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# Synthesis and Properties of Amorphous $SiO_2$ Nanoparticles

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**Abstract**—We have studied the synthesis of amorphous silica nanoparticles through fluorination processing of quartz sand. The results demonstrate that synthesis conditions influence the physicochemical properties of the resultant amorphous silica. We have obtained silica-containing powders 17 to 89 nm in average particle size and 92 to 508 $m^2/g$ in specific surface area.

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## INTRODUCTION

In many areas of science and technology, the past few decades have seen rapid growth in studies based on the use of amorphous silica in relation to its state and purity. Amorphous silica is widely used as a filler for rubber, textile materials, paper, plastics, paints, pigmented lacquers, pharmaceutical substances, and cosmetics; in the production of silicon and silicon ferroalloys; in the growth of quartz single crystals for electronics; in the production of quartz glass, refractories, abrasives, and molds; and as an adsorbent and catalyst in a number of technologies in the chemical, petrochemical, food, and other industries.

Standard methods for the preparation of amorphous silica employ complex, multistep processes and require expensive chemicals and specific raw materials and apparatus [1, 2]. In this context, there is high current interest in developing an economically attractive process for the preparation of amorphous silica nanoparticles from quartz sand, a readily available, inexpensive material containing little harmful impurities.

## EXPERIMENTAL

We studied foundry quartz sand with the following composition (wt %): $SiO_2$, 95.80; $Al_2O_3$, 2.26; $Fe_2O_3$, 0.17; $TiO_2$, 0.23; $Na_2O$, 0.09; $K_2O$, 0.97; loss on ignition, 0.40 (Chalganskoe quartz–kaolin–feldspar sand deposit, Amur oblast, Russia). In our experiments, we used quartz sand ground to a particle size under 0.001 cm.

The sand was fluorinated in a purpose-designed laboratory-scale apparatus, which included a nickel alloy reactor, where the raw material was sintered with ammonium bifluoride ($NH_4HF_2$), and the resultant mixture was heat-treated to give ammonium hexafluorosilicate, $(NH_4)_2SiF_6$. To separate and collect volatile reaction products, we used a two-zone condenser made of stainless steel and Teflon. Ammonia gas was absorbed in a water-filled vessel. Amorphous silica nanoparticles were obtained through precipitation, by adding aqueous ammonia ($NH_4OH$) to an aqueous $(NH_4)_2SiF_6$ solution. The process was run in a laboratory-scale Teflon hydrolizer. $NH_4HF_2$ was regenerated in a laboratory-size evaporator/crystallizer system.

The raw material, intermediate phases, and final products were characterized by chemical analysis, X-ray diffraction, spectral analysis, electron microscopy, differential thermal analysis, and other techniques available at the Amur Mineralogical/Geochemical Research Center, Institute of Geology and Nature Management, Far East Branch, Russian Academy of Sciences.

Elemental analysis of samples was carried out on a Bruker S4 Pioneer spectrometer. Fluorine and ammonia were determined after $H_2SiF_6$ and $NH_3$ removal, by titrating the resultant solutions with thorium nitrate and sulfuric acid, respectively. The phase composition of the samples was determined by X-ray diffraction on an MD-10 EFA X-ray minidiffractometer using ICDD PDF 2008 data. Microimpurities were determined by emission spectroscopy on an STE-1 crossed dispersion spectrograph using pouring in a three-phase arc and evaporation from a carbon channel. Electron-microscopic examination was carried out on a JEOL JSM-6390 LV scanning electron microscope and a SOLVER R47 atomic force microscope (Vladivostok, Russia). Thermogravimetric scans were performed with an STA 449C Jupiter thermal analyzer at a heating rate from 2 to 5°C/min, using lidded platinum crucibles (the initial sample weight was 0.10–0.15 g). The IR spectra of the raw material and amorphous silica were obtained

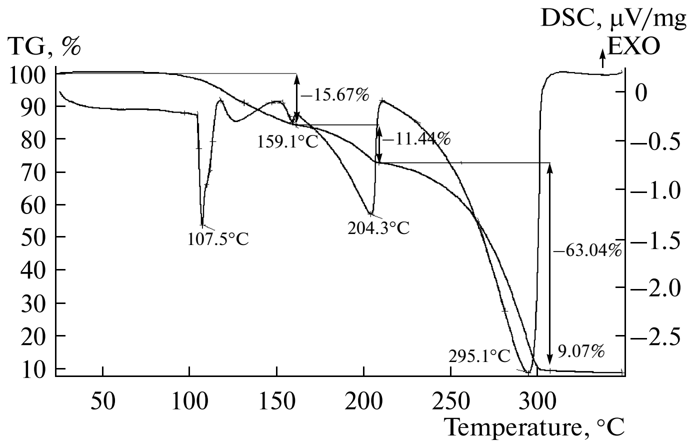

**Fig. 1.** DSC and TG curves for the reaction between quartz sand and ammonium bifluoride.

on an ETIR–Spectrum One spectrophotometer (Perkin Elmer, USA). The specific surface area of the amorphous silica powders was evaluated from nitrogen thermal desorption using a Sorbtometr M specific-surface analyzer (manufactured at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences).

The thermodynamic parameters, rate constants and activation energy of chemical reactions were calculated using the Microsoft Excel 2007 application. Amorphous silica nanoparticles were imaged using the NOVA program and Microsoft Windows Paint application.

## RESULTS AND DISCUSSION

The fluorination processing of quartz sand was studied experimentally in three steps: sintering of the raw material with ammonium bifluoride at temperatures from 100 to 200°C; heat treatment of the resultant powder in the temperature range 300–500°C, resulting in the formation of $(NH_4)_2SiF_6$; and synthesis of amorphous silica nanoparticles at temperatures from 20 to 90°C.

Figure 1 shows differential scanning calorimetry (DSC) and thermogravimetry (TG) curves illustrating the multistep reaction between quartz sand and ammonium bifluoride. Thermodynamic calculations of the corresponding Gibbs energy change suggest that reactions (1) and (2) are possible even at room temperature (Table 1).

The first step is reaction (1), which yields ammonium heptafluorosilicate, $(NH_4)_3SiF_7$. The DSC curve in Fig. 1 shows the corresponding endothermic peak at 107.5°C. Raising the temperature leads to the formation of a mixture of $(NH_4)_3SiF_7$ and ammonium hexafluorosilicate by reaction (2). At 204.3°C, we observe $(NH_4)_2SiF_6$ formation by reaction (3).

In the TG curve in Fig. 1 the weight loss accompanying the endothermic event at 159.1°C is 15.67%, which corresponds to the water and ammonia removal by reaction (1) (calculated weight loss, 16.36%). Raising the temperature leads to the removal of HF and the residual water and ammonia. At 204.3°C, the weight loss evaluated from the TG curve is 11.44%, and the calculated value is 10.93% [reactions (2) and (3)]. The maximum calculated amount of ammonia, 7.17 wt %, was found for reaction (3).

According to the rate constants and activation energies in Table 2, reactions (1)–(3) were kinetically controlled. The rate of the process can be increased by raising the temperature. In molten $NH_4HF_2$ (126.8°C), the reaction has the highest rate. Optimal process conditions can be reached at 200°C in 3.5 h. The ammonia volume evolved then reaches 99% of the theoretical one [3].

During sintering [reactions (1)–(3)], the ammonia gas and water vapor were captured in an aqueous solu-

**Table 1.** Calculated Gibbs energy (kJ) of the chemical reactions underlying the fluorination of quartz sand and the synthesis of silica nanoparticles

| *t*, °C | 25 | 100 | 200 | 300 | 500 |
|---|---|---|---|---|---|
| $2SiO_2 + 7NH_4HF_2 = 2(NH_4)_3SiF_7 + NH_3\uparrow + 4H_2O\uparrow$ (1) | | | | | |
| $\Delta G$ | −39 | −96.45 | −306.05 | −1698.65 | −1851.85 |
| $2SiO_2 + 7NH_4HF_2 = (NH_4)_3SiF_7 + (NH_4)_2SiF_6 + 4H_2O\uparrow + 3NH_3\uparrow + 3HF\uparrow$ (2) | | | | | |
| $\Delta G$ | −36 | −115.5 | −354.5 | −1776.5 | −1988.5 |
| $SiO_2 + 3NH_4HF_2 = (NH_4)_2SiF_6 + 2H_2O\uparrow + NH_3\uparrow$ (3) | | | | | |
| $\Delta G$ | 256 | 181.9 | −49.9 | −1464.7 | −1662.3 |
| $(NH_4)_2SiF_6 + 4NH_4OH = SiO_2\downarrow + 6NH_4F + 2H_2O$ (4) | | | | | |
| $\Delta G$ | −48.7 | −19.1 | 20.3 | 59.7 | 138.6 |
| $2NH_4F = NH_4HF_2 + NH_3\uparrow$ (5) | | | | | |
| $\Delta G$ | 0.5 | −12.0 | −28.7 | −45.4 | −78.8 |

tion to form aqueous ammonia, which was used in the $(NH_4)_2SiF_6$ hydrolysis step. The $NH_3$ and HF released during sintering [reaction (2)] reacted in the second zone of the condenser to form ammonium fluoride, $NH_4F$, which was directed to the evaporator/crystallizer system.

According to X-ray diffraction and chemical analysis data, the powders obtained under reducing or inert conditions at 200°C in 3.5 h consisted of $(NH_4)_2SiF_6$ and Al, Fe, Na, and K compounds, which formed simple fluorides. The $(NH_4)_2SiF_6$ thus obtained was purified by heat treatment. This led to ammonium hexafluorosilicate sublimation, which began at 204.3°C and prevailed at temperatures above 295.1°C, in agreement with previous data [4, 5].

The process had a large rate constant and low activation energy (Table 2). The best temperature for ammonium hexafluorosilicate formation was 500°C: the calculated theoretical amount of this compound was reached in 0.5 h. The volatile compound $(NH_4)_2SiF_6$ was captured and collected in the first zone of the condenser. The resultant fluorides remained precipitated, without subliming.

Electron-microscopic examination showed that the ammonium hexafluorosilicate consisted of platelets less than 100 nm in thickness, which formed fibrous, pyramidal, and dendritic crystalline aggregates. According to spectrochemical analysis data, the $(NH_4)_2SiF_6$ was very pure: the contents of metallic impurities (Al, Fe, Mn, Mg, Cu) were within $10^{-5}$ to $10^{-3}$ wt %. A second sublimation cycle reduced the content of harmful impurities to under $10^{-8}$ to $10^{-6}$ wt %.

Amorphous silica nanoparticles were synthesized at temperatures from 20 to 90°C in an aqueous solution of ammonium hexafluorosilicate (3 to 33 wt %), which was reacted with aqueous ammonia (25 wt % $NH_3$) to give a suspension at pH 8–9. The suspension was left to stand at temperature for 0.5–1.5 h.

Ammonium hexafluorosilicate hydrolyzes in an aqueous alkaline solution by reaction (4) (Table 1). Reaction (4) takes place at room temperature, with $\Delta G_{25} = -48.7$ kJ. Its Gibbs energy increases with temperature: $\Delta G_{100} = -19.1$ kJ.

Boiling down an aqueous $NH_4F$ solution leads to ammonium bifluoride crystallization by reaction (5). The ammonium bifluoride can be used again as a raw material.

It is unreasonable to use ammonium hexafluorosilicate contents below 3 wt %, which lead to the formation of difficult-to-filter $SiO_2$ gel. Raising the $(NH_4)_2SiF_6$ content to above 33 wt % reduces the yield of the process and impairs the quality of the final product. The temperature range used, 20–90°C, was selected because the solvent rapidly vaporized at higher temperatures and the quality of the product was insufficiently high at temperatures below 20°C. Holding the suspension for 1 h at temperatures from 20 to 90°C contributed to gel stabilization and considerably improved the filterability of the gel. The suspension was then filtered and washed with distilled water with mechanical stirring, and the filtrate was dried to constant weight.

**Table 2.** Rate constant $k$ and activation energy $E_a$ for the sintering of quartz sand with ammonium bifluoride and the sublimation of the volatile compound ammonium hexafluorosilicate

| $t$, °C | $k$, min$^{-1}$ | $t$, °C | $k$, min$^{-1}$ |
|---|---|---|---|
| quartz sand sintering | | $(NH_4)_2SiF_6$ sublimation | |
| 100 | 0.002202 | 300 | 0.002268 |
| 150 | 0.005031 | 350 | 0.010620 |
| 175 | 0.006382 | 450 | 0.044069 |
| 200 | 0.008230 | 500 | 0.061729 |
| $E_a$, kJ/mol | 18.3 | | 10.8 |

Figure 2 plots the degree of extraction of amorphous silica against initial ammonium hexafluorosilicate concentration in aqueous solution, which was found as

$$a = (a_p/a_0)C,$$

where $a_p$ is the practical yield of $SiO_2$ gel, $a_0$ is the theoretical yield of $SiO_2$ gel, and $C$ is the amorphous silica content of the $SiO_2$ gel.

It can be seen in Fig. 2 that the degree of extraction of amorphous silica reaches a maximum, 92.36 wt %, in dilute (3 wt % $(NH_4)_2SiF_6$), nearly ideal solutions at

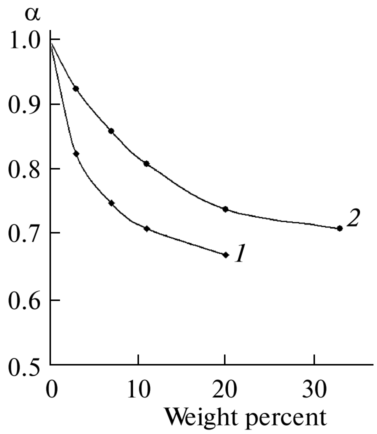

**Fig. 2.** Degree of extraction of amorphous silica against initial ammonium hexafluorosilicate concentration in aqueous solution at (*1*) 25 and (*2*) 80°C.

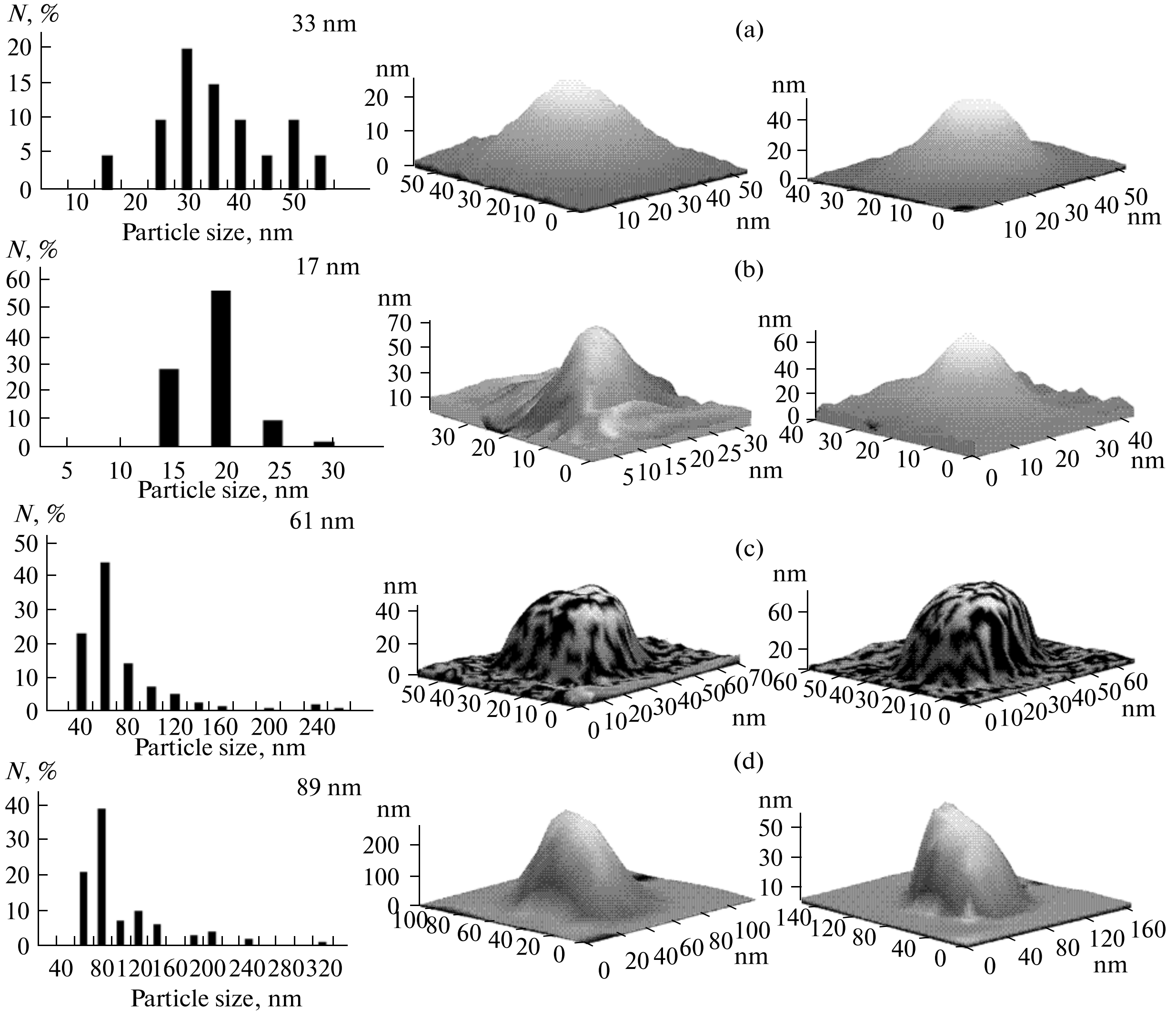

**Fig. 3.** Effect of synthesis conditions on the particle size distribution and three-dimensional images of amorphous silica nanoparticles.

80°C and drops to 71.47 wt % at an $(NH_4)_2SiF_6$ content of 33 wt % and the same temperature. At 25°C, the degree of extraction of amorphous silica is 82.35 wt % at 3 wt % $(NH_4)_2SiF_6$ and drops to 68.53 wt % as the $(NH_4)_2SiF_6$ content increases to 20 wt %. At this temperature, our studies of amorphous silica extraction were limited by the $(NH_4)_2SiF_6$ solubility, which was 20 wt %. Thus, we identified conditions that maximized amorphous silica extraction, which is an important issue in the preparation of this valuable component from various types of mineral raw materials.

From experimental data processing, we obtained the degree of extraction of amorphous silica as a function of temperature in the form of an Arrhenius equation [6]:

$$a = a_0 \exp(E_a/RT).$$

The activation energy was found as

$$E_a = R\Delta \ln a/\Delta(1/T)$$

for each pair of data points in Fig. 2. The average $E_a$ is 1.6 kJ/mol, indicating that reaction (4) is diffusion-limited.

The size of amorphous silica nanoparticles was determined on a SOLVER R47 atomic force microscope (Vladivostok, Russia). The nanoparticles were suspended in high-purity isopropanol placed in a disposable plastic vessel. The suspension was applied to a mica substrate using a mechanical pipette with replaceable tips, which allowed us to avoid mixing of different nanoparticles. In our analyses, we used an NSG 03 cantilever probe, with a nominal tip radius of 10 nm.

Figure 3 illustrates the effect of hydrolysis conditions [reaction (4)] on the particle size distribution and presents three-dimensional images of nanoparticles. The nanoparticles have the smallest average size (17 nm) at

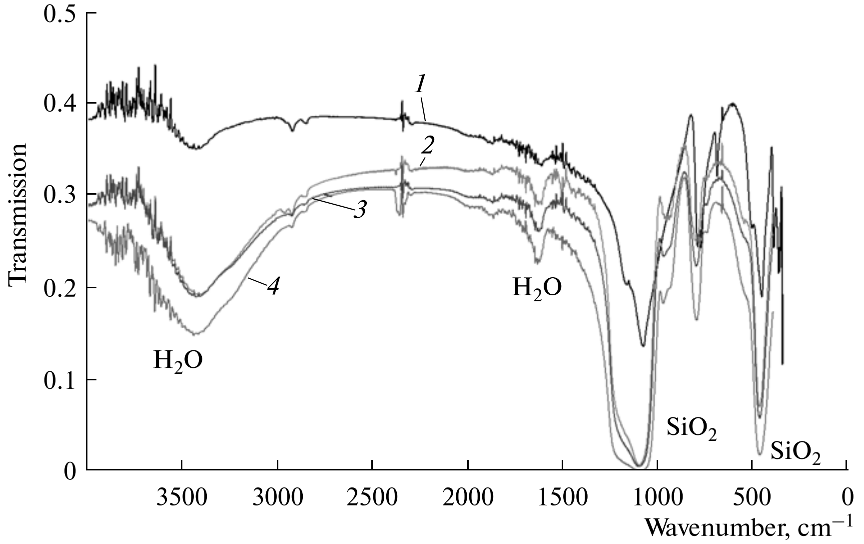

**Fig. 4.** IR spectra of the (*1*) quartz sand and (*2*–*4*) amorphous silica powders prepared at 80°C. The initial $(NH_4)_2SiF_6$ content of aqueous solution was (*2*) 33, (*3*) 20, and (*4*) 3 wt %.

an initial $(NH_4)_2SiF_6$ content of 3 wt % and synthesis temperature of 80°C (Fig. 3b). At a synthesis temperature of 80°C and ammonium hexafluorosilicate contents of 20 and 33 wt %, the average particle size is 61 (Fig. 3c) and 89 nm (Fig. 3d), respectively. At an $(NH_4)_2SiF_6$ content of 3 wt %, lowering the synthesis temperature to 25°C increases the average particle size to 33 nm (Fig. 3a).

Our results demonstrate that, by varying the initial $(NH_4)_2SiF_6$ content of aqueous solution from 3 to 33 wt % and the synthesis temperature from 25 to 80°C, one can increase the specific surface area of the amorphous silica powder from 92 to 508 $m^2/g$ and the specific pore volume from 0.096 to 0.225 $cm^3/g$.

According to chemical analysis data, the silica powders contained trace levels of fluorine and 2.53 to 7.65 wt % water. The loss on ignition ranged from 3.73 to 5.76 wt %, in agreement with previous data [7]. Spectrochemical analysis indicated that the amorphous silica powders contained very little harmful impurities (less than 1 ppm by weight). The X-ray diffraction patterns of the powders showed an amorphous halo, with no crystalline reflections.

The structure of the amorphous silica nanoparticles was studied by infrared spectroscopy [8]. Figure 4 presents the IR spectra of the parent quartz sand and amorphous silica. The line of the quartz sand lies above the lines of the amorphous silica powders, attesting to structural transformations and suggesting that the particle size of the powders depends on synthesis conditions. All of the IR spectra show well-defined $H_2O$ stretching ($\nu = 3250–3550$ $cm^{-1}$) and bending ($\nu = 1600–1650$ $cm^{-1}$) bands.

The spectral range 400 to 1600 $cm^{-1}$ characterizes the structure of atomic groups in the samples studied. Both the parent quartz sand and amorphous silica powders had absorption bands in the range $\nu = 900–1200$ $cm^{-1}$, corresponding to stretches of $SiO_2$ tetrahedra. The absorption bands in the range 720–780 $cm^{-1}$ are due to stretching modes of the $SiO_2$ group, and the bands at $\nu = 500$ $cm^{-1}$ and lower frequencies arise from bending modes of this group.

A comparative analysis of the spectra indicates that the amorphous silica powders prepared at 80°C and low solution concentrations consist of smaller particles in comparison with the samples prepared at 80°C and high solution concentrations.

## CONCLUSIONS

The present results demonstrate that the fluorination processing of ground quartz sand involves three steps: chemical interaction of the raw material with ammonium bifluoride at temperatures from 100 to 200°C, which yields sintered powder; heat treatment of the resultant powder in the temperature range 300–500°C, resulting in the formation of high-purity ammonium hexafluorosilicate; and synthesis of amorphous silica nanoparticles from an aqueous $(NH_4)_2SiF_6$ solution at temperatures from 20 to 90°C. Synthesis conditions influence the physicochemical properties of the resultant amorphous silica and the degree of silica extraction. We have developed an economically attractive process for the preparation of amorphous silica nanoparticles from readily available, inexpensive quartz sands, which involves almost complete ammonium bifluoride recycling.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Rakov, E.G., *Khimiya i tekhnologiya neorganicheskikh ftoridov* (Chemistry and Technology of Inorganic Fluorides), Moscow: Mosk. Khimiko-Tekhnologicheskii Inst., 1990.
2. Zemnukhova, L.A., Sergienko, V.I., Kagan, V.S., and Fedorishcheva, G.A., RF Patent 2 061 656, *Byull. Izobret.*, 1996, no. 16.
3. Rimkevich, V.S., Pushkin, A.A., Malovitskii, Yu.N., and Girenko, I.V., Study of Fluoride Treatment of Silica-Containing Raw Material, *Russ. J. Appl. Chem.*, 2011, vol. 84, no. 3, pp. 345–350.
4. Mel'nichenko, E.I., Krysenko, G.F., Epov, D.G., and Marusova, E.Yu., Thermal Properties of $(NH_4)_2SiF_6$, *Russ. J. Inorg. Chem.*, 2004, vol. 49, no. 12, pp. 1803–1806.
5. Medkov, M.A., Krysenko, G.F., and Epov, D.G., Combined Processing of Datolite Concentrate with Ammonium Bifluoride, *Vestn. Dal'nevost. Otd. Ross. Akad. Nauk*, 2010, no. 5, pp. 63–66.
6. Stromberg, A.G. and Semchenko, D.P., *Fizicheskaya khimiya* (Physical Chemistry), Moscow: Khimiya, 1999.
7. Rimkevich, V.S., Malovitskii, Yu.N., and Dem'yanova, L.P., RF Patent 2 286 947, *Byull. Izobret.*, 1996, no. 31.
8. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.