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Effect of structural changes on luminescent and dosimetric properties of nanoscale aluminum oxide

S.V. Zvonarev, V.S. Kortov*, T.V. Shtang, D.V. Ananchenko, K.A. Petrovykh

Institute of Physics and Engineering, Ural Federal University, 21 Mira Street, Yekaterinburg 620002, Russia

HIGHLIGHTS

- Dosimetric ceramics are synthesized from α-Al_2O_3 nanopowder.
- Proportion of small particles grows with the synthesis temperature increase.
- TL peak with the same exposure dose is higher in small grainy ceramics.
- Fine grainy ceramics can be used for measurements of higher doses.

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ABSTRACT

Variations of the particle size and porosity of the alumina ceramics synthesized by annealing compacted nanopowder at 1500–1700 °C in vacuum for various periods of time have been studied by SEM. Particle size distributions, which depend on the conditions of the ceramics synthesis, were obtained and discussed. The formation of fine grains and the growth of their fraction with the increasing annealing temperature increase the thermoluminescence intensity and expands the usable dose range upwards.

1. Introduction

Luminescent and dosimetric properties of various materials proposed for measurements of high doses have been intensely studied in recent years (Bilski et al., 2008; Teixeira and Caldas, 2012; Polymeris and Kitis, 2012; Saraee and Kharieky, 2013; Kortov et al., 2014). High-dose irradiations are used to sterilize medical products, to modify properties of materials, and for other purposes. A large part of these studies is devoted to nanostructured phosphors, such as alkali halide crystals (Salah et al., 2007), sulfates (Salah et al., 2008), sulfides (Yazici et al., 2007), or oxides (Salah et al., 2011).

Nanostructured dosimetric phosphors are usually similar to their microcrystalline analogs and single crystals in their chemical macro- and microcomposition. The luminescent and dosimetric properties of the microcrystalline analogs and single crystals are well known. Nanostructured phosphors were found to be less sensitive to low and medium doses of radiation than their microcrystalline analogs. This implies that, at the same exposure in this dose range, the thermoluminescence (TL) peak intensity of the nanostructured samples is lower. In contrast, in the high dose range, the TL peak intensity increases with the increasing dose, whereas the intensity of the dosimetric TL peaks of the microstructured analogs gets saturated and tends to decrease. As a result, the dose range of nanostructured detectors is 1.5–2 orders of magnitude wider than the dose range of the corresponding microcrystalline phosphors (Kortov, 2010; Kortov and Ustyantsev, 2013). This is also true for anion-defective nanoscale aluminum oxide as compared with its single-crystalline Al_2O_3:C analog, which is the basis of the highly-sensitive TLD-500 detectors of ionizing radiation widely used today.

It is viable to commercially produce nanostructured radiation detectors in the form of synthetic ceramics instead of compacted powder tablets. Nanostructured ceramics are stronger

* Correspondence to: 19 Mira Street, Yekaterinburg, Russia. Tel.: +7 343 375 44 43; fax: +7 343 375 44 15.
E-mail addresses: s.v.zvonarev@urfu.ru (S.V. Zvonarev), vskortov@mail.ru (V.S. Kortov), t.v.shtang@gmail.com (T.V. Shtang), ananchenko.daria@mail.ru (D.V. Ananchenko), kspetrovyh@mail.ru (K.A. Petrovykh).

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mechanically, and their properties are more stable. Moreover, ceramics can be used to produce detectors of arbitrary shapes and sizes. However, high-temperature synthesis of luminescent ceramics is accompanied by an increase of the grain size. The effects of the synthesis conditions on the ceramics structure and their luminescent and dosimetric properties are not well studied yet. Thus, the aim of this work was to study the effects of the synthesis conditions on the structure of the oxygen-deficient ceramics of α-alumina as well as on their luminescent and dosimetric properties.

2. Experimental

The experimental ceramic samples were synthesized from the commercial high-purity α-Al_2O_3 nanopowder produced by "VNIIOS NK" (Russia). The powder with the particle size of 50–70 nm was obtained using the alcoholate method (Schinkel et al., 2008). The samples were subjected to 8–9 kg/cm^2 static pressure. The following synthesis of the ceramics was carried out in a vacuum electric furnace (10^{-3}–10^{-4} Torr) at the temperatures varying from 1500 to 1700 °C and the annealing time varying from 30 min to 3 h. Vacuum is a good reducing medium, which helps to obtain 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 and the whole sample bulk. A Clinker C7 analyzer of solid fragment microstructure (SIAMS, Russia) was used to estimate particle size distributions. The optical system and software of the analyzer were able to find all nanoparticles in each SEM image and to size them up accurately to within tenths of nanometer. Particle size distribution for each type of the samples was determined based on the analysis of over 1500 particles.

The standard method was used to perform TL measurements with a FEU-142 photomultiplier at the linear temperature change from 300 to 820 K at the rate of 2 K/s. To find the parameters of the dependence of the TL peak on the absorbed dose, the ceramic samples were 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.

3. Results and discussion

The obtained SEM images were used to analyze the structure of the alumina samples synthesized under various heating conditions. Fig. 1 shows typical SEM images of the ceramics nanopowder synthesized from alumina at 1500 °C (3 h), 1600 °C (1 h), and 1700 °C (0.5 h).

An analysis of the SEM images shows that the synthesis in vacuum at 1500 °C (3 h) gives rise to agglomerates with the mean size of about 600 nm (Fig. 1a). The sample is highly porous, and the pore size is commensurate with the agglomerate size. Increasing synthesis temperature reduces the number of pores and the agglomerate mean size. The reduction of the number of pores is due to ceramics firming with growing synthesis temperature. The temperature growth above 1500 °C affects the agglomerate size only slightly, but particles below 100 nm in size emerge under this condition. It is also noteworthy that annealing at a higher temperature (1600 °C, 1 h) produces a stratified structure of the sintered particles in the form of a polyhedron with well-defined facets (Fig. 1b). Further increase of the synthesis temperature up to 1700 °C increases the fraction of the small particles (Fig. 1c). Some of these particles are just 10–40 nm in size, i.e., they are smaller than the particles in the original nanopowder. Thus, the synthesis conditions described above produced α-Al_2O_3 ceramics with a wide particle size distribution.

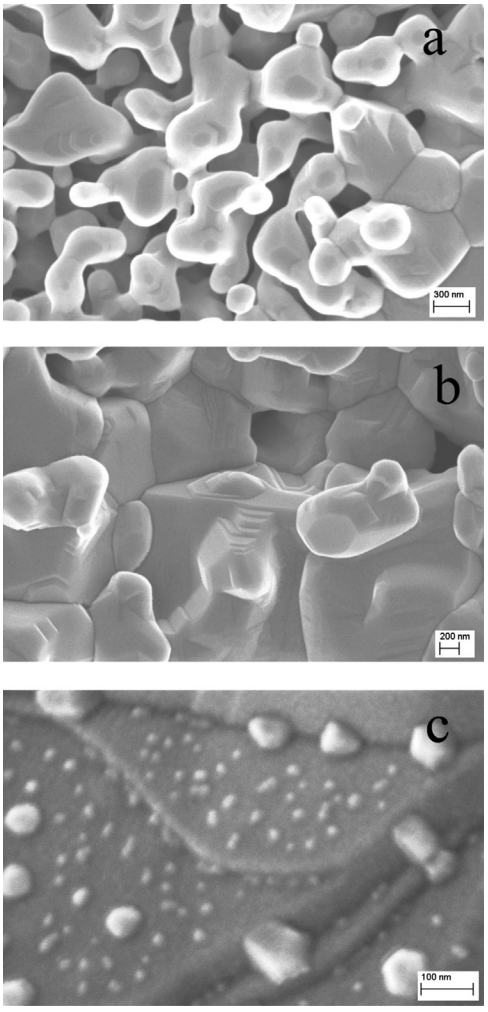

Fig. 1. SEM-images of nanocrystalline Al_2O_3 ceramics synthesized by annealing at 1500 °C for 3 h (a), at 1600 °C for 1 h (b), and at 1700 °C for 0.5 h (c).

Fig. 2 shows the obtained particle size distributions. At 1500 °C (3 h), most of the particles in the sample (89%) were agglomerates formed in the sintering, with the 500-nm particles being most common. The fraction of particles smaller than 200 nm did not exceed 11%. With increasing annealing temperature (1600 °C, 1 h), the fraction of the smaller particles in the sample grew. The fraction of the particles smaller than 200 nm increased to 67%, while the fraction of the particles bigger than 500 nm decreased to 33%. The particle distribution in the sample annealed at 1700 °C (30 min) shows that the particles 35–200 nm in size resulting from sintering prevailed (approximately 54%). The samples also contained 45% of the 200–1500 nm particles. The particles smaller than 30 nm, but still visible in the SEM image (Fig. 1c), constituted 9% of the sample.

One can conclude that, with increasing temperature of the synthesis of the alumina ceramics in vacuum, some large agglomerates decompose to form small nanoparticles. It is possible to hypothesize that that one of the causes of the changes in the ratio of the particles with different sizes is strong thermal stresses at temperatures above 1500 °C, which reduces the sizes of the

agglomerates. Violation of the stoichiometric oxide composition may also be a factor because the high-temperature heating in vacuum results in oxygen deficiency in the synthesized samples. An analysis of X-ray diffraction patterns showed that the phase composition of the ceramics had not change: it was still 100% α-phase with the structural changes described above.

It is of special interest to consider the effects of the structural changes in alumina ceramics on their luminescent and dosimetric properties.

Fig. 3 shows TL glow curves of the ceramic samples under study exposed to 18 Gy of β-radiation. They feature several peaks, namely, two low-temperature peaks at 410 K and 460 K, as well as a high-temperature peak at 600 K. The high-temperature peak is not as intense as the low-temperature peaks. It is noteworthy that the ceramics synthesized at 1700 °C (30 min), which contained a large number of particles smaller than 200 nm, exhibited more intense thermoluminescence. This may be due to the fact that the ceramics with smaller particles have more luminescent centers on the particle borders. Furthermore, at a higher temperature of annealing in vacuum, the number of oxygen vacancies increases, which results in their higher overall concentration in aluminum oxide. These oxygen vacancies form F^- and F^+-centers engaged in the thermoluminescence process. The TL curve of an oxygen-deficient α-Al_2O_3 single crystal features only one isolated peak with the maximum at 460 K. The peak results from thermofluctuational restructuring of a complex defect center (F^-, F^+-centers and impurity effects). In a nanostructured sample (as mentioned above) TL is most intense at 410 K. The TL is believed to be caused by surface analogs of the *F*-type centers. There is also an excessively rapid growth of the TL intensity in the range from 1600 to 1700 °C. One can assume that 1700 °C is a threshold temperature after which formation of small particles increases drastically and the concentration of oxygen vacancies in the ceramics grows.

Fig. 4 shows the dependence of intensity of the TL peak at 410 K on the exposure dose of the ceramics annealed at 1600 °C (1 h) and 1700 °C (30 min). The dose response is superlinear. One of the causes of the nonlinear dose response is competition between the dosimetric and deep traps (Kortov et al., 2007). Luminescence in a nanophosphor can be more complex than in a single crystal due to a growing number of competing TL traps. Such traps are formed, for example, on the numerous borders of nanoparticles. Superlinear dose response has been found experimentally in nanostructured Al_2O_3 obtained by the solution combustion synthesis (Blair et al., 2010). Fig. 4 also shows that the TL sensitivity to radiation increases with increasing synthesis temperature. The useful dose range widens, too. For the sample annealed at 1600 °C, it is 3.2×10^{-2}–9×10^{1} Gy. In the case of the sample annealed at 1700 °C, the upper limit of the meausrable doses is shifted up to 200 Gy. One should recall that the usable dose range of the single crystals of oxygen-deficient aluminum oxide (TLD-500 detectors)

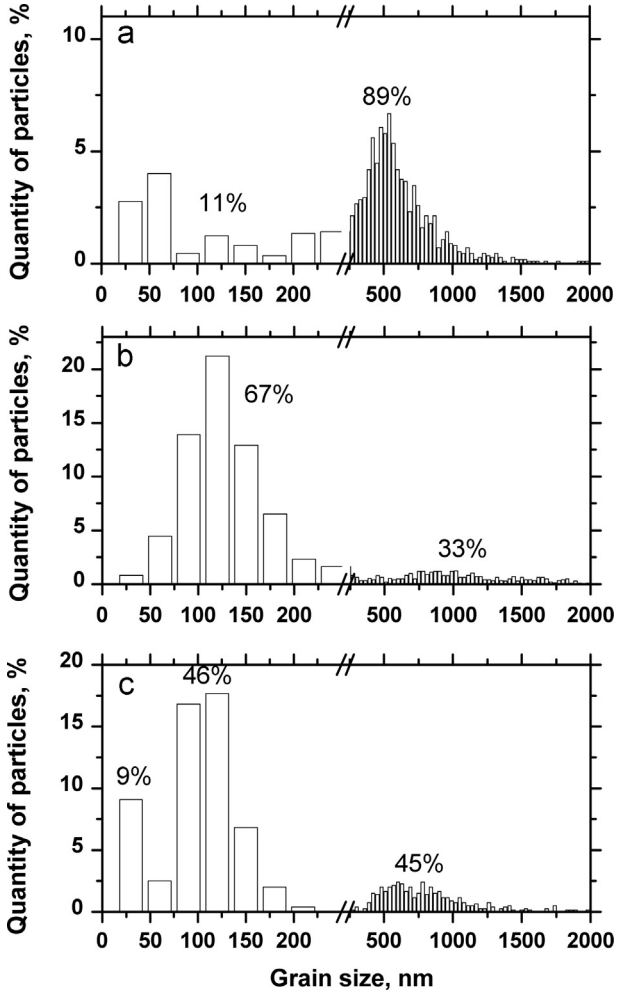

Fig. 2. Particle size distribution of the nanoscale α-Al_2O_3 synthesized by annealing at 1500 °C for 3 h (a), at 1600 °C for 1 h (b), and at 1700 °C for 0.5 h (c).

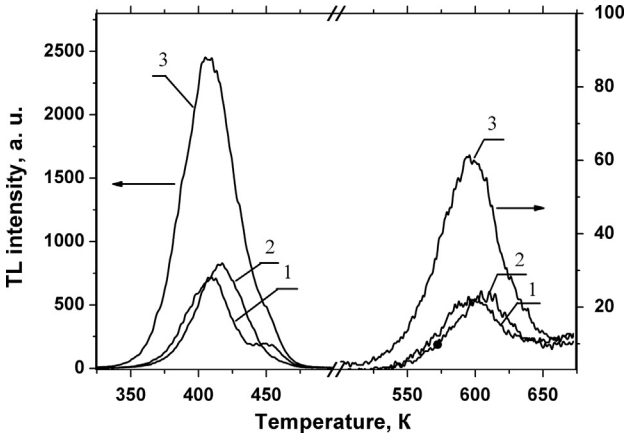

Fig. 3. TL curves of the α-Al_2O_3 ceramics exposed to 18 Gy of β-radiation. Synthesis conditions: (1) 1500 °C, 3 h; (2) 1600 °C, 1 h; (3) 1700 °C, 0.5 h.

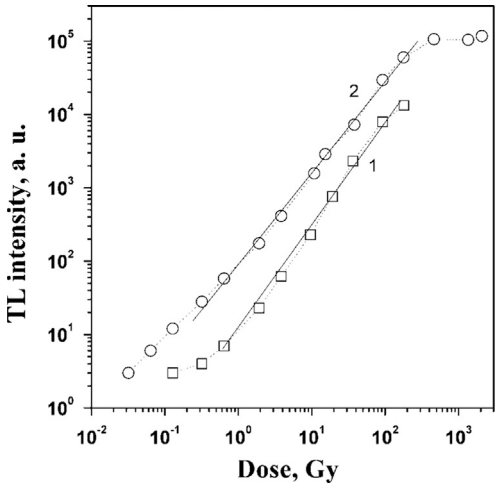

Fig. 4. Dose response of the TL peak at 410 K of the α-Al_2O_3 ceramics annealed at (1) 1600 °C for 1 h and (2) at 1700 °C for 0.5 h.

is limited to 20 Gy (Kortov, 2007). The results obtained in this work show that fine grainy ceramics of aluminum oxide can be utilized as a material for detectors uded for measuring higher exposure doses. The nonlinearity of the dose response should be taken into account while measuring doses.

4. Conclusion

Synthesis conditions were found to affect the structure, luminescent and dosimetric properties of oxygen-deficient α-Al_2O_3 ceramics. It has been shown that, with an increase of the temperature of the synthesis of the ceramics in vacuum, the fraction of the particles smaller than 200 nm and new particles 10–35 nm in size grew. Luminescent and dosimetric characteristics also depend on the conditions of the synthesis. In particular, the maximal TL intensity and the widest range of the measurable doses are observed in the case of the ceramics synthesized in vacuum at 1700 °C.

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