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Experiment Report Form

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(next page)

DUBBLE	**Experiment title: Single Scattering Characterization of Thin Photonic Crystals with Large Band Gaps**	**Experiment number**: **26-02-121**
Beamline: BM-26B 'DUBBLE'	**Date(s) of experiment**: From: 11-11-2002 To: 15-11-2002	**Date of report**: 8-01-2003
Shifts: 9	**Local contact(s)**: Igor Dolbnya	

Names and affiliations of applicants (* indicates experimentalists):

A. Imhof*, J. Hoogenboom*, A. van Blaaderen* (Soft condensed matter, UU), A. Petukhov* (van 't Hoff, UU), I. Dolbnya* (DUBBLE, NWO/ESRF)

Report:

During this experiment we have studied various colloidal systems, which strongly diffract visible light. The samples include thin colloidal crystals of silica spheres deposited on glass substrates, composite colloids made of a silica core and a metal shell, and concentrated suspensions of silica spheres. Below we present some of the results achieved.

One of the samples, which we have studied, is a body-centred tetragonal (bct) crystal. This unusual crystal structure is prepared by colloidal crystallization in an external electric field, and subsequent fixation in a polymer gel. The nearest-neighbour distance is about 1.6 μm. This sample is the first in our group, which has been studied in detail by two complementary techniques, the real-space confocal microscopy and the reciprocal-space x-ray diffraction. Figure 1 shows an image taken with the confocal fluorescence microscope.

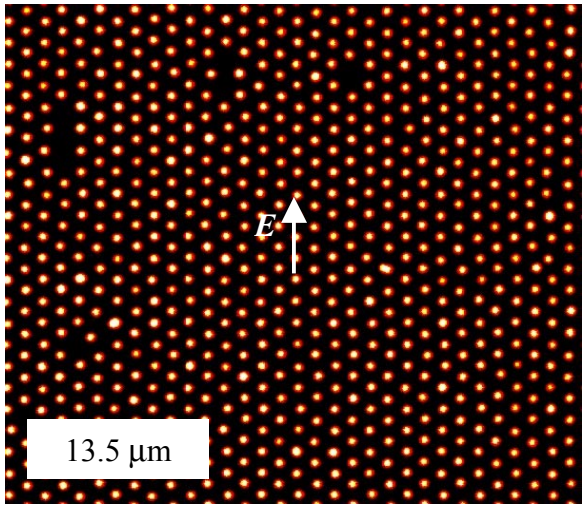

Fig. 1 Confocal image of a BCT crystal grown in an external electric field applied along the white arrow. The cores of silica spheres are labeled with fluorescent dye.

This sample is very challenging for x-rays since its period in real space is larger than one micron or more than ten thousand times the wavelength λ (here we used 12.38 keV radiation with λ = 0.1 nm). In this situation, to resolve diffraction peaks one needs a beam with transverse coherence length much larger than $10^4 \times \lambda$, a detector with sufficient resolution and optimisation of the whole optical setup. Such an optimisation was achieved in the experiment 26-02-101 (experiment proposed by I. Dolbnya) in March 2002 [1]. Optics was carefully aligned and slits sizes were optimised. For the present sample we used a CCD (charge-coupled device) camera borrowed from the ESRF detector pool (pixel size corresponds to about 60 μm distance on the phosphor screen) to record the diffraction pattern. The maximum possible sample-detector distance (which is slightly larger than 8 m) and the smallest lead beam stop (5×5 mm^2) were used.

To illustrate the scale in the reciprocal space, Fig. 2a [2] displays the fibre diffraction pattern from the rat tail collagen (q-space calibration sample). The white arrows point to the first-order diffraction peaks originating from the 65 nm period of the collagen. Note how narrow the collagen arcs are – they are now much better resolved than with the ordinary set-up at DUBBLE. Here the diffraction angle 2θ is 1.5 mrad. In panel (b) we show the diffraction pattern obtained with x-rays normal to the substrate. The beam stop is shifted such that only its corner absorbs the direct beam. To clearly see the diffraction peaks, the image is magnified 5 times. Note the difference in the scale, which is given in pixels of the camera on the left and bottom sides of the image. The white arrow points onto the lowest-order diffraction (110) peak corresponding to the interplanar spacing of d = 1.33 μm (as estimated from the diffraction pattern) in the real space. This value compares well with the confocal microscopy result of d = 1.35 μm obtained from

the image in Fig. 1. Thus, we have managed to clearly resolve the diffraction peaks corresponding to the *d* spacing, which is about 20 times larger than that in the rat tail collagen, and has diffraction angle 2θ as little as 75 microradian or 15 seconds of arc. The pattern in Fig.2b gives information on sample structure in two dimensions. To study that in the third dimension, the sample was rotated by 18.44° around the vertical axis. For a bct crystal at this orientation one expects that the Ewald sphere crosses four (211)-class reflections. As shown in Fig.2c, three of these reflections are indeed clearly visible as bright spots (white arrows point on them). Our diffraction data thus unambiguously confirm the bct crystal structure. A detailed rocking curve was measured (sample orientation was scanned in small steps around the one used in Fig.2c). This measurement allows us to evaluate the intrinsic (not limited by the instrument resolution) width of the reflections [3].

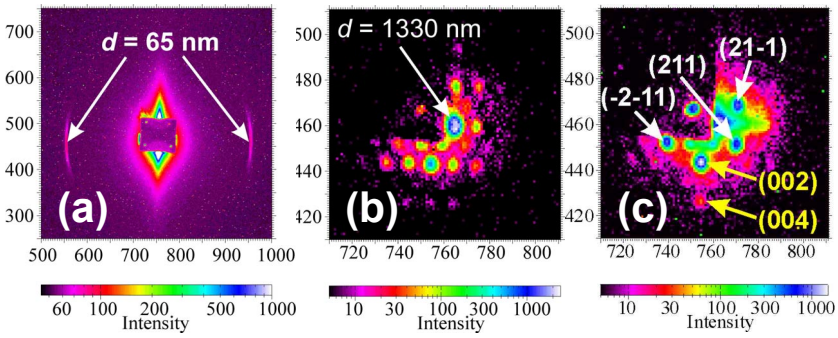

Fig.2(colour). (a): Diffraction pattern of rat tail collagen; (b) and (c): magnified (×5 relative to panel a) diffraction patterns of the bct crystal obtained with x-rays incident along the (1-10) and (1-20) crystallographic directions, respectively. White arrows in (c) indicate three (211)-class reflections. Yellow arrows point on the reflections, which are present in both (b) and (c) panels since the axis of rotation crosses them. The electric field was applied along the vertical (001) direction.

Another example of our results is illustrated in Figure 3. Here we have studied colloidal suspensions of charged silica particles with radius of 50 nm. Here we used the gas-filled detector (which has a dynamic range much larger than that of the CCD camera) and 9 keV x-ray beam (λ = 0.138 nm). Panel (a) displays the measured SAXS radial profiles $I(q)$ (corrected for the detector response and the background) for different colloid concentrations in suspensions with 10^{-3}M ionic strength. Structure factors $S(q)$ in panel (b) are obtained by dividing the $I(q)$ by the particle form factor obtained from the $I(q)$ measured for the smallest concentration. These data allow us to follow in detail the development of various peaks in the structure factor $S(q)$ and their shift to higher q resulting from the reduction of the average spacing between the particles. Similar results are obtained with ionic strength of 10^{-5}M (much larger Debye screening length). We note that the minima of the $I(q)$ dependence in Fig.3a are rather shallow, but from electron microscopy we know that the colloid is highly monodisperse. Therefore, it is an effect of the too low resolution of the gas-filled detector, which does not allow us to resolve the intrinsic depth of the minima. The colloidal particles have only 2% size polydispersity, it is also clear from Fig. 3a since the oscillations of the $I(q)$ dependence decay rather slowly.

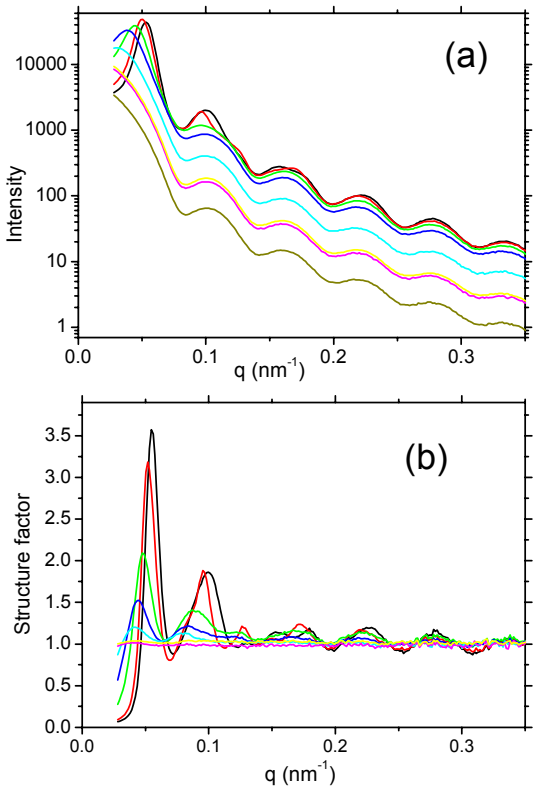

Fig.3 Radially-averaged scattered x-ray intensity (a) and the structure factor (b) of silica suspensions at volume fractions from 0.01-0.5.

The results of the experiment 26-02-101 and of the present experiment show that at the DUBBLE one can achieve much higher resolution in the detector plane. Within the ordinary installation the resolution is severely limited by the gas-filled detector while optics allows one to significantly reduce the minimum accessible wavevector and to achieve much more detailed information [1]. We believe that many users of the DUBBLE can significantly profit if a new CCD detector with resolution of the order of 25 microns is added to the standard set-up of the SAXS/WAXS station.

References

[1] report of experiment 26-02-101, March 2002.

[2] higher-resolution pictures of Fig.2a and 2b are also available at http://www.chem.uu.nl/fcc/www/peopleindex/andrei/bct/index.htm (click on the images to enlarge)

[3] A.V. Petukhov et al., *Phys. Rev. Lett.*, **88**, 208301 (2002); A.V. Petukhov et al., *Phys. Rev. Lett.*, in press; reports of experiments 26-02-77 and 26-02-90, April & September 2001.