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# High-pressure, high temperature synthesis of a mesoporous $\alpha$ -quartz/bismuth nanowire composite

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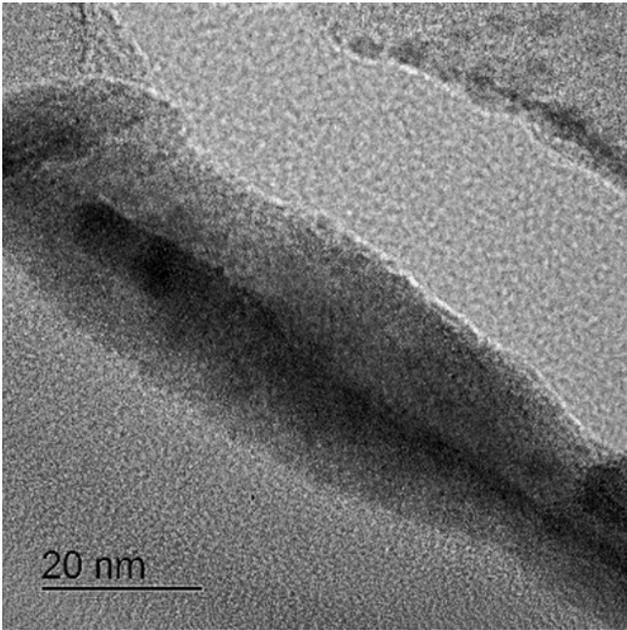
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## ABSTRACT

High temperature, high pressure conditions were used to insert liquid bismuth in 4-6 nm diameter amorphous silica nanotubes. A combination of transmission electron microscopy and neutron powder diffraction indicate that the final composite consists in 5-6 nm semi-conducting Bi nanowires confined in insulating mesoporous  $\alpha$ -quartz. Such a nanostructured material could be of considerable interest for thermoelectric applications.



## HIGHLIGHTS:

- Bismuth was inserted into 4-6 nm silica nanotubes under high-pressure, high-temperature conditions
- The host amorphous nanotubes crystallize in the form of  $\alpha$ -quartz
- The obtained nanocomposite consists of 5-6 nm Bi nanowires imbedded in mesoporous  $\alpha$ -quartz
- The formation of Bi nanowires modifies their physical properties compared to bulk Bi

## KEYWORDS:

Nanocomposites; Silica nanotubes; High Pressure; Guest Insertion; Bismuth

## 1. Introduction

Nanostructuring has been proposed as a solution to improve the efficiency of thermoelectric materials, which are characterized by their figure of merit  $ZT = \alpha^2 T / \rho \lambda$  with  $\alpha$  being the Seebeck coefficient,  $T$  the temperature,  $\rho$  the electrical resistivity and  $\lambda$  the thermal conductivity.[1, 2] The decrease of the dimensionality not only can lower the thermal conductivity by increasing the phonon scattering, but also can improve the electronic properties by quantum confinement.[1-6] Bismuth and its alloys are materials of choice for thermoelectric applications at low temperature in Peltier devices for cooling of optoelectronic systems, superconductors and for thermal management of electronic devices.[5, 7, 8]

Bismuth nanowires have been prepared using different techniques such as physisorption, vapor phase deposition, liquid phase deposition with organic liquids and liquid injection under high pressure [5, 9-15]. Although more efficient for obtaining complete pore filling of the mesoporous matrices, the last technique has been investigated in a limited number of studies [9-13]. It was shown that molten Bi can be inserted in the nanometric channels of porous materials at high pressure and high temperature.[5, 9-13] Various systems have been studied as host for insertion of liquid Bi including mesoporous silica, chrysotile asbestos, Vycor glass and opal.[9-13] These materials are ideal for designing a network of Bi nanowires. This nanostructuring resulted in major changes to the electrical and thermal conductivities and the Seebeck coefficient.[5, 9, 11, 16]

In the present study, high pressure and high temperature are used to inject liquid bismuth in 4-6 nm diameter pure amorphous silica nanotubes. The critical insertion pressure was estimated to be about 0.1 GPa based on the work of Bogomolov.[9] The Bi insertion was performed in a diamond anvil cell and millimeter-sized samples were prepared in a conac28 large volume press. The successful synthesis of Bi nanowires was confirmed by transmission electron microscopy (TEM). Neutron powder diffraction (NPD) provided structural information on the phases present in the synthesized nanocomposite and preliminary electronic properties were measured.

## **2. Experimental details**

The silica nanotubes were prepared from pure chrysotile fibers by using a nitric acid solution [17]. Then, the nanotubes were washed with distilled water and dried in air at 600 °C for 12 hours to remove water and hydroxyl groups from the silica walls of the nanotubes (Fig. 1).

A resistively-heated, membrane diamond anvil cell (DAC) was used for the high pressure, high temperature experiments. Ruby and  $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$  were placed in the 200  $\mu\text{m}$  hole in a 115  $\mu\text{m}$  thick rhenium gasket placed on one diamond anvil. These materials were used to measure the pressure and temperature by optical luminescence.[18-20] 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 the silica nanotubes and Bi powder

were added in a glovebox under argon. A 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. The pressure was increased to 0.5 GPa and the bismuth was melted at close to 500 K, then the liquid Bi was inserted in the nanotubes by increasing the pressure to 2.4 GPa at temperatures around 550 K.

Preparation of millimeter-sized sample Bi/silica nanotubes was carried out using a conac28 high-pressure apparatus. A mixture of bismuth and silica nanotubes with approximately a 1:3 volume ratio was placed in a 5mm inner diameter PTFE capsule in a glovebox and sealed under vacuum in a glass tube. The tube was then heated in order to melt the bismuth to form a compact sample. The PTFE capsule was inserted in the graphite furnace of the lithographic stone gasket, which was then placed between the two WC anvils of the conac press. Pressure was increased to 1 GPa to connect the graphite furnace. The temperature was increased to 613 K to ensure melting of Bi followed by pressure increase up to 2.1 GPa for insertion. The PTFE capsule was intact and was easily removed after the high P-T treatment. The melting point of PTFE rises steeply with pressure[21] and already reaches 692 K at 0.06 GPa, and will be even higher between 1 and 2 GPa at which the heating was performed. The diameter and thickness of the sample were 4.494 mm and 0.674 mm, respectively. The P-T conditions used ensure both filling of the nanotubes and full densification of the resulting pellet.

The millimeter-sized samples were studied by NPD on the D20 diffractometer at the Institut Laue Langevin. An incident wavelength of  $1.87\text{\AA}$  was used. Acquisition times were of the order of 30-60 minutes. Fullprof[22] was used to perform Le Bail fit in order to obtain the unit cell parameters.

The recovered sample from the DAC was placed in IR-white Resin (Sigma Aldrich). This sample and the millimeter-sized samples were cut into 70 nm slices using ultramicrotomy. TEM and electron diffraction measurements were performed with FEG JEOL 2200 FS – 200 KV electron microscope equipped a CCD GATAN USC camera with  $4092\times 4092$  pixels and a 200 kV electron gun. The probe diameter in STEM mode is about 1nm with a resolution, which can reach  $1\text{\AA}$ .

The electrical resistivity and the Seebeck coefficient were measured at room temperature by using respectively the Van der Pauw and the hot probe method on the millimeter-sized nanocomposite.

### 3. Results and discussion

The initial sample consists of nanotubes with typical outer and inner diameters of 30-35 nm and 4-6 nm [17], respectively (Fig. 1). The TEM results on the Bi containing samples after HP-HT treatment (Fig. 2) show that Bi atoms had been inserted in the initial nanotubes and form nanowires with a diameter of 5-6 nm (Fig. 3) corresponding to the inner diameters of initial nanotube. Some nanowires are found to retain the initial curvature of the chrysotile fibers (Fig. 3). The distance between the atomic planes in the nanotubes are found to be in the order of 6-7 Å, which is similar to the Bi-Bi distance along the c direction in the rhombohedral form. STEM-EDX results confirm that the Bi nanowires are surrounded by SiO<sub>2</sub>. Importantly, the oxygen distribution is identical to that of Si. Electron diffraction data (Fig. 4) from zones with the same morphology as those corresponding to SiO<sub>2</sub> could be indexed based on the  $\alpha$ -quartz lattice (Table 1) indicating that the nanotubes had crystallized in the form of the  $\alpha$ -quartz.

Due to the high level of absorption of bismuth in the visible and x-ray regions of the spectrum, NPD appeared to be the technique of choice to obtain structural information on the synthesized nanocomposite. Two phases were observed in the NDP pattern of the mm-sized nanocomposite prepared at 2.1 GPa and 613 K (Fig. 5), highly oriented rhombohedral bismuth (cell parameters:  $a = 4.5518(5)$  Å,  $c = 11.882(1)$  Å) and  $\alpha$ -quartz (cell parameters:  $a = 4.9217(6)$  Å,  $c = 5.4169(9)$  Å) obtained due to the crystallization of the silica nanotubes. The strong preferred orientation present did not allow quantitative analysis to be performed using the Rietveld method.

Preliminary global measurements of the electronic properties were performed on the millimetre-sized nanocomposite. The measured electrical resistivity of 0.3 m $\Omega$ .cm is 2.5 times higher than that of bulk Bi.[23] It is known that Bi nanowires present a higher resistivity than the bulk form due to quantum confinement, which induces a semimetal to semiconductor transition.[24-27] Therefore, this higher measured resistivity may indicate that the confined Bi nanowires increase the electrical resistivity of the nanocomposite. In addition, the insulating quartz also contributes to composite's resistivity. The value obtained for the Seebeck coefficient of  $-46 \pm 2$   $\mu$ V/K (Fig. 6) is comparable to values obtained for Bi nanowires

with larger diameters in previous work.[5, 28-31] This negative value indicate that electrons are the major charge transport carriers. Finally, the thermoelectric power factor for the nanocomposite is about 11  $\mu\text{W}/\text{cmK}^2$ .

#### **4. Conclusion**

These results clearly show that the HP-HT treatment resulted in the insertion of the liquid bismuth to form 5-6 nm wires and in the crystallization of the nanotubes to form  $\alpha$ -quartz. This nanostructuration can be expected to modify the properties of Bi with respect to its bulk form. In addition, as in previous work[15], selective dissolution may provide a route to obtain isolated 5-6 nm bismuth nanowires. According to theoretical calculations[24], these nanowires may have an exceptional thermoelectric efficiency due to their modified physical properties such as electronic conductivity, Seebeck coefficient and thermal conductivity. Preliminary global electrical measurements on a nanocomposite pellet are consistent with the properties expected due to nanostructuration.

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Table 1. Electron diffraction data for a SiO<sub>2</sub>-containing zone in Bi-filled nanotubes with indexation based on an  $\alpha$ -quartz lattice.

$d$ (Å)	$hkl$
3.34	101
2.32	102
1.98	201
1.53	211
1.36	212

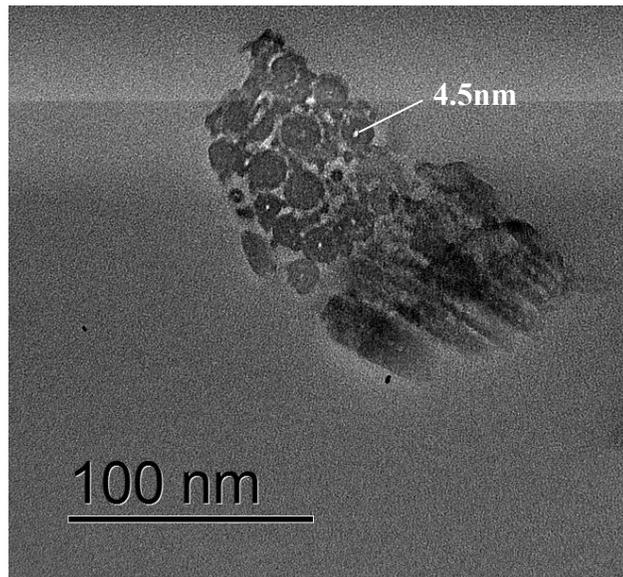
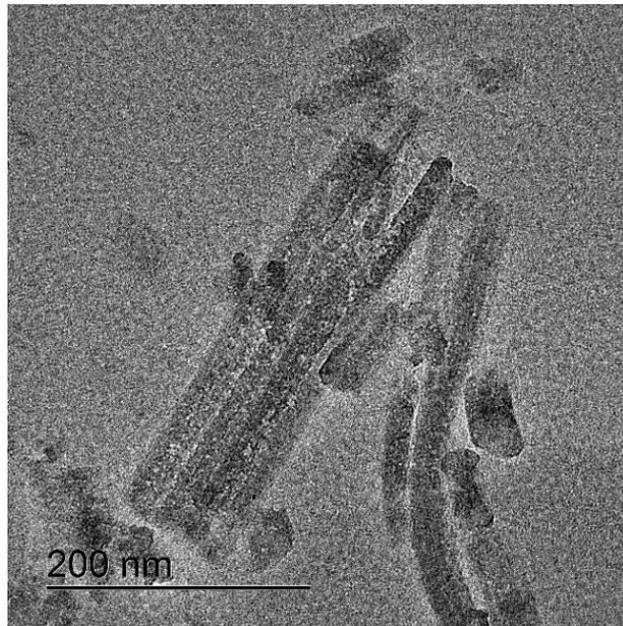


Fig. 1. TEM images of pure SiO<sub>2</sub>-nanotubes after acid treatment of chrysotile fibers

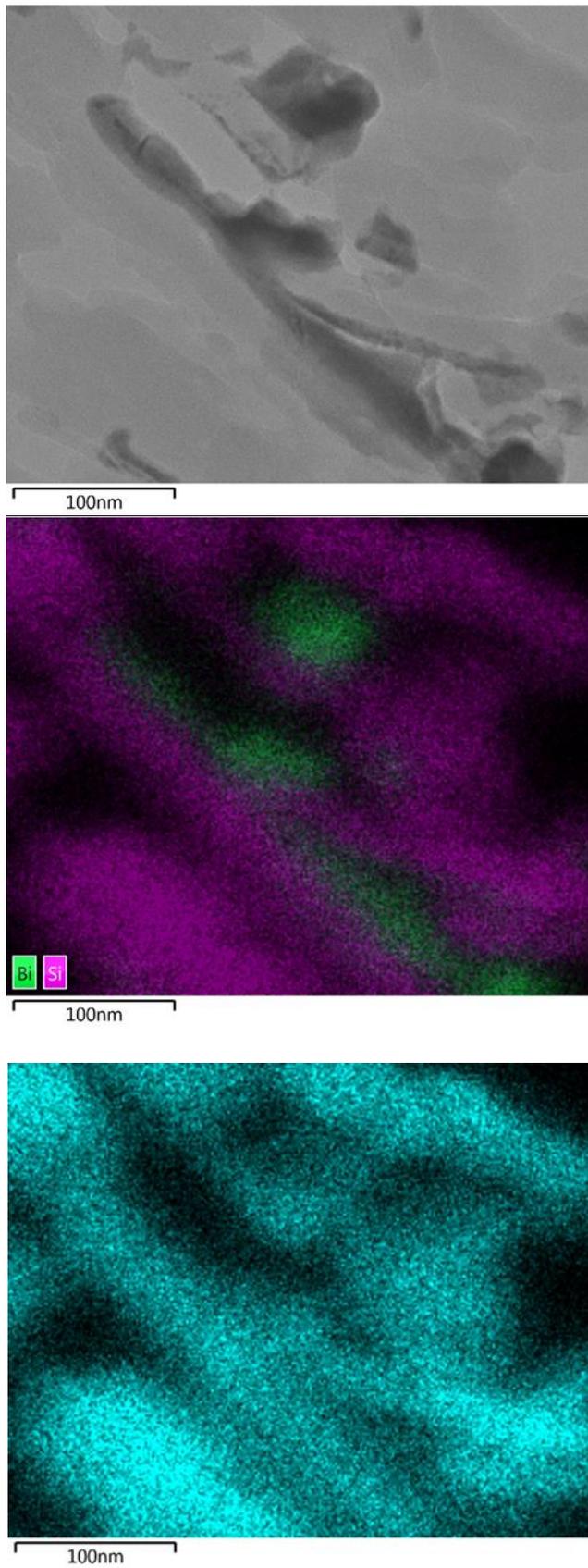


Fig 2. TEM images (top) of a Bi nanowire in a SiO<sub>2</sub> matrix and STEM-EDX L $\alpha_1$  data of Bi and K $\alpha_1$  data of Si (middle) and O (bottom).

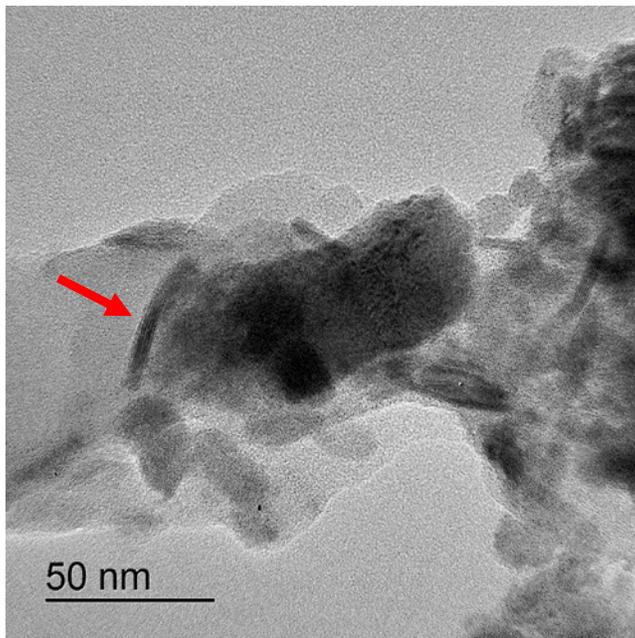
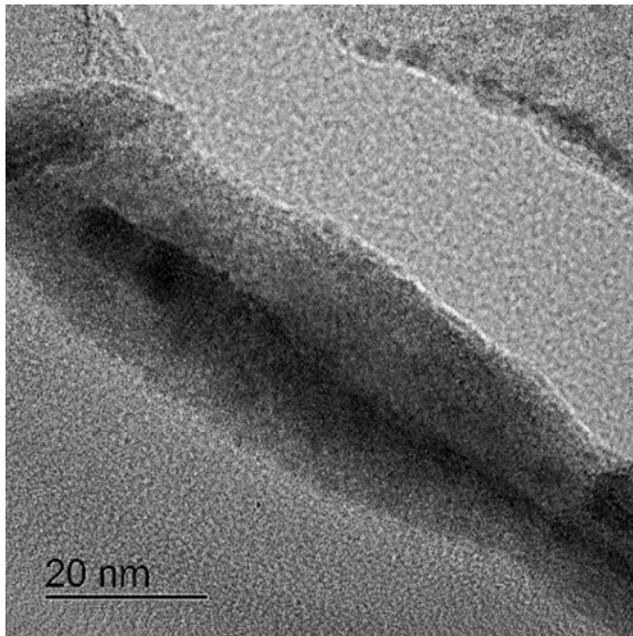


Fig. 3. TEM images of Bi nanowires surrounded by SiO<sub>2</sub>. A typical zone retaining the curvature of the chrysotile fibers is indicated by a red arrow.

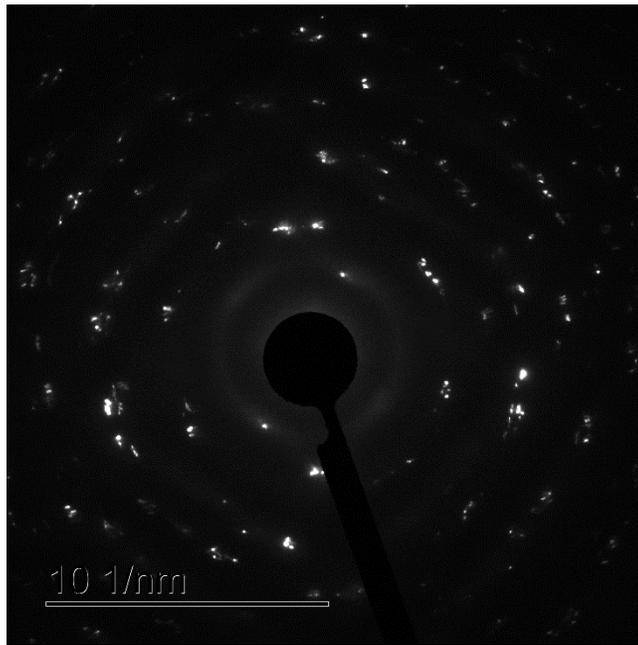


Fig. 4. Electron diffraction pattern of zones with the same morphology as the  $\text{SiO}_2$  containing zones in Fig. 2.

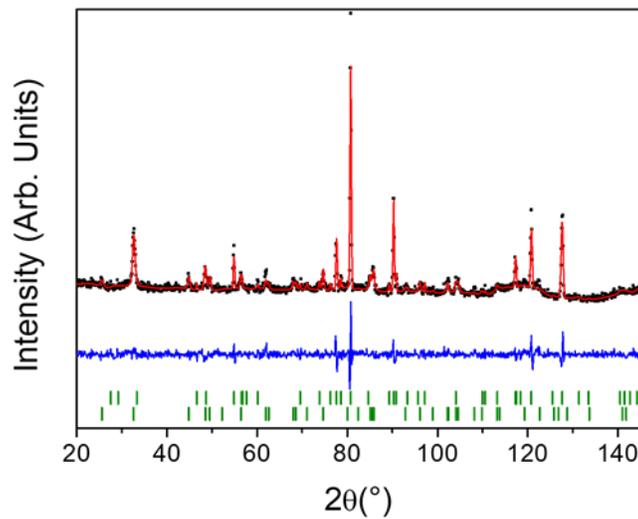


Fig. 5. Experimental (black), calculated (red) and difference (blue) profiles from the fit to the NPD data from the Bi-filled silica nanotubes sample processed at 2.1 GPa and 613 K. Vertical bars indicate the calculated positions of the Bragg reflections of rhombohedral Bi (above) and  $\alpha$ -quartz (below).

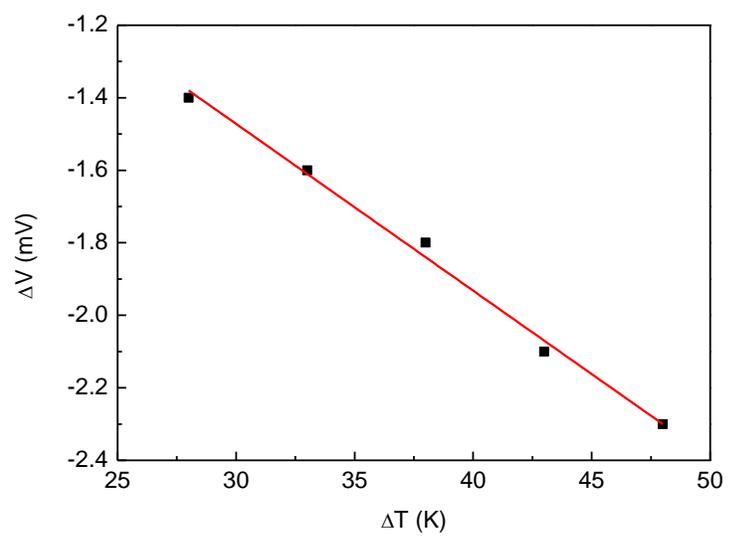


Fig. 6. Voltage-temperature difference plot for the Bi-filled nanotubes.