POROUS STRUCTURE OF SYNTHETIC OPALS

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Abstract: The apparent density, porosity, specific surface and annihilation characteristics of positronium were measured for synthetic opals. It was shown that the total porosity consists of micropores and nanopores connected with narrow channels, which are closing under opal heat treatment. The sizes of primary SiO_2 particles and nanopores were estimated.

Synthetic opals are candidates for producing photonic crystals [1] and various nanocompositions on the base of spatially ordered dielectric matrix. The microstructure of opals is defined as close-packed monodisperse spheres of amorphous silicon dioxide, i.e. comparable with the wavelength of light. The voids between the spheres form a system of micropores whose volume fraction is 26% (the model of contacting undeformed spheres [2]). The density measurements of the initial (not subjected to high temperature annealing) opals [3] been witness to the presence in them of additional porosity possibly related to the spheres substructure. In fact, it has been repeatedly argued that the spheres in question consist, in turn, of finer α-SiO_2 particles [3, 4] the voids between which form a system of nanopores. The information on this system's parameters (the related specific surface, characteristic sizes of nanovoids, "adsorptive" capacitance with respect to a particular adsorbate, etc.) is of prime importance for the a priori modeling of an opal-based composite. The goal of this work was to derive precisely such information. In our study we employed along with the traditional adsorption and structural methods (BET, gravimetry, electron microscopy) the original method of electron-positron annihilation which is sensitive to the presence of voids of sub- and nanometer scale [5].

The α-SiO_2 particles were synthesized using SFB's technique [6, 7]. The objects to be examined were opals consisting of spheres 160 and 900 nm in dia, both initial (dried at a temperature 150^0C to remov e water) and annealed at 800^0C (900 nm) and 1020^0C (260 nm). For comparison, we additionally examined samples of natural opal sintered at 1200^0C and of commercial quartz glass. Generally the samples were plates measuring 15x15x2 mm. We measured the apparent density ρ_a (by the hydrostatic weighting technique), the kinetic curves of water

evaporation from opals, the isotherms of nitrogen adsorption, the angular correlation of annihilation radiation (ACAR) upon positron injection into the samples being investigated. The α-SiO_2 spheres substructure was revealed through measurements on a transmission electron microscope JEM-100CX. Based on those measurements, we defined the following parameters: the total porosity ε = 1 - ρ_a /ρ_t (ρ_t = 2.22 g/cm^3 being the true porosity of α-SiO_2), "liquid" porosity ε' (relative sample volume accessible for a particular liquid), characteristic times τ of water evaporation from opals, specific surface S_{BET} of opals, the sizes of nanopores (from the analysis of the ACAR spectra) the sizes of primary SiO_2 particles (from the analysis of the electron microscopic images). In the table are listed the values obtained by us for the main parameters of the adsorption and annihilation characteristics of the samples under study. The ε' values were defined for four liquids (H_2O, C_2H_5OH, C_7H_8, CCl_4) but only water and ethyl alcohol appear in the table because the results for the three "large-molecule" liquids are practically coincident. The comparison of the ε and ε' values shows that the initial opal samples demonstrate the molecular-sieve effect: small water molecules fill micro- and nanopores whereas for larger molecules the system of nanopores is unaccessible. For the annealed opals the ε' values are the same for all molecules and noticeably smaller than the corresponding ε values. It may be assumed that the nanopores are separated from the micropores by annealing, get jointed first of all.

Table. Values of the apparent density ρ_a, total (ε) and liquid (ε') porosity, specific surface S_{BET}, halfwidths of the broad (Γ_B) and narrow (Γ_B) components of the ACAR spectrum, intensity of the narrow component I_N and mean diameter of the nanopores D_{mean} for the investigated opal and quartz glass samples.

Sample	ρ_a, g/cm^3	ε, %	ε' (water), %	ε' (ethyl alcohol) %	S_{BET}, m^2/g	Γ_B, mrad	Γ_N, mrad	I_N, %	D_{mean}, nm
Opal natural	1.95	11.8	-	-	-	10.2	3.22	11.4	0.76
Opal sintered	2.23	-	-	-	-	10.4	3.80	14.4	0.58
Quartz glass	2.21	-	-	-	-	10.4	3.70	15.3	0.60
Opal 900 nm (800^{0}C)	1.31	41.0	28.0	29.6	3.52 (3.05)	10.2	2.44	18.6	1.16
Opal 260 nm (150°C)	1.15	48.2	46.0	34.5	14.3 (15.0)	10.1	2.90	9.60	0.89
Opal 260 nm (1020°C)	1.40	37.0	32.5	32.3	12.7 (12.3)	10.3	2.16	13.9	1.40

The S_{BET} values, listed in the table, fairly agree with the calculated S_{calc} values into account only the outer surface of the SiO_2 spheres. This implies that in the initial opals nanopores are

unaccessible even for nitrogen molecules which are just slightly larger than the water molecules (nitrogen molecule is 0.37 nm in dia, water molecule is 0.26 nm in dia) [8]. Note, that the closeness of the S_{BET} and S_{calc} values was reported in the work [9] for opals with the sphere of diameter 500 nm.

It should be remembered in analyzing the annihilation characteristics that the broad ACAR spectrum component is stipulated by annihilation of positrons with outer valence electrons, and in the case of silicon dioxide its halfwidth Γ_B is governed by the chemical Si-O bond parameters which can differ for the surface and bulk atoms. The closeness of the Γ_B values for all the investigated samples evidences for an insignificant influence of the surface bonds on the broad component parameters in opals. On the contrary, the narrow component is

connected exclusively with the occurrence of structural defects: in quartz crystals this component is absent ($I_N = 0$) whereas in fused quartz (quartz glass) it is quite intensive [10]. It is seen from the table that in opals as well I_N reaches large values (15-20%). The narrow component is stipulated by annihilation of positronium atoms localized in the nanopores, its Γ_N halfwidth being connected with the nanopores size. We used the Γ_N values to calculate the mean diameters of the nanopores (on the assumption that they are spherical in shape). These are listed in the last column of the table. The nanopores sizes in quartz glass are seen to be much smaller than in opals. It is natural to suggest that in the latter case the nanopores are voids between the above mentioned α-SiO_2 particles constituting the spheres. This suggestion is supported by our electron-microscope results. Fig.1 demonstrates the image of the sphere edge from which it is inferred that the size of the spheric SiO_2 particles is approximately 5-7 nm. These particles being close-packed, the voids between them will measure 1.5-2.0 nm, in good agreement with the nanopores sizes in opals, listed in the table.
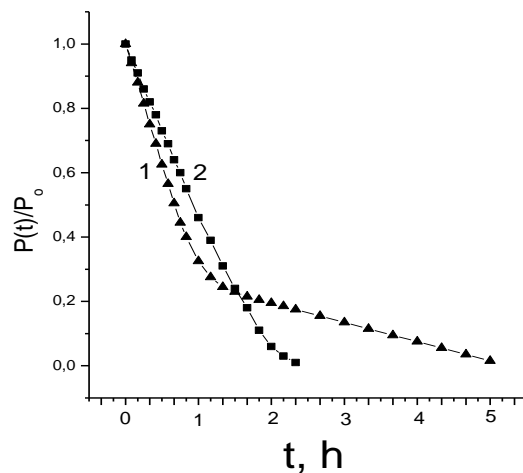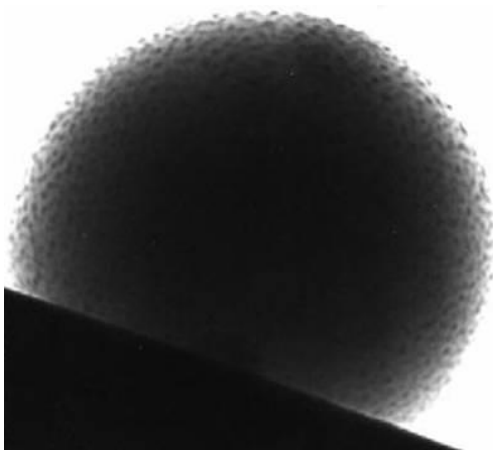

Fig.1 TEM image of the 225 nm dia α- SiO_2 sphere. Fig.2 Kinetics of water evaporation from opal samples: *1 –* initial, *2 –* annealed.

The above said idea of the system of nanopores separated from the micropores by narrow channels has been convincingly supported by the measurements of the kinetic curves for the water escape from opals due to its natural evaporation at 20^OC (see fig.2). For the annealed sample (curve 2) the evaporation time $\tau \cong 2$h, for the initial one (curve 1) $\tau \cong 5$h (with the same sample shape). Such a great τ in the initial samples may be attributed to show diffusion of water molecules from nanopores via the narrow channels. In the process of annealing the opals the channels join and water does not get into the nanopores.

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