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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Effect of the Nature of Anions of Aluminum Salts Used to Synthesize a Precursor of the Al_2O_3–ZrO_2 Ceramics on the Stabilization of the Tetragonal Modification of Zirconium Dioxide

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Abstract—Samples of a precursor for an aluminum oxide ceramics reinforced with zirconium oxide were synthesized by hydrolysis of various aluminum salts in the presence of a ZrO_2 sol under conditions of urea decomposition at 90°C and pH < 4 maintained, with hydrolysis products deposited onto the surface of ZrO_2 sol particles. It was found that the nature of a salt anion affects the interaction of hydrolysis products of the aluminum cation with the surface of ZrO_2 sol particles. The structure of products formed in thermal treatment of samples of a precursor for Al_2O_3–ZrO_2 (T = 1250°C) was characterized by X-ray phase analysis and scanning electron microscopy. The phase transition temperatures of the oxides Al_2O_3 and ZrO_2 contained in the precursor were estimated using the results of thermal analysis of the samples in the temperature range 20–1300°C.

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The Al_2O_3–ZrO_2 system is a basis for synthesis of aluminum oxide ceramics reinforced with zirconium dioxide (ZTA ceramics) [1, 2]. The strength and crack resistance of the material is provided by the transformation strengthening associated with the conversion of the tetragonal phase of ZrO_2 to the monoclinic phase at mouths of propagating cracks, crack deviation (branching), microcracking, and modular load transfer [2]. The t-ZrO_2 modification is metastable and its preservation in the material depends on the size and defectiveness of particles [3, 4]. One way to solve the problem of t-ZrO_2 stabilization under thermal treatment conditions is to preserve the ZrO_2 phase in the finely dispersed state by deposition of aluminum hydrolysis products onto the surface of ZrO_2 sol particles in the stage of mixing of the starting components [5]. This can restrict the growth of ZrO_2 particles in thermal treatment of the materials synthesized and thereby can diminish the probability of nucleation of the m-ZrO_2 phase.

Analysis of studies concerned with chemistry of ionic and molecular precursors for composite materials shows that their properties are determined not only by the chemical and phase composition, but also by the activity of the precursors, related to their chemical and thermal prehistory, and also by the homogeneity of intermediates and their ability to retain this property in the subsequent stages of product synthesis [6]. For example, when choosing the synthesis conditions of the aluminum oxide component of materials belonging to the Al_2O_3–ZrO_2 system, it is necessary to take into account that the composition, structure, and properties of the Al_2O_3 phase being formed are affected by the nature of an aluminum salt and specific features of its hydrolysis [7]. As applied to solving the problem of deposition of hydrolysis products of aluminum salts onto the surface of ZrO_2 colloid particles, the role of these factors has not been studied.

The aim of this study was to determine the influence exerted by the nature of aluminum salt anions in the conditions of joint hydrolysis of aluminum salts and

Precipitation conditions of mixtures of starting components and the phase composition of samples of mixed oxides Al_2O_3–ZrO_2 upon a thermal treatment

Sample	Composition of a mixture of starting components	pH values of a mixture of components		Intensity ratio of *t*/*m* ZrO_2 phases	$b_{1/2}/h$ ratio for the d = 3.84 Å line for α-Al_2O_3
		pH_{in}	pH $\Delta\tau$ = 2 h		
S7	ZrO_2(T_{ripen}=7 days), $A1_2(SO_4)_3 \cdot 18H_2O$, $CO(NH_2)_2$	2.7	2.6	3.61	0.149
S15	ZrO_2(T_{ripen} =15 days), $A1_2(SO_4)_3 \cdot 18H_2O$, $CO(NH_2)_2$	2.5	2.7	3.15	0.134
Ch7	ZrO_2(T_{ripen} =7 days), $A1C1_3 \cdot 6H_2O$, $CO(NH_2)_2$	1.8	2.4	6.20	0.191
Chl5	ZrO_2(T_{ripen} =15 dyas), $A1C1_3 \cdot 6H_2O$, $CO(NH_2)_2$	1.7	2.3	3.21	0.125
Ac7	ZrO_2(T_{ripen} =7 days), $A1(CH_3COO)_3$, $CO(NH_2)_2$	3.4	3.6	7.30	0.294
Acl5	ZrO_2(T_{ripen} =15 days), $A1(CH_3COO)_3$, $CO(NH_2)_2$	3.2	3.6	6.80	0.300

urea at pH < 4 and T = 90°C in the presence of ZrO_2 sol particles on the efficiency of stabilization of the *t*-ZrO_2 phase in composite materials of the Al_2O_3–ZrO_2 system in their thermal treatment.

EXPERIMENTAL

We used in experiments $AlCl_3 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, and $Al(CH_3COO)_3$ salts of chemically pure grade and ZrO_2 sols. The sols were synthesized by the precipitation-peptization method, with products of $ZrOCl_2 \cdot 8H_2O$ hydrolysis used. A nitric acid solution was used as a peptizing agent. The molar ratio NO_3^-/Zr^{4+} was strictly fixed. The ZrO_2 sol concentration was 2.5 wt %. The particle size distribution of the ZrO_2 sols synthesized with different ripening times (7 and 15 days) was analyzed by small-angle X-ray scattering method.[a] The surface charge of colloid particles was determined by electrophoresis in a Kehn instrument [5].

The contents of the components in a composite were 75 wt % Al_2O_3 and 25 wt % ZrO_2. This ratio was accepted in accordance with the recommendations of [8, 9]. A mixture of a solution of an aluminum salt and ZrO_2 sol was thermostated on a water bath at 90°C in the presence of urea $CO(NH_2)_2$ added to the solution of the components in a twofold excess with respect to the aluminum salt. The process of a conjugate hydrolysis of the aluminum salt and urea occurred in the course of 2 h to a constant solution pH. The precipitate formed was dehydrated by evaporation, dried at 105 ± 5°C for 48 h in an SNOL-1,6.2.5.1/9-IZ chamber furnace and then was calcined in a VTP low-inertia furnace. The rate at which the temperature was raised to a prescribed value was 10 deg min^{-1}.

Precursor samples were subjected to differential-thermal (DTA) and X-ray phase (XPA) analyses. The DTA was performed with an MOM OD-101 derivatograph, and the XPA, with a DRON-2 X-ray diffractometer ($Cu_{K\alpha}$ radiation, quartz monochromator in the primary beam, counter rotation rate 2 deg min^{-1}). The ratio between the *t*-ZrO_2 and *m*-ZrO_2 phases in thermally treated samples was found from the intensity ratio of reflections from the (111) planes for *t*-ZrO_2 and (111) and (111) for *m*-ZrO_2 [10, 11]. The dispersity of α-Al_2O_3 was evaluated indirectly from the ratio between the full width at half-maximum (FWHM) and height of the peak at d = 3.48 Å [12]. The gas evolution from the samples heated in the derivatograph was determined by chemical analysis. The residual content of the NO_3– and SO_4^{2-} ions in different stages of heating was found by IR spectroscopy with a Nicolet 380 IR Fourier spectrometer.

The microstructure of a thermally heated Al_2O_3–ZrO_2 sample was examined with a Hitachi-4800 scanning electron microscope (accelerating voltage 1.0 kV, magnification up to 50 000). The grain size was estimated using the special software shipped with the instrument.

The XPA data for Al_2O_3–ZrO_2 samples synthesized in the presence of urea and thermally treated at 1250°C

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[a] The measurements were made at the Institute of Crystallography, Russian Academy of Sciences, Moscow.

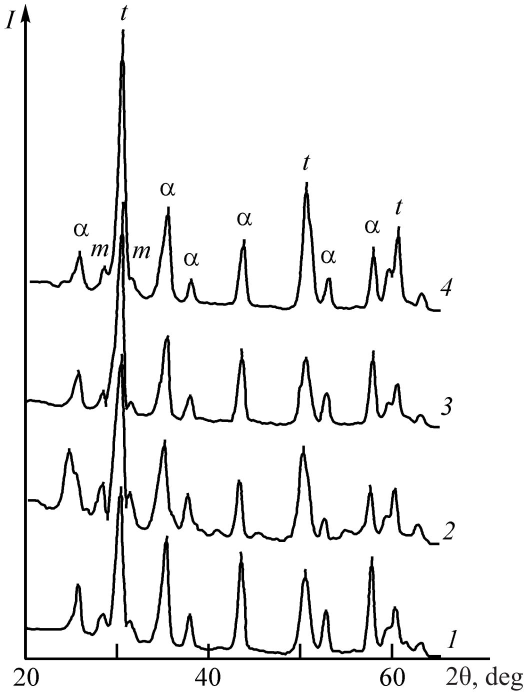

Fig. 1. X-ray diffraction patterns of samples: (*1*) S7, (*2*) Ch15, (*3*) Ch7, and (*4*) Ac7. (*I*) Intensity and (2θ) Bragg angle. Designations: α, α-Al_2O_3; *t*, *t*-ZrO_2; and *m*, *m*-ZrO_2.

are shown in the form of X-ray diffraction patterns in Fig. 1. In the course of calcination, both the precursor components undergo polymorphic transformations. In all of the thermally treated samples, aluminum oxide is present only in the form of α-Al_2O_3, and zirconium dioxide, in the tetragonal and monoclinic modifications. No chemical interaction between the aluminum and zirconium oxides is observed. A qualitative analysis of the X-ray diffraction patterns shows that the crystallinities of the samples under study and the amounts of the *t*-ZrO_2 and *m*-ZrO_2 phases they contain are different.

The quantitative data characterizing the *t/m* ZrO_2 ratio and the $b_{1/2}/h$ ratio for the diffraction peak at $d = 3.84$ Å of the α-Al_2O_3 phase (where $b_{1/2}$ is the FWHM of the peak and h is its height) for Al_2O_3–ZrO_2 samples calcined at 1250°C are listed in the table.

An important condition for preservation of a large *t/m* ZrO_2 ratio in calcination of the material is that zirconium dioxide should be distributed in the form of finely dispersed particles in a homogeneous aluminum oxide matrix. The homogeneity of a system containing a mixture of oxides is predetermined in the stage of precursor synthesis, and this is achieved via deposition of hydrolysis products of the aluminum salt onto the surface of ZrO_2 sol particles. This result is confirmed by the fact that the isoelectric point of modified ZrO_2 sol particles is at pH 8.2–8.8, which corresponds to values of similar parameters of an individual pseudoboehmite sol [5].

The *t/m* ZrO_2 phase intensity ratio in Al_2O_3–ZrO_2 samples subjected to a thermal treatment increases in the sample order S7 < Ch7 < Ac7. According to the variation of the $b_{1/2}/h$ ratio of the $d = 3.84$ Å line of the α-Al_2O_3 phase, the dispersity of aluminum oxide particles in a mixture of the oxides Al_2O_3 and ZrO_2 increases in the same order.

Aluminum salts are hydrolyzed via a number of successive stages, and hydrolysis products have a variable composition. As a rule, soluble hydroxyl-aluminum polymeric cations are formed at pH < 4 and their composition can be expressed by the general formula $Al_m(OH)_n(H_2O)^{(3m-n)+}_{4m+2-2u}$ at $(m - 1)\,2 + 2u \le n \le 3m$ [7]. It is important to note that, as the number of aluminum atoms in a polymeric cation increases, the specific charge of the polycation, $I^- = (3m - n) : m$ may decrease from +3 to +0.33. The surface charge of ZrO_2 sol particles is also positive [5], and the interaction between ZrO_2 and aluminum-containing polycations will be facilitated as I^- decreases. In a wide range of variation of the hydrolysis conditions, the most typical is the polycation of composition $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (designated as Al_{13}) for which $I^- = 0.54$. However, hydrolysis upon addition of a strong base to an aluminum salt solution leads, especially at a high neutralization rate, to formation of neutral species $[Al(OH)_3]^0_n$, and a precipitate is formed at $n \to \infty$. In hydrolysis of aluminum salts in the presence of urea (on heating the solution to 70–100°C), premature formation of floccules can be precluded [5, 13]. In these conditions, urea decomposes and OH^- ions are formed:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2,$$
$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-.$$

OH^- ions are released gradually and in the whole volume of the liquid phase, which does not lead to local solution supersaturations. In the initial stages of the processes, the solution pH changes only slightly (see table) because of the consumption of OH– ions formed in hydrolysis of the aluminum salt.

Singly charged ions (the role of Cl^- ions was examined in [13]) do not hinder formation of aluminum polycations. Moreover, the formation of a colloid in hydrolysis of the $AlCl_3$ salt may be delayed up to pH 5.16 [13]. By contrast,

SO_4^{2-} ions hinder formation of polynuclear aluminum cations, and especially Al_{13}. Hydrolysis of aluminum sulfates yields neutral forms $Al_4(OH)_{10}SO_4$. Floccules of hydrolysis products of aluminum sulfate were observed at pH 3.72 [13].

Comparison of the XPA data for synthesized and calcined samples of a mixture of Al_2O_3 and ZrO_2 makes obvious that the highest stability of the tetragonal modification of ZrO_2 are achieved for Ac7 and Ac15 samples synthesized from $Al(CH_3COOO)_3$. The hydrolysis occurs at the cation and anion:

$$[Al(H_2O)_6]^{3+}_{(sol)} + H_2O_{(liq)} \leftrightarrows [Al(H_2O)_5(OH)]^{2+}_{(sol)} + H_3O^+_{(sol)},\ K_{a1} = 5.0;$$

$$CH_3COOH_{(sol)} + H_2O_{(liq)} \leftrightarrows CH_3COO^-_{(sol)} + H_3O^+_{(sol)},\ K_{a2} = 4.8.$$

The close acidity constants K_{a1} and K_{a2} [14] favor a shift of the pH value of the salt solution to the neutral region, which is manifested in that the pH values increase in the course of precursor synthesis (see table, Ac7 and Ac15 samples). Possibly, it is also important that, exhibiting surface-active properties, the acetate ion CH_3COO^- readily enters, because of the low hydrophobicity of its hydrocarbon radical, into interaction with aluminum complexes [14] and thereby hinders growth of its particles. As a consequence, the α-Al_2O_3 phase is formed in a highly dispersed state in thermal treatment of Ac7 sample. Surfactants are widely used in nanochemistry to restrict growth of colloid particles [15].

With a ZrO_2 sol with a ripening time increased to 15 days used to synthesize samples, the t-ZrO_2/m-ZrO_2 ratio in calcined Al_2O_3–ZrO_2 samples decreases as compared with the set of samples S7, Ch7, and Ac7, synthesized with a ZrO_2 sol ripened for 7 days.

A study of the samples by the small-angle X-ray scattering method demonstrated that the average diameter of ZrO_2 sol particles is 25 nm at a ripening time of 7 days.

The positive charge is formed on the surface of sol particles primarily via rupture of Zr–O–Zr bonds and appearance of cationic polymeric forms on the surface of ZrO_2 particles [17]. Zirconium in their composition can coordinate OH– ions, which allow interaction with aluminum polycations. In the course of aging, there occurs polycondensation of OH groups to give oxo bonds, which is the reason for weakening of the interaction of ZrO_2 sol particles with aluminum polycations.

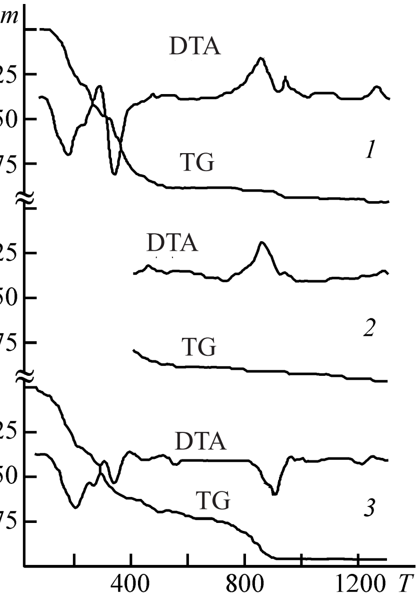

Fig. 2. Results of a thermal analysis of samples: (*1*) Ch7, (*2*) Ac7, and (*3*) S7.

The hydrolysis of aluminum salts ends in the stage of evaporation of the liquid phase retained by synthesis products. The specific properties of anions of aluminum salts contained in the evaporation products are also manifested in the stage of calcination of samples of the precursor for the ZTA ceramics.

In evaporation of colloid solutions, HCl starts to be removed from their composition, which favors completion of the hydrolysis of $AlCl_3$. Acetic acid also partly evaporates in these conditions. The hydrolysis of $Al(CH_3COO)_3$ is particularly favored by an increase in temperature. SO_4^{2-} ions are fully retained by the dry residue and, as noted in [13], form a basic aluminum salt.

According to the results of a thermal analysis (Fig. 2), Ch7 sample, preliminarily dried at 105°C, loses physically adsorbed water and HCl in the temperature range 100–290°C (as confirmed by qualitative chemical analysis) and boehmite γ-AlOOH crystallizes in the sample. Above 150°C, nitrogen oxides are released as decomposition products of the excess amount of HNO_3. The endothermic effects and a weak exothermic effect at 290–480°C reflect the reaction of dehydroxylation of boehmite to give Al_2O_3:

$$2\gamma\text{-AlOOH} \rightarrow Al_2O_{3(am)} + H_2O.$$

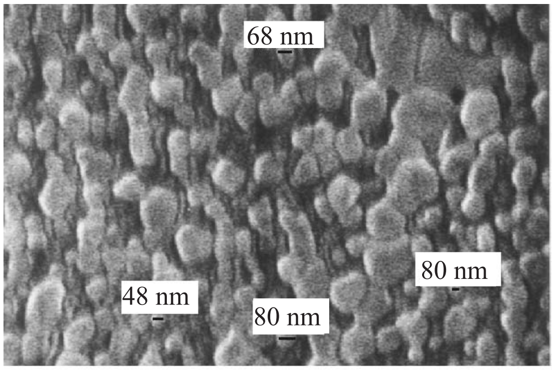

Fig. 3. Micrograph of a part of the surface of a thermally treated Ac7 sample.

$Al_2O_{3(am)}$ crystallizes at 770–840°C to give γ-Al_2O_3 with an admixture of θ-Al_2O_3. The complex nature of the phase transformation can be attributed to the inhomogeneous state of aluminum hydrolysis products, including their accumulation on the surface of ZrO_2 particles. On being heated to temperatures of 900–940°C, Ch7 sample mostly contains γ-Al_2O_3. The phase transition γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ was recorded at 1230–1250°C.

A thermal analysis of Ac7 sample is technically impossible because of its foaming in the temperature range 100–400°C. However, transformations similar to those described above occur at higher temperatures. The principal difference is in the somewhat higher temperature of α-Al_2O_3 formation (1240–1260°C).

When S7 sample is heated, the effects associated with the formation of boehmite γ-AlOOH and its subsequent dehydroxylation(250–330°C) are less pronounced, compared with Ch7 sample. It contains basic aluminum sulfate [13]. In the composition of calcination products obtained above 370–400°C, the $Al_2O_{3(am)}$ phase and aluminum salts containing sulfate ions coexist. Aluminum sulfates decompose at 820–900°C, which is confirmed by IR spectral data for samples calcined at different temperatures. The phase transition γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ occurs at 1230–1250°C.

The efficiency of the restrictions imposed by aluminum hydrolysis products deposited onto the surface of ZrO_2 particles on the growth of their size is confirmed by a study of calcined Al_2O_3–ZrO_2 samples by scanning electron microscopy. Figure 3 shows an electron micrograph of a part of the surface of A7 sample calcined at 1250°C for 2 h. The micrograph clearly demonstrates individual grains rather uniformly distributed in the surface layer of the material. Their size is 40–80 nm, i.e., is smaller than the value of 113.5–136.2 nm, the grain size in the micrograph of a previously synthesized S7 sample [5]. The assumption is confirmed that the size of ZrO_2 nanoparticles can be stabilized by their deposition onto the surface of the aluminum oxide phase, which is the most pronounced when aluminum acetate is used as a precursor for synthesis. The phase composition of the material obtained satisfies the requirements to a precursor for a ZTA ceramics characterized by a disintegration viscosity K_{1c} of up to 17 MPa $m^{0.5}$ and a bending strength σ_{bend} of up to 1700 MPa [2].

CONCLUSIONS

(1) It was shown that hydrolysis of various aluminum salts under the action of NH_3 formed in decomposition of urea at 90°C leads to deposition of aluminum hydrolysis products onto the surface of ZrO_2 sol particles, which restricts growth of zirconium dioxide particles in a subsequent thermal treatment of the precursor for the Al_2O_3–ZrO_2 ceramics and provides stability of the t-ZrO_2 phase it contains.

(2) It was demonstrated that the effect of t-ZrO_2 stabilization in thermally treated and cooled Al_2O_3–ZrO_2 samples increases in the following order of aluminum salt anions: $SO_4^{2-} < Cl^- < CH_3COO^-$, which reflects the sequence in which grows the ability of these compounds to form, in hydrolysis at pH < 4, aluminum polycations with a lowered relative charge on the aluminum atom in their composition.

(3) The temperatures at which Cl^-, CH_3COO^-, and SO_4^{2-} ions are removed from the precursor samples synthesized in the study and phase transformations of the crystalline modifications of Al_2O_3 occur in the temperature range 100–1300°C were determined.

(4) A study by scanning electron microscopy confirmed the high efficiency of the method developed for stabilization of the tetragonal modification of ZrO_2 in an Al_2O_3–ZrO_2 sample synthesized from $Al(CH_3COO)_3$.

REFERENCES

1. Podzorova, L.I., Il'icheva, A.A., and Pen'kova, O.I., *Ogneupory Tekhn. Keram.*, 2005, no. 11, pp. 2–5.
2. Shevchenko, A.V., Ruban, A.K., and Dudnik, E.V., *Ogneupory Tekhn. Keram.*, 2000, no. 9, pp. 2–8.
3. Podzorova, L.I., Il'icheva, A.A., Mikhailina, N.A., et al., *Neorg. Mater.*, 2002, vol. 38, no. 12, pp. 1455–1461.
4. Andrievskii, R.A., *Ross. Khim. Zh.*, 2002, vol. 46, no. 5,

pp. 50–56.

5. Zharnyl'skaya, A.L., Vol'khin, V.V., Shcherban', M.G., and Reuther, H., *Zh. Prikl. Khim.,* 2008, no. 7, pp. 1069–1074.
6. Tret'yakov, Yu.D., *Usp. Khim*., 2004, vol. 73, no. 9, pp. 899–916.
7. Bi, S., Wang, C., Cao, Q., et al., *Coord. Chem. Rev*., 2004, vol. 248, pp. 441–455.
8. Messing, G.L. and Kumagai, M., *J. Am. Ceram. Soc*., 1989, vol. 72, no. 1, pp. 40–44.
9. Srdic, V.V. and Radonjic, L*., J. Am. Ceram. Soc*., 1997, vol. 80, no. 8, pp. 2056–2060.
10. Garvie, R.S. and Nicholson, P.S., *J. Am. Ceram. Soc*., 1972, vol. 55, no. 6, pp. 303–305.
11. Mitra, N., Vijayan, K., Pramila Bai, B.N., et al*., J. Am. Ceram. Soc.,* 1993, vol. 76, no. 2, pp. 533–535.
12. *Rentgenografiya: Spetspraktikum* (X-ray Diffraction Analysis: Special Practical Course), Katsnel'son, A.A., Ed., Moscow: Mosk. Gos. Univ., 1986.
13. Feng, C., Wei, Q.,Wang, S., et al., *Colloids Surfaces A: Physicochem. Eng. Aspects*, 2007, vol. 303, pp. 241–248.
14. Stumm, W. and Morgan, J.J., *Aquatic Chemistry*, New York: J. Wiley & Sons, Inc., 1996.
15. Ochs, M., Cosovic, B., and Stumm, W., *Geochim. Cosmochim. Acta*, 1994, vol.58, no. 2, pp. 639–650.
16. Summ, B.D. and Ivanova, N.I*., Usp. Khim*., 2000, vol. 69, no. 11, pp. 995–1008.
17. Nazarov, V.V., Yuan' Dou Shen, and Frolov, Yu.G., *Kolloid. Zh*., 1992, vol. 54, no. 3, pp.119–122.