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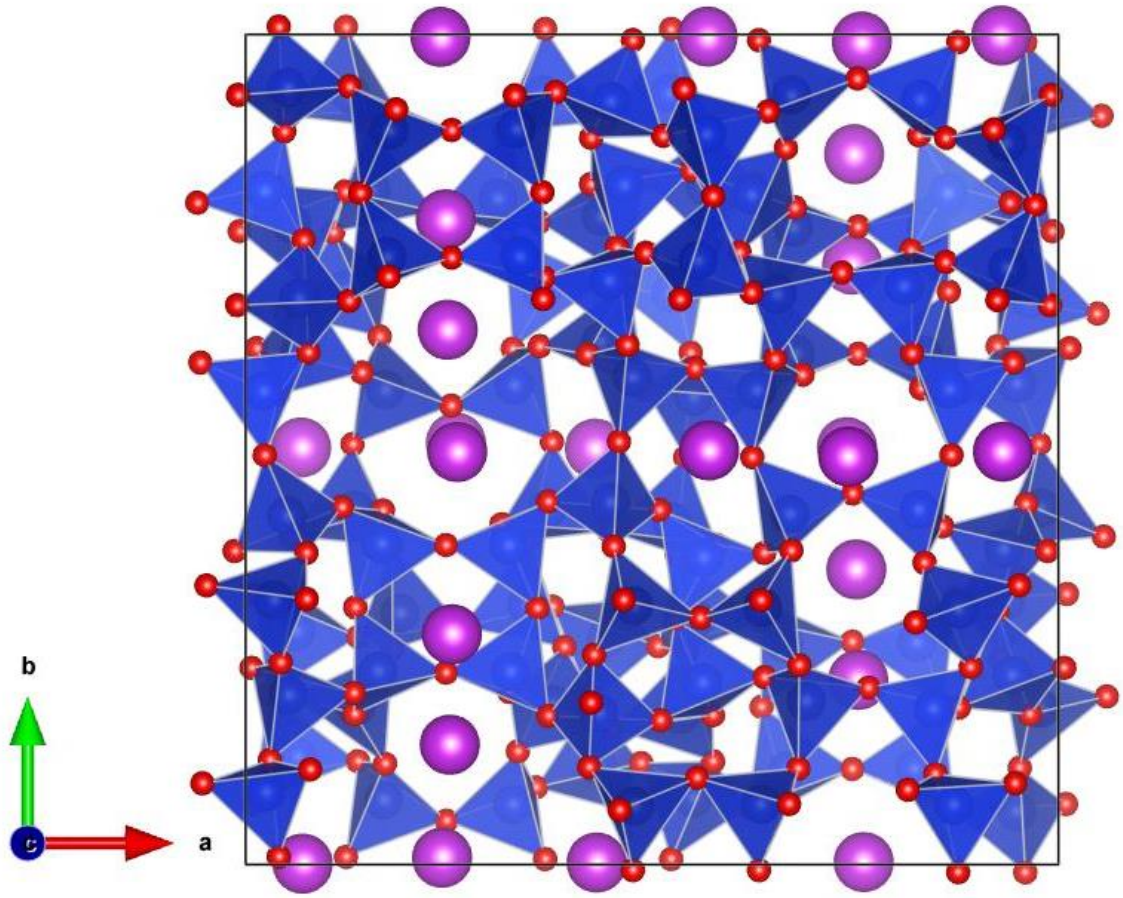
ABSTRACT

A silicalite-1/bismuth composite was synthesized by insertion of liquid bismuth in the 5.5 Å diameter pores of the zeolite under high-pressure, high-temperature conditions. The insertion of bismuth stabilizes the structure with respect to pressure-induced amorphization. Transmission electron microscopy indicated the presence of chains of atoms, which correspond to the 5.5 Å diameter of the host silicalite-1 structure. Neutron powder diffraction also confirmed the insertion of Bi in the pores of silicalite-1. Density functional theory calculations indicate that the insertion of bismuth results in formation of chains with short and long Bi-Bi distances in the pores of the host silicalite-1 linked to the framework by van der Waal's interactions. The material is predicted to be a semiconductor with a band gap of 0.4 eV.



HIGHLIGHTS:

- Bismuth enters the pores of silicalite-1 under high-pressure, high-temperature conditions
- The Bi-filled silicalite-1 structure is stabilized with respect to pressure-induced amorphization
- Density functional theory calculations show that Bi atoms form atomic chains with short and long Bi-Bi distances linked to the framework by van der Waal's interactions
- The calculated eDOS show that the Bi-silicalite-1 composite material is a semiconductor with a band gap of 0.4 eV.

KEYWORDS:

Silicalite-1; High Pressure; Guest Insertion; Bismuth; Semiconductor

1. Introduction

Zeolites are microporous aluminosilicates with pore diameters typically less than 10 Å. These materials have a large number of applications as molecular sieves, in catalysis, as selective adsorbers among others. Confinement of guest species, in particular metal atoms, in zeolites opens the way to design new composite materials with novel electronic, optical and magnetic properties.

Previous studies[1, 2] have shown that molten metals can be inserted into the nano- and subnanometric channels of porous materials at high pressure and high temperature. The interest of this method compared to more conventional methods of metal insertion, such as vapor adsorption, intrazeolite cation reduction and incorporation directly during hydrothermal synthesis, is that a much higher degree of pore filling can be obtained. Oxidization of the metal can also readily be avoided. The critical pressure for insertion of a liquid metal in a porous solid (P_c) is defined in the general case[3] by the Laplace-Washburn equation:

$$P_c = -4\gamma_L \cos\theta / D \tag{1}$$

where γ_L is the surface tension of the nonwetting liquid, θ is the contact angle between the liquid and the solid and D is the pore diameter.

According to Bogomolov[1], an interface transition gap between channel surfaces and metallic layer should be considered in the case of metallic dielectric liquid due to its nonwetting properties and a new equation was thus proposed:

$$P_c = \frac{0.4(\gamma_o - \gamma_c)}{D\left(1 - \frac{2\delta_o(\gamma_o - \gamma_c)}{D\gamma_o}\right)^2} \tag{2}$$

where γ_o is the surface tension of liquid, γ_c is the adhesion energy and δ_o is the Tolman length.

Pressures of 0.6 to 2.9 GPa are necessary to insert the molten metal in microporous zeolites with pores between 8.4 and 6.6 Å[1].

The electronic structures of nanowires were also investigated by different authors[2, 4]. A model for the electronic structure for metals inserted into zeolite was established in order to calculate the density of

states, the conductivity and even optical properties[4]. Bi quantum wires have been reported to be incorporated in natural mordenite with pore diameter of 6.7 Å under high pressure[2]. Based on a comparison between x-ray powder diffraction patterns of mordenite with that of mordenite/Bi, an enhancement of the intensity of the peak at 6.5° was proposed as proof of the wire synthesis; however, x-ray diffraction has a very low penetration depth in such a sample containing bismuth and no structure refinements were performed. This increase in intensity is however evidence of incorporation of Bi in the pores. The electronic structure of this composite material was determined based on optical absorption spectroscopy and its current-voltage characteristics. A double zigzag chain was proposed for the structure of the wires with a bond length of 3 Å, a 90° bond angle and a period of the chain of 4.2 Å. This proposition was not verified using x-ray diffraction data nor by theoretical calculations.

Little is known on how the insertion of metals affects the host zeolite nor on the quantity and location of the inserted metal atoms. In the present study, even a higher degree of confinement of metals (bismuth) inside the siliceous zeolite silicalite-1 with a monoclinic MFI (Mobil-Five) structure, space group $P2_1/n$ and 5.5 Å diameter pores[5] is studied by injecting liquid bismuth in the host zeolite under high-pressure-high-temperature conditions. Up to now, liquid Bi has not been inserted in such small channels, which requires a pressure exceeding about 4 GPa based on equation (2). The use of a purely siliceous zeolite is an advantage compared to the use of a natural zeolite as no counter ions are present in the pores, thereby allowing a greater degree of filling with metal atoms and reducing any tendency to oxidation. A combination of transmission electron microscopy (TEM), synchrotron x-ray and neutron diffraction and density functional calculations are used to obtain information on the amount and the nature of the inserted Bi atoms in silicalite-1.

2. Experimental and computational details

2.1 Synthesis and calcination of silicalite-1

Silicalite-1 was prepared using a fluoride route in order to minimize the amount of structural defects[6]. Structural defects could hinder the insertion of bismuth. The reactants employed were: NH_4F(2.8 10^{-3}

mol), tetrapropylammonium bromide TPABr (5.3 10^{-3} mol), silica (6.8 10^{-3} mol), and water (24g). TPABr acts as a structure directing agent. These precursors were mixed under stirring to obtain a homogeneous silica-based gel. The resulting gel was heated in a PTFE-lined autoclave at 473K for 30 days. The as-synthesized silicalite-1 was recovered by filtration and dried overnight at 333 K. Porous silicalite-1 was obtained by calcining the as-synthesized zeolite under air at 823K for 6 h. Then, silicalite-1 was ground in a McCrone XRD mill and placed in the drying oven at 70 °C for one night to obtain micron-sized crystallites. Silicalite-1 single crystals with maximum dimensions of 100x50x50 µm were obtained from SOMEZ (Montpellier, France).

2.2 Insertion of liquid Bi at high-temperature and high pressure in a diamond anvil cell.

A resistively-heated Almax Easylab Helios membrane diamond anvil cell (DAC) was used for the high pressure, high temperature experiments. Ruby and SrB_4O_7:Sm^{2+} were placed in the 200 µm hole in a 115 µm thick rhenium gasket placed on one diamond anvil. These materials were used to measure the pressure and temperature by optical luminescence[7-9]. NaCl was then added and pressed to form a pellet to protect these materials from the molten bismuth. Half of the pellet was then removed and three silicalite-1 single crystals and Bi powder were added in an argon atmosphere in a glove box. An Alan Bradley E150 programmable heater controller was used to control the heater power and a thermocouple placed inside the heater near the diamond was used to measure the temperature.

2.3 Preparation of millimetric samples under HP-HT conditions in a CONAC28 apparatus.

Preparation of millimetric Bi/silicalite-1 samples, in order to have enough material for neutron powder diffraction, TEM and magnetization measurements, was carried out using a CONAC28 high-pressure apparatus. A mixture of Bismuth and silicalite-1 powder were placed in a polytetrafluorethylene capsule in the graphite furnace in the lithographic stone cell for the CONAC device, which was then placed between the two WC CONAC anvils. Pressure was firstly increased to 2GPa to connect the graphite furnace. Bi was then heated at 593 K to ensure melting followed by pressure increase up to 5GPa for insertion**.**

Two syntheses were performed with a Bi/SiO_2 volume ratio of 1/3. The samples obtained have diameters of 5.35 mm and 4.94 mm and thickness of 0.694 mm and 0.645 mm, respectively.

2.4 Single crystal x-ray diffraction. X-ray diffraction on single crystals of Bi-filled silicalite-1 in the Re gasket were performed on the ID27 beamline at the ESRF. The incident wavelength was 0.3738 Å and a MAR165 CCD was used as a detector. Phi-scans from -38° to 38° were performed with an acquisition time of 10s. Data analysis was performed with Crysalis Pro (Rigaku).

2.5 Transmission electron microscopy (TEM).

TEM measurement was performed with FEG JEOL 2200 FS – 200 KV electron microscope equipped a CCD GATAN USC camera with 4092×4092 pixels and an electron gun of 200 kV. The probe diameter in STEM mode is about 1nm with a resolution, which can attain 0.1 nm.

2.6 Neutron powder diffraction. 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[10] 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[11].

2.7 Magnetization. Magnetic properties were measured on one of the millimetric samples using a Squid Magnetic Properties Measurement System (MPMS) from Quantum Design using 100 Oe magnetic field. Both zero field cooling (ZFC) and Field Cooling (FC) were performed.

2.8 Density Functional Theory calculations.

Density functional theory (DFT) based calculations were performed on empty silicalite-1 to test the method and on silicalite-1 with 12 and 24 Bi-atoms placed inside the pores to determine the effect of a high degree of pore filling. We used the SIESTA package[12] and the generalized gradient approximation to the exchange correlation functional as proposed by Perdew, Burke and Ernzerhof[13]. Core electrons are replaced by nonlocal norm-conserving pseudopotentials.

The $5d^{10}$ electrons have not been considered in the Bi-pseudopotential. The valence electrons are described by a double-zeta singly polarized basis set. The localization of the basis was controlled by an energy shift of 50 meV. Real space integration was performed on a regular grid corresponding to a plane-wave cutoff of 350 Ry. Integrals over the Brillouin zone are approximated by sums over a 2×2×4 mesh of special *k*-points according to the Monkhorst-Pack scheme[14]. Theoretical lattice parameters and atomic positions were fully relaxed using a Broyden-Fletcher-Goldfarb-Shanno algorithm until the maximum stresses and residual forces were less than 0.01 GPa and 0.04 eV/Å, respectively.

3. Results and discussion

Several silicalite-1 single crystals with maximal linear dimensions of 80-100 µm were pressurized with bismuth in the diamond anvil cell to 0.8 GPa and then heated to 525 K. The pressure was then increased gradually up to 6.3 GPa. The temperature was then lowered to 323 K resulting in a pressure increase up to 11 GPa. The pressure was then decreased to ambient pressure and the gasket containing the sample removed from the diamond anvil cell.

This recovered sample was studied by synchrotron x-ray diffraction. Mapping of the sample was first performed with 50 µm resolution. The zones containing NaCl and Bi were readily identified by their powder diffraction patterns. The Bi-containing zones were then reinvestigated with 20 µm steps. Spots from silicalite-1 single crystals were observed at several locations. These crystal were then centered on the beam and phi scans were performed, Figure 1. Weak low angle reflections were observed a d-spacings corresponding to silicalite-1. Due to the very strong absorption of Bi, reliable intensities could not be extracted for the single crystals. However, the single crystals were recovered after pressurization up to 11 GPa, which is well above the pressure that amorphization[15, 16] is observed in the same empty-pore silicalite-1 sample, both without a pressure transmitting medium or in the presence of a non-penetrating pressure transmitting medium such as silicone oil. In contrast in this previous work, no amorphization occurred in penetrating pressure transmitting media such as Ar or CO_2 up to 25 GPa, which is well above the solidification pressure of the medium. This absence of amorphization is consistent with the insertion

of liquid bismuth, which acts as a penetrating pressure transmitting medium, in the pores of these silicalite-1 single crystals under HP-HT conditions.

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 belt-type apparatus. This sample was analyzed by transmission electron microscopy. Evidence is found for layers of atomic chains (Figure 2), which correspond perfectly to the 5.5 Å pores of silicalite-1. EDX analysis indicate regions which exhibit a very homogeneous distribution of silicon and subnanometer Bi zones, some of which are aligned, distributed in the SiO_2 matrix down to the unit cell level (< 2nm).

Neutron powder diffraction was performed on the millimetric powder sample (Figure 3). 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 4): 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[15].

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 3). 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 5). 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 [2] 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.

In the past, it was shown that the insertion of liquid K metal into K-exchanged zeolite-A (LTA type structure) under high pressure and high temperature leads to ferromagnetic behavior[17]. The present Bi-filled silicalite is different as the framework is neutral and there are no cations in the pores. In order to determine the behavior in the case of neutral metal-filled zeolitic system, we performed magnetization experiment on millimetric sample and found a weak Pauli paramagnetic behavior probably due to residual rhombohedral Bi and no traces of superconductivity nor magnetic order. The presence of charged clusters of metal atoms in the K-filled LTA appears thus to be an important element for the presence of ferromagnetic behavior.

4. Conclusion

In conclusion, liquid bismuth was found to enter the siliceous zeolite, silicalite-1, at temperatures above 525K and pressures above 5 GPa. X-ray diffraction indicated that single crystals of this new material could be recovered after the HP-HT cycle under conditions at which pressure-induced amorphization is observed. Transmission electron microscopy indicates the presence of atomic chains which correspond to the 5.5 Å of the pores in silicalite. Neutron powder diffraction also confirms the insertion of bismuth. The results of DFT calculations show the structure of Bi-filled silicalite-1 contains Bi chains with short and long Bi-Bi distances, which interact with the silicalite-1 framework via van der Waal's forces.

Supporting Information. Crystallographic information files (CIF) file containing the structural data for silicalite-1 and the DFT model for Bi-filled silicalite-1 have been supplied as supporting information.

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5. Acknowledgments

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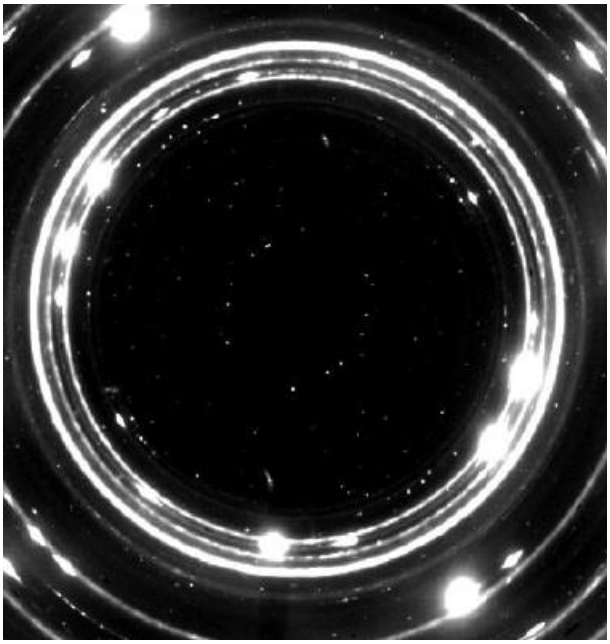

Figure 1. Single crystal reflections of silicalite-1 (small weak low-angle spots) in diffraction pattern of the composite material in the gasket after pressurization to 11 GPa obtained with high-energy x-ray radiation (33keV) on the ID27 beamline at the ESRF. The strong spots and powder lines are due to remaining bulk Bi.

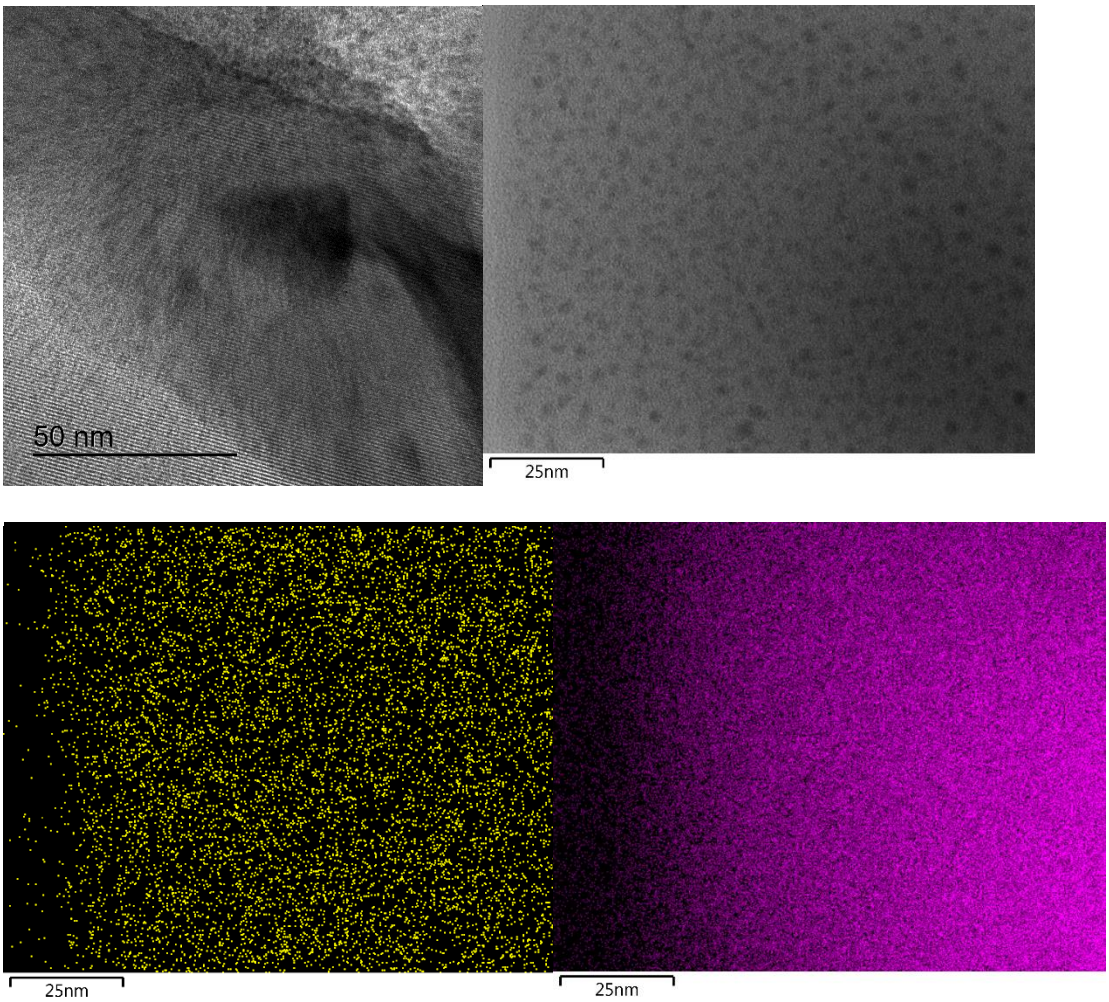

Figure 2**.** TEM (upper left) and STEM images (upper right) and STEM-EDX Bi $L\alpha_1$ (lower left) and Si $K\alpha_1$ data (lower right) from the Bi/silicalite-1 sample.

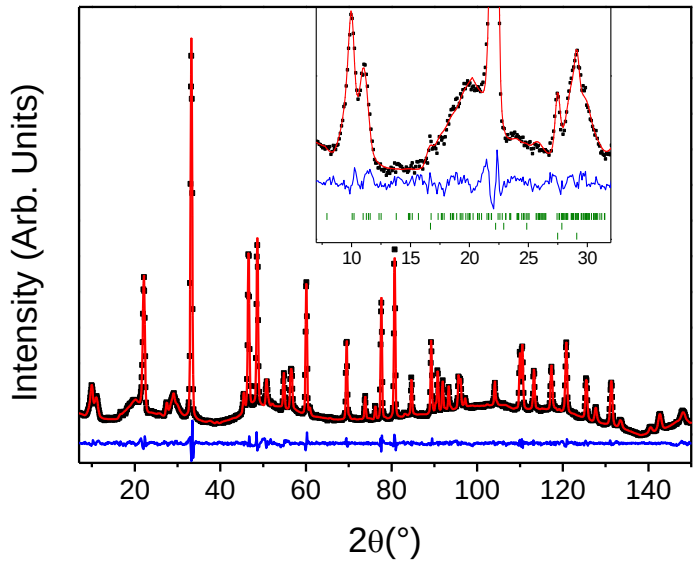

Figure 3. Experimental (black), calculated (red) and difference (blue) profiles from the fit to the NPD data from the Bi-filled silicalite-1 sample processed at 5 GPa and 593 K. The low angle part of the pattern is shown in the inset. Vertical bars indicate the calculated positions of the Bragg reflections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

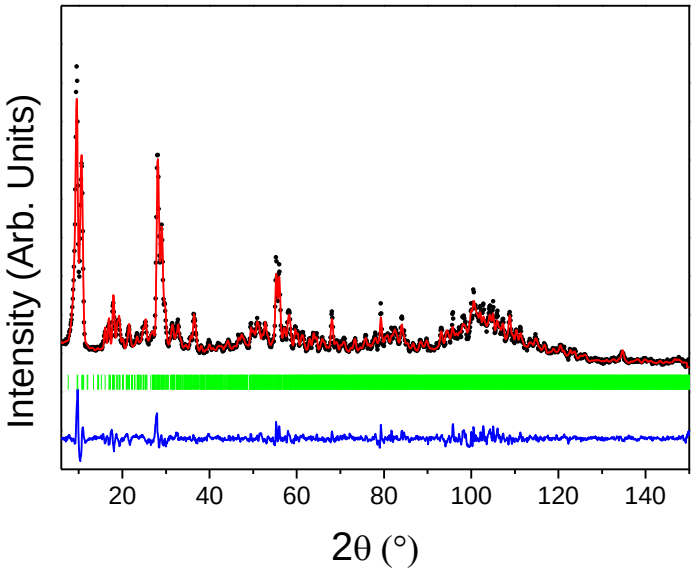

Figure 4. Experimental (black), calculated (red) and difference (blue) profiles from the fit to the NPD data from the initial silicalite-1 sample using the Rietveld method. Vertical bars indicate the calculated positions of the Bragg reflections of silicalite-1.

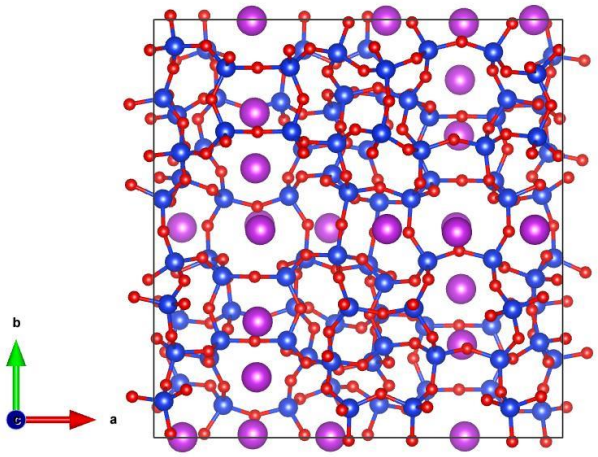

Figure 5. Relaxed structure of Bi-filled silicalite-1. Silicon, oxygen and bismuth atoms are represented by blue, red and purple spheres, respectively.

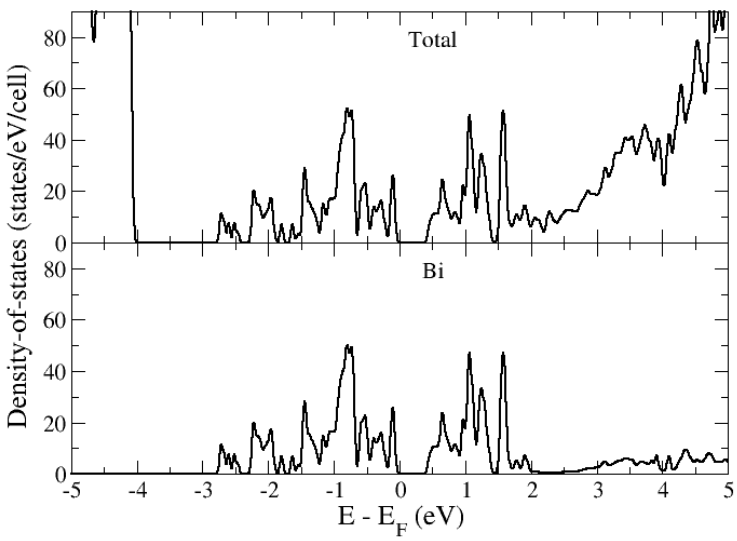

Figure 6. Electronic density of states of Bi-filled silicalite-1 (above) and the contribution of the inserted Bi atoms (below).