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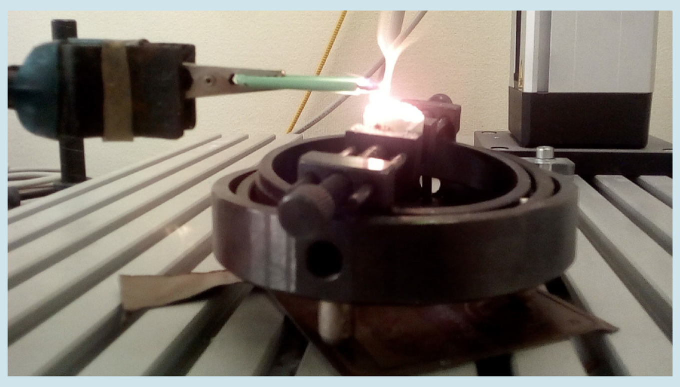
Band gap and antioxidant properties of cerium dioxide nanoparticles

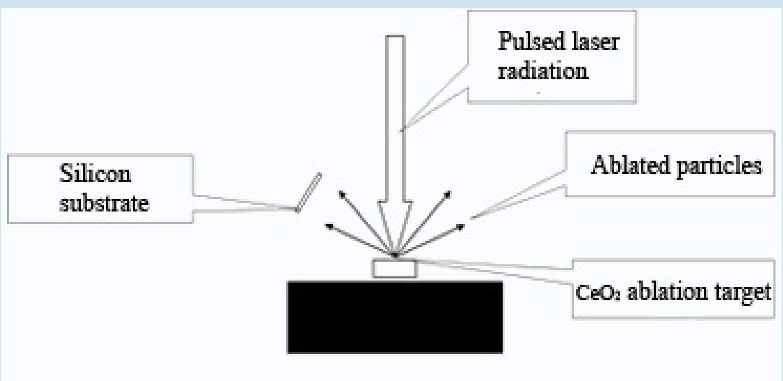
Cerium dioxide has a wide range of applications in various fields of both science and technology, as a catalyst in automobile exhaust systems or solid state energy [1]. It is noted in the works [2-5] that cerium dioxide nanoparticles have the prospect of being used in the biomedical field due to their powerful antioxidant properties. That is, nanosized cerium dioxide inactivates various radicals in biological systems, such as superoxide O^{2-}, a highly reactive short-lived hydroxyl radical OH*. The antioxidant properties of cerium dioxide nanoparticles increase due to structural defects on surface of the particles such as an oxygen vacancy. Laser ablation makes it possible to obtain particles with these structural defects [6,7].

Experiments aimed at revealing the difference in the effectiveness of antioxidant properties between ablated nanoparticles and mechanical grinding cerium dioxide particles ground in a mortar in a photocatalytic reaction of methylene blue dye degradation were completed.

The photocatalytic reaction was carried out in the presence of zinc oxide, and the oxidation of methylene blue was recorded spectrophotometrically in the wavelength range from 550 to 750 nm. Layers of cerium dioxide nanoparticles were deposited on silicon wafers by laser ablation. This method allows one to obtain CeO_2 nanoparticles with surface structural defects of the oxygen vacancy type, which determines their antioxidant properties [7]. The source of laser radiation for the deposition of CeO_2 nanoparticles was a pulsed fibre laser activated by diode pumping IPG Photonics, with the "High Contrast" option (radiation wavelength 1.06 μm, laser radiation intensity ~ 10^9 W/m^2, pulse duration 200 μs, pulse repetition rate up to 1 kHz). Pressed cerium dioxide of the class "chemically pure" was used as a target. Also, a mechanical grinding cerium dioxide powder was obtained from the same material which was the target for ablation by grinding in a mortar.

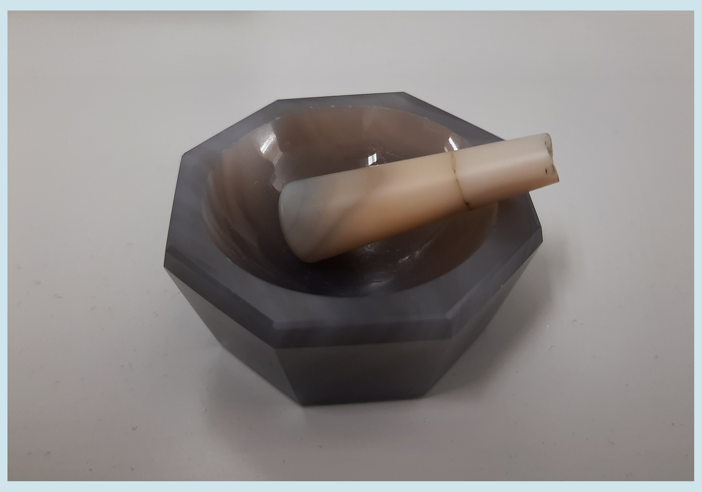
The method of obtaining nanoparticles of cerium dioxide is the method of laser ablation and by mechanical grinding in a mortar.





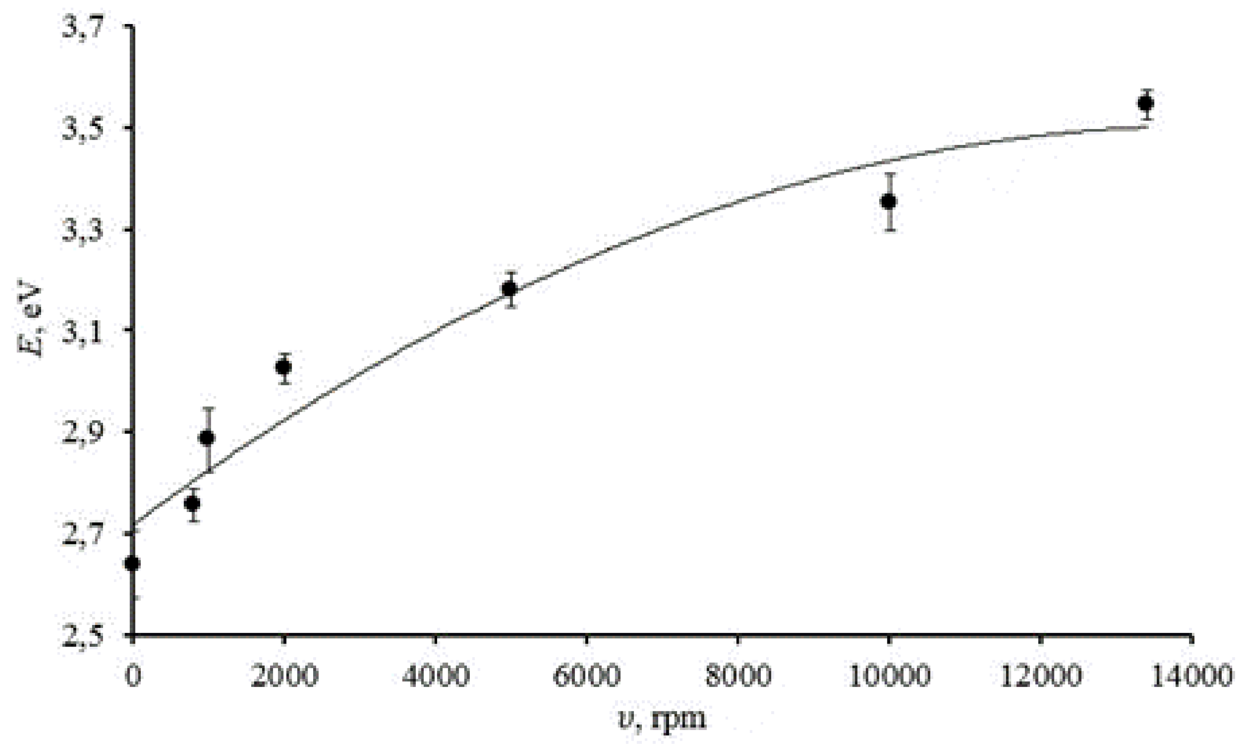
Experimental scheme of the formation of layers of ablated CeO_2 particles on a silicon substrate.

Mechanical grinding in a mortar.

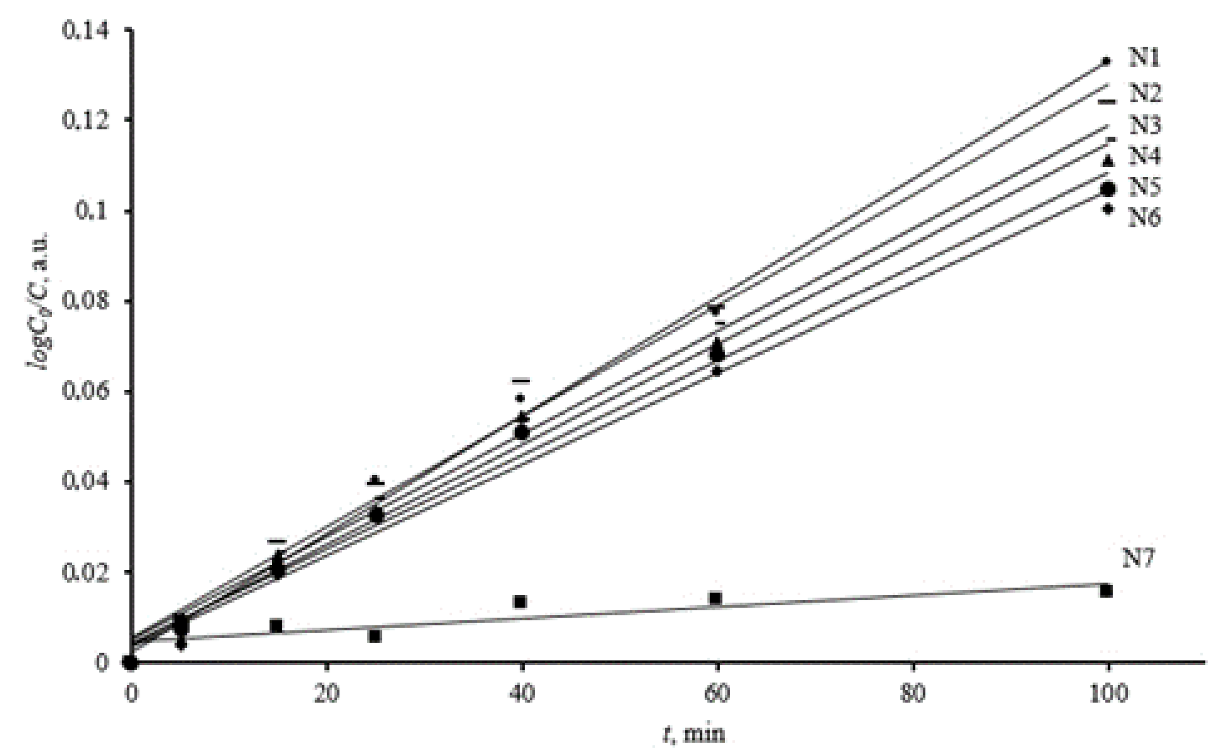


Subsequently, the ablated cerium dioxide nanoparticles, ground cerium dioxide powder and zinc oxide powder were dispersed. The dispersion was 40 minutes for each solution.

Then dispersed solutions were centrifuged in a microcentrifuge. For two solutions of cerium dioxide, the time and speed range of the centrifuge were from 10 minutes from 1000 to 5000 rpm, respectively, and for zinc oxide were 5 minutes and 1000 rpm. From the upper part of the microtubes, centrifuged solutions were drawn up with a syringe and a volumetric syringe of solutions constituting 80% of the volume of the microtube. Note that, from each microtube, solutions of centrifuged zinc oxide particles were poured into one solution to achieve homogenety of solid particles. Then the solutions were placed in cuvettes, a solution of methylene blue was added, and the photocatalytic process, which lasted 100 minutes, was carried out.



Dependence of the band gap on the speed of centrifugation of nanodispersed solutions of cerium dioxide, the solid line is the approximating curve.



Dependence of the logarithm of the residual concentration of methylene blue solution on the time of the photocatalytic reaction with the presence of zinc oxide particles in the systems, the decoding of the designations on the graph is given in the text, solid lines are approximating curves.

№	N1	N2	N3	N4	N5	N6	N7
k, (min^{-1})	0.0013	0.0012	0.0011	0.0011	0.001	0.001	0.0001

Values of the rate constants of reactions k in systems in the course of a photocatalytic reaction with the presence of zinc oxide particles.

Evaluation of the size of grinded particles of cerium dioxide by the method of small-angle X-ray scattering diffractometry showed that after the process of centrifugation of the dispersed solution at a centrifuge frequency of 1000 rpm, the limiting particle size did not exceed 80 nm, at 5000 rpm - 40 nm, and without centrifugation - 100 nm. Experimental data showed that ablated CeO_2 nanoparticles had more pronounced antioxidant properties than mechanically ground particles.

It was determined that with an increase in the speed of centrifugation of nanodispersed aqueous systems of cerium dioxide the width of the band gap of nanoparticles of cerium dioxide increases.

It follows from the tabular data that the rate constant of methylene blue degradation increases in systems with mechanical grinding cerium dioxide nanoparticles, which indicates their weak antioxidant effect in comparison with nanoparticles obtained by laser ablation.

[1] E. Aneggi, C. M. de Leitenburg, Boaro, P. Fornasiero, A. Trovarell Cerium Oxide (CeO2): Synthesis, Prop. and Appl. ed. S. Scirè and L. Palmisano (Amsterdam: Elsevier) (2020) 402.
[2] M. A. Pugachevskii, A. N. Chibisov, V. A. Mamontov, A. P. Kuzmenko Phys. Status Solidi a (2021) 2100355.
[3] A. Filippi et al. RSC Advances 9 (2019) 11077.
[4] M. A. Pugachevskii, V. A. Mamontov, N. V. Aung, A. S. Chekadanov, A.P. Kuz'menko, Tech. Phys. Lett. 46 (2020) 1032.
[5] M. A. Pugachevskii, Tech. Phys. Lett. 43 (2017) 698.
[6] K. RB. Singh, V. Nayak, T. Sarkar, R. P. Singh J. The Royal Society of Chemistry 10 (2020) 27194.
[7] M. A. Pugachevskii, A. N. Chibisov, A. P. Kuzmenko, A. S. Fedorov, Solid State Phenom. 312 (2020) 68.