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Short Communications

The Photoluminescence Properties of Ablated ZrO_2 Nanoparticles

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The method of optical spectroscopy determined photoluminescence properties of zirconia nanoparticles produced by laser ablation. The effect of annealing of nanoparticles in the range from 400 to 1000 °C on their luminescence is investigated. It is shown that the emission of the luminescence make it possible to conclude about the type of defects in the structure of nanoparticles and their dynamics during annealing. A qualitative explanation of the detected patterns is provided.

Keywords: Photoluminescence, Nanoparticles, ZrO_2.

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1. INVESTIGATION RESULTS

Zirconium dioxide is of interest as a promising material for the production of optical coatings with high heat-resistant characteristics [1]. With this in view, studying its optical properties is a vital problem. It is known that pure zirconium dioxide is polymorphic material. It can be in a low-temperature monoclinic phase (< 1400 °C) and high-temperature tetragonal (1400-2300 °C) and cubic (> 2300 °C) phases. In the previous works [2-4] zirconium dioxide nanoparticles were produced by method of laser ablation. It is shown that after ablation the high-temperature tetragonal and cubic phases are formed in them. Their emergence can be explained by the formation of the surface defects that are due to a fast crystallization during laser ablation. These defects can serve as the centers of luminescence, thereby defining special optical characteristics of the produced coatings. Thus, the purpose of this work was the research of luminescent properties of the zirconium dioxide nanoparticles produced by laser ablation and also studying how annealing influences them.

Nanoparticles were produced by ablation of a zirconium dioxide target by pulse radiation with a solid-state YAG:Nd^{3+} laser with 1.06 μm wavelength, which was a constituent of the laser KVANT-15 complex. Intensity of radiation was 109 W/m^2, pulse duration 4 ms, pulse repetition rate from 1 to 25 Hz. As the target, the alloyed chemically pure powder ZrO_2 was used. In the ablation, zirconium dioxide nanoparticles were deposited on the object carriers located at a distance of 10 mm from the target. Time of dispersion was varied from 1 to 10 min.

Temperature processing of ZrO_2 ablated particles was made on air in the SNOL-furnace 0.2/1250 in the temperature range of 400 to 1000 ºC. Time of annealing was 3 hours, which, as shown in work [5], is enough for the phase transformations to occur.

The luminescent properties of the ZrO_2 nanoparticles were studied using a spectrometry system from "Spektr OKB" [specialist design office] based on an MDR-41 monochromator, the spectral range of which is 200-25,000 nm. Deuterium and halogen lamps and also a DRT-125 mercury lamp were used as the emission source.

Optical microscopy showed that on the substrate surface in the course of ZrO_2 laser ablation the continuous, uniform covering of white color is formed. According to translucent microscopy, ablated particles have spherical shape, and their size range from 10 to 200 nm.

The conducted researches of luminescent properties of ablated ZrO_2 nanoparticles showed that at radiation of samples with a mercury lamp DRT-125, photoluminescence peaks of both in the ultraviolet and in the visible range appear. In Figure 1 for ZrO_2 nanoparticles luminescence peaks with an intensity maximum at 1.6 eV and 3 eV are shown.

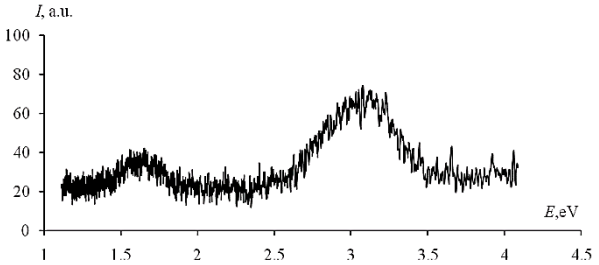

Fig. 1 – Photoluminescence spectrum of zirconium dioxide nanoparticles

According to researches, the shape of photoluminescence peaks of nanoparticles partially changes depending on the Li intensity at ablation. So, for nanoparticles ablated at the Li intensity of 1010 W/m^2 intensity, half-width of photoluminescence peaks is more than for the nanoparticles obtained at 109 W/m^2. Increase in half-width of peaks can be explained by the growth of defect number in surface layers of nanoparticles at higher intensions of laser radiation.

Processing in a furnace of ablated ZrO_2 nanoparticles leads changes luminescence properties.

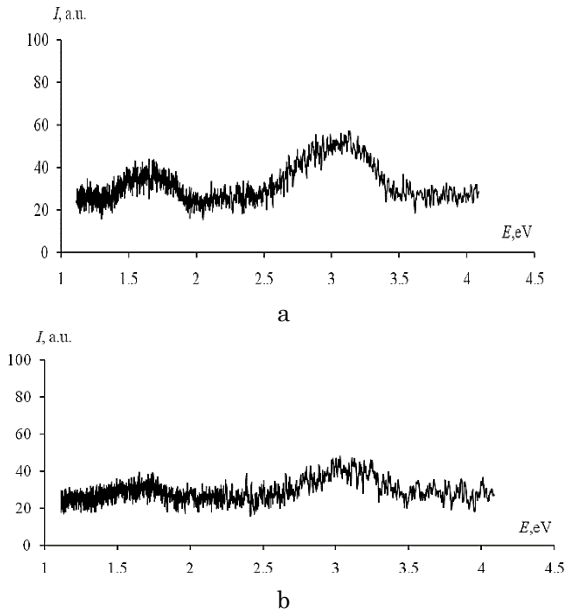

Fig. 2 – Photoluminescence spectra of ZrO_2 nanoparticles ablated at the Li intensity of 1010 W/m^2 and annealed further during 3 hours at temperatures: a – 600 ºC; b – 1000 ºC

Figure 2 shows luminescence spectra of nanoparticles ablated at the Li intensity of 1010 W/m^2 and further annealed in 3 hours at 600 ºC and 1000 ºC. It can be seen that after annealing at 600 ºC at luminescence spectra the peak at 3 eV becomes smaller (Fig. 2, a), whereas the peak at 1.6 eV decreases only after annealing at 1000 ºC (Fig. 2, b).

In [5] it is shown that in systems of oxides of transitional metals the dynamics of luminescence peaks can be due to the change in concentration of structural defects in nanoparticles in the annealing. So, annealing at 600 ºC can lead to a decrease in oxygen defects, which for ZrO_2 nanoparticles manifests itself in reduction of peak at 3 eV. In [6-7] the link between the photoluminescence glow in the optical ranges 3.2÷3.6 eV and 2.3÷2.5 eV with oxygen vacancies is also noted. After annealing at 1000 ºC, annealing of zirconium defects is also possible which attests to a decrease in peaks at 1.6 eV. Thus, the photoluminescence of ZrO_2 nanoparticles indicates that defects of oxygen atoms in this oxide belong to Schottky defects and defects of zirconium atoms to Frenkel defects.

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