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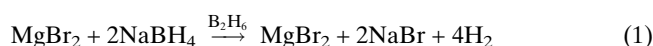
A Simple Sol–Gel Synthesis of Superconducting MgB₂ Nanowires**

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The discovery of superconductivity in the binary boride MgB₂ with a transition temperature (T_c) of near 39 K,^[1] has sparked intense interest in this compound. This interest is in part due to the high T_c compared to other bimetallic compounds, and the fact that traditional solid-state synthesis routes can be used to prepare this compound.^[2] Traditional synthesis routes have been employed for the preparation of crystals,^[3] thin films,^[4] macroscopic wires,^[5,6] and tapes^[7] of this material. Although solid-state synthesis methods using elemental Mg and B have been successful in producing bulk MgB₂ phases, the preparation is made difficult by the large differences in vapor pressure between Mg and B, and also the high reactivity of Mg towards O, which requires these reactions to be performed under carefully controlled conditions, since doping or contamination of the MgB₂ phase affects the superconducting transition temperature.^[4,8,9] It is of fundamental and applied interest to study the effect of size on the superconducting nature of MgB₂. Till now there have been only a few reports of the synthesis of MgB₂ nanowires^[10–12] or other MgB₂ nanostructures.^[13,14] Most of these synthesis methods are multistep, involving a vapor-transport process,^[10] mechanical alloying,^[13] or pyrolysis of MgB₂ nanoparticles formed in situ.^[11] However, a soft-chemical synthetic approach, which allows more control over the stoichiometry and nanostructure morphology of this potentially important material, is long overdue. Here we report a simple, high-yield bulk synthesis that produces pure MgB₂ nanowires that show a superconducting T_c of 38.6 K. Our technique utilizes room-temperature sol–gel chemistry followed by pyrolysis in a controlled atmosphere of diborane (B₂H₆) and N₂ under ambient pressure. The sol–gel technique is an attractive synthetic method since its flexibility allows for optimization of the synthesis.^[15]

The MgB₂ nanowires were synthesized in two steps. Initially a precursor gel was obtained by mixing the magnesium bromide and sodium borohydride reagents in the presence of cetyltrimethylammonium bromide (CTAB). Pyrolysis of this gel under a diborane–N₂ atmosphere yielded a black powdery product. The powder X-ray diffraction pattern of the black product shows the presence of the MgB₂ phase (see Supporting Informa-

tion, Fig. S1) while scanning electron microscopy (SEM) revealed that the product was predominately nanowires. Use of other magnesium halides, such as MgCl₂ or MgI₂, also yielded nanowires under similar reaction conditions; however, the yield of the nanowires in the product was reduced compared to when using MgBr₂. The chemical reaction can be written as:



Extensive SEM of the black product revealed that nanowires are essentially the exclusive product. Bulk crystals or other morphologies (such as 2D plates or tapes) were rarely observed. Figure 1a shows a typical SEM image of the prod-

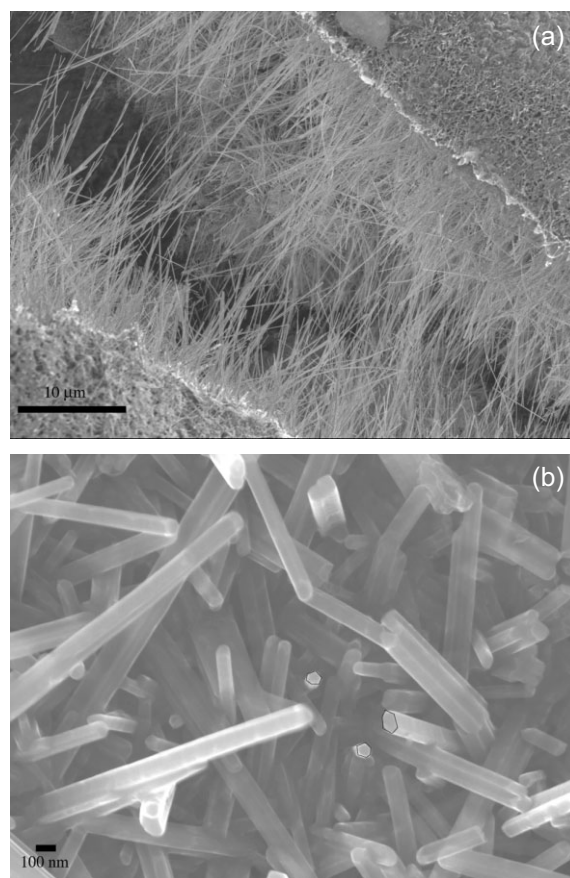


Figure 1. SEM images of the MgB₂ nanowires. a) A thick mesh of nanowires, where individual nanowires with lengths up to 15–20 μm can be seen in the center of the image. b) Higher-magnification image of the vertically oriented nanowires, showing that some of the nanowires have a hexagonal cross section, as outlined in black.

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uct, revealing a thick mesh of nanowires. The nanowires are ca. 50–100 nm in diameter with very smooth surfaces and have lengths up to at least 20 μm . A few nanowires appear to be ribbonlike, but nanowires oriented vertically with respect to the electron beam reveal a hexagonal cross section (see Fig. 1b) consistent with a degree of crystallinity. EDAX (energy dispersive analysis by X-rays) of individual nanowires also revealed the presence of Mg and B in the nanowires.

Transmission electron microscopy (TEM) images show that the nanowires are solid, straight, and quite uniform in diameter along their lengths (Fig. 2a). Some of the nanowires reveal a rounded tip, while others have a flat rectangular or polygonal tip. Some of the nanowires are single-crystalline and show lattice fringes, as shown in the high-magnification TEM image in Figure 2b. The layer separation estimated from the lattice

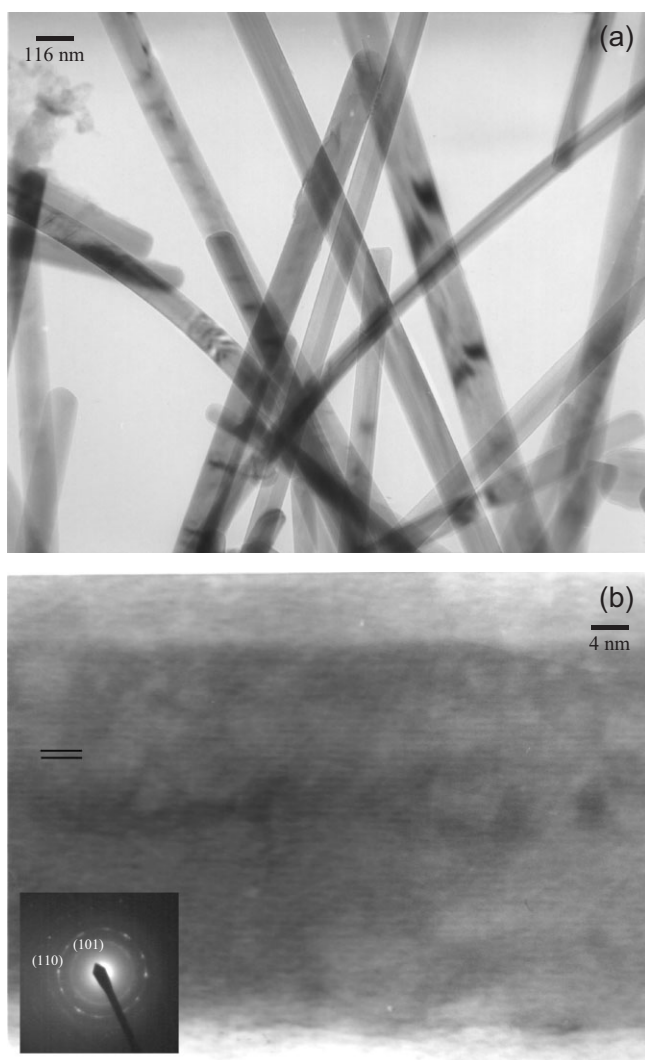


Figure 2. TEM images of the MgB_2 nanowires. a) Low-magnification TEM image showing nanowires with rounded as well as flat rectangular tips. b) High-magnification TEM image of an individual nanowire showing the lattice fringes. Inset shows the corresponding electron diffraction pattern.

fringes is approximately 2.6 \AA , corresponding to the (100) spacing of bulk MgB_2 (Joint Committee on Powder Diffraction Standards (JCPDS) file, card number 38-1369), indicating that the wires probably grew perpendicular to the a -axis. The hexagonal cross section of some of the wires (Fig. 1b) also suggests that the growth axis of the wires may be parallel to the c -axis.^[16] Selected area electron diffraction (SAED) patterns (inset of Fig. 2b) on some individual nanowires indicate that the nanowires are crystalline. The diffraction spots in the ED pattern could be indexed to $d(100)$, $d(101)$, and $d(110)$ lattice planes of bulk MgB_2 .

The formation of the gel in the initial reaction mixture may be the key to the formation of the nanostructured products. A gel is typically composed of a dense fibrous network or mesh of ultrafine particles.^[17] This prearrangement of the precursor particles, with the participation of the CTAB surfactant, could template the formation of the one-dimensional morphology of the nanowires. Gel-and-surfactant-assisted synthesis of nanowires and nanotubes of several inorganic materials has been previously reported in the literature.^[18–20] Since the melting point of MgBr_2 is ca. 650 $^\circ\text{C}$, the reaction could be occurring from a molten salt solvent that allows for intimate intermixing of the precursors and diffusion of the diborane vapors. However, the absence of any features at the tip of the nanowires argues against any catalytic growth or vapor–liquid–solid (VLS) mechanism. The use of B_2H_6 gas is crucial since it maintains a B-rich atmosphere and completely prevents oxygen (impurity in the N_2 gas or from the quartz reaction chamber) from coming into contact with the reactants. B_2H_6 reacts with even minute amounts of O_2 to form solid B-oxide phases,^[21] thus preventing reaction of O_2 with Mg that may form along with MgB_4 when MgB_2 is heated above 700 $^\circ\text{C}$.^[22,23] In some experimental runs, trace amounts of MgB_4 impurity could be identified in the products. If the reaction is done under a nominally pure N_2 atmosphere, the product contains a mixture of phases—white oxide phases and black boride phases. It has been shown recently that heating MgB_2 at 700 $^\circ\text{C}$ in an Ar atmosphere produces MgO nanowires.^[24]

Magnetic susceptibility data on a bulk sample containing an ensemble of MgB_2 nanowires was collected using a SQUID (SQUID: superconducting quantum interference device) magnetometer. The powdered sample was zero-field-cooled from room temperature to 5 K and the DC magnetization was then measured as a function of temperature under an applied field of 50 Oe (1 Oe = 1000/4 π A m⁻¹). A strong Meissner effect, indicating the onset of superconductivity, was observed at ca. 38.6 K (Fig. 3). It is interesting to note that T_c is essentially the same as the bulk value. The T_c in the MgB_2 system is generally sensitive to the presence of impurities. Boron substitution with C or O and magnesium substitution with other metals all result in a lowering of T_c with even trace amounts of impurities, and a further reduction in T_c with increasing amounts of impurities.^[4,9] Although we could not reliably quantify the amount of C/O in the nanowires, the sharp T_c at ca. 39 K suggests that the nanowires are chemically pure. It

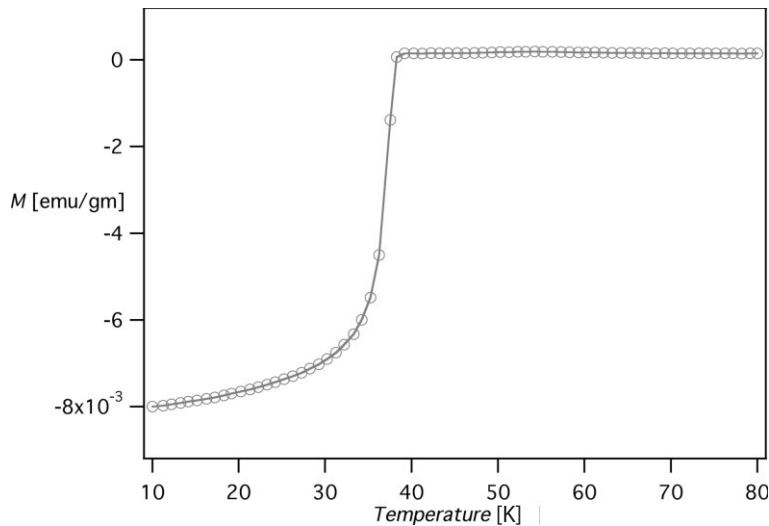


Figure 3. The DC magnetization (M) as a function of temperature obtained on a randomly oriented ensemble of MgB_2 nanowires under an applied field of 50 Oe, showing a superconducting transition at 38.6 K.

also suggests that the nanowire morphology does not affect the transition temperature.

The magnetization (M) versus field (H) measurement, carried out on the MgB_2 nanowires at 5 K, showed the presence of a hysteresis loop (Supporting Information, Fig. S2), commensurate with the fact that MgB_2 is a type II superconductor. Since the intermediate mixed state of type II superconductors is most important for applications, the value of the lower and upper critical fields (H_{c1} and H_{c2} , respectively), which define the mixed state, and their dependence on temperature is of significance. We carried out some analysis of our preliminary data to estimate the H_{c1} and H_{c2} values from the magnetic measurements. However, since the temperature dependence of the upper critical field is anisotropic (i.e., $H_{c2}^c \neq H_{c2}^{ab}$)^[25] and the present set of measurements was carried out on a randomly oriented ensemble of nanowires, more precise measurements on single nanowires or oriented nanowire bundles are required to obtain better values for these parameters. In our preliminary studies, H_{c1} was estimated from the deviation from linearity of the M – H plot measured at different temperatures in the low-field region. The dependence of H_{c1} on temperature is almost linear and extrapolation of this curve to 0 K gives a value of ca. 338 Oe for $H_{c1}(0)$. This value is comparable to that reported by other researchers.^[26] The temperature dependence of H_{c2} is derived from the magnetic susceptibility measurement done under different applied fields. The H_{c2} -versus-temperature plot shows a pronounced positive curvature near T_c , as was previously reported in the MgB_2 system.^[27,28] Although there have been numerous studies that estimate the upper and lower critical fields in pure and doped MgB_2 , to our knowledge there have been no reports of critical-field measurements on MgB_2 nanowires. However, there are several reports where the temperature dependence of the critical fields was estimated for macroscopic

polycrystalline wires of MgB_2 that show similar behavior to sintered pellets.^[6] It will be interesting to carry out measurements of resistivity, supercurrents, and critical fields on individual nanowires. These studies are currently in progress.

Recently, it was reported that when the diameter of the superconducting nanowire of Sn is smaller than almost five times the phase coherence length, $\xi(T)$, of bulk Sn, its behavior changed from that of a bulklike to that of a more quasi-one-dimensional system.^[29] The superconducting coherence length of MgB_2 is ca. 5 nm,^[27,30] which is much smaller than the average diameter of the nanowires obtained in this study. This might explain the fact that the nanowires show bulklike behavior.

In conclusion, bulk quantities of superconducting MgB_2 nanowires have been successfully synthesized from magnesium halides and sodium borohydride precursors via a simple method utilizing room-temperature sol–gel chemistry and pyrolysis under a diborane– N_2 atmosphere. The nanowires show a T_c of 38.6 K. The successful bulk preparation of MgB_2 nanowires by simple sol–gel-assisted methods suggests that it may be possible to extrude and pyrolyze the precursor gel in a continuous process to produce long MgB_2 superconducting nanowire cables.

Experimental

Synthesis of Precursor Gel: 0.2958 g of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ (ca. 1 mmol) and 0.078 g of NaBH_4 (ca. 2 mmol) were dissolved separately by sonication in 3.2 and 6.8 mL of ethanol, respectively. 0.025 mmol of CTAB was then added to each solution. The sodium borohydride solution was then added dropwise to the Mg-halide solution (large evolution of gas observed and the solution turned turbid) and the reaction mixture was sonicated for several minutes. This reaction mixture thickened over time and formed a gel when left open to the atmosphere for several hours.

Synthesis of MgB_2 Nanowires by Pyrolysis of the Gel: The thickened gel was loaded into a quartz boat, placed inside a horizontal tube furnace and the furnace temperature was ramped to 800 °C at ca. 10 °C min⁻¹. Pyrolysis was carried out for approximately 5 min at 800 °C in an atmosphere of diborane and N_2 (200 sccm) and then the furnace was switched off and cooled to room temperature over a period of 12–14 h. A black, powdery product was formed in the quartz boat. The product was washed rapidly with deionized water followed by ethanol to remove the by-products, including sodium bromide, formed in the reaction shown in Equation 1.

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