Determination of void arrangements in inverse opals by transmission electron microscopy

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Abstract. Three-dimensionally ordered macroporous (3DOM) materials, also known as inverse opals, have been extensively investigated for use as photonic crystals that operate in the visible and near-IR region of the spectrum. Because the template for 3DOM materials is made by a colloidal self-assembly process, they can easily incorporate defects that degrade or eliminate their desired light-restricting properties. We have developed a method that uses transmission electron microscopy (TEM) to probe the interior of individual sections of 3DOM photonic crystals by bright-field imaging followed by two-dimensional Fourier image analysis. The technique permits the viewing of stacking faults in the crystal. Analysis of samples of 3DOM ceramics has allowed us to confirm that the voids in the structures are arranged on the points of a face-centred cubic lattice.

1. Introduction

Photonic crystals are dielectric materials that have a periodic variation in their refractive index in one, two, or three dimensions. The structure of the photonic crystal controls the dispersion of light (or other electromagnetic radiation) with a wavelength comparable to the crystal’s repeat distance [1]. Interest in photonic crystals centres on their ability to restrict, guide, and confine light.

Three-dimensionally ordered macroporous (3DOM) materials are one type of photonic crystal made from a colloidal crystal template. Colloidal crystals consist of a three-dimensional arrangement of uniformly sized spheres. In opals, these colloidal crystals are comprised of hydrated silica beads arranged along face-centred cubic (fcc) lattice points. The iridescence of opals is a result of the diffraction of light off the planes of spheres in the structure [2]. To make 3DOM materials, the empty space of an artificial opal is replaced with a second material, then the original opal is removed chemically or thermally [3]. These “inverse opals” offer enhanced photonic properties, including the possibility of a full, three-dimensional photonic band gap, in which a range of wavelengths is forbidden from propagating in any direction [4].

The self-assembly process that creates the template for 3DOM materials is, however, prone to spontaneously occurring point defects and stacking faults that degrade or eliminate the photonic...
properties [5]. Small-angle X-ray scattering (SAXS) has been used to study the arrangement of spheres in the template material and their level of disorder [6]. This work describes a complementary method by which the ordering of the voids and planar defects in the final, inverted material can be examined by transmission electron microscopy (TEM).

2. Experimental and sample analysis

The synthesis of 3DOM materials has been extensively reviewed [7]. The images shown in this work are of a silica inverse opal that incorporates lacunary $\gamma$-SiW$_{10}$O$_{36}$ clusters in the structure [8], prepared from 280 nm polystyrene spheres and a solution of clusters, silicon alkoxides, water, ethanol and acid. The opal was removed by dissolving the template in a refluxing mixture of tetrahydrofuran (THF) and acetone. The inverse opal product typically contained 22 wt% tungsten.

The sample was prepared for TEM analysis by dispersing < 5 mg of the solid in ethanol by sonication; several drops of the suspension were placed on a holey carbon grid and allowed to dry. The grid was mounted on a double-tilt holder with a range of 90° along one axis. Goniometer angles were measured to the nearest degree. Images were recorded digitally on a 1k × 1k, Peltier-cooled CCD camera. Diffractograms were calculated using the fast Fourier transform (FFT) function in ImageJ 1.62 and using the entire image (rather than a smaller selected area).

Particles were selected by size, location, and orientation. That is, a suitable particle is one large enough to show < ~20 voids in any direction, is located far enough away from potentially interfering particles, shows $p4mm$ or $c2mm$ plane symmetry, and is aligned to allow several high-symmetry orientations to be visible while tilting through 90°.

The spatial arrangement of the voids in the sample was established by comparing the images and their respective diffractograms to simulations based on five plausible void arrangements: face-centred cubic (fcc), body-centred cubic (bcc), simple cubic (sc), hexagonal close-packed (hcp) and random hexagonal close-packed (rhcp). The rhcp structure was treated as an fcc lattice with random stacking faults between close-packed planes [9]. A more extensive mathematical description of the creation of the projections is described elsewhere [10].

There were three areas for comparison with the model systems: relative goniometer tilt between images/simulations, the relative angle between reciprocal lattice vectors and the relative length of reciprocal lattice vectors in the diffractogram.

Figure 1 shows a set of bright-field micrographs taken of one particle oriented in four directions. To facilitate a comparison with the simulated projections, the images have been cropped. The fcc simulation (figure 2) shows the closest match to the plane symmetry in the micrographs and the overlap and relative orientation of the circular projections. The slight mismatch between the figure 1a and figure 2a is a result of reaching the goniometer tilt limit when recording the image series.

The match between reality and simulation can be quantified by comparing the relative lengths and angles of the reciprocal lattice vectors. Figure 3 shows an enlargement of the diffractograms of the images from figure 1. The diffractograms were calculated from the full 1k × 1k image rather than the cropped images shown in figure 1. For comparison, the calculated diffractograms for projections of an fcc lattice are shown in figure 4. All the relative vector lengths and angles (including those for the image in figure 1a) match the theoretical values within the precision of the measurement. The other systems analysed (not shown) matched, at best, half of the vector lengths and two-thirds of the relative angles. Also, with the exception of figure 1a, all the goniometer tilts matched those predicted for fcc.

3. Discussion

One of the key orientations for all the cubic lattices is along the [011] zone axis. In an fcc lattice, this orientation would show the presence of stacking faults: shift vectors in the family $\frac{a}{6}<2\overline{1}1>$ lie in the plane of the image (dashed lines in figure 1d). The non-appearance of stacking faults in the bright-field images allows an rhcp arrangement of voids to be ruled out. Both bcc and sc lattices produce high-symmetry projections at relative goniometer angles identical to those from the fcc lattice. However, these differ markedly in appearance. Figure 5 shows, as an example, the difference between the [011] orientations of the cubic lattices examined. A full graphical analysis appears in [10].
**Figure 1.** Bright-field micrographs of a single particle of 3DOM silica viewed in four high-symmetry orientations. The relative goniometer angles were: (a) 86°, (b) 56°, (c) 36°, (d) 0°.

**Figure 2.** Simulated projections based on an fcc lattice, viewed along the (a) [100] zone axis, (b) [211] zone axis, (c) [111] zone axis, (d) [011] zone axis. The dashed lines in (d) show how a stacking fault would appear in the image. The theoretical relative tilt angles are (a) 90.0°, (b) 54.7°, (c) 35.4°, (d) 0°.

**Figure 3.** Magnified diffractograms of the images shown in figure 1.

**Figure 4.** Calculated diffractogram for the projection of an fcc lattice of scatters oriented along (a) 100, (b) 211, (c) 111, (d) 011. Theoretical vector length ratios are: \( L_2/L_1 \), 1.15; \( L_3/L_1 \), 1.63; \( L_3/L_2 \), 1.41; \( L_4/L_1 \), 1.91; \( L_4/L_3 \), 1.17. Theoretical angles between vectors are: \( \alpha_1 \), 45°; \( \alpha_2 \), 31.48°; \( \alpha_3 \), 58.52°; \( \alpha_4 \), 60°; \( \alpha_5 \), 35.26°; \( \alpha_6 \), 54.74°. The spots shown are limited to those within \( 2.2/( \text{sphere radius} ) \) from the central spot.
An hcp lattice presents a more unusual situation in which several high-symmetry orientations of the structure appear the same as or similar to projections from an fcc lattice. Three examples are shown in figure 6. Both figure 6a and 6c are subtly different from the listed projections in the fcc lattice. The difference between figure 2d and figure 6a, for example, is a result of the difference in stacking of close-packed planes (the stacking direction runs left to right in the plane of the page). The more easily noted difference between hcp and cubic lattices, however, is in the goniometer angles [10].

4. Conclusions
This method of structural determination in the TEM is ideal for small, low-density samples. It uses commonly available equipment and a simple sample preparation method. Additionally, it allows areas to be selected in real space, then to be analysed in reciprocal space. Thus, it could be applied to the study of colloidal phases, defects and “grain” boundaries.

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