ESRF	**Experiment title:** STRUCTURE OF LARGE SINTERED ARTIFICIAL OPALS	**Experiment number**: 26-02/537
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Scientific background

Photonic crystals (PhCs) have attracted much attention in the past decade since they can be used for light manipulation. They are candidates for the creation of negative refractive index metamaterials [1]. Their magnetic and transport properties can be controlled by their mesoscale architecture [2]. Colloid self-assembly is one of the promising routes to inexpensive large-scale fabrication of the opal-like materials. By filling up the dried colloidal crystals with another material and etching the colloidal spheres away, one can obtain various inverted PhCs. Artificial opals can be fabricated with a procedure based on combination of self-assembly and sol–gel method (sedimentation) [3], or self-assembly onto polished conductive substrates by the vertical deposition method (convective assembly, or controlled drying) [4,5]. The structure and long-range periodic order of wet sedimentary colloidal crystals was studied in great detail [6,7]. These crystals of hard spherical colloidal 'atoms' form an important model system, which is able to mimic crucial aspects of the crystallization process and the (growth-induced) defects. However, these wet sedimentary crystals were not directly applicable as templates for inverted PhCs. The later can be conveniently achieved using thin opal-like crystalline films made by vertical deposition technique [4,5]. Recently, detailed investigations of such samples were performed in collaboration between Delft, Utrecht, St. Petersburg and the DUBBLE beamline [4,8]. Now we have obtained crystals, which combine the advantages of the two systems studied previously. The opals are made on the basis of sedimentary crystals similar to those studied in Refs. [6,7]. By exploiting careful drying with subsequent sintering large single opals are obtained. Because the colloidal particles are 'baked' together, these crystals are self-supporting and can now be used as templates to fabricate photonic materials [9] in contrast to the system investigated in [6,7]. On the other hand, the new samples do not need any substrate and they are much thicker, which can allow for true 3 dimensional applications.

Samples and experimental techniques

The microradian x-ray diffraction setup [10], was exploited to obtain unprecedented angular resolution, which is crucial to characterize the large scale structures ordered on the large distances (100 lattice periods). A set of beryllium compound refractive lenses was used to focus the beam at the detector. We used the detector with 9 μm pixels to obtain the highest angular resolution, which is purchased by Utrecht group specifically for microradian studies. A number of samples was obtained by sedimentation of highly monodisperse SiO_2 colloidal spheres with diameter ranged between 300 nm and 2200 nm from aqueous solution. The resulting crystals were carefully dried to obtain large porous opals, which were subsequently sintered by annealing at 750^{o}C for between 1 and 5 hours. Than, the rods of about 100 μm × 100 μm × 5 mm were cut out of the bulk samples for the x-ray studies. In order to obtain the information on the full 3D crystal structure, the diffraction patterns were collected with different sample orientations in the rotation angle range of 0 ÷ 180 degree that allows us to reconstruct the full 3D reciprocal lattice of the crystals. The corresponding software has been recently developed [11]. In addition, it is crucial to quantify the typical size of single crystalline domains and the presence of crystal distortions. These parameters are characterized by

collecting the 3D data at a few positions within the same sample accompanied by a sequence of 2D diffraction patterns taken with the beam along a few low-index crystallographic directions.

Results.

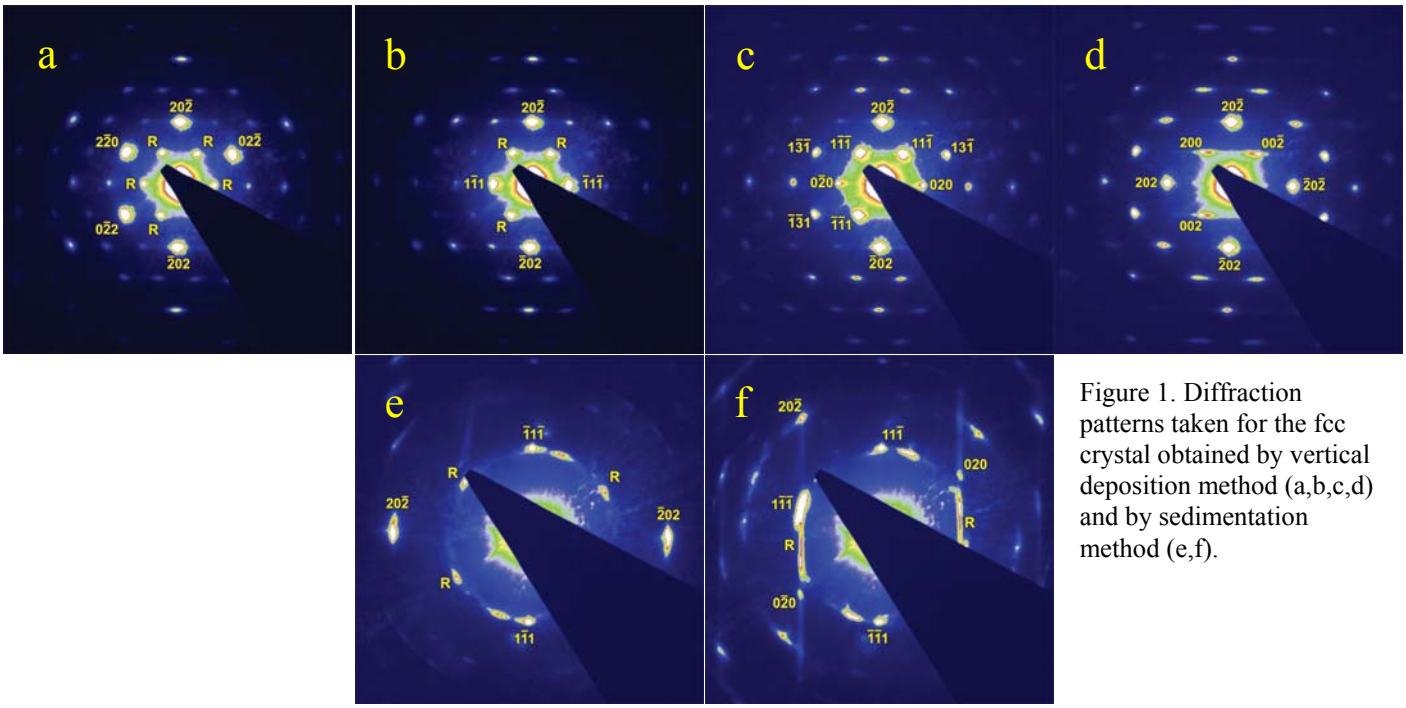

Figure 1. Diffraction patterns taken for the fcc crystal obtained by vertical deposition method (a,b,c,d) and by sedimentation method (e,f).

Microradian diffraction patterns shown in Figure 1 are taken from an fcc crystal obtained by vertical deposition method and measured with the beam normal to the substrate (111 crystallographic direction, panel a) and after the sample rotation by 19, 35 and 55 degrees around the vertical axis (002 crystallographic direction) panel b,c and d, correspondingly. The hexagonally arranged set of reflections (Panel a) demonstrates the 3-fold symmetry along the 111 direction normal to the substrate surface. One can easily follow the reflections appeared in Panels (b-d) so distinctively inheritent in the fcc structure. The corresponding indexes are added to the pictures. Panels e and f show the similar patterns taken for the crystal obtained by sedimentation method. The observed reflexes can be also ascribed to the fcc structure. However, in addition to the well-pronounced fcc reflection, one can also see additional reflections, which are forbidden for a perfect fcc crystal. They originate from intersections of the Ewald sphere by so-called Bragg rods, which are induced by stacking disorder in the direction normal to the substrate. These additional reflections are denoted by designation R on the pictures.
Preliminary results presented above illustrate similarities and differences between the PhCs obtained by the vertical deposition method and sedimentation method in the light of the microradian X-ray diffraction.

References

1. D.R. Smith, J.B. Pendry, M.C.K. Wiltshire, Science, **305**, 788 (2004).
2. S.V. Grigoriev, K.S. Napolskii, N.A. Grigoryeva, *et al.*, Phys. Rev. B **79**, 045123 (2009).
3. Advanced Materials, **13**, №6 ,369 – 450. Photonic crystals are the central theme of this issue.
4. K.S. Napolskii, N.A. Sapoletova, *et al.*, Langmuir, **26**(4), 2346 (2010).
5. Jiang P., Bertone J.F., Hwang K.S., Colvin V.L., *Chem. Mater.* **11,** 2132 (1999).
6. A.V. Petukhov, D.G.A.L. Aarts, I.P. Dolbnya *et al.*, Phys. Rev. Lett. **88**, 208301 (2002); see also ESRF Highlights 2002, p. 19-20.
7. A.V. Petukhov, I.P. Dolbnya, D.G.A.L. Aarts *et al.*, Phys. Rev. Lett. **90**, 028304 (2003);
8. J. Hilhorst, V.V. Abramova, A. Sinitskii *et al.*, Langmuir **25**, 10408 (2009); see also ESRF spotlight on science www.esrf.eu/news/spotlight/spotlight95/ (24 Nov 2009).
9. M.E. Kozlov, N.S. Murthy, I. Udod *et al.*, Appl. Phys. A 86, 421 (2007).
10. J.H.J. Thijssen, A.V. Petukhov, D.C. 't Hart *et al.*, Adv. Mater. **18**, 1662–1666 (2006).
11. A.A. Eliseev, D.F. Gorozhankin, K.S. Napolskii *et al.*, JETP Lett., **90**, 272 (2009).
12. I.P. Dolbnya, A.V. Petukhov, D.G.A.L. Aarts *et al.*, Europhys. Lett., 72, 962 (2005).