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NEW TECHNOLOGIES OF PREPARATION AND TREATMENT OF MATERIALS

Effect of Temperature on Annealing Products of Synthesized Opal Matrices

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Abstract—In this paper, we describe the synthesis of opal matrices by the sol-gel method and the α-cristobalite production from them by high-temperature annealing. Both the conditions for preparing synthetic opal matrices by the hydrolysis of tetraethoxysilane in a binary ethanol-water solvent using an ammonia solution as a catalyst and the reagent concentrations for this process are described in detail. The silica particles were prepared by multistage growth to the required size at addition of tetraethoxysilane to the reaction mixture. A temperature regime for drying the siliceous xerogel with the production of porous matrices for further use and annealing to obtain high-purity α-cristobalite is proposed. Structural adjustments, such as an increase in the matrix density, their hardening, and a temperature-dependent change in the matrix porosity, are described. Open-pore matrices consisting of amorphous silicon dioxide are prepared by annealing up to 1100°C. The prepared matrices can later be used for their impregnation with various compositions to obtain various types of sensors, composite materials, and inverted matrices. The transition of a silica xerogel from an amorphous state to a crystalline state with the formation of low-temperature α-cristobalite with an α-tridymite admixture by drying and annealing at 1300°C is shown. Further annealing at 1650°C leads to the formation of a transparent nonporous sample of α-cristobalite. All processes were performed under the control of scanning electron microscopy, Raman spectroscopy, and X-ray diffraction analysis.

Keywords: α-cristobalite, synthetic opals, sol-gel method, Raman spectroscopy, X-ray diffraction analysis, SEM

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INTRODUCTION

Photonic crystals are the most promising materials for the development of new quantum electronics devices. Their use in developing telecommunication systems of the new generation contributes to reducing the attenuation coefficient of optical fibers and creating low-threshold laser emitters of the visible and near-infrared ranges, ultrafast optical switches, amplifiers, filters, high-performance emitters, etc. Photonic crystals are spatially periodic solid-state structures that are characterized by a periodic change in the refractive index in various spatial directions on scales comparable to the wavelength of light. The first materials which were considered as photonic crystals were synthetic opals [1] that are varieties of quartz and SiO_2 nanostructures with certain metals.

At present, the sol-gel method has been widely developed in the production of new generation materials. This allows producing products with new preset properties, controlling the size of the constituent particles, etc. This method is widely used in the preparation of amorphous synthetic opal matrices that can later be used as the basis for the production of various composites and sensors. Composite materials can be produced directly by the sol-gel synthesis or by infiltration of finished opal matrices with various suspensions, salt solutions, etc. [2]. Moreover, if silicon dioxide is removed from the treated opal matrices, an inverted structure based on impregnating components is retained in most cases [3, 4].

One of the ways to use opal matrices is to obtain high-purity α-cristobalite, which is a raw material for quartz glasses and optical fiber and is added as a flour to some types of paints and varnishes. α-cristobalite has good optical characteristics, high hardness (about 6.5 units), and UV resistance. Cristobalite can also be used as a filler for the production of various plastics and artificial stone based on polyester and acrylic resins and in the cable industry; it can serve as a raw material for the production of quartz glass and can be used in ceramics. Natural cristobalite is a rather rare mineral and so synthetic cristobalite is mostly used in industry. Although its synthesis has been widely described in the literature, a universal method for obtaining high-purity cristobalite has not been developed yet.

The sol-gel method that allows controlling the composition and diameter of spherical silicon nanoparticles [5] is mainly used to produce synthetic opal matrices. The most common method for producing monodisperse SiO_2 particles of a certain size is the hydrolysis of tetraalkyl silicates in the presence of a catalyst that was developed by Stöber, Fink, and Bohn [6].

The microstructure of the opal matrices obtained by this method is a dense package of monodisperse amorphous silica balls. This research is aimed at obtaining both synthetic opal matrices for the further possible production of composite materials for various purposes as well as α-cristobalite by high-temperature calcination.

EXPERIMENTAL

Reagents

In the experiment, the following reagents were used: tetraethoxysilane (TEOS, Aldrich) with content of the basic substance of ≥99.0%, ethanol (purum fine spirit, Fluka) with 96% content of the main substance, and ammonia water solution (purity 25-5, Sigma Tek) with content of the basic substance of 25%.

Ethanol was initially dried by boiling under reflux for 3 h in the presence of anhydrous calcium oxide and distilled in a "dry" atmosphere [7]. Calcium oxide was preliminarily annealed at 1100°C for 8 h. Next, the middle fraction of ethyl alcohol was distilled in a "dry" atmosphere with preliminary boiling with metallic magnesium flakes for 2 h and further selection of the middle fraction with a vapor temperature of 78.3°C. The water content in the dried ethanol was determined by amperometric titration with Fisher's reagent and did not exceed 0.002 wt %. Tetraethoxysilane and an ammonia aqueous solution were used without further purification.

Equipment

Scanning electron microscopy (SEM) was performed using a Tescan Vega 3 scanning electron microscope (accelerating voltage of 10 and 20 kV depending on the sample). X-ray diffraction patterns of the samples were obtained using a Bruker D2 PHASER multifunctional X-ray diffractometer equipped with $CoK_{\alpha 1}$ radiation source (λ = 1.788892 Å), monochromatic Bragg–Brentano X-ray optics, zirconium β filter, in the range of angles of 6°–75° (2θ) with a step of 0.020° (2θ). The X-ray scattering intensity was recorded with a LYNXEYE position-sensitive high-performance semiconductor linear detector.

Raman spectra were obtained by using a Renishaw inVia RM1000 spectrometer (excitation: 532-nm laser; registration: CCD detector cooled by a Peltier module) equipped with a 250-mm stigmatic short-focus monochromator, a Leica optical microscope (1000×), and a three-coordinate sample holder.

A high-temperature chamber furnace SNOL 12/16 with a maximum temperature of 1700°C achieved by using chromite lanthanum heaters and a thyristor power supply with microprocessor controller-programmer for 20 ranges was used for drying, calcining, and annealing the samples.
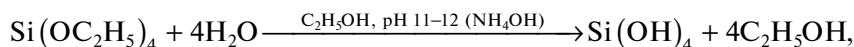
Synthesis

The four-component system of TEOS–water–ethanol–ammonia precursors was chosen as the most suitable for the practical use in preparing xerogels samples and, further, opal matrices. TEOS is known not to mix with water. Therefore, ethanol is used as a solvent in the synthesis. The ammonia solution acts as a catalyst in this reaction. The use of catalysts accelerates the hydrolysis and makes its reaction more complete. Particle sizes are known to be strongly dependent on the hydrolysis conditions [8]. Of great importance is the mixing rate, temperature, composition, and the order of adding reagents. Earlier [9], it was shown that particles closest in size are obtained if the turbulent regime is used when mixing.

The rapid nucleation and uniform growth of colloidal particles with a size of 8–10 nm occur in the TEOS hydrolysis at a large catalyst concentration. Next, aggregation and the growth of particles of amorphous silica occur. This stage can be adjusted by mixing and changing the temperature and pH of the solution. At a low ammonia concentration, a white precipitate of $H_2SiO_3 \cdot H_2O$ does not fall out, and a gel with a regular structure is formed instead [10].
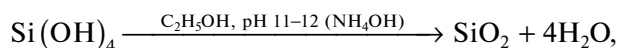
Produced by the sol-gel method when using ammonia as the catalyst, all the opal-like matrices consist of monodisperse spherical particles. The size of the grown particles is determined by both the silica concentration and the chemical kinetics of direct and reverse reactions [11]. The solvent used in hydrolysis and polycondensation during gelation also plays an important role in the formation of the gel structure.

The opal matrices under study were obtained using the modified Stöber-Fink-Bohn method [6]. This method is based on the reaction of hydrolysis of silicon alkoxides in aqueous alcoholic solution in the presence of ammonia as a catalyst. This process is multistage:
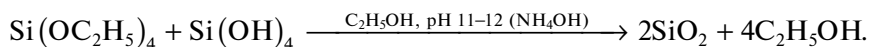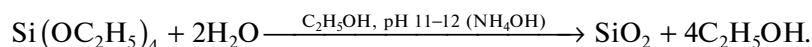
1. Hydrolysis

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{\quad C_2H_5OH,\ pH\ 11-12\ (NH_4OH) \quad} Si(OH)_4 + 4C_2H_5OH,$$

2. Water condensation

$$Si(OH)_4 \xrightarrow{\quad C_2H_5OH,\ pH\ 11-12\ (NH_4OH) \quad} SiO_2 + 4H_2O,$$

3. Alcohol condensation

$$Si(OC_2H_5)_4 + Si(OH)_4 \xrightarrow{\text{C}_2\text{H}_5\text{OH, pH 11–12 (NH}_4\text{OH)}} 2SiO_2 + 4C_2H_5OH.$$

The combination of these processes can be represented as follows:

$$Si(OC_2H_5)_4 + 2H_2O \xrightarrow{\text{C}_2\text{H}_5\text{OH, pH 11–12 (NH}_4\text{OH)}} SiO_2 + 4C_2H_5OH.$$

At the first stage, tetraethoxysilane was hydrolyzed. An aqueous solution of ethanol (16−20 M of water) was prepared, then an aqueous solution of ammonia (1−5 M) was added as a catalyst, and TEOS (0.14 M) was added at the last stage. The ethanol content was ~50% of the mixture. The process was carried out at 50°C with constant stirring for 2 h. Adding TEOS to the mixture was carried out in a multistep manner. The synthesis was carried out using a magnetic stirrer with heating. At mixing of the mixture, a turbulent mode was used. Particles with sizes from 80 nm to 2 μm were obtained by multistep regrowth to the required sizes. The amorphous silica obtained in the previous synthesis step was used as seeds in the next stage. Consequently, additional portions of tetraethoxysilane were added to the reaction vessel [12−14].

After gelling was completed, the suspension was left for natural sedimentation of the obtained silica particles that later formed opal matrices.

The most time-consuming process in obtaining opal-like matrices is drying. The choice of the drying and annealing mode is the key to obtain opal matrices.

Drying, Sintering, and Annealing

The next and most important stage is drying amorphous silica and its annealing. At the first stage, drying is carried out at room temperature in a desiccator under the pressure of saturated ethanol vapor. Ethanol vapors compensate for the hydrostatic pressure of the solvent in the matrix capillaries, thereby protecting the matrix from destruction. The duration of this stage reaches six months depending on the geometric dimensions of the sample.

The next stage of drying is multistage heating.

The heating of the opal matrix prepared for drying was performed according to the mode presented by the temperature curve in Fig. 1.

Gradual heating to 135°C and holding at this temperature for 6 days results in removal from the matrix of the solvent physically unbound to the matrix.

At the next stage of heating (400°C), gradual removal of the organosilicon residues, sorbed water, and the remaining solvent from the pores in the deep of the sample occurs. In the case of incomplete drying at the first stage, the pores can be "sealed," and the remaining moisture in them will break the matrix upon further annealing, while the organic solvent components when burning will change the matrix transparency, making it unsuitable for further use. At the same time, the sample volume is reduced owing to the closer contact of particles.

Annealing at 600°C allows removing bound solvent and organic matter from the matrix without significant changes in the porosity of the structure with some of its hardening [15].

At further heating to temperatures of about 1000°C, a gradual increase in the matrix density with the collapse of the nanopores is observed.

At continued heating to 1100−1200°C, a sharp increase in the opal density occurs. This stage is accompanied by the collapse of micropores and complete sintering of the matrix structural units. As a result, the opal matrix loses the signs of ordering and turns into quartz glass.

After drying, it is necessary to anneal the sample to obtain α-cristobalite. With increasing temperature, its density increases. In the temperature range of 1250−1300°C, the transition of amorphous quartz to β-cristobalite occurs. The latter becomes α-cristobalite upon cooling. This is confirmed by the temperature diagram of phase transitions given in [16]. The transition of β-cristobalite to α-cristobalite is reversible and was previously studied in detail [17]. For the further transition of α-cristobalite to quartz, it is necessary to process it at elevated pressures and temperatures.

Annealing of the obtained matrices for the formation of α-cristobalite was sequentially carried out at 1100, 1300, and 1650°C.
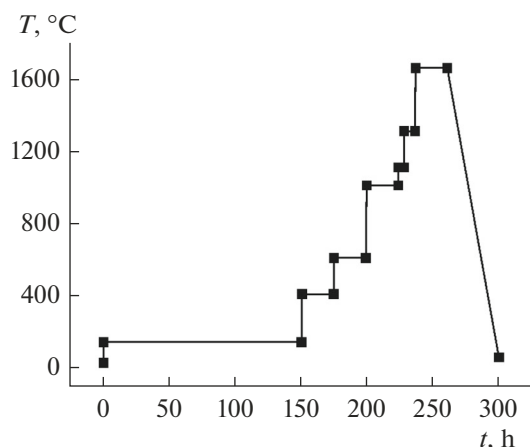

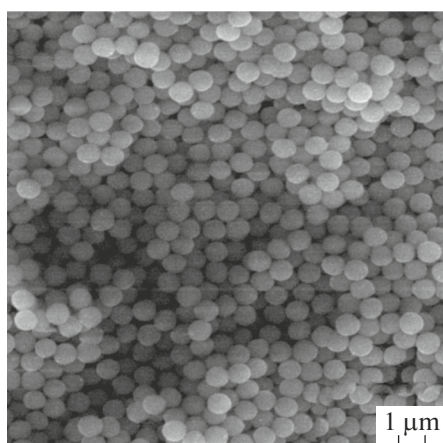**Fig. 1.** Temperature regime of opal matrix drying and annealing.
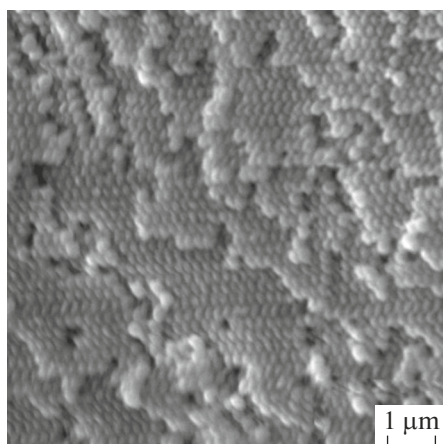
Fig. 2. SEM image of SiO$_2$ sol.

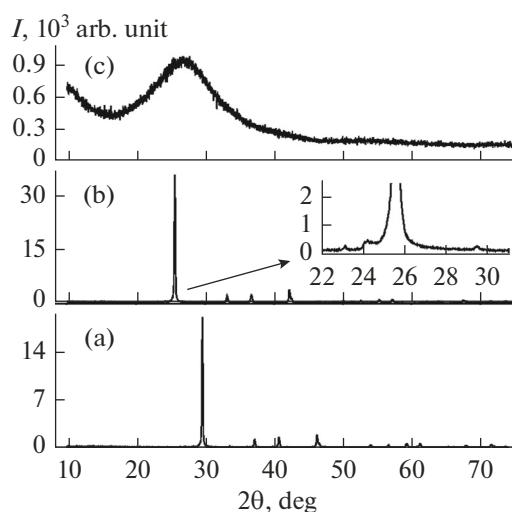**Fig. 3.** SEM image of synthesized opal matrix.

Fig. 4. X-ray spectra of initial opal-like matrix: (a) the heating at 1100°C for 4 h, (b) annealed at 1300°C, and (c) annealed at 1650°C.

RESULTS AND DISCUSSION

To study the obtained matrices, scanning electron microscopy, X-ray diffraction analysis, and Raman spectroscopy were used. The structural and morphological characteristics of the obtained particles were performed by using SEM. A suspension of silica particles was deposited on an aluminum substrate and, after drying at room temperature, was introduced into an electron microscope column. At imaging of the matrices, a thin layer of carbon was deposited on the samples to improve the visualization of the particle structure. SEM images were analyzed to estimate the average size and dispersion of the primary particles of SiO$_2$, the conglomerate of which is a separate sphere. As can be seen in the images, both the sol (Fig. 2) and the dried matrices (Fig. 3) consist of spherical silica particles that are disordered in the case of the sol and ordered for the matrices.

X-ray structural analysis showed that it is possible to obtain both amorphous silicon dioxide and the crystalline form of SiO$_2$, α-cristobalite, depending on the annealing temperature of the opal matrix.

When annealed under mild conditions (up to 1100°C), white matrices of amorphous SiO$_2$ (Figs. 4a and 5a) with open pores are obtained. The open pores allows them to be infiltrated with suspensions containing single-walled carbon nanotubes [18−20] for production of materials of various types.

As can be seen in the radiograph presented in Fig. 4a, when an opal-like matrix is annealed at 1100°C for 4 h, the sample remains completely amorphous since the amorphous halo does not have a crystallinity peak ($2\theta \approx 36°$) appearing at the beginning of the formation of cristobalite, which is in agreement with the study [21].

According to [10], the powder of silica particles remains X-ray amorphous even after annealing at 1100°C for several days. The cristobalite phase appears after annealing at temperatures above 1300°C, as can be seen on the radiographs in Figs. 4b and 4c. Similarly, Raman spectroscopy confirms the amorphism of a SiO$_2$ sample (Fig. 5a). The shape and frequency of the bands with an intensity maximum at 406, 480, 600, and 807 cm^{-1} coincide with the spectrum of amorphous silica given in [22].

The result of further annealing of the dried opal-like matrix at 1300°C is a sample of a milky white color, low-temperature α-cristobalite with an insignificant admixture α-tridymite (reflections 23.170 and 29.511° (2θ) with an intensity of 0.4% and 24.264° (2θ) with an intensity of 0.8%, inset in Fig. 4b). Its X-ray diffraction pattern and Raman spectrum are shown in Figs. 4b and 5b.

Annealing at 1650°C for 24 h leads to structural and phase changes observed in the sample. As a result of annealing, the α-tridymite phase disappears with simultaneous compaction of the SiO$_2$ structure, which results in a transparent nonporous sample of α-cris-
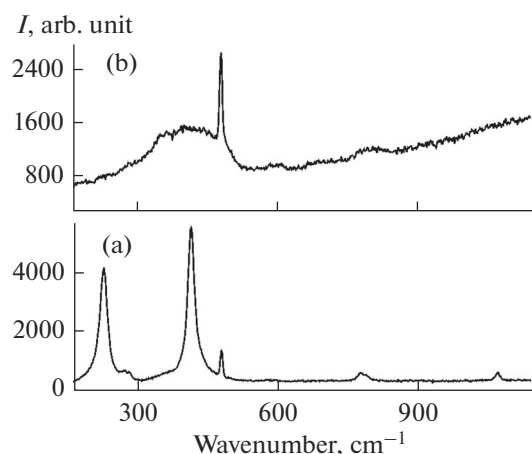
I, arb. unit

Fig. 5. Raman spectra of initial opal-like matrix: (a) the heating at 1100°C for 4 h and (b) annealed at 1300°C.

tobalite (tetragonal syngony, space group P4(1)2(1)2) (Fig. 4c). The type of X-ray pattern coincides with the spectrum of α-cristobalite given in [21].

CONCLUSIONS

An analysis of the published data is given, and various methods of growing and drying synthetic opals that were tested in practice are systematized.

The optimal mode and concentration of precursors for obtaining synthetic opal matrices were selected. The temperature regime of drying and annealing of the synthesized opals was developed and successfully tested. The resulting material can be then used to obtain various composites and as a raw material for the optical production.

As a result of the synthesis and prolonged multistage annealing of opal matrices, high-purity α-cristobalite was obtained.

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