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Complete inheritance of fractal properties during first-order phase transition

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ABSTRACT

We present experimental evidence of complete fractal properties inheritance in the course of first-order phase transition from amorphous to monoclinic or tetragonal zirconia under hydrothermal conditions. This phenomenon takes place either under rapid microwave heating or conventional heating regardless of starting fractal dimension value. Exactly the same effect is observed for hafnia. The similarity of the local structures of amorphous and crystalline zirconia as well as relatively soft crystallization conditions could be the definite reasons for the conservation of the mesostructure in the course of phase transition.

Recent studies of the structural organization of colloid materials (sols, gels, etc.) have shown that many of them exhibit surface or volume fractal properties, i.e. self-similarity of the structural elements. It has been further established that the fractal dimension is a key factor affecting physical and chemical properties of the materials, including their reactivity, catalytic activity, sorption capacity, etc. [1].

Formation of fractal structures as a result of colloid particle aggregation is thought to be a very common phenomenon. Numerous examples indicate that variation of the synthesis conditions affects the mechanism of aggregation thus allowing them to obtain colloid systems with given fractal dimension [2,3]. For instance, we recently proposed a technique of hydrous zirconia gel preparation allowing surface fractal dimension fine tuning from 2.03 to 2.60 simply by changing the acidity of the reaction medium [4]. Unfortunately, materials formed in this way are typically of amorphous nature. Moreover, any attempt to obtain their crystalline counterparts by high temperature treatment results in a dramatic decrease in the fractal dimension (and, finally, disappearance of fractality) and shrinkage of self-similarity range [5,6]. A comprehensive discussion of restructuring fractal clusters upon annealing was recently provided by Bahadur et al. [7].

In this paper, we report the first evidence of the possibility of a complete inheritance of fractal properties during first-order phase transition, namely, crystallization of amorphous zirconia gels under hydrothermal conditions.

Starting amorphous zirconia gels possessing different fractal properties were prepared as follows [4]: zirconium oxynitrate hydrate was separately dissolved in distilled water so that the final concentration of zirconium was 0.25 M. To obtain hydrous zirconia gels, aqueous ammonia (2.7 M) was added dropwise to corresponding solutions until the pH reached the desired value (4, 7, 8 and 9). The resulting precipitates were centrifuged, washed repeatedly with distilled water and dried under air flow at 60 °C overnight. The same procedure was used to synthesize amorphous hafnia gels.

Microwave-hydrothermal (MWHT) treatment of amorphous zirconia gels precipitated at pH=4, 7, and 9 (3 g of each sample in 50 ml of water) was performed in a Berghof Speedwave MWS-3* microwave system at 130 °C, 180 °C, and 225 °C for 1–5 h. Conventional hydrothermal (HT) treatment of zirconia gel precipitated at pH=8 was performed in Parr 4793 autoclave at 140 °C and 240 °C for 3 h. The resulting precipitates were separated by centrifugation, washed with distilled water, and dried at 50 °C.

Powder X-ray diffractograms (PXRD) of the gels and the products of their HT and MWHT treatment were obtained on a Rigaku D/MAX 2500 diffractometer (CuK_α radiation) over a 2θ range of 5°–60° (0.02°/step). The mean crystallite size was evaluated from X-ray diffraction data using the Scherrer equation. The microstructure of specimens was examined with a Leo912 AB Omega transmission

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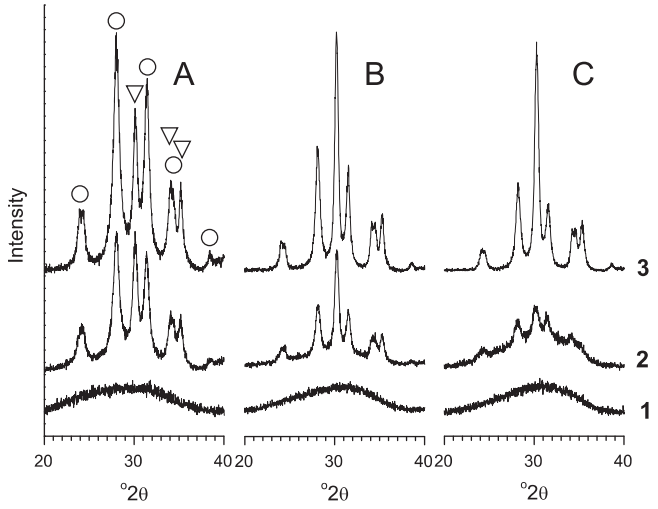

Fig. 1. PXRD data for hydrous zirconia precipitated at pH 4 (A), 7 (B), and 9 (C). 1 – as precipitated xerogels, 2 – after hydrothermal treatment at 225 °C for 1 h, 3 – after hydrothermal treatment at 225 °C for 5 h. t-ZrO_2 peaks are denoted by triangles and the most intensive m-ZrO_2 peaks by circles (A).

electron microscope (TEM). Thermal analysis (TGA/DTA) was performed using a Perkin-Elmer Pyris Diamond instrument (20–1100 °C).

PXRD (Fig. 1) and TGA/DTA data indicates that hydrothermal crystallization of amorphous zirconia gels takes place only upon heating up to 225 °C. Samples treated at this temperature for 1 h are partially crystalline, while almost complete crystallization is observed only when the duration of treatment is extended to 5 h. These findings are also supported by TEM and electron diffraction data. According to DTA data, the content of the amorphous phase decreases with increasing pH of zirconia gel synthesis. It is worth noting that exactly the same behavior is typical for hafnia gels precipitated from $HfCl_4$ solutions at pH=4, 7, and 9. However, hydrothermal crystallization of amorphous hafnia proceeds considerably slower and even the samples treated at 225 °C for 5 h contain a small admixture of amorphous hafnia. This corresponds with our earlier *in situ* Calvet calorimetry data [8]. PXRD data indicates that the only crystalline product formed upon HT and MWHT treatment of amorphous hafnia gels is monoclinic hafnia (m-HfO_2), while crystallization of amorphous zirconia gels results in formation of a mixture of monoclinic (m-ZrO_2, PDF #37-1484) and tetragonal (t-ZrO_2, PDF #42-1164) zirconia phases. The monoclinic zirconia content in the products of HT and MWHT treatment increases with the decrease in gel precipitation pH.

Small angle neutron scattering (SANS) measurements were performed on the SANS-2 setup (FRG1 neutron reactor, GKSS Research Centre, Geesthacht, Germany), which operates in near point geometry using neutrons with the wavelength $\lambda=5.8$ Å with $\Delta\lambda/\lambda=10\%$ and allows us to measure the scattering in the range of the momentum transfer $4.3\times10^{-3}<q<2.5\times10^{-1}$ Å^{-1}. Due to experimental limitations we could not investigate the scattering in a wider q range in this work, but recently [4] we conducted corresponding experiments for hydrous zirconia and hafnia synthesized under similar conditions in a momentum transfer range $8\times10^{-4}<q<0.25$ Å^{-1}. We have proved such systems to be self-similar in three decades of scaling.

Figs. 2–4 show the experimental curves of a differential neutron macroscopic cross section $d\Sigma(q)/d\Omega$ for both amorphous xerogels of hydrous zirconia synthesized at various pH values and the products of their MWHT treatment at $T_h=130$, 180 and 225 °C. It is clear that MWHT treatment at $T_h\le180$ °C does not significantly affect the scattering pattern or the intensity of scattering. The only exception is the high q region where the scattering

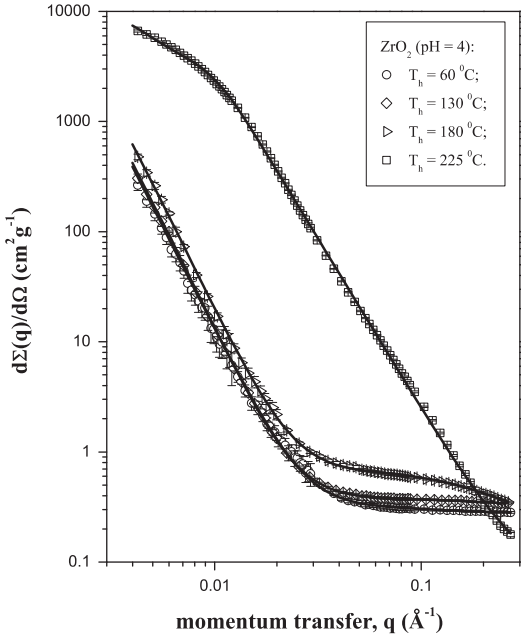

Fig. 2. SANS cross-sections $d\Sigma(q)/d\Omega$ for zirconia specimens synthesized at pH=4 and subjected to HTMW treatment at different temperatures as a function of the momentum transfer q. Solid lines represent results of experimental data fitting Eqs. (1) and (2).

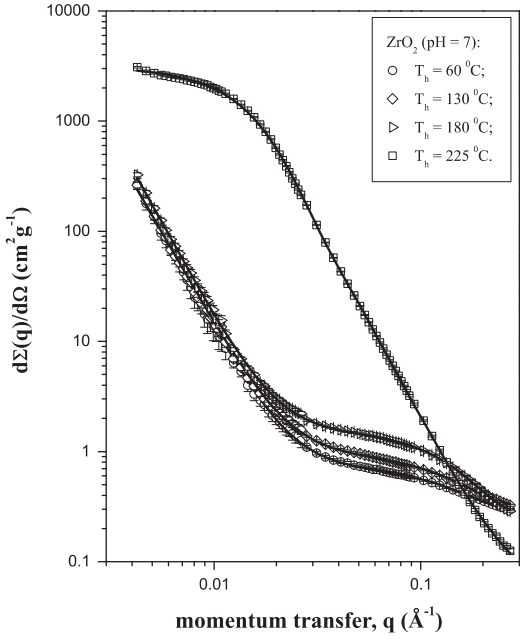

Fig. 3. SANS cross-sections $d\Sigma(q)/d\Omega$ for zirconia specimens synthesized at pH=7 and subjected to HTMW treatment at different temperatures as a function of the momentum transfer q. Solid lines represent results of experimental data fitting Eqs. (1) and (2).

intensity increases with the increase in the temperature of MWHT treatment. A common property for all the samples synthesized at $T_h\le180$ °C is that two various q ranges exist, where the behaviors of the SANS cross section $d\Sigma(q)/d\Omega$ are significantly different. For low values $q<q_c\approx0.025$ Å^{-1}, the scattering cross section $d\Sigma(q)/d\Omega$ satisfies the power law q^{-n}. In the region $q>q_c$, the scattering curves exhibit a shoulder indicating the presence of small monodisperse inhomogeneities with the effective gyration radius r_g.

The exponent n values found from the slope of the straight-line sections of the experimental curves $d\Sigma(q)/d\Omega$ plotted in log–log