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ScienceDirect
Mendeleev Commun., 2004, 14(4), 165–167

Mendeleev Communications

Synthesis and microstructure of silica photonic crystals

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DOI: 10.1070/MC2004v014n04ABEH001968

Synthetic opals based on monodisperse 270 nm diameter silica microspheres were synthesised, and their microstructure and optical properties were studied.

Photonic crystals are dielectric materials with a highly periodic structure in which the refractive index varies on a scale of light wavelengths.[1,2] Being transparent for a wide range of electromagnetic waves, a photonic crystal does not permit light with a certain wavelength to propagate through it due to Bragg diffraction if the wavelength is close to the lattice spacing of the photonic crystal. Hence, photonic crystals are expected to be optical analogues of semiconductors having an optical wavelength band gap termed as a photonic band gap (PBG). The potential applications of photonic crystals are highly prospective ranging from high performance light-emitting diodes and optical fibers to low-power microlasers and photonic very large scale integration (VLSI) systems.[3]

Opals are the first naturally observed photonic crystals composed of the fcc arrangement of monodisperse amorphous silica spheres with similar (relative standard deviations lower than 5%) diameters of 150–900 nm.[4] However, the refractive index ratio n_{silica}/n_{air} up to 1.487 (cristobalite) or even 1.544 (quartz) is below the value actually needed for a full PBG.[5,6] Nevertheless, the existence of photonic pseudogaps or nonoverlapping gaps in ordered monodisperse silica spheres was demonstrated.[7,8] For this reason, synthetic opals can be regarded as suitable models for studying the photonic properties of PBG materials. The aim of this work was to synthesise high-quality silica photonic crystals and to study their microstructure and optical properties.

Monodisperse silica microspheres were synthesised through the hydrolysis of tetraethoxysilane $Si(OEt)_4$ (98%, Aldrich) in a water–ethanol liquor in the presence of ammonium hydroxide as a catalyst. Microspheres with an average diameter of 270 nm and a relative standard deviation of about 5% were obtained under the strict control of reaction conditions.[9] The molar ratio of components in the reaction mixture was NH_3:H_2O:EtOH:$Si(OEt)_4$ = 1:20:11:0.1. The size and the size distribution of microspheres were calculated from SEM images. Over 300 spheres were sized using SEM in order to obtain data for statistical calculations.

In order to produce materials with a long-range order of microspheres, suspensions of particles with a narrow size distribution are preferable. Therefore, preliminary separation of microspheres according to size was performed in a gravitational field. After the synthesis, the suspension of particles was diluted with distilled water and left undisturbed in a burette sealed to avoid evaporation and pollution. Obviously, the sedimentation

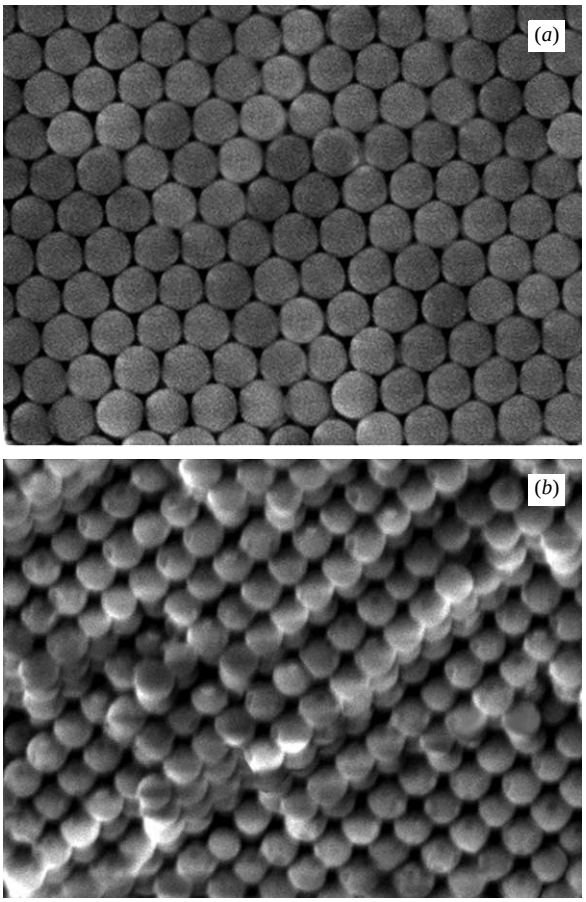

Figure 1 SEM images of the sample of opal made of 270 nm spheres: (*a*) image of the surface in <111> growth direction and (*b*) several (100) planes of an fcc lattice.

rate of heavy particles is greater than that of light particles. Therefore, the size distribution of microspheres in any fixed horizontal layer of the suspension becomes more and more narrow with time. Afterwards, a chosen suspension layer with a desirable size distribution can be separated and then used for the preparation of photonic crystals.

According to SEM data, the above procedure allowed us to produce suspensions of silica microspheres with relative standard deviations of about 2–3%, and these values were in a good agreement with the results of preliminary estimations.

Sedimentation relying solely on gravity is a very slow process, requiring typically weeks or months, especially if sphere diameters are smaller than 300 nm,[10] as in our case. However, even very slow sedimentation results in polycrystalline opals with disoriented domains of varying sizes. Therefore, in order to produce quasi-three-periodic structures of silica microspheres, we used natural sedimentation[10,11] combined with solvent evaporation.[12] To improve the mechanical properties of the materials thus produced and to increase the refractive index ratio n_2/n_1 up to 1.470–1.487, the samples were finally sintered at a relatively high temperature of ~600–700 °C. Optimal time–temperature conditions of sintering were determined by thermal analysis.

The SEM image of a surface layer of the samples is shown in Figure 1(*a*). Silica particles are stuck in a close-packed arrangement with each sphere neighbouring six others in a layer. Although such images confirm a relatively regular close-packed arrangement, they cannot be used to distinguish between the face-centered cubic (fcc, ABCABC…) and hexagonal close-packed (hcp, ABABAB…) structures. However, according to theoretical calculations, the equilibrium structure of a colloidal crystal made of hard spheres is known to be fcc, although an entropy difference between the fcc and hcp structures is quite small.[13] Experimentally, the preferred fcc 'crystallization' for three-dimensional arrangements of silica microspheres was confirmed in previous publications,[7,8] as well as in this work. One of the typical SEM images of characteristic (100) planes of a fcc structure is shown in Figure 1(*b*). Therefore, we assumed that our spheres were packed in the fcc arrangement when analysing optical measurement results.

The presence of different defects is typical of photonic crystals as for crystals with atomic, ionic and molecular bondings. Point defects are typically seen at intervals of hundreds of unit cells [Figure 2(*a*)]. Some examples of line defects are shown in Figure 2(*a*) (low-angle boundaries) and Figure 2(*b*) (the shift of the microsphere rows could happen because of some intrinsic stresses). The SEM images indicate the presence of disordered regions dividing well-ordered domains [Figure 2(*c*)]. Such a domain structure is not a result of incorrect actions in a synthetic sequence but forms due to the mechanism of fcc stacking formation in the sedimentation process. Formation of a layer begins at several different points onto the surface where first particles have been settled. Several silica microspheres already ordered in a close-packed arrangement compose a nucleus for further 'crystallization' (self-assembling). This well-ordered region influences the neighbouring particles and causes the motion of a crystallization front. Note that every well-ordered region grows

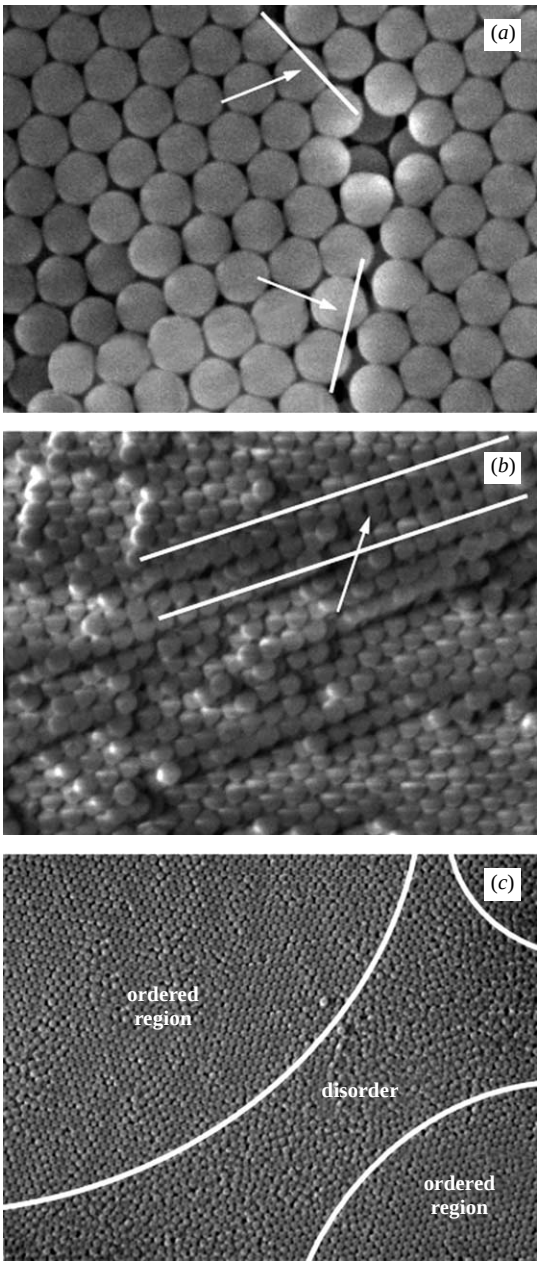

Figure 2 Defects in the fcc arrangement of silica microspheres: (*a*) vacancies and low-angle boundaries (indicated by arrows); (*b*) line defect similar to stacking fault (indicated by an arrow) and (*c*) domains and intermediate disordered regions.

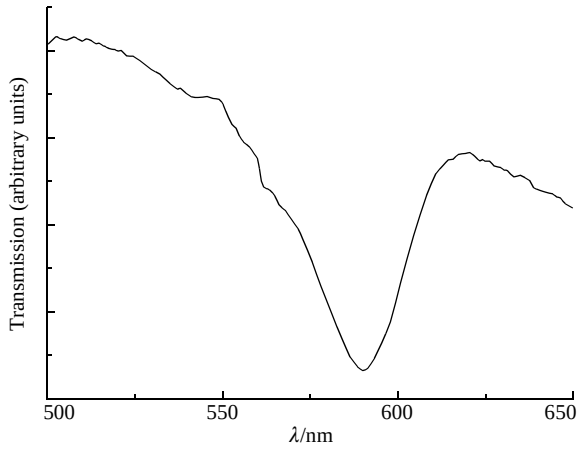

Figure 3 Transmission spectrum of the opal sample taken at normal incidence to the (111) plane.

independently; therefore, the interaction of different crystallization fronts results in the formation of disordered regions with high- and low-angle boundaries between the domains.

In general, it was shown that the mechanisms of defect formation in the packings of microspheres could be other than that in crystals with atomic, ionic and molecular bonding. The ratio between defects of various types was different from that in 'usual' crystals.

Despite the presence of all the above defects, the samples exhibited strong photonic properties. Lattice constants in the crystalline sediment were of the order of the wavelength of visible light. Therefore, the dried and annealed samples possessed bright iridescence. The surface of samples looked brightly red at some angles confirming the results of transmission measurements.

A typical transmission spectrum from opal samples acquired at normal incidence to the (111) plane is shown in Figure 3. The absence of a peak from the transmission spectra of samples with a mechanically destroyed periodicity could mean that this minimum can be interpreted as a reflection from periodical planes in the fcc structure. We can estimate the position of this peak using the Bragg law for normal incidence:

$$2dn\sin\theta = k\lambda, \quad (1)$$

where d is the interplanar spacing, θ is the angle measured in the direction of light incidence to the planes, k is the order of diffraction (k = 1, 2, 3...), and λ is the wavelength of radiation in a vacuum. We used the effective (average) refractive index n of the silica–air medium as a function of wavelength:

$$n = n_{\text{silica}}(\lambda)f_{\text{silica}} + n_{\text{air}}(1 - f_{\text{silica}}), \quad (2)$$

where $f_{\text{silica}} \approx 74\%$ is the volume fraction occupied by silica in a close packed structure, and $n_{\text{air}} \approx 1$. It was found that the peak is caused by first-order diffraction from (111) planes of the fcc structure. The calculated wavelength of diffracted light is λ = 593 nm, whereas the centre of the peak observed is at ~591 nm (Figure 3). This minimum also corresponds to the first pseudogap at the L-point of a photonic band structure.[6] The relative stop-band width of $\Delta\lambda/\lambda_0$, where $\Delta\lambda$ is the peak width at half-maximum, and λ_0 is the centre wavelength of the peak, is about 0.06.

These well-ordered silica opals are promising materials for photonics, and they can also be used as templates for the synthesis of inverted opal-based structures filled with high-refractive-index materials.[11,14]

This work was supported by the Russian State Programme 'Universities of Russia' (grant no. UR.06.02.001). We are grateful to E. A. Goodilin for valuable discussions.

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Received: 4th June 2004; Com. 04/2293