Experimental report

16/09/2019

Proposal:	**5-22-761**	**Council:**	4/2018

Title: Neutron diffraction study of bismuth wires incorporated within powdersilicalite-1F

Research area: Chemistry

This proposal is a new proposal

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Samples: SiO2/Bi

Instrument	Requested days	Allocated days	From	To
D20	1	1	10/09/2018	11/09/2018

Abstract:

Bismuth is the one of the best thermoelectric materials for Peltier cooling, we hope to improve its properties by reducing its dimensionality and by designing bismuth nanowires for which large enhancement of the thermoelectric properties have been predicted. Porous materials are ideal for designing a network of nanowires.

The objective of this experiments is to confirm successful synthesis of silicalite-1F/Bi composite and to determine the structure of Bi nanowires within silicalite-1F and how the structure of the zeolite is modified by the incorporation of bismuth. Neutron diffraction is suitable for such bulk sample due to its high penetration depth, which will permit to probe the whole sample despite of the presence of residual bismuth outside the zeolite. A 25mm3 sample will be prepared from zeolite powder and Bi at 7.5 GPa and 300°C in a belt press for this experiment.

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In order to reduce the difficulties encountered in X-ray diffraction due to the strong absorption of Bi, a millimetric, polycrystalline sample of Bi-silicalite-1 was prepared by heating the zeolite in liquid Bi at 5 GPa and 593 K in a CONAC28-type apparatus. The starting silicalite-1 and the recovered millimetric samples were studied by neutron powder diffraction on the D20 diffractometer at the Institut Laue Langevin. An incident wavelength of 1.87Å was used. Acquisition times were of the order of 15 minutes for the pure silicalite-1 sample and 4-12h for the bismuth filled samples. The program Fullprof[1] was used to perform Rietveld refinements on the starting material and to calculate the pattern for the model structure of the recovered sample and Le Bail fits was performed for describing the residual rhombohedral Bi and trace PTFE from the capsule in the sample. Crystal structures are displayed using the program Vesta[2].

Neutron powder diffraction was performed on the millimetric powder sample (Figure 1). The data are still dominated by scattering from rhombohedral Bi. The unit cell parameters of the Bi-silicalite-1 phase were found to be: *a* =19.39(1) Å, *b* = 19.87(1) Å, *c*=12.99(1) Å, β = 91.0(2) ° and V = 5003(5) Å^3. These values can be compared to the corresponding ones for the initial pure silicalite-1 material obtained on the same diffractometer (Figure 2): *a* =19.905(1) Å, *b* = 20.139(1) Å, *c*=13.3869(6) Å, β = 90.648(4) ° and V = 5365.9(4) Å^3 (See CIF file in SI). This indicates that the unit cell volume contracts by 6.8% with respect to the initial empty pore silicalite-1. This contraction after compression to 5 GPa in the Bi-containing silicalite-1 can be considered to be moderate as it only equivalent to that observed at close to 1 GPa in empty silicalite-1in *in situ* high pressure x-ray diffraction experiments[3].

The data of the sample recovered from HP-HT conditions were not suitable for refinement of the structure by the Rietveld method due to the relatively weak signal from such a small sample. The relative intensities of the many prominent diffraction lines change due to insertion of Bi atoms in the pores. In particular, the relative intensities of the 200 and 501 reflections increase by 48 % and 89 %, respectively, whereas a 32% decrease is observed for the 011 reflection. The observed intensity distribution can be modelled by using the structure obtained from DFT calculations (see below) (Figure 1). The calculated pattern of the Bi-silicalite-1 phase was obtained by using the cell parameters of the recovered sample, the fractional atomic coordinates of Si, O and Bi from the DFT model structure (see CIF file in SI) and by refining the occupation factor of Bi. The refined value of 0.60(1) corresponds to 14 Bi atoms per unit cell statistically distributed on partially occupied sites close to the center of the pores. The reflections of the remaining bulk Bi and the polytetrafluorethylene from the capsule were fit using the Le Bail method (agreement factors: r_p=8.9%, r_{wp}=9.3%).

In order to have an insight to the filling of silicalite-1 by Bi on an atomic level, DFT calculations were performed. Twenty-four Bi atoms were placed in the pores of silicalite-1, which was the maximum corresponding to a stable configuration, and the structure was relaxed (Figure 3). The parameters of the relaxed unit cell are: *a* =19.66 Å, *b* = 20.08 Å, *c*= 13.43 Å, β = 91.57° V = 5300 Å^3. These lattice parameters exhibit a similar tendency with respect to experiment with a decrease in *a* and *b* and the volume an increase in the β angle. A configuration with twelve Bi atoms in the pores was also tested giving a relaxed cell exhibiting a similar tendency (*a* =19.744 Å, *b* = 20.129 Å, *c*= 13.322 Å, β = 91.65° V = 5292 Å^3). This configuration was unusual as it implied that the pores were partially filled with clusters arranged in an arbitrary ordered manner. Experimentally the unit cell is more compressed with respect to theory. This is certainly due to the high pressure treatment, which induced some collapse of the structure, and the lower average Bi content. The 24 Bi atoms are aligned in the pores in the linear and sinusoidal pores of the silicalite-1 structure. The minimum Bi-Bi distance is 2.69 Å, which is slightly lower than twice the atomic radius of Bi. Subsequent distances are 2.75 Å and 3.37-3.74 Å indicating pairing of Bi atoms along the pore direction separated by shorter and longer Bi-Bi-distances. The minimum Bi-O distance is 3.58 Å is much longer than a bonding distance and is equal to the sum of the van der Waal's radii of Bi and O. This confirms the nature of the atomic scale chains in the inserted Bi. A double chain proposed previously in the case of 6.7 Å pore diameter mordenite [4] with a Bi-Bi distance of 3 Å would have a van der Waal's diameter of about 7 Å and thus not fit in the 5.5 Å free diameter of the pores of silicalite-1.

The electronic density of states of silicalite-1 filled with 24 Bi atoms were also calculated. The eDOS is dominated by bismuth and insertion transforms the wide-gap insulator silicalite-1 to a semiconducting composite with a gap of 0.4 eV (Figure 6). A very similar gap is calculated if the SiO_2 framework is removed. The gap is opened with respect to semimetallic bulk bismuth. The eDOS are also characteristic of a 3D array of Bi due to the occupation of both the direct and sinusoidal channels of silicalite-1.

REFERENCES

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[3] J. Haines, C. Levelut, A. Isambert, P. Hébert, S. Kohara, D.A. Keen, T. Hammouda, D. Andrault, J. Am. Chem. Soc., 131 (2009) 12333-12338.
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ASSOCIATED PUBLICATION

High-pressure, high temperature insertion of bismuth in the siliceous zeolite silicalite-1
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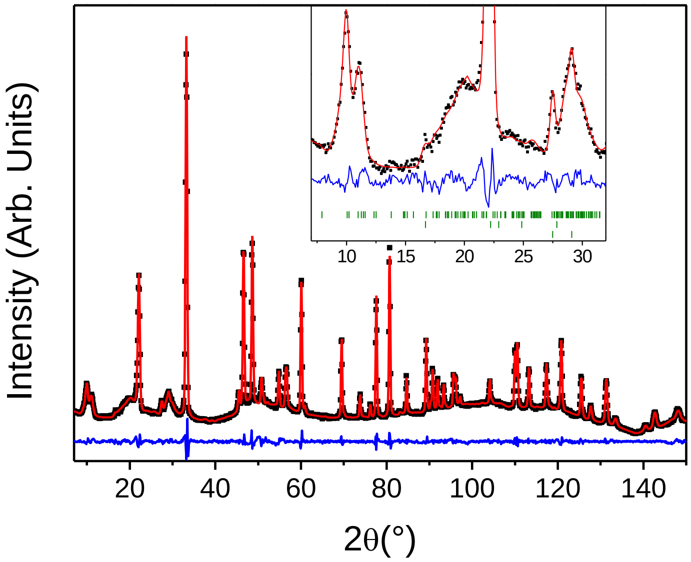

Figure 3. Experimental (black), calculated (red) and difference (blue) profiles from the fit to the NPD data from the Bi-filled silicalite-1 sample processed at 5 GPa and 593 K. The low angle part of the pattern is shown in the inset. Vertical bars indicate the calculated positions of the Bragg reflections of Bi-filled silicalite-1 (top), polytetrafluorethylene (middle), rhombohedral Bi.

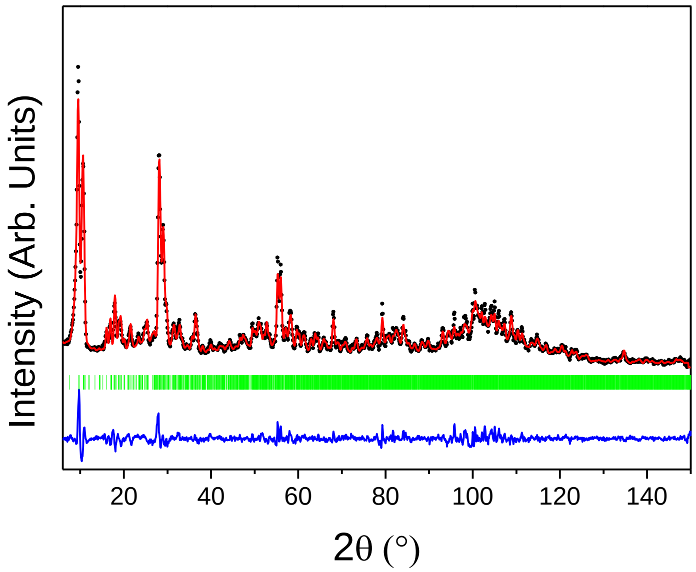

Figure 4. Experimental (black), calculated (red) and difference (blue) profiles from the fit to the NPD data from the initial silicalite-1 sample using the Rietveld method. Vertical bars indicate the calculated positions of the Bragg reflections of silicalite-1.

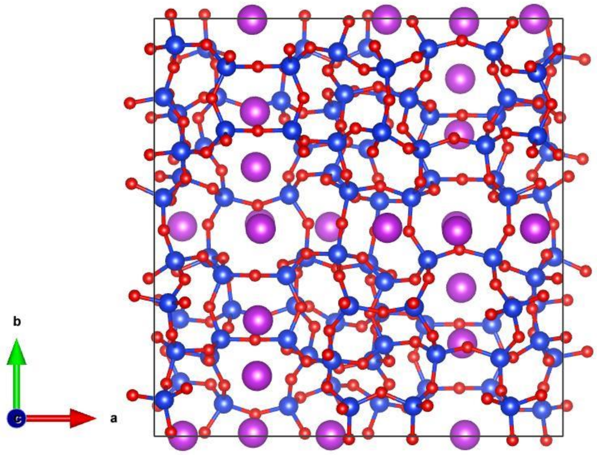

Figure 5. Relaxed structure of Bi-filled silicalite-1. Silicon, oxygen and bismuth atoms are represented by blue, red and purple spheres, respectively.