# High-pressure, high temperature insertion of bismuth in micro- and mesoporous silica

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Confinement of guest species, in particular metal atoms, in porous materials, such as zeolites and mesoporous silica, opens the way to design new composite materials with novel electronic, optical and magnetic properties. Previous work has shown that molten Bi can be inserted in the nanometric channels of porous materials at high pressure and high temperature. The insertion pressure is inversely proportional to the pore diameter. Various systems have been studied including several zeolites, mesoporous silica, chrysotile asbestos and Vycor glass [1-4]. These materials are ideal for designing a network of Bi nanowires, which could be of interest for thermoelectric applications, as nanostructuration and quantum confinement not only can improve the electronic properties of such materials, but also lower their thermal conductivity.

In the present work, a composite was synthesized by insertion of liquid bismuth in the 5.5Å diameter pores of the silicieous zeolite, silicalite-1, under high-pressure, high-temperature conditions, both in diamond anvil cells and a large-volume CONAC28 press. The insertion of bismuth stabilizes the structure with respect to pressure-induced amorphization. Transmission electron microscopy (TEM) indicated the presence of chains of atoms with a diameter of 5-6Å, corresponding to the diameter of the host silicalite-1 structure. Neutron powder diffraction (NPD) also confirmed the insertion of Bi in the pores of silicalite-1 (*Figure 1*). Density functional theory calculations indicate that the insertion of bismuth results in formation of chains in the pores of the host silicalite-1 linked to the framework by van der Waal's interactions interactions.

In order to probe different degrees of nanoconfinement, high temperature, high pressure conditions were also used to insert liquid bismuth in 4nm diameter amorphous silica nanotubes. A combination of TEM and NPD indicate that the final composite consists in 4nm nanowires confined in insulating quartz. Such a nanostructured material could be of considerable interest for thermoelectric applications. Additionally, selective dissolution would provide a route to obtain isolated 4nm bismuth nanowires.

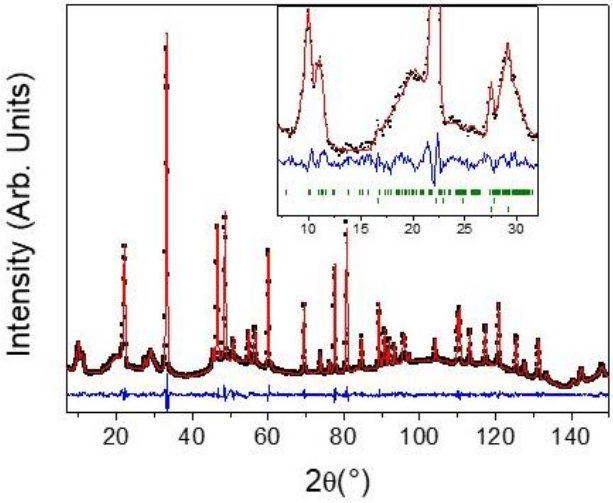


*Figure 1*. Experimental (black), calculated (red) and difference (blue) profiles from the fit to the NPD data from the Bi-filled silicalite-1 sample prepared at 5 GPa and 320°C. The calculated pattern of the Bi-silicalite-1 phase was obtained by using the cell parameters of the recovered sample and the fractional atomic coordinates of Bi, Si and O from the DFT model structure. The low-angle data are shown in the inset. Vertical bars indicate the calculated positions of the Bragg reflections of Bi-filled silicalite-1, PTFE, and Bi.

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