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Short Communication

The Hydrothermal Autoclave Synthesis of the Nanopowders of the Refractory ZrO_2 and HfO_2 Oxides

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The nanopowders of the transition metal ZrO_2 and HfO_2 oxides were obtained by the hydrothermal autoclave synthesis. The nanoparticles possess a rounded shape and a size range of 40 to 80 nm (ZrO_2), of 10 to 40 nm (HfO_2). X-ray diffraction analysis and electron microscopy show that the structure of the nanoparticles is monoclinic.

Keywords: Hydrothermal synthesis, Nanoparticles, Refractory oxides, Zirconium, Hafnium.

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In the last years, problems of producing nanopowders of refractory transition metal oxides of transit metals such as zirconium dioxide and hafnium dioxide [1] have become intensively studied. Great attention to them is dictated by a number of distinctive properties. In addition to the high melting temperature (ZrO_2 –2700 °C, HfO_2 – 2800 °C), strength, corrosive resistance they have a record low, among oxides, heat conductivity they keep in the wide temperature range, which dictates their relevance in powder metallurgy when heat isolators are manufactured [2] Distinctive optical properties due to a stable reflection coefficient in the UV range (up to 220 nm), in the visible and the IR ranges determine their application also in reflecting coatings of space vehicles that work under tough temperature conditions [3]. Nanopowders of ZrO_2 and HfO_2 of high chemical purity are used in atomic technology where zirconium and hafnium have found various applications. On the basis of zirconium, one can made thermal insulation coatings of nuclear reactor walls. Nanopowders of hafnium can be used for control rods of nuclear reactors since it is well known that hafnium features big cross-section of neutron capture In this connection, the production of chemically pure nanopowders of hafnium and zirconium is an urgent task. Hydrothermal synthesis [4, 5] can be one of the means for production of oxide ceramics nanopowders. The present work deals with the results on synthesizing nanopowders of ZrO_2 and HfO_2 with the autoclave method. Morphological and structural features of particles obtained are also provided.

Synthesis of ZrO_2 and HfO_2 nanopowders was conducted by the hydrothermal method in a steel autoclave with a 50-ml volume Teflon liner. As precursors, zirconium propoxide (IV) in propanol (70 %, ACROS, USA) and hafnium isopropoxide (IV) in $(OOCH(CH_3)_2)_4{\cdot}HOCH(CH_3)_2$ (99 %, Alfa Aesar, Germany) were used. At first, the precursors were solvated in a relevant spirit and hydrolyzed in 10 ml of distilled water with further aging for one day. After that, diethylamine and oleic acid in the ratio 1 : 1 : 1 and distilled water were added. The autoclave was kept at a temperature of 160 °C for 24 hours. From the obtained solution, solvent was removed and the particles were dried at a dynamic heating of up to 400 °C for one day and further at an isothermal additionally 24 hours at a temperature of 400 °C.

The structure and phase composition of synthesized nanopowders were studied in transmission electron microscope ZEISS Libra-120 (accelerating voltage 120 kV) which featured a HAADF detector and an energy Ω- filter. Calibration of electronograms in the microdiffraction mode was done with a test sample for the transmission electron microscopy (TEM) on the basis of a polycrystalline Au film. Qualitative and quantitative phase composition were also determined with X-ray diffractometer DRON-7M. The chemical structure was examined by the Raman light scattering with microspectrometer OmegaScope^{tm} (AIST NT, Zelenograd, Russia) that was integrated with scanning probe and confocal microscopes. Morphology and the particle sizes of HfO_2 were studied with atomic-force microscope NTEGRA Prima and AIST-NT Smart. Granulometric investigations were conducted both in a hand mode and with the help of a program packet Gwyddion to atomic-force microscope Aist-NT Smart.

Investigations by atomic-force microscopy and electron microscopy have revealed that the nanopowders of both ZrO_2 and HfO_2 were synthesized as particles of a round shape. Fig. 1 shows TEM images of synthesized nanoparticles of zirconium dioxide (a) and hafnium dioxide (b). According to granulometric study, the particle sizes were within the limits from 40 to 80 nm for ZrO_2 and from 10 to 40 nm for HfO_2 (Fig. 2).The average particle size was 54 nm for ZrO_2 and 23 nm for HfO_2.

By using diffraction of electrons from synthesized nanopowders, phase analysis was conducted. Interplanar distances derived from diffraction maxima on electronograms (inserts in Fig. 1) for samples of ZrO_2 and HfO_2 are given in Table 1. Comparison of these values with crystallographic database shows that the synthesized nanoparticles of both ZrO_2 [6] and HfO_2 [7] were in a monoclinic modification.

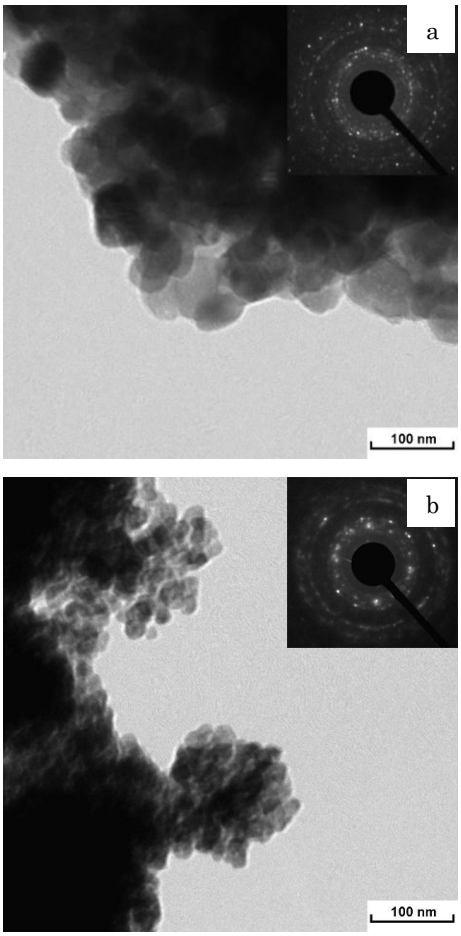

Fig. 1 – TEM images of nanopowders of ZrO_2 (a) and HfO_2 (b) synthesized by the hydrothermal method

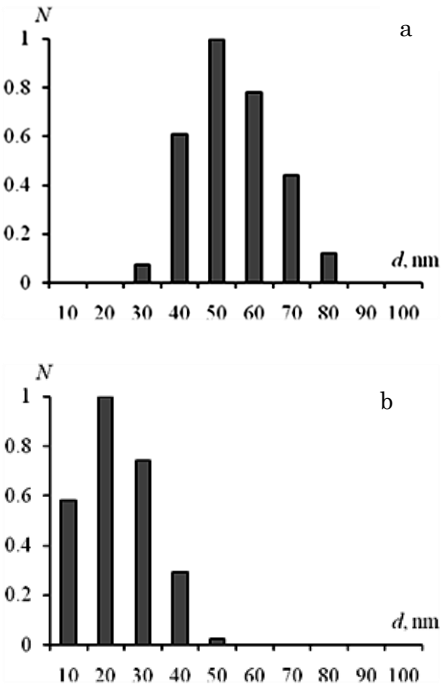

Fig. 2 – Granulometric composition of the nanopowders obtained: a) ZrO_2 (a); b) HfO_2

Electron microscopy data are corroborated by X-ray phase analysis. In Fig. 3 depicted are X-ray diffractograms of ZrO_2 and HfO_2 nanopowders. The interplanar spacings determined by the maxima on the X-ray pictures are also given in Table 1. X-ray phase data also indicate that nanoparticles of zirconium and hafnium oxides obtained by the hydrothermal method were in a monoclinic phase.

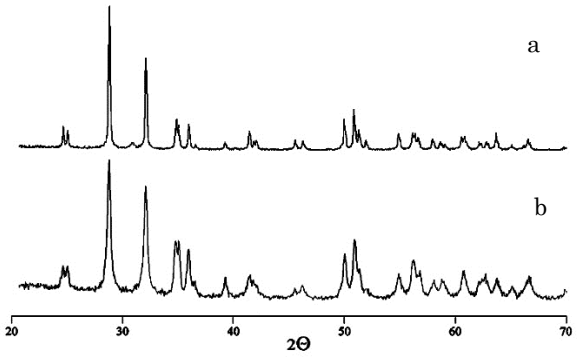

Fig. 3 – X-raydiffractograms of synthesized nanopowders: a) ZrO_2 and (b) HfO_2

Table 1 – Comparison of phase analysis of TEM and X-ray phase analysis with crystallographic database. The values are given in angstroms

Card 3-515 Monoclinic ZrO_2	,,,,,,,,,	X-RPA	Card 6-318 Monoclinic HfO_2	ПЭМ	X-RPA
3,70	3,67	3,72	3,68	3,73	3,71
3,64	3,62	3,66	3,61	3,62	3,62
3,17	3,18	3,18	3,15	3,17	3,16
2,84	2,83	2,84	2,82	2,85	2,83
2,63	2,63	2,65	2,59	2,59	2,60
2,56	2,58	2,57	2,52	2,55	2,54
	2,51	2,53	2,48	2,50	2,50
2,34	2,37	2,37	2,32	2,34	2,36
2,22	2,21	2,24	2,196	2,19	2,18
2,02	2,02	2,04	1,981	1,99	2,00
1,85	1,84	1,86	1,838	1,83	1,85
1,82	1,81	1,83	1,807	1,81	1,82
1,69	1,68	1,70	1,684	1,68	1,68
1,65	1,65	1,66	1,653	1,64	1,65

It is known that a dimension effect, when a critical size is achieved, can stabilize high-temperature phases of polymorphic materials such as ZrO_2 and HfO_2. In work [8], experimentally and theoretically was shown that the critical size for ZrO_2 is less than 2 nm. As was earlier demonstrated, the particles synthesized in the present work were of significantly greater than the critical size. Therefore, the monoclinic structure is energetically favorable in them. In our papers [9-11] it was shown that with laser ablation one can stabilize high-temperature tetragonal and cubic phases of both ZrO_2 and HfO_2 in nanoparticles with the size of up to 50 nm. This stabilization is achieved owing to the formation of structural defects in surface layers of nanoparticles.