MANUFACTURING OF ZrO_2 BASED TETRAGONAL AND CUBIC SOLID SOLUTIONS WITH LANTHANIDE OXIDES: THE EFFECT OF XEROGELS AND PRECURSOR POWDERS PROPERTIES

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High-symmetric (tetragonal and cubic) ZrO_2 modifications are considered as perspective materials for modern industry, such applications as solid electrolytes in electrochemical devices and dentistry materials could be mentioned. The most appropriate approach to obtain desirable high symmetric zirconia phases is ZrO_2 stabilization by the addition of some bivalent and trivalent metal oxides resulting in solid solutions formation. Sol-gel synthesis is widely used here due to the possibility to control the phase composition and the dispersity of the precursor powders obtained. The goal of the present work was the application of the above approach for the manufacturing of ZrO_2 stabilized by lanthanides, i.e., the synthesis of ZrO_2 tetragonal and cubic solid solutions with La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er, and Yb oxides. The paper reports the study of the thermal effects in xerogels, the dispersity of products at all stages of powder manufacturing, and the phase composition of the obtained precursor powders.

The reagents used for lanthanides stabilized zirconia (LnSZ) synthesis are listed below: aqueous ammonia solution, $ZrO(NO_3)_2 \cdot 6H_2O$ and lanthanide hydrates $A(NO_3)_3 \cdot 6H_2O$, where A – La, Ce, Pr, Sm, Gd, Tb; $B(NO_3)_3 \cdot 5H_2O$, where B – Ho, Er, Yb. Systems $92ZrO_2$-$8Ln_2O_3$ (mol.%, Ln = Pr, Nd, Sm, Gd, Ho, Er, Yb), $91ZrO_2$-$9CeO_2$, $90ZrO_2$-$10La_2O_3$, and $88ZrO_2$-$12Tb_2O_3$; $97ZrO_2$-$3Nd_2O_3$, $97ZrO_2$-$3Sm_2O_3$, $96ZrO_2$-$4Ln_2O_3$ (Ln = Ce, Gd, Tb, Ho, Er, Yb), $95ZrO_2$-$5La_2O_3$ and $95ZrO_2$-$5Pr_2O_3$ were chosen for the investigation and corresponding 0.1M aqueous salts solutions were prepared. Then, the salts solution was added by drops at a rate of ~ 1–2 ml/min into the 1M ammonia aqueous solution; the pH level of about 9–10 was kept constant. Co-precipitation in an ice bath (0–5 °C) at permanent mixing by a multiblade mechanical agitator resulted in the hydroxide mixture formation. The obtained gel was aged for two days, then filtered using the Buchner funnel with the ashless paper filter (Grade 589/3 blue ribbon filter with an average pore size of ~ 2 μm) to remove the mother solution and then washed. The freshly formed metal hydroxides gel was dehydrated via freeze drying. The received amorphous powders were annealed at 450, 600 and 800 °C for 2 hours. Samples investigation was performed by thermal analysis, the X-ray diffraction analysis and particle size distribution analysis. It was found that experimental values of exothermic effects in xerogels agree well with crystallization enthalpy value for the cubic zirconia crystallization being ~ -9 kJ/mol and for the tetragonal zirconia crystallization being ~ -15 kJ/mol. It was shown that the increase in the calcination temperature up to 800 °C increases powders dispersity with mean particle size reduction up to ~ 20–40%.

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