ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 3, pp. 385–390. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © O.V. Al'myasheva, V.V. Gusarov, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 3, pp. 359–364.

Features of the Phase Formation in the Nanocomposites

O. V. Al'myasheva[a] and V. V. Gusarov[b]

[a] *Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31, St. Petersburg, 199004 Russia*

[b] *St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia*
e-mail: almjasheva@mail.ru e-mail: almjasheva@mail.ru

Received July 16, 2009

Abstract—Thermodynamic conditions of formation of critical nuclei in the composites that are the phase forming medium, a matrix with inclusions of nanoparticles of the other phase, are considered. It is shown that depending on the nature of the spatial distribution of nanoparticles in the matrix, critical nuclei of different shapes may appear at the phase formation. In some cases the formation and stable existence of metastable phases, including amorphous ones is possible. The conditions of formation in the nanocomposites of the critical nuclei of heterogeneous structure are determined. The experimental data on the phase formation in the nanocomposites ZrO_2–$Al(OH)_3$ and ZrO_2–SiO_2 were analyzed and the earlier described feature of formation of the new phase nuclei is confirmed theoretically.

DOI: 10.1134/S1070363210030023

INTRODUCTION

The interest in chemical and phase transformations in the media localized in the areas of nanometer scale with spatial constraints of nanometrer scale, in one or more basic directions, i.e., in the so-called nano-reactors, in the recent years steadily increased [1–7]. This originates from the often unusual character of the processes in the nanoreactors compared with the analogous macro-scale processes and by a set of new properties which possess the newly formed substances, and by the increasing number of nano-sized objects that can be used as reactors. The influence of conditions on the process of chemical reaction [8], as well as effect of the change in the size of the reaction zone (the effect of reactor scaling of the process) was noted long ago [9], but the changes in the chemical and phase transformations at the variation in the reactor size and shape were usually considered on quantitative level only. However, the spatial limitation of the reaction environment in the nanometer scale in some cases leads to chemical and phase transformations of a fundamentally new nature (see, for example, [2, 4, 6, 7]).

It was shown experimentally in [10, 11] that in the nanocomposites consisting of a matrix that can potentially undergo chemical and phase transformations with nanoparticles of another phase distributed in it, these transformations under certain conditions can proceed in unusual way. Such nanocomposites, i.e., the reaction medium with spatial constraints in the form of inclusions of nanoparticles of another phase, may also be considered as nanoreactors. The systematic investigation of the phase formation in these nanoreactors is of interest.

Let us consider a nanocomposite consisting of a matrix, i.e., the reaction environment, with the inclusions of nanoparticles of another phase. As a first approximation, we assume that the initial (going to be transformed) substance, the forming phase, and the phase of nanoscale inclusions are isotropic. If uniform distribution of nanoparticles in the reaction environment is presumed and, for simplicity, they are considered as spherical inclusions in the nodes of a cubic lattice (Fig. 1), then for the nanocomposites with nanoparticles of diameter d and the volume fraction v the maximal free (unoccupied with nanoparticles) space for the formation of the particles of new phase will have a characteristic size δ, defined by the dependence $\delta = \delta(d, v)$ presented in Fig. 2. The area of the characteristic sizes corresponding to the most typical dimensions of critical nuclei formed in the solid phase, which usually are of a few or of tens of nanometers [12, 13], is marked out in Fig. 2. This area

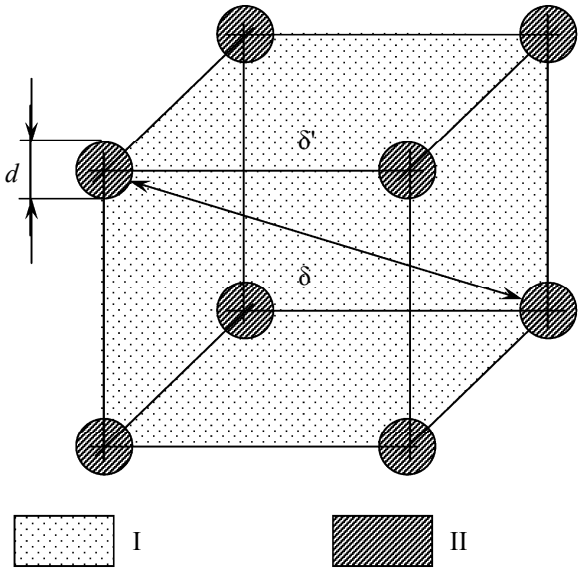

Fig. 1. Cubic packing of nanoparticles in the reaction medium. (I) is the substance constituting the reaction medium and (II) is the substance of nanoparticles inclusions; (*d*) is the diameter of nanoparticles; (δ') is the minimum distance between the nanoparticles; (δ) is the maximum distance between the nanoparticles.

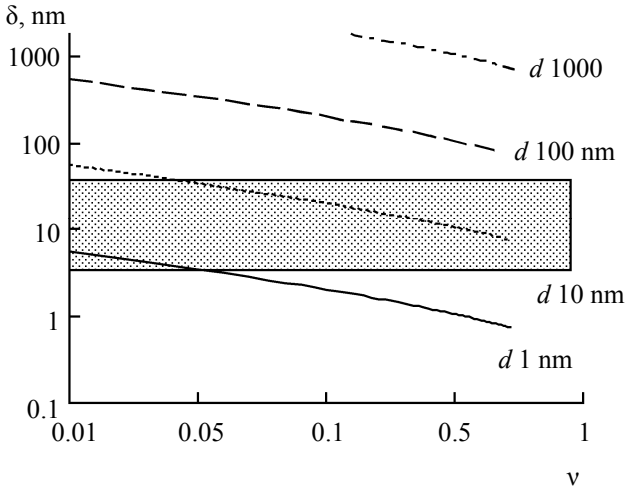

Fig. 2. Dependence of the maximum distance between the nanoparticles (δ) on their size (*d*) and volume fraction (ν). The marked area corresponds to characteristic values of the size of critical nuclei of oxide phases.

to some extent is boundary: at the higher values of δ the nanopaticles of another phase are obviously not an obstacle for the formation of nuclei, and for smaller values of δ the formation of critical nuclei along the classical scheme [13] becomes impossible. As can be concluded from the analysis of the data described in Fig. 2, critical for the formation of a new phase nuclei in the reaction medium are the nanocomposites with inclusions particles smaller than 100 nm.

Let us consider the potential opportunity of the phase formation in the cases when the size of a normal critical nucleus of equilibrium phase is consistent with the characteristic size δ of the area in which it is formed. As in this case the formation of critical nucleus of the equilibrium phase with the optimal volume/surface ratio is hampered by heterophase nano-sized inclusion (see Fig. 2), for the phase formation in such an environment potentially remain the following opportunities: (1) the formation of a critical nucleus of non-isometric form (laminar or stretched in one direction), located between the particles of inclusions, (2) the formation of a heterogeneous critical nucleus, i.e., inside of it will be located the particle of another phase, and (3) the formation of a critical nucleus of a phase which is not in equilibrium at the given temperature and pressure, but with a ratio of specific surface energy and Gibbs energy of formation of this phase that provides the size of its critical nucleus less than δ. It should be noted that the feasibility of these options for the formation of critical nucleus can be affected by both thermodynamic and kinetic factors.

Let us consider the thermodynamic restrictions to the formation of critical nuclei in isotropic medium with distributed in it heterophase nanosize inclusions. In the case of the first of the above options for the formation of nuclei, the analysis of specific values of surface energy σ_i and Gibbs energy of formation of the equilibrium phase i $g_{Vi} < 0$ shows that if for the critical nucleus of isometric shape (a ball), the value of the characteristic size is $d_{cri}^{ball} = 4(\sigma_i/|g_{Vi}|)$, then for the the critical nucleus this phase in the form of layer (flat cylinder) with a maximum thickness corresponding to the gap between the nanoparticles of the other phase (δ'), the value of the width (diameter) is expressed as follows:

$$h_{cri} = \frac{\delta'}{2\delta'/d_{cri}^{ball} - 1}. \quad (1)$$

Note that this expression is obtained at the assumption of equidistant location of the second phase nanoparticles in the environment. Analysis of expression (1) shows that the formation of critical

nucleus of the phase i in a layer of width h_{cri} and the thickness corresponding to the distance (δ') between the particles of the second phase, is possible only at the value

$$\delta' > \frac{d_{cri}^{ball}}{2} \quad . \tag{2}$$

As far as d_{cri}^{ball} for various phases i is different, the condition (2), generally speaking, in some cases can be fulfilled at the crystallization of metastable phases and not fulfilled at the formation of equilibrium phase. Such options are possible if the increase in g_{Vi} (decrease in $|g_{Vi}|$) for the metastable phases is compensated by a simultaneous decrease in σ_i, so that d_{cri}^{ball} decreases until fufilling the condition (2).

Generally, this situation with the phase formation in a restricted space is typical for all geometric forms of critical nuclei. For example, if the size of the critical nucleus of equilibrium phase i, is $d_{cri}^{ball} > \delta$, i.e., larger than the area in which it could be formed, then there are alternative options for the formation of critical nuclei. In this case, not only the critical nuclei of non-isometric form or nuclei with a heterogeneous structure on the basis of equilibrium phase i may be formed, but may appear the critical nuclei of metastable phase j, if a condition $d_{cri}^{ball} < \delta$ (formation of a spherical nucleus) or $d_{cri}^{ball} < 2\delta'$ (formation of a laminar nucleus) is fulfilled. Thus at the stage of nucleation in an environment with distributed spatial constraints in it created by the nanoparticles of the other phase a certain selection of phases may occur along the thermodynamic possibility of their formation.

The analysis of the expression for the critical size of nucleus of elongated shape (long cylinder) shows that for isotropic materials the elongation of nucleus does not compensate the decrease in its cross section, i.e., values $d_{cri}^{(cylinder)}$ and $d_{cri}^{(sphere)}$ coincide regardless of its length. As a consequence of this result it is expectable, in particular, that some oxide materials being localized in hydrosilicate nanotubes whose inner diameter as a rule falls in the range of 1–5 nm [14], will not crystallize, because the size of critical nuclei for many oxides exceeds the specified value [12].

Another possibility of the formation of the critical nucleus in these environments with nanoparticles distributed in them, as mentioned above, is the formation of heterogeneous nucleus, i.e., nucleus that includes the nanoparticles of another phase. Assuming, as above, that the formed phase and nanoparticles are isotropic for the characteristic size (diameter) of spherical critical nucleus can be written the following expression

$$d_{cri}^{het} = \frac{d_{cri}^{ball}}{1 - \left(1 + \frac{3}{2}\frac{d_{cri}^{ball}}{d}\cdot\frac{\sigma_l'}{\sigma_l}\right)\cdot\nu}, \tag{3}$$

where d is the size (diameter) of nanoparticles distributed in the environment; σ_i' is the surface energy of the phase boundary of nanoparticle with the emerging phase i; v is the volume fraction of nanoparticles in the environment.

The analysis of expression (3) shows that the formation of the critical heterogeneous nucleus is thermodynamically possible only at fulfilling the condition

$$\nu < \frac{1}{1 + \frac{3}{2}\frac{d_{cri}^{ball}}{d}\cdot\frac{\sigma_l'}{\sigma_l}} \, . \tag{4}$$

Note that if the values d_{cri}^{ball} and d are close in magnitude, then from expression (4), follows that $v \leq 0.4$, and for cases $d_{cri}^{ball} << d$ and/or $\sigma_i' << \sigma_i - v < 1$, i.e., in the latter case the environment can be quite densely packed with the nanoparticles. To these limiting cases correspond d_{cri}^{het} to such extent much larger than d_{cri}^{ball}, so that for kinetic reasons they seems practically impossible.

The analysis of expressions (1) and (3) shows a sharp increase in the characteristic size of the critical nuclei at the reduced value of d and increased parameter v. This fact shows that, as far as the combination of the values of the parameters included in Eqs. (1) and (3), which will give the values of the characteristic size of the critical nuclei not significantly differing from d_{cri}^{ball} may not be frequent, then the formation of nuclei of the considered types would be rather rare event by kinetic reasons. Formation of these nuclei likely requires prolonged exposure of the considered nanogeterogenous media in an environment where nucleation is possible thermodynamically in accordance with expressions (1)–(4).

In [10–12] the phase formation was experimentally studied in systems ZrO_2–$Al(OH)_3$ and ZrO_2–SiO_2 where nanoparticles of ZrO_2 (d ~ 15 nm) served as heterogeneous inclusions. The systems differed not only in chemical composition, but also by the method of obtaining the initial composition, by the conditions of the chemical transformations, and by the nature of reactions in them [12].

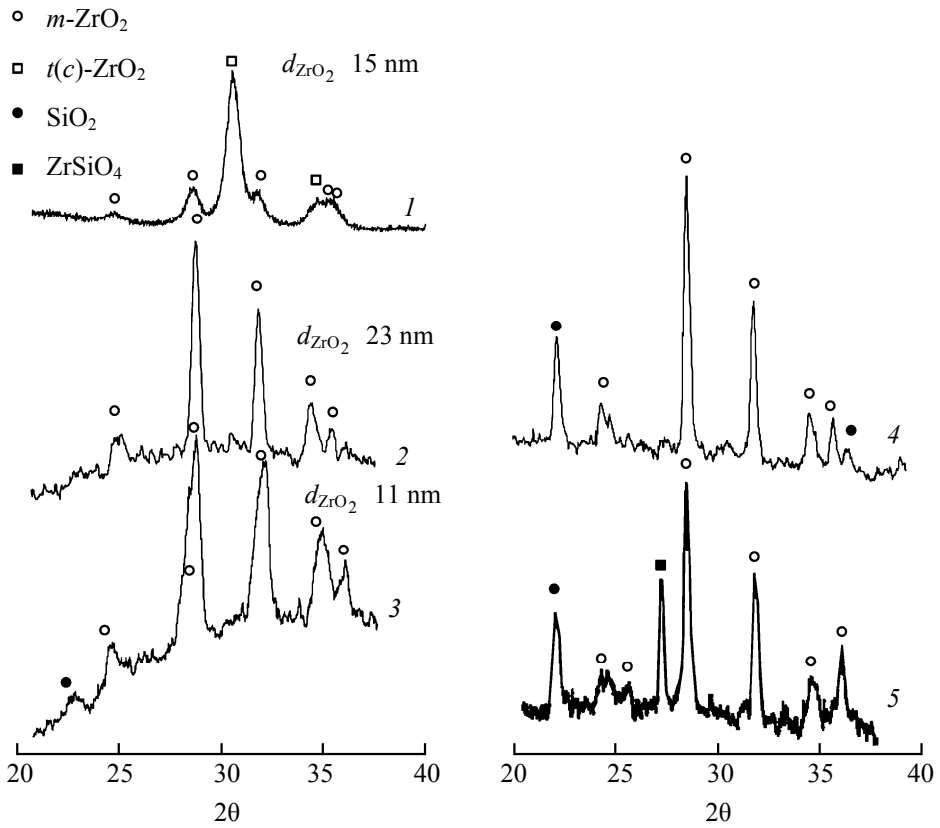

Fig. 3. The results of X-ray diffractometery of the samples on the basis of the system ZrO_2–SiO_2. The size of ZrO_2 crystals (d_{ZrO_2}) is calculated with Sherrer formula. (*1*) is the initial mixture of nanoparticles ZrO_2 and amorphous SiO_2 (nanocomposite); (*2*)–(*4*) are nanocomposites after heat treatment at a temperature 1500°C for 30 min, 1 h, and 1.5 h respectively; (*5*) is a mixture of particles of micron size of ZrO_2 and amorphous SiO_2 after thermal treatment for 1.5 h.

The initial reactive nanocomposition ZrO_2–$Al(OH)_3$ was obtained by the precipitation of aluminum hydroxide on the zirconium dioxide nanoparticles synthesized primarily by the method described in [15]. Dehydration of $Al(OH)_3$ was carried out under hydrothermal conditions in accordance with the procedure described in [12]. As an experiment for comparison we give the results of the synthesis of aluminum oxide under the same conditions but in the absence of ZrO_2 nanoparticles in the matrix of $Al(OH)_3$ [16].

The comparative analysis of the results obtained in [16] and [12] shows that if in the system Al_2O_3–H_2O in hydrothermal conditions (450°C, 75 MPa) occurs dehydration of $Al(OH)_3$ with the formation of well crystallized particles of α-Al_2O_3 (corundum structure), as would be expected based on the results of thermodynamic calculations [12, 17] and of the experimental data on the phase diagram of Al_2O_3–H_2O [18], then in the system ZrO_2–Al_2O_3–H_2O, in which ZrO_2 is in the form of nanosized inclusions, at the dehydration of aluminum hydroxide amorphous aluminum oxide is formed not crystallizable even at temperatures of calcination amounting to 1200°C [19]. This fact might originate from the distance between the nanoparticles of ZrO_2 in the reactive composition ZrO_2–$Al(OH)_3$ being smaller than the size of critical nuclei of α-Al_2O_3, and other its metastable crystalline forms, which according to [12] is 40–60 nm under these conditions. Therefore, as follows from expressions (1)–(4), at the dehydration of $Al(OH)_3$ can be formed either amorphous aluminum oxide or nuclei of crystalline Al_2O_3 with non-isometric shape or of heterogeneous structure. The formation of a salt type nucleus in this case is not possible owing to the condition (2), because the distance between the nanoparticles of ZrO_2 does not exceed δ' ~10 nm (Fig. 1), while the size of the critical nucleus of crystalline aluminum oxide under the conditions of the experiment by all estimates exceeds 40 nm [12], i.e., the condition for the possibility of salt type nucleus (2) cannot be attained.

The formation of a critical nucleus with heterogeneous structure in this case, it seems, is hampered by the slow process of formation of the nuclei of crystalline forms of Al_2O_3 under hydrothermal conditions [16] that, in accordance with the data shown in [20] does not contribute to the incorporation into the crystallizing substance of the particles of other phases. Thus, the most realistic way of development of the process in nanocomposite ZrO_2–$Al(OH)_3$ at the dehydration of $Al(OH)_3$ is the formation of amorphous aluminum oxide, which is confirmed by experiment.

Nanocomposite ZrO_2–SiO_2 was prepared as described in [10, 12] by mechanical mixing of equimolar quantities of ZrO_2 nanoparticles (particle size 15±3 nm [15]) and amorphous SiO_2 (aerosil A-300). For a comparative study was prepared also a mixture of similar composition but containing ZrO_2 particles of micron size (passing through a sieve with the gap 63 μm). Thus, unlike the nanocomposites ZrO_2–$Al(OH)_3$, in this case ZrO_2 serves as a heterophase component of the reaction composite and as one of the reactants simultaneously. A heat treatment at 1500°C of the considered mixtures, as showed the results of experimental studies given in [11, 12] and the data of X-ray phase analysis (Fig. 3), revealed that in the composite containing micron particles of ZrO_2 the reaction of $ZrSiO_4$ formation was largely completed, but in the nanocomposite where the particles of ZrO_2 were a thousand times smaller and in accordance to the known laws [22] the reaction was expected to proceed much faster, actually the formation of $ZrSiO_4$ did not occur. However, in the system ZrO_2–SiO_2 at the initial stage of interaction between ZrO_2 nanoparticles and amorphous SiO_2 a decrease of ZrO_2 particle size was observed and then crystallization of amorphous SiO_2 with the formation of crystobalite nanoparticles (Fig. 3) with simultaneous growth of the crystals of ZrO_2.

The results may mean that the size of critical nucleus of $ZrSiO_4$ significantly exceeds the distance between the ZrO_2 nanoparticles, that in accordance with the conclusions made above prevents the process of formation of $ZrSiO_4$ nuclei. However, the size of the critical nucleus of crystobalite is comparable with the size of free space between the ZrO_2 nanoparticles in nanocompositee ZrO_2–SiO_2, which leads to the formation of nanocrystals of a phase nonequilibrium under these temperature conditions on the basis of SiO_2 with the structure of crystobalite [18] (Fig. 3) according to the theoretical conclusion made earlier about the possibility of phase selection processes at the nucleation in nanocomposites. The changes the size of crystals of ZrO_2 in the process of heat treatment illustrated in Fig. 3 probably originate from the fact that, as is known, ZrO_2 can dissolve in appreciable quantities in amorphous silicon dioxide [23] and the size of ZrO_2 nanoparticles decreases. At the crystallization of the amorphous phase on the basis of SiO_2 containing ZrO_2 with the formation of crystobalite occurs the reverse process, the crystallization of zirconium dioxide on the surface of ZrO_2 nanoparticles due to its very low solubility in the crystalline modifications of SiO_2 [18, 21], that in turn leads to an increase of zirconium dioxide nanoparticles.

Thus, experimental data confirmed the conclusion of theoretical analysis on the opportunity of the formation of critical nuclei of nonequilibrium phase and its stable existence in the nanocomposites. However, in the cases examined the formation of nuclei of new phase with layer morphology or heterophase structure was not revealed, although the possibility of their formation could be predicted on the basis of expressions (1) and (3). This fact, apparently, is due to kinetic difficulty of these processes.

ACKNOWLEDGMENTS

This work was financially supported by the Presidium of Russian Academy of Sciences, Program no. 18 “The development of methods for obtaining chemicals and creating new material,” and the Russian Foundation for Basic Research (project no. 09-03-90449-Ukr_f_a).

REFERENCES

1. Rusanov, A.I., *Zh. Obshch. Khim*., 2002, vol. 64, no. 4, pp. 532–549
2. Suzdalev, I.P. and Suzdalev, P.I., *Usp. Khim.*, 2006, vol. 75, no. 8, pp. 715–752
3. Buchachenko, A.L., *Usp. Khim.*, 2003, vol. 72, no. 5, pp. 419–437.
4. Tret’yakov, Yu.D., Lukashin, A.V., and Eliseev, A.A., *Usp. Khim.*, 2004, vol. 73, no. 9, pp. 974–998.
5. Ablyazov, P.N., Vasilevskaya, V.V., and Khokhlov, A.R., *Kolloid. Zh.*, 2007, vol. 69, no. 3, pp. 293–299.
6. Maslennikova, T.P., Korytkova, E.N., and Gusarov, V.V., *Zh. Prikl. Khim.*, 2008, vol. 81, no. 3, pp. 289–292.
7. Al’myasheva, O.V. and Gusarov, V.V., *Dokl. Akad. Nauk*, 2009, vol. 424, no. 5, pp. 641.
8. Mendeleev, D.I., *Osnovy khimii* (Fundamentals of

Chemistry), vol. 1, 12th ed., Moscow: ONTI Goskhimizdat, 1934, p. 47.

9. Kafarov, V.V. and Meshalkin, V.P., *Analiz i sintez khimiko-tekhnologicheskikh system* (Analysis and Synthesis of Chemical Technological Systems), Moscow: Khimiya, 1991.
10. Al'myasheva, O.V. and Gusarov, V.V., *Fizika i Khimiya Stekla*, 2006, vol. 32, no. 2, pp. 224–229.
11. Al'myasheva, O.V. and Gusarov, V.V., *Zh. Neorg. Khim*., 2007, vol. 52, no. 8, pp. 1194–1196.
12. Al'myasheva, O.V., *Candidate Sci. (Chem.) Dissertation,* St. Peterburg, 2007.
13. Fol'mer, M., *Kinetika obrazovaniya novoi fazy* (Cinetics of a New Phase Formation), Moscow: Nauka, 1986.
14. Chivilikhin, S.A., Popov, I.Yu., and Gusarov, V.V., *Dokl. Akad. Nauk*, 2007, vol. 412, no. 2, pp. 201–203.
15. Pozhidaeva, O.V., Korytkova, E.N., Romanov, D.P., and Gusarov, V.V., *Zh. Obshch. Khim*., 2002, vol. 72, no. 6, pp. 910–914.
16. Al'myasheva, O.V., Korytkova, E.N., Maslov, A.V., and Gusarov, V.V., *Neorg. Mater*., 2005, vol. 41, no. 5, pp. 540–547.
17. Al'myasheva, O.V. and Gusarov, V.V., *Al'ternativnaya Energiya i Ekologiya*, 2007, no. 1, pp. 113–115.
18. Toropov, N.A., Barzakovskii, V.P., Lapin, V.V., and Kurtseva, N.N., *Diagrammy sostoyaniya silikatnykh system. Spravochnik. Vypusk pervyi. Dvoinye sistemy* (Diagrams of State of Silicate Systems. Handbook. Issue 1. Dual Systems), Leningrad: Nauka,1969, pp. 1–822.
19. Al'myasheva, O.V., Vlasov, E.A., Khabenskii, V.B., and Gusarov, V.V., *Zh. Prikl. Khim*., 2009, vol. 82, no. 2, pp. 224
20. Kazin, P.E. and Tret'yakov, Yu.D., *Usp. Khim.*, 2003, vol. 72, no. 10, pp. 960–977.
21. Toropov, N.A. and Galakhov, F.Ya., *Izv. Akad. Nauk SSSR*, *Otd. Khim. Nauk*, 1956, no. 2, p. 158.
22. Tret'yakov, Yu.D., *Tverdofaznye reaktsii* (Solid Phase Reactions), Moscow: Khimiya, 1978.
23. Mazurin, O.A. and Strel'tsina, M.V., and Shvaiko-Shvaikovskaya, T.P., *Svoistva stekol i stekloobrazuyushchikh rasplavov: Spravochnik* (Properties of Glasses and Glass-Forming Melts. Handbook), vol. 1, Leningrad: Nauka, 1973.