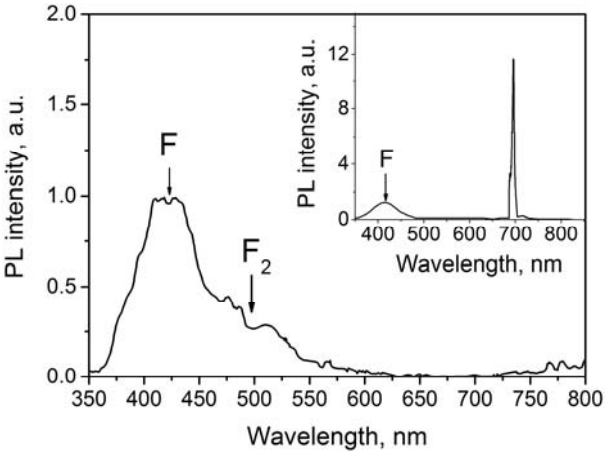

Figure 2. PL spectrum of alumina ceramics synthesized at 1500˚C for 180 min. In the inset: PL spectrum of single crystal

A narrow emission band at 695 nm, which appeared in the PCL spectrum of anion-defective Al_2O_3 single crystal, caused by the presence of Cr^{3+} impurity ions and corresponded to the transition $^2E \rightarrow {}^4A_2$ in the Cr^{3+} ions [3]. In the spectrum of ultrafine ceramic this emission band was not registered because of the great disorder in the sample structure in comparison with single crystal.

PL spectra of single crystal and ceramics (Fig. 2) were measured under photon excitation with wavelength 205 nm, which corresponds to the maximum of F-center optical absorption in alumina [4]. Distinct emission bands of F-centers (420 nm) and R-line of Cr^{3+} impurity ions (695 nm) were

observed in the PL spectrum of a single crystal. In the PL spectrum of ceramics, the emission band of F-centers was broadened, and in addition there was PL band near 500 nm. The band mentioned above is associated with the presence of aggregate F_2-centers (two oxygen vacancies, captured 4 electrons) in the ceramic. It is known that these defects are typical of highly disordered alumina samples, also after neutron irradiation of single crystals [5]. In that context, R-line of chromium ions did not appear in the PL and PCL spectra of ceramic. Therefore, disorder of the samples greatly affects spectral characteristics of ultrafine oxygen-deficient alumina ceramics. High disorder in alumina ceramics synthesized from nanopowder was also confirmed by EPR spectra measurements.

Fig. 3 shows EPR spectra of Al_2O_3 single crystal and ultrafine ceramic after β-irradiation with the dose of 12 Gy. EPR spectrum of ceramics contained complex signal which is a superposition of a broad resonance absorption line with the magnetic field induction of 2964 G and a narrow line at 3363 G.

A broad signal can be attributed to the presence of a large number of surface defects typical of ultrafine materials. G-factor of resonance absorption line at the magnetic field induction of 3363 G is equal to 1.97. In a number of papers, the EPR-signal with g=1.96-2.01 in alumina is associated with absorption of singly ionized oxygen vacancies [6]. The spectrum of single-crystal sample in addition to the main absorption line at the magnetic field 3492 G contained absorption lines at 2000 G and 5500 G, related to chromium ion impurities [7].

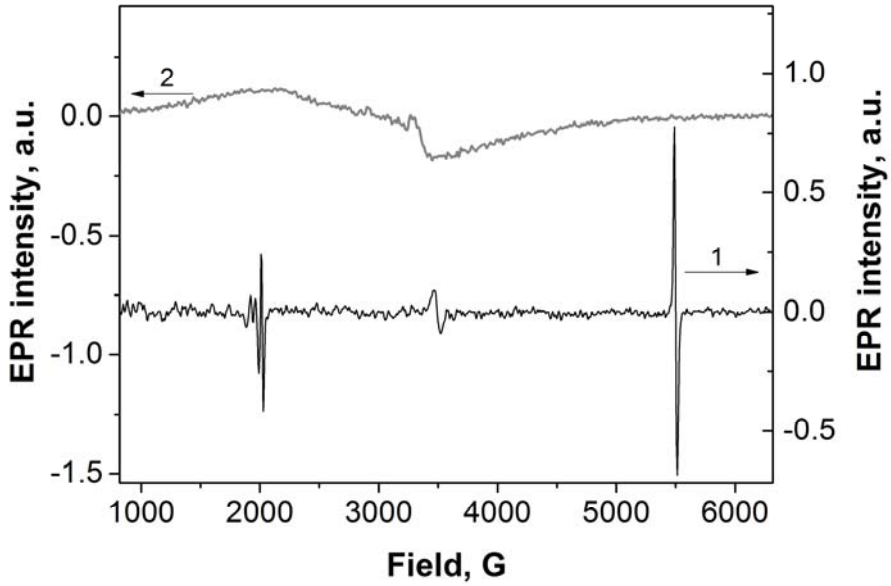

Figure 3. EPR spectra of oxygen-deficient alumina single crystal (1) and ultrafine ceramics (2)

TL curves of the samples (Fig. 4) were measured after β-irradiation with the dose of 18 Gy. TL maximum of ceramics was registered at T = 145˚C. In comparison with the single-crystal sample, it was shifted at 30˚C towards lower temperatures. Such TL maximum shift is also common for other oxide nanopowders [2]. It is caused by high concentration of surface defects that create charge carriers with lower activation energy. High temperature TL peak registered in ceramics at T = 330˚C after β-irradiation with the doses above 10 Gy has an intensity comparable to the same peak in the single crystal. It is known that high temperature TL peaks in alumina single crystal are associated with deep traps [8]. TL measurements confirmed the deep traps formation in the oxygen-deficient alumina ceramics.

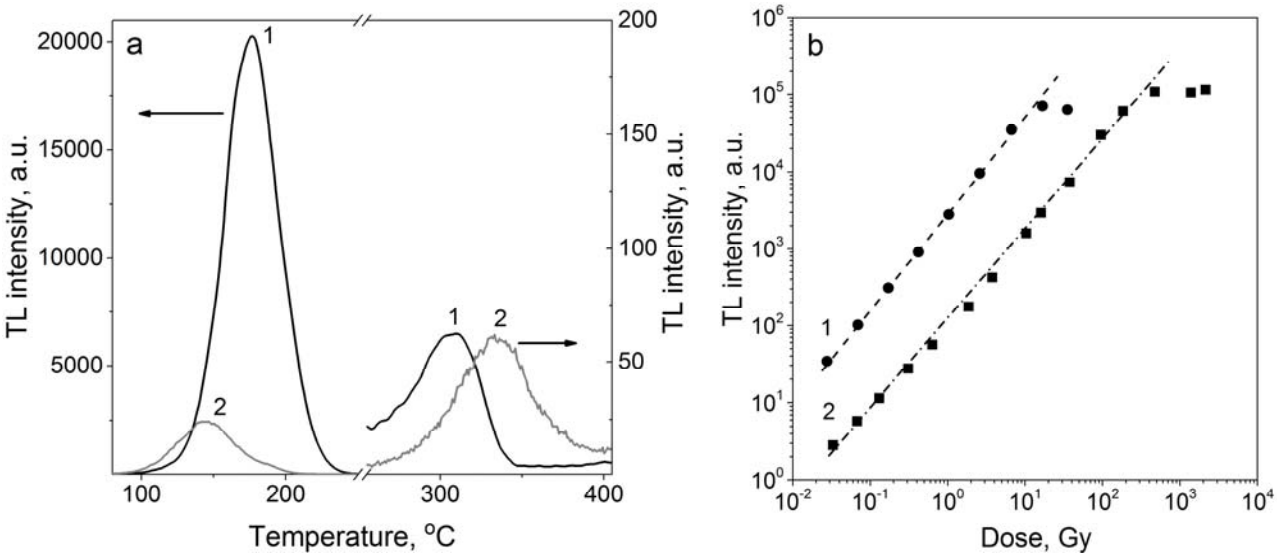

Figure 4. TL (a) and dose responses (b) of the oxygen-deficient alumina single crystal (1) and alumina ceramics synthesized at 1700˚C, 30 min (2)

TL peaks with the maxima in the range 120-180˚C belong to dosimetric peaks. Dose responses of TL peak intensity (T = 175˚C) in alumina single crystal and ultrafine ceramic (T = 145˚C) after β-irradiation are shown in Fig. 4. The TL peak dose response of single crystals changed linearly in the dose range up to 10 Gy. In ceramics synthesized at T = 1700 ºC for 30 min, the dose response of TL peak increased linearly over a wider range of high doses (up to 300 Gy). Therefore, the maximum dose of ionizing radiation registered with the use of ultrafine alumina ceramics is much higher than that with a single crystal.

Conclusions

1. High-temperature annealing of nanopowder α-Al_2O_3 compacts in vacuum in strongly reducing medium leads to the formation of oxygen vacancies in the oxide.
2. PCL and PL spectra of synthesized ceramic contain a band at 420 nm caused by the emission of F-centers, created by oxygen vacancies.
3. EPR of irradiated ceramics features complex signal which is a superposition of broad resonance absorption line at the induction of the magnetic field 2964 G, and narrower line at 3363 G. The broad signal can be attributed to the presence of a large number of surface defects typical for ultrafine materials. The g-factor (1.97) for resonance line at 3363 G indicates it's probably relation to absorption of singly ionized oxygen vacancies.
4. Dosimetric TL peak of ultrafine ceramic was shifted at 30˚C towards temperatures in comparison with the single-crystal sample.
5. Dose response of TL peak 145 ˚C in ceramic after β-irradiation is linear up to 300 Gy and saturates at doses near 1 kGy. From this it follows that ultrafine oxygen-deficient alumina ceramics synthesized from nanopowders is promising material for producing high-dose detectors of ionizing radiations.

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