INTRODUCTION

Natural and artificial opals are packets of quartz spheres with a diameter greatly exceeding the interatomic distances in quartz [1]. They contain a certain amount of water and belong to the photonic crystal family. It is known [2] that, when affected by temperature and pressure, quartz undergoes many polymorphic transformations to $\alpha$ and $\beta$ quartz, tridymite, and $\alpha$ and $\beta$ cristobalite upon temperature variation and to coesite and stishovite at high pressures. The aim of this study was to investigate the structure of artificial opals in order to clarify structural transformations that occur in artificial opals affected by temperature and pressure.

EXPERIMENTAL

Experimental samples were pieces of white opals with inherent irisation (Technomash).

The samples were fabricated by the deposition of an opal–like precipitate from a monodisperse suspension, preliminarily prepared by the hydrolysis reaction of tetraethoxysilane (TEOS) in an alcohol–ammonia medium containing amorphous spherical silica globules, with the subsequent drying, thermal treatment of the precipitate, and impregnation by silica sol. The thermal treatment involved pneumatolytic annealing in water vapor for 2–10 h at temperatures of $350–400^\circ C$ and pressures of $80–200$ atm and repeated annealing at $400–600^\circ C$ for 1–2 h after the silica sol impregnation. The amount of silica sol used for impregnation ensured a vitreous silica content of 5–15 vol % of the total amount of silica in the product after repeated annealing.

The large- and small-scale structural characteristics of the synthetic opals were determined using small-angle neutron and synchrotron diffraction methods and neutron diffractometry. Small-angle neutron scattering was investigated on a STOIK neutron spectrometer [4], IR-8 reactor, and Mediana and STM stations of the Kurchatov synchrotron radiation source; the diffractometry investigations were carried out on a DISK multidetector neutron diffractometer [5]. Possible phase transformations were investigated by microcalorimetry and thermogravimetry on an STA 49C facility.

RESULTS

It can be seen in Fig. 1 that the small-angle synchrotron diffraction pattern obtained on a double-crystal spectrometer contains peaks at scattering angles of several tens of seconds of arc. Similar peaks appear in the small-angle neutron diffraction patterns; they correspond to the formation of a cubic superlattice with a period close to that of the light wave (see the table).
The small-scale structure of the opals was studied by neutron diffractometry. In the neutron pattern in Fig. 2, one can see several amorphous halos and an enhanced incoherent background, which is obviously related to the water-containing component, and small-angle scattering indicative of inhomogeneities. Comparison of the halo positions with the positions of the strongest lines in the diffraction patterns of different quartz crystal modifications showed that they correspond only to the lines of the highest temperature modification, i.e., $\beta$ cristobalite (Fig. 3). If the opals were based on quartz rather than on cristobalite, the halos in the neutron pattern would correspond to the halos in the positions of the strongest lines of $\alpha$-quartz.

The data show that the opals produced by the above-described technology should be called cristobalite rather than quartz opals.

**TEMPERATURE EFFECT**

Since cristobalite is the highest temperature quartz modification, no polymorphic transformations characteristic of the low-temperature modification should be expected during its heating. Indeed, the microcalorimetry and gravimetry data (Fig. 4) show no phase transformations, except for those at 200 and 800°C, which are accompanied by mass loss and are, apparently, related to the loss of water and water-containing component. These effects are not observed upon repeated heating (Fig. 5). In this case, the incoherent scattering background related to hydrogen disappears from the neutron patterns, and the positions of some halos slightly shift toward larger scattering angles. Thus, the water-containing component is lost upon heating. Upon annealing at 800 and 1000°C, the opal changes color from white to blue, with irisation retained (Fig. 6).

Sometimes, depending on the thermal treatment regime, black areas arise in blue opals and additional diffraction lines occur in neutron patterns which correspond to $\beta$-cristobalite and indicate the partial crystallization of the opals in the temperature range where crystalline cristobalite is thermodynamically unstable. This proves again the cristobalite character of the synthetic opals under study. With a further increase in annealing temperature to 1150°C, the cristobalite-

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![Fig. 2. Neutron diffraction patterns of the SiO₂-based synthetic photonic crystal: (1) initial synthetic crystal and (2) blue opal obtained at SiO₂.]