ESRF	**Experiment title:** STRUCTURE OF INVERTED PHOTONIC CRYSTALS BASED ON LARGE SINTERED ARTIFICIAL OPALS	**Experiment number**: 26-02/553
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Scientific background

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 one can obtain various inverted systems whose size and chemical composition are tuned by the size of the colloids and by the structure/density of infiltration precursor(s), respectively. The general interest for the study of nanoscale metallic structures based on opal-like structures (OLS) is related to their wide application in spintronic devices, and high density storage devices. Magnetic and transport properties of such devices are controlled by their mesoscale architecture [1].

The aim of the experiments was the structural characterization of a new type of inverse OLS derived by infiltration of the three-dimensional net of voids of the template artificial opal under an applied pressure with Bi, Sn and Sb, as well as bimetallic Bi/Sb structures. The results of the study provided us with key structural information, which is crucial for the fabrication of high-quality and large-volume (up to $1\times1\times1$ cm^3) inverted crystals for photonics and nanoelectronics applications.

Samples and experimental techniques

The microradian x-ray diffraction setup at the BM-26B (DUBBLE) beamline [2] 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 on the detector. We used the CCD detector with the pixel size a 22 μm square, which is available at the beamline, to obtain the highest angular resolution and to collect larger-view diffraction data. Construction and alignment of the setup took more than 1 day. A new mounting for the lenses was tested for the first time by the beamline team. It turned out that it did not work so that the old design had to be used. As a result, more than 4 shifts of the beamtime were lost.

The 3D opal-like matrices were obtained by sedimentation of highly monodisperse SiO_2 colloidal spheres with diameter ranged between 170 nm and 550 nm from aqueous solution [3]. 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. The inverse OLS are prepared by infiltrating melts of Bi, Sn, or Sb under an applied pressure [4]. Bi/Sb bimetallic structures are obtained by filling the voids of the Sb inverted opal with Bi. In total up to 15 crystals had been investigated. Rods of about 100 μm × 100 μm × 5 mm were cut out of the bulk samples for the x-ray diffraction study. 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 recently been developed [5].

Results.

Microradian diffraction patterns shown in Figure 1 were taken from (a) Sn inverse opal and (b) Bi inverse opal. They demonstrate two extreme examples of the opal-like structure. The diffraction pattern shown in Fig.1 a can be interpreted taking into account that (i) the lines of scattering intensities correspond to the [001] axis of Random Hexagonal Close Packing (RHCP) structure ([111] in terms of the Face Centered

Cubic (FCC) structure) and that (ii) the line perpendicular to them corresponds to the [100] axis of RHCP structure ([1-21] in terms of FCC structure). In general it is clear that the structure is close to the RHCP. On contrary, the diffraction pattern shown in Fig.1 b for Bi inverse opal can be interpreted as the FCC structure. Indeed, the Bragg reflections can be interpreted as belonging to the plane (101) of the FCC structure of the Bi inverse opal. In fact the FCC crystal obtained by the sedimentation method is a very rare case and most of the measured crystals appeared to be close to RHCP structure. Moreover, the fabrication of series of crystals with different periodicity made of Bi or Sn appeared to be rather succesful while all the samples made of Sb (as well as bimetallic Bi/Sb structures) did not display any long–range periodicity.

The periodicity of the crystal structure can be determined from the positions of the Bragg reflections.

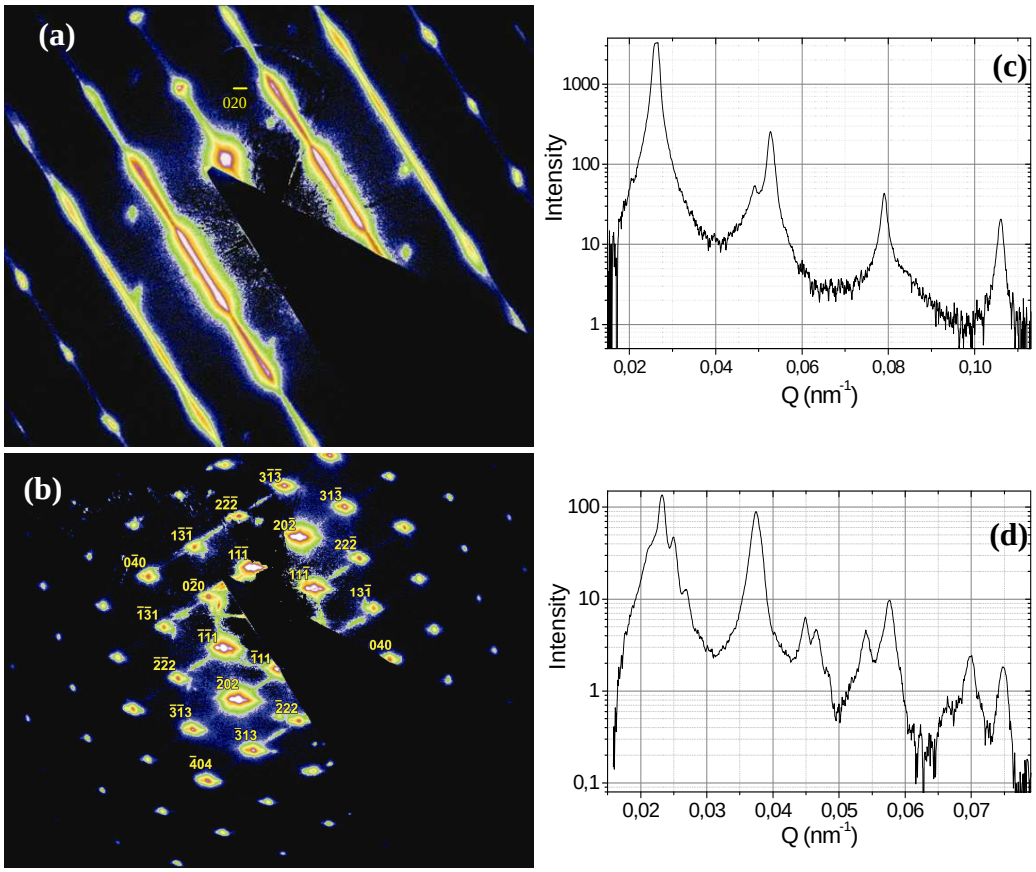

Figure 1. Diffraction patterns taken for (a) Sn inverse opal, (b) Bi inverse opal. Q-dependence of the scattered intensity for (c) Sn inverse opal, (d) Bi inverse opal.

Fig.1 (c) gives the momentum transfer dependence of the scattering intensity along the [100] axis of the RHCP structure for Sn inverse opal. The intensity was averaged over the angle of 10 degrees. Fig.1 (d) shows the azimuthally-averaged radial profile of the scattering intensity of the FCC structure for Bi inverse opal. The lattice constant of the FCC structure is found to be a = 475 ± 5 nm for Bi inverse opal. The average dimension of crystallographic domains was obtained from the width of the reflections in the radial direction and correspond the value of 6 lattice parameters for Bi inverse opal and 12 lattice parameters for Sn inverse opal.

References

1. S.V. Grigoriev, K.S. Napolskii, N.A. Grigoryeva, *et al.*, Phys. Rev. B **79**, 045123 (2009).
2. J.H.J. Thijssen, A.V. Petukhov, D.C. 't Hart *et al.*, Adv. Mater. **18**, 1662–1666 (2006).
3. C. Lopez, L. Vazquez, F. Meseguer, *et al.*, Superlattice Microstruct. **22**, 399 (1997).
4. M.E. Kozlov, N.S. Murthy, I. Udod, *et al.*, Applied Physics A **86**(4), 421 (2007).
5. A.A. Eliseev, D.F. Gorozhankin, K.S. Napolskii *et al.*, JETP Lett., **90**, 272 (2009)