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Dosimetric phosphor based on oxygen-deficient alumina ceramics

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HIGHLIGHTS

- Oxygen-deficient Al_2O_{3-x} ceramics was synthesized in a reducing medium.
- Particle size and mass of the ceramics depend on temperature of synthesis.
- Luminescence centers are created by oxygen vacancies arising during the synthesis.
- Luminescence of ceramics is observed at 420 nm under UV-excitation.
- The synthesized ceramics can be used as a dosimetric phosphor.

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ABSTRACT

Oxygen-deficient alumina ceramics with blue luminescence was synthesized in reducing medium (vacuum, presence of carbon) from nanopowder at varying temperatures and annealing time. The structure of the samples, particle size distribution, changes in mass of the samples at different synthesis temperatures were studied. In the obtained ceramics the spectra of photoluminescence are registered in the band centered at 420 nm, which is associated with the F-centers created by oxygen vacancies. The luminescent intensity grows with increasing temperature and annealing time. The thermoluminescence curves feature two peaks whose intensities depend on the temperature of the ceramics synthesis. Dose response of the thermoluminescence peaks of alumina ceramics synthesized at 1700 °C was measured under beta-irradiation.

1. Introduction

Luminescent dosimetry of ionizing radiations is of great importance among numerous applications of phosphors in science and technology. Luminescent detectors of radiations are widely used in personal dosimetry of the staff at nuclear power plants, for radiation monitoring of environment, in medicine, to control the radiation situation in space.

Anion-defective alumina single crystals are known materials for the manufacture of highly sensitive radiation detectors (Akselrod et al., 1990). Oxygen-deficient Al_2O_{3-x} single crystals can be obtained when they are grown from the melt ($T = 2053°C$) with the presence of carbon. At high temperatures gaseous carbon monoxide (CO) forms in the growth vessel. It is a good reducing agent. An alumina loses a part of its oxygen in a highly reducing medium at a particular rate of crystal growth. Oxygen vacancies emerge in the crystal, they trap two or one electron forming luminescent F and F^+-centers respectively.

In recent years there has been a growing interest in developing dosimetric phosphors for high dose measurements. A need in measuring fluxes of highly intensive ionizing radiation is growing due to development of radiation technologies to sterilize medical products and modify material properties. High-dose measurements are required also for dosimetric control of the equipment at nuclear power plants, to assess radiation situations in spent fuel storage facilities. There are successful applications of high-dose luminescent detectors (Obryk et all, 2013; Kortov et al., 2014a).

A prospective trend of development of dosimetric phosphors for middle and high-dose measurements is a synthesis of luminescent ceramics from nanoscale powders. Nanopowders are promising initial materials for synthesis of luminescent ceramics. Using nanopowders one can obtain dense compacts under lower static pressure while they are pressed. When dense compacts are used at further annealing, less porous ceramics can be obtained. Such ceramics are mechanically strong and suitable for making detectors of radiation with different forms and sizes. Moreover, lower

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temperatures are necessary to synthesize ceramics from nanopowders. In spite of the growth of particles at high-temperature annealing, the synthesized ceramics is ultrafine and the mean grain size is 2–4 μm (Kortov et al., 2014b). Such ceramics are radiation – resistant. Quantum - size effects cannot occur with such particles. However, ultrafine ceramics have more extended surface in comparison with the ceramics synthesized from large-grained powders (20–40 μm). Surface defects on the numerous interfaces of particles of ultrafine ceramics can create luminescence centers increasing its photon yield. The reported factors are important for dosimetric phosphors.

A possibility of creating luminescent oxygen-deficient ceramics from alumina nanopowder was shown (Kortov et al., 2008). However, the synthesis processes of such ceramics which provide a high luminescence yield at irradiation are little studied.

This work is devoted to studies of the effects of the ceramics synthesis conditions on their structure, luminescent and dosimetric properties.

2. Experimental

The experimental ceramic samples were synthesized from the commercial high-purity α-Al_2O_3 nanopowder with the particle size of 50–70 nm produced by "VNIIOS NK" (Russia). The powder was pressed into pellets (compacts) 5 mm in diameter and 1.3 mm thickness under 1000 kg/cm^2. The pellet weighed 40 mg. The synthesis of ceramics was carried out in the vacuum (10^{-3} - 10^{-4} Torr) electric furnace at the temperature range from 1100°C to 1700°C and the annealing time varying from 30 min to 3 h.

A great number of the samples were synthesized with the presence of carbon. For this purpose a highly pure graphite (99.99%) rod with the mass of 20 g was placed 5 mm from the samples in the vacuum chamber of the furnace. It was done to create a strong reducing medium which is needed to synthesize oxygen-deficient samples of alumina ceramics.

The surface structure of the obtained ceramics was studied with a SIGMAVP scanning electron microscope (Carl Zeiss, Germany) and a secondary electron detector (In-lens) in high vacuum with a 5 kV accelerating voltage. The samples had been preliminary coated with a 10 nm-thick gold layer using Quorum Q150T ES high-vacuum system. Over 50 SEM images of various surface and chipping sectors were obtained for each sample under study. The scanning areas were chosen randomly to obtain representative data on the surface topology. A Clinker C7 analyzer of solid fragment microstructure (SIAMS, Russia) was used to estimate particle size distributions. Particle size distribution for each sample was determined based on the analysis of over 1500 particles.

To define the luminescent properties of the ceramics, the photoluminescence (PL) spectra and the thermoluminescence (TL) curves were measured. The PL spectra were obtained using a luminescent LS-55 spectrometer (Perkin Elmer, USA) in the range of (200–800) nm. The samples were excited ($\lambda_{exc} = 205$ nm) near the absorption band of F-center. The measurements were made in the phosphorescence mode under excitation with a pulse xenon lamp of 150 W power, 10 Hz frequency and 20 m delay of PL registration after the pulse. The spectrometer was equipped with a built-in filter with the bandpass more than 290 nm. The experimental setup with FEU-142 photomultiplier with the maximum spectral sensitivity 350 nm was used in registering TL. The setup provided linear heating of the irradiated ceramics in the range of 300–820 K at a rate of 2 K/s. A filter BGG 9 («Optics-M » Ltd., Russia) with the bandwidth 300–700 nm was applied for protection from the thermal background of the heater. The characteristics of the BGG 9 filter are similar to those of BG 39 (SCHOTT AG, Germany).

To find the dependence of the TL peak intensity on the absorbed dose, the ceramic samples were preliminarily exposed from the $^{90}Y/^{90}Sr$ β-source.

3. Results and discussion

The obtained SEM images were used to analyze the microstructure of the ceramics. Fig. 1 shows SEM images and particle size distributions of the initial alumina compact and the ceramics synthesized for 1 h at 1400°C, 1600°C. It can be seen that in the initial compact alongside with the particles 50–70 nm in size there are also aggregates which emerged under pressing. The sizes of the aggregates were up to 500 nm, thus an average size of particles was 173 nm. The samples synthesized at 1400°C consists of agglomerates with an average size of 617 nm, they contain a large number of pores. With an increasing synthesis temperature up to 1600°C, the particle size distributions widen, the particles grow further, and a number of pores decrease. For example, synthesis at 1600°C gives rise to large plate like agglomerates with an average size of 2.24 μm. Formation of large agglomerates and a decrease in a number of pores are the results of particle sintering and sample compacting.

Fig. 2 presents a dependence of the mean particle size in alumina ceramics on the annealing temperature in the range of 1400–1700°C. A rate of particle growth is seen to be increasing at T > 1500°C. The ceramics synthesized at 1700°C have an average particle size about 3.5 μm. Thus, the end-products of reducing synthesis under the above reported conditions are the samples of ultrafine alumina ceramics.

Formation of non-stoichiometric alumina samples was accompanied by decomposition of Al_2O_3 into gaseous lower oxides (Al_2O, AlO) with creation of CO_2. The gaseous products of the reactions are pumped out with a vacuum system. As a result, oxygen deficiency Al_2O_{3-x} occurs in the samples, which leads to their decreasing mass due to evaporation. This effect is presented in Fig. 3. When the ceramics is synthesized in vacuum without carbon in the range of 900–1700°C, the samples almost do not lose their mass, though vacuum is a reducing medium. When the ceramics is synthesized under strong reducing conditions with the presence of carbon, the loss of the mass in the samples is remarkable at 1400°C and becomes dramatically bigger when the temperature rises up to 1600°C.

Sintering and partial loss of the mass of the samples, when they are annealed in a reducing medium, cause a temperature-dependent descent in diameter and, thus, leads to decreasing surface area of the compacts. In this regard, the intensities of luminescence of all the ceramics under study were evaluated in terms of area units of the samples.

As mentioned earlier, the oxygen vacancies in alumina create F-centers when trap two electrons. Excitation of such centers under irradiation with photons or charged particles gives rise to intracenter $3p \rightarrow s_0$ transitions which are accompanied by emission in the blue spectral region with the intensity maximum at 420 nm (Evans, 1995). Therefore, while observing changes in the intensity of the emission band centered at 420 nm, one can estimate a relative variation in concentration of oxygen vacancies.

The measurements of PL spectra allowed clarifying the association of the emission band at 420 nm with the presence of oxygen vacancies in the sample. The F-centers in alumina are known to have an optical absorption band centered at 205 nm near the border of the UV-region (Evans, 1995). Fig. 4 shows that with the selective excitation into the mentioned optical absorption band, PL with the maximum at 420 nm was registered as a result of the excitation of F-centers in the ceramics. The PL intensity was growing with longer time of isothermal annealing of the samples, i.e. it depended on the concentration of the emerged oxygen vacancies. A band was seen near 500 nm in the PL spectrum. The