

# Encapsulation of One-Dimensional Potassium Halide Crystals within BN Nanotubes

Wei-Qiang Han, C. W. Chang, and A. Zettl\*

Department of Physics, University of California, Berkeley, California 94720, and The Molecular Foundry, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received April 14, 2004; Revised Manuscript Received May 3, 2004

## ABSTRACT

One-dimensional crystals of potassium halides, including KI, KCl, and KBr, were inserted into boron nitride nanotubes. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectrometry were used to characterize their microstructures and compositions. The fillings are usually single crystals with lengths up to several micrometers.

Hexagonal boron nitride (BN) is a covalently bonded system with exceptionally strong  $sp^2$  planar bonds. This material forms the basis for a growing number of nanostructures including nanotubes (NTs).<sup>1,2</sup> The desirable mechanical, electronic, thermal, and chemical properties of these materials suggests that BN nanotubes could be a useful component in many complex nanosystems. In particular it may be possible to functionalize their outer surface with other materials<sup>3</sup> or to fill their interior with other crystals. The filling of BN nanotubes with some one-dimensional crystals, including carbides, nitrides, oxides, and fullerenes, has already been demonstrated.<sup>4–9</sup> These filled BN nanotubes are usually synthesized through a simultaneous phase separation process during the synthesis of nanotubes and nanowires.

The highly ionic nature and low vapor pressures of alkali halides make them fundamentally interesting and experimentally challenging molecules to study. Alkali halides form the most comprehensive series of currently characterized filling materials for single-walled carbon nanotubes.<sup>10,11</sup> Different from carbon nanotubes, BN nanotubes have an energy gap of 5 eV independent of wall number, diameter, or chirality and thus constitute desirable insulating structures for geometrically and electronically confining atomic, molecular, or nanocrystalline species. Here we describe the synthesis and structural characterization of one-dimensional potassium halide filled BN nanotubes.

There is a two-step process to create the potassium halide filled BN nanotubes. First, bare (i.e., unfilled) BN nanotubes are synthesized through a carbon nanotube substitution reaction followed by an oxidation treatment.<sup>2,12</sup> The outside diameter of BN nanotubes is usually less than 8 nm while

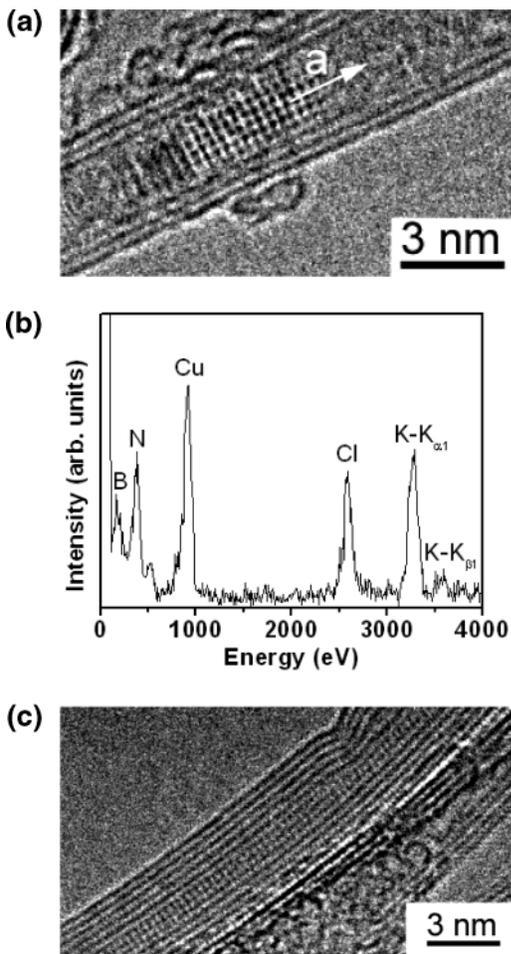
**Table 1.** Reaction Temperatures and Reaction Times

filled materials	filling temp °C	reaction time (hours)
KCl	740	4
KI	670	4
KBr	720	4

the inside diameter usually ranges from 1 to 5 nm. The nanotubes form either as isolated units or as tubes arranged in aligned bundles. The oxidation-treated BN nanotubes are then sealed in different evacuated ( $10^{-6}$  Torr) quartz ampules together with different commercially obtainable potassium halides (KI, KCl, and KBr) in about a 4:1 halide/BN NT mass ratio. The experimental conditions are listed in Table 1. The ampules are broken open, and the resultant materials are ultrasonically dispersed in methanol and dropped onto a holey carbon coated grid for characterization by high-resolution transmission electron microscopy (HRTEM) using a Philips CM200 FEG equipped with an energy-dispersive X-ray spectrometer (EDS).

Figure 1a is a high-magnification TEM image of a three-walled BN nanotube filled with KCl crystals. The incident electron beam direction is along  $\langle 001 \rangle$ , and the long axis of the crystal is parallel to the crystalline  $a$  direction. The crystal structure can be indexed to rock salt KCl. The inner diameter of the BN nanotube is about 2.16 nm. The width of the KCl crystal is 1.56 nm. This is a six-layer KCl crystal. The dark spots are spaced at average intervals of  $\sim 3.1$  Å, corresponding to the  $3.15$  Å  $\{200\}$   $d$  spacing of bulk rock salt KCl. Figure 1b is the corresponding EDS spectrum, which is consistent with the nanotube's core being composed of pure KCl. Figure 1c shows a three-layer crystal inside a five-

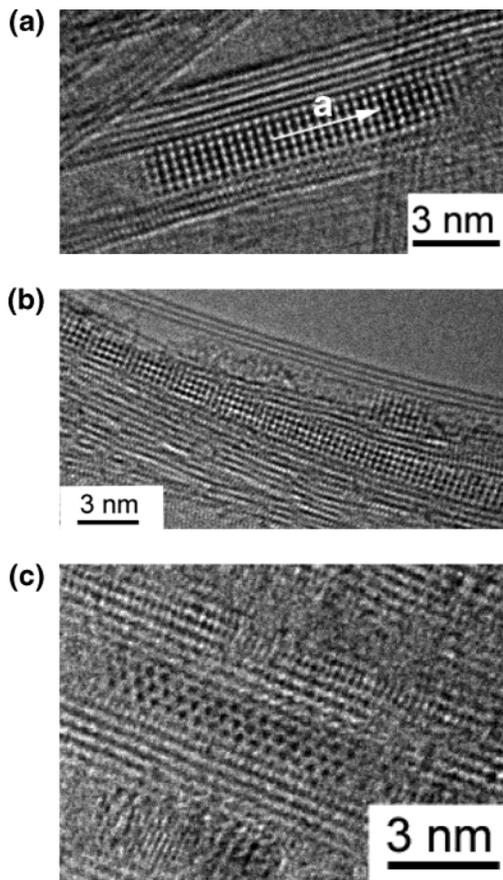
\* Corresponding author. E-mail: azettl@physics.berkeley.edu.



**Figure 1.** (a) High-magnification TEM image of a KCl-filled BN nanotube. The incident electron beam direction is along  $\langle 001 \rangle$ , and the long axis of the crystal is parallel to the crystalline  $a$  direction. (b) EDS spectrum taken the filled nanotubes of Figure (a). (c) High-magnification TEM image of a three-layers crystal filled inside BN nanotube.

walled BN nanotube. The inner diameter of the BN nanotube is about 1.32 nm. This narrow crystal is also rock salt KCl, and its long axis runs parallel to the crystalline  $a$  direction. Significant lattice distortions are observed in the three-layer crystal. Along the long axis the dark spots are spaced at average intervals of  $d_1 \sim 3.0 \text{ \AA}$ , less than the  $3.15 \text{ \AA}$   $\{200\}$   $d$  spacing of bulk rock salt KCl. The distortion ratio is about 4.8%. Perpendicular to the long axis across the crystal, the spacing increases to  $d_2 \sim 3.45 \text{ \AA}$ , much larger than the  $3.15 \text{ \AA}$   $\{200\}$   $d$  spacing of bulk rock salt KCl. Here the distortion ratio is about 9.5%. The percent difference between  $d_2$  and  $d_1$  is about 15%. Similar distortions in the lattice spacing perpendicular to the long axis of the filled crystal were observed in a bilayer of KI-filled single-walled carbon nanotubes, but there was no distortion of the spacing along the long axis of the crystal.<sup>13</sup>

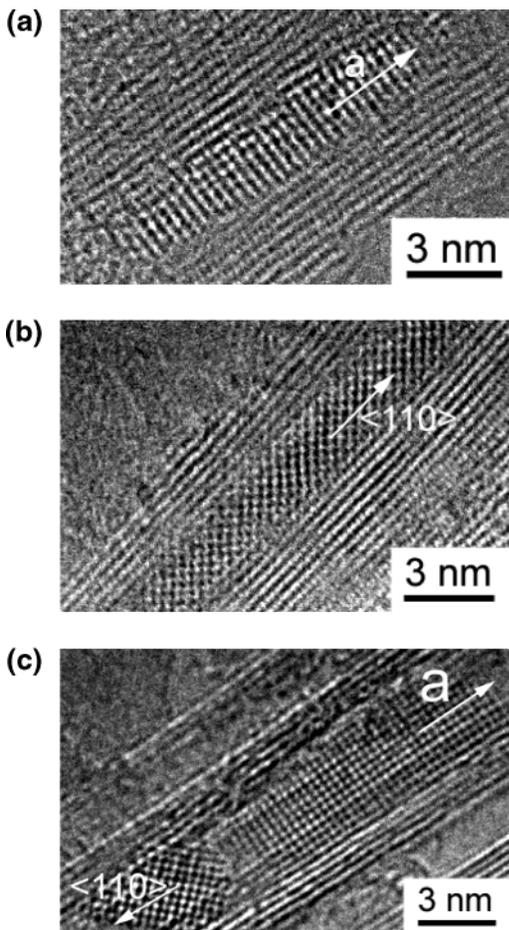
Figure 2a is a high-magnification TEM image of a KI-filled BN nanotube. The length and width of the KI crystal are 11.6 and 1.40 nm, respectively. This is a five-layer KI crystal. The incident electron beam direction is along  $\langle 001 \rangle$ , and the long axis of the crystal is parallel to the crystalline  $a$  direction. The crystal structure can be indexed to rock salt



**Figure 2.** (a) High-magnification TEM image of a KI-filled BN nanotube. The incident electron beam direction is along  $\langle 001 \rangle$  and the long axis of the crystal is parallel to the crystalline  $a$  direction. (b) High-magnification TEM image of two KI-filled BN nanotubes. (c) High-magnification of a three-layer crystal encapsulated by a BN nanotube.

KI. Figure 2b is a high-magnification TEM image of two KI-filled BN nanotubes. One nanotube encapsulates a very long crystal. Surveying the entire nanotube in the TEM, we find it to be fully filled. The length of the filling is up to several micrometers. The four-layer crystal structure is also rock salt KI, and the long axis of the crystal is parallel to the crystalline  $a$  direction. The shape of the filled crystal follows the shape of the nanotube, straight or bent. Another nanotube has a short filling. Figure 2c shows a three-layer crystal inside a BN nanotube. The width of crystal is  $7.4 \text{ \AA}$ . EDS spectra confirm the crystals are KI.

Figure 3a is a high-magnification TEM image of a KBr-filled BN nanotube. The width of the KBr crystal is 1.83 nm. The incident electron beam direction is along  $\langle 001 \rangle$ , and the long axis of the crystal is parallel to the crystalline  $a$  direction. The crystal structure can be indexed to rock salt KBr. Figure 3b shows a long crystal encapsulated by a BN nanotube. This thin crystal is also rock salt KBr, and its long axis is parallel to the  $\langle 110 \rangle$  direction. The width of crystal is 2.13 nm. Figure 3c shows a BN nanotube filled with two connected crystals. The widths of both crystals are 3.46 nm. Both crystals are cubic KBr. The long axes of the longer crystal and the shorter crystal are parallel to the crystalline



**Figure 3.** (a) High-magnification TEM image of a KBr-filled BN nanotube. The incident electron beam direction is along (001), and the long axis of the crystal is parallel to the crystalline  $a$  direction. (b) High-magnification TEM image of a long crystal encapsulated by a BN nanotube. This thin crystal is cubic KBr, and its long axis is parallel to the  $\langle 110 \rangle$  direction. (c) High-magnification TEM image of two connected crystals encapsulated by one nanotube.

$a$  direction and the  $\langle 111 \rangle$  direction, respectively. EDS spectra confirm that the crystals are KBr.

We demonstrate the successful encapsulation of various potassium halides within BN nanotubes using a capillary technology. It is found that BN nanotubes filled with fullerenes often have irregular crystal structures, or “silo” structures, even when the inner diameters of the BN nanotubes are quite large.<sup>9</sup> In contrast, it is difficult to find such structures in BN nanotubes filled with potassium halides. The filled halides maintain their usual crystal structure, although distortions exist for the narrowly filled

crystals. This suggests that not only are the tubes’ inner diameters important in the formation of “silo” structures but also that the bonding type of the filling may play an important role. The ionic bonding of potassium halides is very strong, so they tend to form regular crystal structures. Whereas the van der Waals interaction between fullerenes is very weak, so it is easy for them to form silo structures. Compared to carbon nanotube filled halides, we have not only observed the similar distortions in the lattice spacing perpendicular to the long axis of the filled crystal inside BNNTs, but have also observed the distortion of the spacing along the long axis of the crystal. BN nanotubes not only confine the halide crystals but also act effectively as chemically and electrically inert protecting layers and could enhance the stability of potassium crystals in harsh chemical, thermal, and electrical/optical environments. Finally, the interaction between potassium halides and BN nanotubes suggests that new properties might arise for encapsulated halide crystals.

**Acknowledgment.** This research was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under contract number DE-AC03-76SF00098, administered through the  $sp^2$  and Interfacing Nanostructures initiatives.

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NL0494452