Synthesis and Research of Nanopowders Composed of 0.97ZrO2 · 0.03La2O3

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Abstract—This work is devoted to the preparation of zirconium oxide nanopowders stabilized by lanthanum oxide using the method of codeposition in the presence of hydrogen peroxide. Nanopowders composed of 0.97ZrO2 · 0.03La2O3 with particles of 10–20 nm are obtained. It is found that in the temperature interval of 500–1100°C the tetragonal and monoclinic points of the zirconium oxide phase crystallize at the same time.

Keywords: zirconium oxide, lanthanium oxide, composite, codeposition method, nanopowders, structure stabilization, thermal analysis
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INTRODUCTION
Ceramics based on stabilized zirconium oxide are considered to be a promising material. Zirconium dioxide and the compositions based on it are widely applied as solid electrolytes, carriers of catalysts, and oxygen detectors; and in protective coatings for optical mirrors and filters, microelectronics, ceramic biomaterials, thermoprotective coatings, etc. [1–3]. Zirconium oxide can exist predominantly in three crystalline modifications: monoclinic (M), tetragonal (T), and cubic (C). The quantitative relationship between the M and T phases determines the efficiency of the transformational hardening mechanism of the ceramics based on zirconium dioxide and appreciably affects many of their properties [4, 5]. Numerous studies of ceramics based on zirconium dioxide have shown that the materials containing completely stabilized zirconium dioxide (based on a solid solution of the cubic modification) possess low strength properties [6, 7]. Partially stabilized zirconium dioxide (PSZD), which along with cubic zirconium dioxide also contains monoclinic and tetragonal phases, is particularly hard as a result of the ceramics’ transformational hardening effect [8]. The partial stabilization of zirconium dioxide occurs by adding less than 5 mol % of oxides of calcium, magnesium, rare-earth elements (e.g., a system of ZrO2–Y2O3 containing 3 mol % of Y2O3 is used in stomatology) [8]. In order to stabilize zirconium dioxide, the doping oxide should have the corresponding size of the metal ion and form a solid solution with zirconium dioxide [9, 10].

The widely known solid-phase method of obtaining zirconium ceramics presents few possibilities for adjusting the structural-phase state of solids. Currently, the methods of “soft chemistry”, obtaining powdered products (codeposition, sol–gel, cryochemical, etc.) to create preconditions for the formation of materials in a nanosized state with diverse structures [11], are being increasingly widely applied.

The resulting powders possess a rather high specific area and, as a consequence, chemical activity in the processes of further solid-phase interaction. The peroxo-compounds containing in their composition active oxygen in the form of groups of OOH and O—O can be successfully used as the precursors of oxide materials [12–14]. These compounds are less hydrated than hydroxides, and by thermal treatment they are transferred into oxides at lower temperatures than carbonates, oxalates, and other salts of the corresponding metal cations.

EXPERIMENTAL
For the synthesis of solid solutions in a ZrO2–La2O3 system containing 3 mol % La2O3 (0.97ZrO2 · 0.03La2O3), we used ZrO(NO3)2 · 2H2O and La(NO3)3 · 6H2O salts. The deposition was carried out by gradually adding into the mixture solutions of nitrates of freshly prepared ammonium hydrocarbonate solution salts in the presence of 30% H2O2 up to the point of achieving a pH of 7.5 according to the method described in [12]. The resulting solution was stored at a temperature of +5°C, filtered by decantation, and rinsed with water and alcohol. The precipitate was dried at a temperature of 100°C and baked at temperatures of 500, 700, 900, and 1100°C.

The thermal analysis of the samples was carried out on a Netzsch STA 449 F1 Jupiter device for synchronous thermal analysis, with the simultaneous analysis
of gaseous products on a Netzsch QMS 403 CF Aeolos mass spectrometer. The heating was carried out in an argon atmosphere at a rate of 10°C/min up to 1050°C. The results were processed using a Netzsch Proteus Analysis. In order to study the morphology of the nanopowders, we used a JSM-6380LV scanning electron microscope in the mode of secondary electrons.

The X-ray phase analysis was carried out on a DRON-2 diffractometer with CuKα-radiation. The phase composition of the samples was determined using the ICDD PDF-2 data base. The specific area was measured on a GH-1 gasometer using low-temperature nitrogen adsorption.

RESULTS AND DISCUSSION

Figure 1a shows the results of the thermal analysis of a 0.97ZrO2 · 0.03La2O3 sample. It is seen from the