Irreversible phase transitions in structural elements of synthetic opal

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Abstract. The globular photonic crystal of artificial opal was synthesized by Stöber process in order to study its internal structure. Two methods were used to measure density and to determine porosity, which was 0.368. A fractal model of pores formation was considered for different silica phases, including the amorphous one. Assumptions were made on the type of pores inside globules. The differential scanning calorimetry method was used to reveal the fine multisection structure of the heat flow thermogram through the sample. The second-order phase transition was revealed. The experimental substantiation was given that phase transition is connected with the creation of β-cristobalite. A model was proposed for calculation of the number of component molecules leaving a sample at heating. Independent confirmation of calculation as per the proposed model was obtained by the gravimetric analysis.

1. Introduction
The superlattice with a constant of about a half-wavelength is studied for the transition from electronics to photonics. Artificial opal matrices with a forbidden band in the visible spectrum area have the best properties [1]. The photonic crystals highly-homogeneous in globule sizes are necessary for technical implementation. So, the actual task is to study the growth process of such crystals [2].

2. Experiment and discussion
The globular photonic crystal (PC) of artificial silica was synthesized using a self-assembling effect in the frames of the sol-gel technology by Stöber process [3]. The synthesis took place with the following ratio of component moles: TEOS: ethanol: ammonia: water = 1:84:17:170. Stirring rate is approximately 450 rpm with the use of an over-head stirrer, temperature 25 °C. Reactive chemicals of ACS (ultra high purity) grade by “Component-Reactive” company, distilled water. The solution was concentrated and precipitated in a natural way for two months; total volume of components - 100 ml; reaction vessel - cylindrical, made of glass. The sample was tempered at 600°C for three hours.

Sample density of the obtained photonic crystal was measured by two methods - weighing and measurement of geometric parameters in the air, and water displacement method. The values were 1.20±0.03 and 1.90±0.03 g/cm³, respectively.
2.1 Porosity

Let us evaluate the obtained results with the help of the fractal theory. Let us assume that each globule making part of the face-centered cubic (FCC) arrangement consists, in its turn, of smaller solid spheres packed in a similar way. In this case, sample density shall be determined by formula:

\[ \rho = \rho_b (1 - \eta_0)^p, \]

where \( \rho_b \) - density of small spheres, \( \eta_0 \) – porosity coefficient, \( p \) – number corresponding to the number of generations of spheres, beginning from the maximum one. For FCC-arrangement, the porosity coefficient \( \eta_0 \) is 0.26. In order to specify \( p \) value, a calculation was made with the use of densities of different silica phases. The known forms of silica were considered, which have the ordered structure (quartz \( \alpha, \beta \); tridymite \( \alpha, \beta \); cristobalite \( \alpha, \beta \) and amorphous silica - containing and not containing water).

The cases have been analyzed where \( p=1, 2, 3 \). Numeric data on densities of these silica forms are known in literature [4]. Calculation results are given in Table 1.

### Table 1. Analysis of \( p \) value influence on the density of PC consisting of different silica phases.

| \( p \) | Quartz | Tridymite | Cristobalite | \( \text{SiO}_2 \) |
|---|---|---|---|---|
| \( \alpha \) | \( \beta \) | \( \alpha \) | \( \beta \) | \( \alpha \) | \( \beta \) | \( \alpha \) | \( \beta \) | \( n\text{H}_2\text{O} \) |
| 1 | 2.65 | 2.53 | 2.30 | 2.26 | 2.33 | 2.23 | 2.21 | \( \approx 2.10 \) |
| 2 | 1.97 | 1.87 | 1.70 | 1.67 | 1.73 | 1.65 | 1.64 | 1.60 |
| 3 | 1.46 | 1.39 | 1.26 | 1.24 | 1.28 | 1.22 | 1.21 | 1.20 |

The data in Table 1 indicate that the best compliance with the experimental value of density in the air is achieved at \( p=2 \) for amorphous silica containing water.

Taking into account the density obtained by the water displacement method, a calculation was made with the use of porosities of the globular PC.

In this regard, the formula for porosity \( \eta \) was refined while maintaining the condition \( p = 2 \):

\[ \eta = 1 - (1 - \eta_1)(1 - \eta_2), \]

where \( \eta_1 \) - porosity of sample made of globules, \( \eta_2 \) - porosity of small spheres. Then for \( \eta_2 \) we have the formula:

\[ \eta_2 = \frac{\eta - \eta_1}{1 - \eta_1}. \]

It is known that for FCC-arrangement \( \eta_1 = 0.26 \). By using the value for total porosity of the synthesized sample we obtain \( \eta_2 = 0.146 \). Thus, the porosity of small balls which is less than that of FCC-arrangement is indicative of that small balls can be highly deformed and have a wide diameter spread.

In this case, the formula for density is as follows:

\[ \rho = \rho_b (1 - \eta) \]

Using the formula (4) and data of Table 1, let us evaluate the porosity of a structure consisting of different silica types. The data are given in Table 2.

### Table 2. Density of silica phases with account of experimental porosity of the globular PC.

| Phase | Quartz | Tridymite | Cristobalite | \( \text{SiO}_2 \) |
|---|---|---|---|---|
| \( \rho, \text{g/cm}^3 \) | \( \alpha \) | \( \beta \) | \( \alpha \) | \( \beta \) | \( \alpha \) | \( \beta \) | amorphous | \( n\text{H}_2\text{O} \) |
| \( \rho(1-\eta) \) | 1.68 | 1.60 | 1.45 | 1.43 | 1.47 | 1.41 | 1.40 | 1.33 |

From Table 2 it is seen that the synthesized sample has a significantly smaller density than the data represented in the literature on the known silica forms. Porosity determined experimentally by water is attributed to open pores into which water penetrates freely and escapes at heating up to temperatures of approximately 130 °C. Based upon the density of the sample, it contains a significant volume of closed pores. These pores can be considered as nanoreactors in which the process of silica solid phase clusters growth takes place.
2.2. Calorimetric tests

Change in the microstructure of the annealed sample was analyzed at heating from room temperature to a temperature close to the silica melting point. Measured with the help of differential scanning calorimetry (DSC) was the dependency of heat flow passing through the sample to sample weight on the temperature at constant pressure. Measurements were carried out with the help of DSC 404 F1 Pegasus device. The temperature was increased with constant speed 5 deg/min in the inert gas (nitrogen) atmosphere. Measurement speed was 10 m/sec. The thermogram is given in Figure 1. Let us analyze this.

It is known from the literature data that water escapes from the amorphous silica only at temperatures close to 900 °C. So, it was assumed that abnormal dependency of the graph first half is connected with the escape of the liquid phase component molecules that had remained in the sample after annealing. The process was considered with the use of the equation for molecules flow from the sample:

\[ \frac{dN}{dt} = F(t), \]

where \( F(t) \) - heat flow through the sample, normalized to the energy of one molecule leaving the sample. The sample mass decreases gradually. The molecule escape heat determines the endothermic nature of processes up to a temperature of 900 °C.

![Figure 1. Dependence of heat flow through the sample on temperature. Let us consider the first half of Fig. 1, and represent is in the form of a broken line consisting of "j" number of line links marked in Figure 2.](image-url)
Figure 2. Linearization of the initial section fine structure links.

Let us proceed to the theoretical analysis of such section and obtain the equation (5) with an evident right part.

Let us consider the difference in ordinates of the initial and current points on the curve:

$$\Delta A(T) = \frac{1}{m(T_0)} \cdot \left( \frac{dQ}{dT} \right)_{T_0} - \frac{1}{m(T)} \cdot \left( \frac{dQ}{dT} \right)_{T},$$

where $m(T_0), m(T)$ - sample weight in the initial and current point, respectively, \( \left( \frac{dQ}{dT} \right)_{T_0}, \left( \frac{dQ}{dT} \right)_{T} \) - heat flow at the same temperatures.

The value of elementary heat quantity change $\Delta dQ$ depends on the energy $\varepsilon(T)$ and the number $dN$ of molecules which have escaped the sample:

$$\Delta dQ = \varepsilon(T) \cdot dN(T),$$

Let’s normalize the heating temperature to the silica melting point ($T_L$) and represent the molecule heat energy in the form of Taylor’s theorem limited to its three summands:

$$\varepsilon_j(\theta) = 3kT_L \left[ \frac{\theta_j \theta_0}{2} + (\theta - \theta_j) \frac{1}{2} \frac{(\theta - \theta_j)^2}{\theta_j - \theta_j^0} \right],$$

where $k$–Boltzmann’s constant, $\theta_j^0, \theta_j$–normalized initial and final temperature of $j$-th link, $j = 1, 2, 3…j_m$, $m$ – total number of links in the abnormal area.

It should be noted that the escape of molecule s-types takes place at each link. Then we have the following equation:

$$N = N_1 + N_2 + \cdots + N_S = N_1 \cdot \left( 1 + \frac{N_2}{N_1} + \cdots + \frac{N_S}{N_1} \right)$$

With the assumption that the equivalence ratio inside the sample is constant in time, we have:

$$N = N_1 \cdot \left( 1 + \frac{v_2}{v_1} + \cdots + \frac{v_S}{v_1} \right)$$

where $v_1, … , v_S$ - the number of moles of the system components.

The heat flow is: $\frac{dQ}{dT} = b_T \frac{dQ}{dT}$, where $b_T = \frac{dT}{dt}$ – rate of temperature increase, which is constant under the experimental conditions.

Let’s represent the molecules flow in the form of the temperature function:

$$\frac{dN}{dT} = \frac{dN}{dF(T)} \cdot \frac{dF(T)}{dT} = b_T \cdot \frac{dN}{dT}$$

Then the equation (5) shall transform as follows:
For small quantity of sample weight change within the link after summing the equalities (6) - (11) the explicit form of equation (5) can be obtained:

$$\frac{dN_1}{d\theta} = \frac{m_0 T L \Delta A(\theta)}{b_T \left(1 + \frac{v_2}{v_1}\right) e(\theta)}$$  \hspace{1cm} (12)

The equation (12) determines the continuous function for the first link of the graph. For j-th link:

$$\Delta A(\theta) = \frac{\Delta A_j(\theta_j)}{(\theta_{j1} - \theta_{j0})}$$  \hspace{1cm} (13)

The following approximate equality was used at integration of the equation (12):

$$\theta - \theta_0 \approx \frac{2}{3} \theta_1 (\theta_1 - \theta_0).$$

Obtained eventually was the expression for calculation of the number of the first grade molecules which have escaped the sample at the j-th link:

$$N_{1j}(\theta_j) = \frac{2}{9} m_{j0} \frac{\Delta A_{j1}(\theta_j)}{b_T k \theta_j \left(1 + \frac{v_2}{v_1}\right)}$$  \hspace{1cm} (14)

The relative loss of the sample weight at the j-th link shall be expressed as follows:

$$\eta_j = \frac{\Delta m_j}{m_{j0}} = \frac{2}{9} \left(1 + \frac{v_2}{v_1}\right) M_1 \frac{\Delta A_{j1}(\theta_j)}{b_T k \theta_{j1} \left(1 + \frac{v_2}{v_1}\right)}$$  \hspace{1cm} (15)

where $M_1, M_2$ - mole weight of the corresponding components, $N_A$ - Avogadro's number. The data of thermal calculation of the relative weight loss are given in Table 3, where $\eta_\Sigma = 1 - \prod_{j=1}^{n} (1 - \eta_j)$.

Let us compare the data in Table 3 with the results of the thermogravimetric analysis carried out for this sample and represented in Figure 3.

| Table 3. Thermal calculation of the relative weight loss. |
|---------------------------------------------------------|
| Link $j$ | Initial temperature $T_{j0}$, K | Final temperature $T_{j1}$, K | Amount of weight loss at the link $\eta_j$ | Total amount of weight loss $\eta_\Sigma$ |
|----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 1        | 373                         | 523                         | 0.093                       | 0.093                       |
| 2        | 523                         | 653                         | 0.082                       | 0.167                       |
| 3        | 653                         | 793                         | 0.138                       | 0.280                       |
| 4        | 793                         | 893                         | 0.085                       | 0.342                       |
| 5        | 893                         | 993                         | 0.076                       | 0.392                       |
| 6        | 993                         | 1073                        | 0.025                       | 0.407                       |
Figure 3. Relative decrease in sample weight at heating.

Highlighted in Figure 3 are the areas corresponding to the first two links of the broken line represented in Figure 2. The calculation data from Table 3 are marked with blackened circles, and linear sections are shown dashed. The experimental curve is a solid line. Comparison of the theory and the experiment was carried out beginning from a temperature of 373 K. This temperature was taken as the initial one for the 1st link marked in Figure 2. Loss of sample weight at a temperature of 523 K is $(12 \pm 1)\%$ according to experimental data; the calculation gives $(9 \pm 1)\%$. Loss of weight to the end of the 2nd link is $(21 \pm 1)\%$ as per the experiment; $(17 \pm 2)\%$ as per the calculation. Taking into account the calculation accuracy and experimental error, the results are in a satisfactory fit.

Let us analyze the ascending part of the experimental curve in Figures 1 and 2. It consists of non-linear links among which there is a peak characteristic of the second-order phase transition. It is convenient to consider the graph ordinate for this section with an account of thermo-dynamic conformities. According to the first law of thermodynamics we have: $dQ = C_v dT + p dV$, then the ordinate shall be expressed by the following formula: $\frac{1}{\gamma} \frac{dQ}{dt} = \frac{b_T}{m} \left( C_v + \frac{pdV}{dt} \right)$. With the normal atmospheric pressure, the second summand for solid bodies is significantly less than the first one, so further we consider that the ordinate is proportional to the heat capacity with the constant volume. The sample weight in this section remains constant. Then the graph ordinate determines the sample heat capacity; and since it has a step-like peak, we consider that the phase transition being observed is the second-order transition. The peak marked in this section corresponds to the heat capacity jump at the transition of hexagonal segments existing in the sample into the $\beta$-cristobalite phase [6]. This fact is confirmed by detection of the $\beta$-cristobalite phase transition into $\alpha$ modification taking place at a temperature of 210 °C at the cooling curve represented in Figure 4, according to Fenner's diagram [7]. The similar transition is revealed in the study [8] while examining the samples by means of neutrons.

To our opinion, transitions between individual non-linear sections are connected with the change in orientation of individual segments of the amorphous silica system.
Figure 4. Cooling and heating curves of the studied sample.

Observed on the cooling curve, in relation to the heating curve, is a minimum shift, changes in positions of the studied links of the broken line at temperatures below 800 °C.

3. Conclusions

1. The obtained sample represents the amorphous silica inside which segments containing the liquid phase components are present. Evaporation of these components leads to the abnormal form of dependence of the heat flow per weight unit on temperature.

2. Observed in the obtained dependence are linear links for which the sample weight losses are calculated. These results are confirmed at initial sections by independent thermal-gravimetric measurements.

3. Proposed is the dependence of heat energy of molecules leaving the sample on temperature.

4. The second-order phase transition from amorphous silica to β-cristobalite is recorded, which is indicative of a presence of hexagonal segments in the synthesized sample.

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