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Formation of ZrO_2 Nanocrystals in Hydrothermal Media of Various Chemical Compositions

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Abstract — Formation of ZrO_2 nanocrystals of various modifications was studied in relation to the chemical composition of the hydrothermal solution and in connection with the kinetic features of the process. The strongest effect on the structure of ZrO_2 is exerted by addition to the hydrothermal solution of alkali metal fluorides or potassium iodide, which induce predominant formation of monoclinic ZrO_2 nanocrystals. The mechanism by which additions of alkali metal hydroxides and halides affect the phase state of ZrO_2 nanocrystals was revealed.

Strong theoretical and practical interest in substances and materials consisting of nanosized particles stimulates development of new (e.g., ion-exchange synthesis of oxide nanocrystals [1]) and improvement of existing (e.g., sol–gel process and its modifications, gas-phase chemical reactions, cryochemical synthesis, hydrothermal synthesis, etc. [2–7]) processes for production of such materials.

Hydrothermal synthesis of ZrO_2 nanocrystals is of interest as allowing preparation of a monodisperse material with preset particle size and crystal structure [7]. The synthesis parameters [chemical composition and degree of agglomeration of the starting formulations, chemical composition of the hydrothermal solution, P–T–τ (pressure–temperature–time) conditions of hydrothermal treatment] affect differently the disperse and phase composition of ZrO_2. No exhaustive theory has been developed to predict quantitatively the formation and growth of nanocrystals with a definite crystal structure as influenced by parameters of a hydrothermal synthesis. Therefore, it seems appropriate to examine systematically the influence exerted by the synthesis conditions (in particular, by the chemical composition of hydrothermal solutions) on the structure of ZrO_2 nanocrystals.

Numerous studies have shown [7–13] that, as the P–T–τ conditions of hydrothermal treatment and the chemical composition of a hydrothermal medium are varied, the phase composition and size of the resulting ZrO_2 nanocrystals vary widely. Although there are certain common trends noted in many papers (increase in the particle size with increasing temperature and time of hydrothermal treatment [9–11]), many data are ambiguous and contradictory, especially those concerning the phase state of ZrO_2. For example, different authors report the formation under the same conditions of monoclinic and tetragonal (pseudocubic) ZrO_2 nanocrystals.

To reveal regular trends in formation of ZrO_2 nanoparticles of definite modification, we have studied systematically how this process is influenced by alkali metal hydroxides and halides added to a hydrothermal solution. The results are presented in Fig. 1.

Figure 1a shows that the relative amount of monoclinic ZrO_2 (*m*-ZrO_2) grows with increasing basicity of the compound in the order H_2O < LiOH < NaOH < KOH. The size of the particles formed also tends to increase in going from LiOH to NaOH and KOH, i.e., with increasing ionic character of the M–OH bond.

With hydrothermal solutions based on alkali metal halides, the trends are as follows. Irrespective of the kind of the alkali metal, chlorides and bromides as components of hydrothermal solutions do not affect significantly the phase composition of the ZrO_2 nanocrystals formed, as compared to straight water as hydrothermal medium (Figs. 1a, 1c, 1d). However, in fluoride hydrothermal solutions, monoclinic ZrO_2 nanocrystals are formed chiefly (in the presence of LiF) or exclusively (in the presence of NaF and KF) (Fig. 1b). Addition of KI to the hydrothermal solution also promotes crystallization of monoclinic ZrO_2 exlusively (Fig. 1e). It should be noted that the ZrO_2 crystals formed in the KI solution are approximately twice as large as those formed in the other media at the same temperature and time of the synthesis. Presumably, the stability of monoclinic ZrO_2 in this case is due solely to the crystal size effect, in view of previous observations that, with increasing particle

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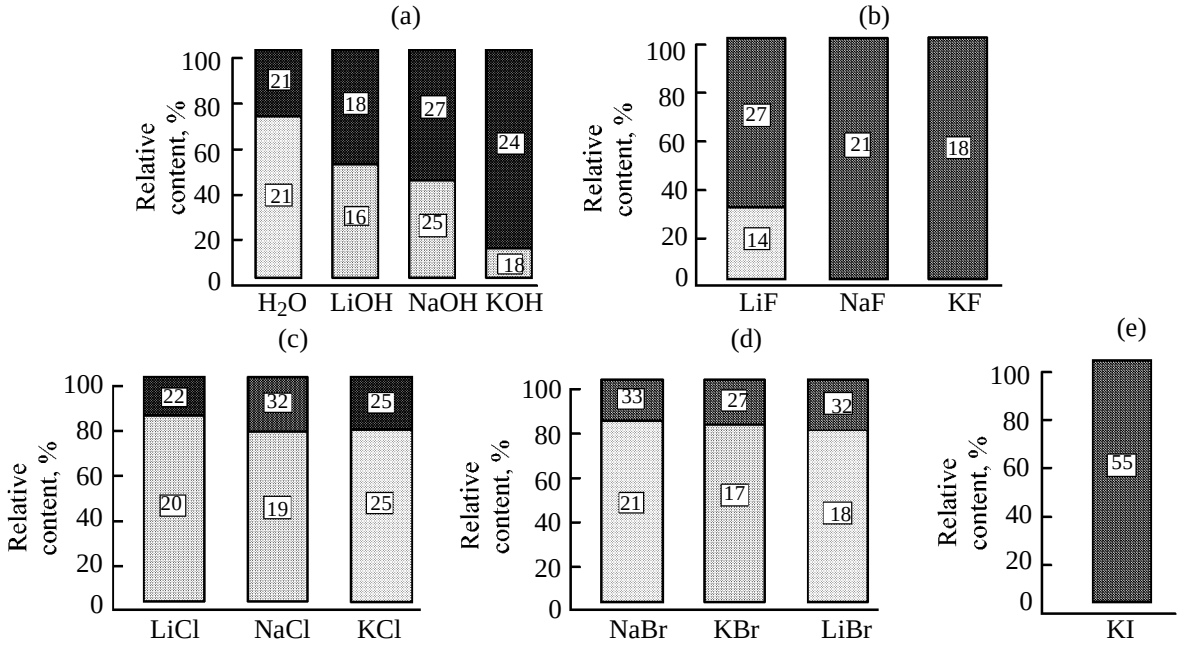
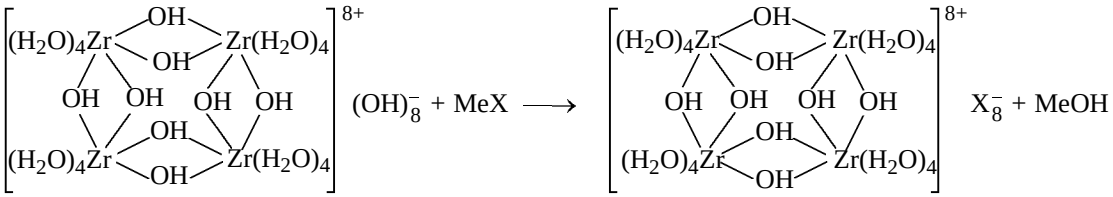


Fig. 1. Phase composition [light bars: tetragonal (pseudocubic) modification; dark bars: monoclinic modification] and size (nm) of ZrO_2 particles prepared in various hydrothermal media: (a) water and alkali metal hydroxides; alkali metal halides: (b) fluorides, (c) chlorides, (d) bromides, and (e) iodide.

size, the content of the monoclinic modification grows and reaches 100% [10].

The particle size of monoclinic and pseudocubic (tetragonal) ZrO_2 nanocrystals formed under hydrothermal conditions is approximately equal, 15–30 nm (Fig. 1); therefore, presumably, the decisive factor governing the structure of nanocrystals is the structural similarity of the nucleation centers and growing nanocrystals. This assumption is supported by the fact that the hydroxide of the polymeric hydroxo complex $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}(OH)_8^-$, which was the ZrO_2 precursor in the hydrothermal synthesis, has a structure similar to that of cubic (or tetragonal) ZrO_2 (Fig. 2). The fact that additions of alkali metal chlorides or bromides to a hydrothermal solution have no effect on the phase state of the ZrO_2 nanoparticles formed (Fig. 1) can be rationalized in terms of the same model, as substitution occurs in the outer sphere of the hydroxo complex and leaves intact its core:



Owing to close ionic radii of oxygen and fluorine {$R_{O^{2-}}$(**IV**) 1.24, R_{F^-}(**IV**) 1.17 Å [12]}, alkali metal fluorides added to the hydrothermal solution partially displace hydroxy groups from the inner sphere of the hydroxo complex, inducing its breakdown, which, in turn, initiates crystallization of monoclinic ZrO_2. A significant content of the pseudocubic modification in ZrO_2 nanocrystals formed from a hydrothermal solution containing LiF (Fig. 1b) is probably due to close ionic radii of Zr and Li {$R_{Zr^{4+}}$(**VIII**) 0.98, R_{Li^+}(**VIII**) ~1.03 Å (extrapolation) [14]}, which promotes partial replacement of Zr ions by Li ions in the

hydroxo complex under the action of the hydrothermal solution; it is known that such heterovalent substitution, $Zr^{4+}_{1-x}Me^{n+}_{x}O_{2-(2-n/2)x}$ (see, e.g., [13]), stabilizes the tetragonal and cubic modifications of ZrO_2. Decreased content of pseudocubic ZrO_2 nanocrystals in the product obtained in the presence of strong alkalis is also quite understandable, because these compounds break down the hydroxo complex [15].

The suggested mechanism is supported by kinetic features of nanocrystal formation under hydrothermal conditions. According to X-ray phase analysis, the starting material is X-ray amorphous (Fig. 3), whereas electron microdiffraction data show that its structure is not fully disordered (Fig. 4). Clusters are detected, which can affect significantly the subsequent phase formation in the system, acting as nuclei of one or another phase. A kinetic study of ZrO_2 crystallization from $[Zr(OH)_2 \cdot 4H_2O]^{8+}_4(OH)^-_8$ in distilled water at T 250°C, P 70 MPa (Fig. 5) shows that these clusters are mainly the nuclei of cubic ZrO_2, which promotes primary crystallization of this modification. After a certain induction period, crystallization of cubic ZrO_2 becomes avalanche-like. Monoclinic ZrO_2 is formed with a certain time lag (Fig. 5), which may be due to nonuniform structure of the initial $ZrO_2 \cdot nH_2O$ and may be primarily associated with crystallization of the residual amorphous fraction of zicronium oxyhydroxide. Longer hydrothermal treatment in the examined range of temperatures and times caused no significant changes in the particle size and phase state.

Thus, the mechanism by which alkali metal hydroxides and halides affect the phase state of nanocrystals is associated with the initial stage of the process: formation of the structure of nucleation centers. The most significant effect on the ZrO_2 structure is exerted by addition to the hydrothermal solution of alkali metal fluorides or KI, inducing formation of chiefly monoclinic ZrO_2 nanocrystals. Under hydrothermal conditions, ZrO_2 nanocrystals are formed in the avalanche-like mode and have a narrow particle-size distribution. The process kinetics can be adequately described by the model proposed in [16].

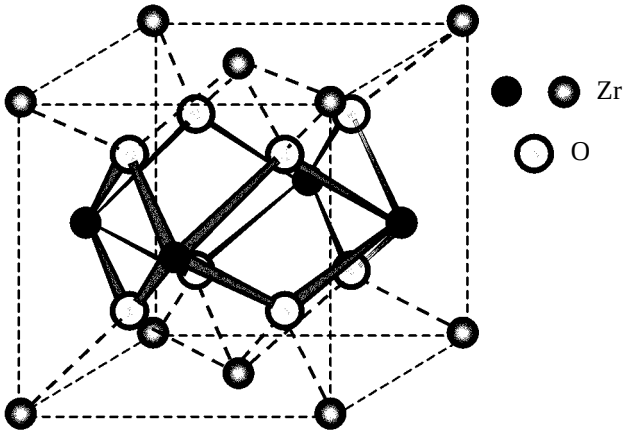


Fig. 2. Arrangement of zirconium and oxygen ions in a Zr_4O_8 fragment of compounds $[Zr_4(OH)_8(H_2O)_{16}]X_8 \cdot 12H_2O$ as a part of the fluorite structure. Gray circles denote zirconium ions in the unit cell of cubic ZrO_2, not incorporated into the $[Zr_4(OH)_8(H_2O)_{16}]X_8 \cdot 12H_2O$ structure.

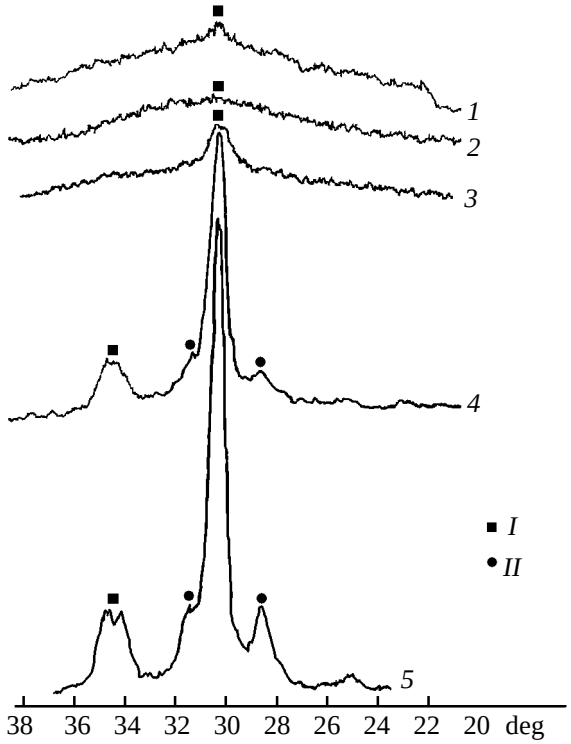


Fig. 3. Diffraction patterns of samples prepared by hydrothermal synthesis in distilled water at 250°C, 70 MPa. Synthesis time, min: (*1*) 80, (*2*) 90, (*3*) 95, (*4*) 100, and (*5*) 120. ZrO_2 modification: (*I*) cubic and (*II*) monoclinic.

EXPERIMENTAL

Zirconium dioxide nanoparticles were prepared by hydrothermal dehydration of zirconium oxyhydroxide ($ZrO_2 \cdot nH_2O$) synthesized as described in [7]. The hydrothermal treatment was performed in platinum crucibles charged with zirconium oxyhydroxide and a mineralizing solution. The charged crucibles were placed in autoclaves, which were heated in furnaces. After isothermal heating at prescribed temperatures, the furnaces were switched off, and the autoclaves were allowed to cool in the furnace. The heat treatment temperature was maintained to within ±5°C. The time of isothermal heating was considered as the heat treatment time. Hydrothermal synthesis of ZrO_2

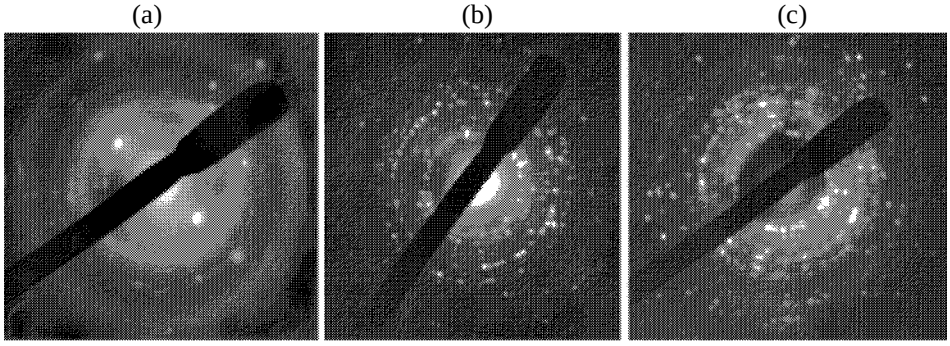


Fig. 4. Microdiffraction patterns of ZrO_2 samples: (a) initial substance before hydrothermal treatment; (b, c) ZrO_2 prepared by hydrothermal treatment in distilled water (250°C, 70 MPa) for 2 and 6 h, respectively.

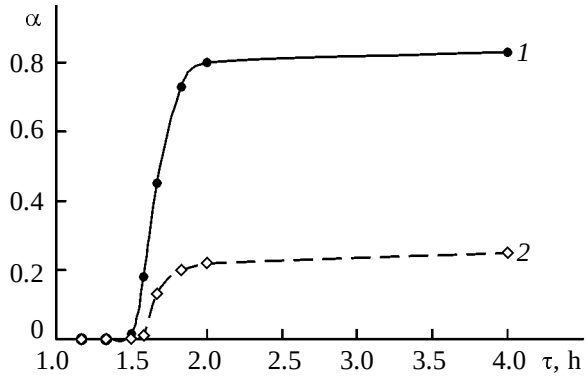


Fig. 5. Crystallization kinetics of ZrO_2 in distilled water under hydrothermal conditions (250°C, 70 MPa): (α) conversion and (τ) time. ZrO_2 modification formed: (*1*) cubic and (*2*) monoclinic.

was performed at 250°C and 70 MPa for 4 h; the chemical composition of hydrothermal solutions was varied within fairly wide limits. As hydrothermal media were used distilled water and solutions of alkali metal halides and hydroxides. The synthesis products were washed with distilled water and dried at 110°C.

Phase analysis was performed with DRON-3 and Siemens D-500HS (Germany) X-ray diffractometers and by electron microdiffraction. The contents of tetragonal (*t*) and cubic (*c*) ZrO_2 were calculated by the formula proposed in [17]:

$$X_{t+c} = \{I(111)_{t+c}/[\mathrm{I}(111)_m + I(111)_{t+c} + I(11\bar{1})_m]\} \times 100\%.$$

The particle size was calculated by the Scherrer formula (the reproducibility was no worse than 5%). The results of Scherrer calculations agree within the experimental error with those obtained by electron microscopy and from surface area measurements (assuming the spherical shape of the particles).

The BET surface area of the material, determined from ethanol adsorption isotherms, was 62 ± 1 m^2 g^{-1}.

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REFERENCES

1. Mamchik, A.I., Vertegel, A.A., Tomashevich, K.V., Oleinikov, N.N., Ketsko, V.A., and Tret'yakov, Yu.V., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 1, pp. 21–25.
2. Gusev, A.I., *Nanokristallicheskie materialy: metody polucheniya i svoistva* (Nanocrystalline Materials: Preparation Methods and Properties), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 1998, p. 199.
3. Gusarov, V.V., Malkov, A.A., Ishutina, Zh.N., and Malygin, A.A., *Dokl. Ross. Akad. Nauk*, 1997, vol. 357, no. 2, pp. 203–205.
4. Ghosh, N.N. and Pramanik, P., *Eur. J. Solid State Inorg. Chem.*, 1997, vol. 34, no. 7, pp. 905–912.
5. Tretyakov, Yu.D., Oleynikov, N.N., and Shlyakhtin, O.A., *Cryochemical Technology of Advanced Materials*, London: Chapman and Hall, 1997.
6. Rakov, E.G., *Zh. Neorg. Khim.*, 1999, vol. 44, no. 11, pp. 1827–1840.
7. Pozhidaeva, O.V., Korytkova, E.N., Drozdova, I.A., and Gusarov, V.V., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 8, pp. 1265–1270.
8. Hu-min, C., Li-jun, W., Ji-ming, M., Zhi-yiang, Z., and Li-min, Q., *J. Eur. Ceram. Soc.*, 1999, no. 19, pp. 1675–1681.
9. Nishizawa, H., Yamasaki, N., Matsuoka, K., and Mitsushio, H., *J. Am. Ceram. Soc.*, 1982, vol. 65, no. 7, pp. 343–346.

10. Tani, E., Yoshimura, M., and Somiya, S., *J. Am. Ceram. Soc.*, 1983, vol. 66, no. 1, pp. 11–17.
11. Pyda, W., Haberko, K., and Bucko, M.M., *J. Am. Ceram. Soc.*, 1991, vol. 74, no. 10, pp. 2622–2629.
12. Hu, M.Z.-C., Zielke, J.T., Lin, J.S., and Byers, C.H., *J. Mater. Res.*, 1999, vol. 14, no. 1, pp. 103–113.
13. Somiya, S. and Akiba, T., *J. Eur. Ceram. Soc.*, 1999, no. 19, pp. 81–87.
14. Shannon, R.D., *Acta Crystallogr., Sect. A*, 1976, vol. 32, no. 5, pp. 751–767.
15. Wells, A.F., *Structural Inorganic Chemistry*, Oxford: Clarendon, 1986. Translated under the title *Strukturnaya neorganicheskaya khimiya*, Moscow: Mir, 1987, vol. 2, p. 376.
16. Antonov, N.M., Gusarov, V.V., and Popov, I.Yu., *Fiz. Tverd. Tela*, 1999, vol. 41, no. 6, pp. 907–909.
17. Kharlamov, A.N., Turakulova, A.O., Lunina, E.V., and Lunin, V.V., *Zh. Fiz. Khim.*, 1997, vol. 71, no. 6, pp. 985–990.