

LETTERS

Massive Icosahedral Boron Carbide Crystals

Bingqing Wei,[†] Robert Vajtai,[†] Yung Joon Jung,[†] Florian Banhart,[‡]
Ganapathiraman Ramanath,[†] and Pulickel M. Ajayan^{*,†}

*Department of Materials Science and Engineering, Rensselaer Polytechnic Institute,
Troy, New York 12180-3590, and Zentrale Einrichtung Elektronenmikroskopie,
Universität Ulm, 89069 Ulm, Germany*

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We have discovered massive icosahedral multiply twinned particles of boron carbide among soot produced during the arc evaporation of carbon and boron in the presence of magnesium. The observation is striking because 5-fold symmetry in large micron size crystals is extremely rare. It is suggested that the icosahedral structural unit that builds up the rhombohedral crystal structure of bulk B_4C provides a template for the formation of these large icosahedral crystals. The physical properties of boron carbide, known for its hardness, could be further improved in these crystals because of their unusually high symmetry.

Large crystals having 5-fold symmetry are rare in nature because these systems have no long-range translational symmetry. However, smaller icosahedral quasicrystal morphologies and local structures showing 5-fold symmetry have been found in several materials systems. Examples of these range from biological materials to minerals, such as viruses,¹ proteins,² surfactant bi-layers,³ diamonds,⁴ and multiply twinned particles (MTP) of metals.⁵ The essence of the structure of these crystals follows the layer by layer stacking of a Mackay icosahedron,⁶ the creation of such large crystals with 5-fold symmetry is very difficult to achieve. Very recently, large compact icosahedra similar to MTPs made from a boron suboxide, B_6O , were fabricated using a high-temperature high-pressure technique.⁷ Here we report that massive crystals of boron carbide, a very common hard material with excellent mechanical, thermal, and electrical properties used for abrasive, electronic, and shielding applications having 5-fold symmetry (Figure 1), can be produced by the relatively simple electric arc-discharge technique.

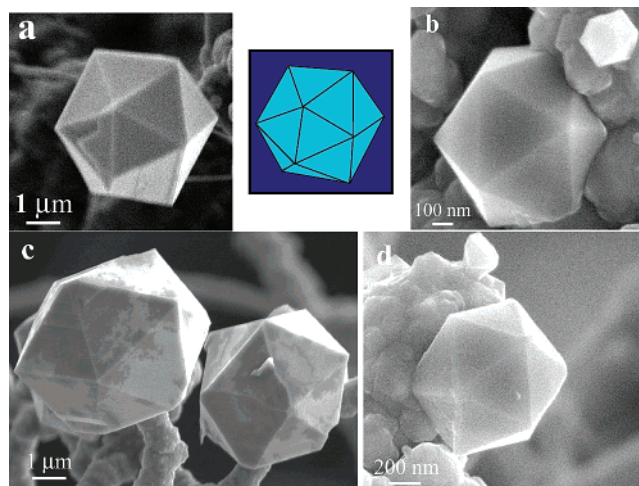


Figure 1. (a) SEM image of a typical icosahedron crystal of boron carbide. The diagonal across the crystal is about $5\ \mu\text{m}$. The inset shows an illustrating model of an isolated icosahedron corresponding to the real crystal shown in a. (b–d) Icosahedral MTP crystals observed in the range from 0.5 to $10\ \mu\text{m}$, with various orientations.

Boron carbide exists as a stable compound in a wide stoichiometry range, from 8 to 20 at. % C, but the composition

* To whom correspondence should be addressed. Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180-3590. E-mail: ajayan@rpi.edu. Fax: (518) 276-8554.

[†] Rensselaer Polytechnic Institute.

[‡] Universität Ulm.

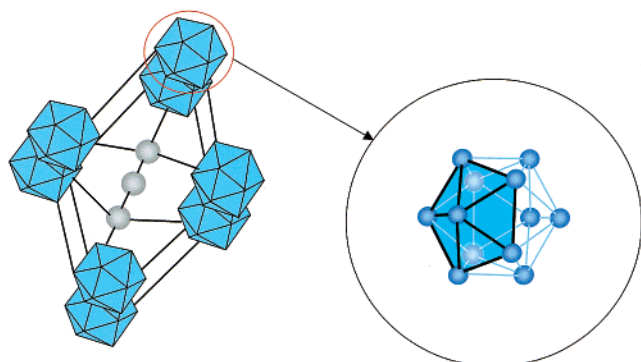


Figure 2. Atomic structure of B_4C .⁹ There are six atoms along the equator of the unit icosahedron, each forming five intraicosahedral bonds and one intericosahedral bond to a terminal atom in the linear chain. There are also six atoms forming three-atom poles on the top and bottom of the icosahedra, which form five intraicosahedral bonds. One of the atoms will be a carbon atom in the case of $B_{11}C$ icosahedron. The atoms in the extreme of the linear chain, either carbon or boron, have a tetrahedral-like coordination to three atoms in three different icosahedra and to the central atom in the chain.

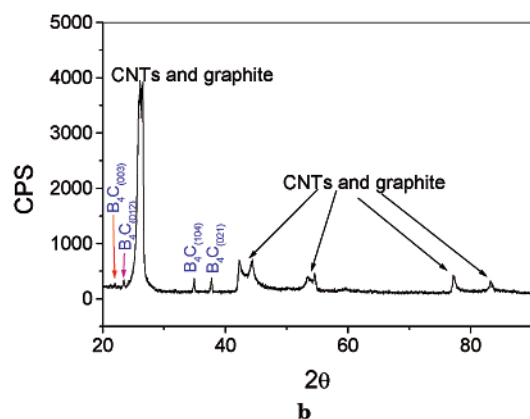
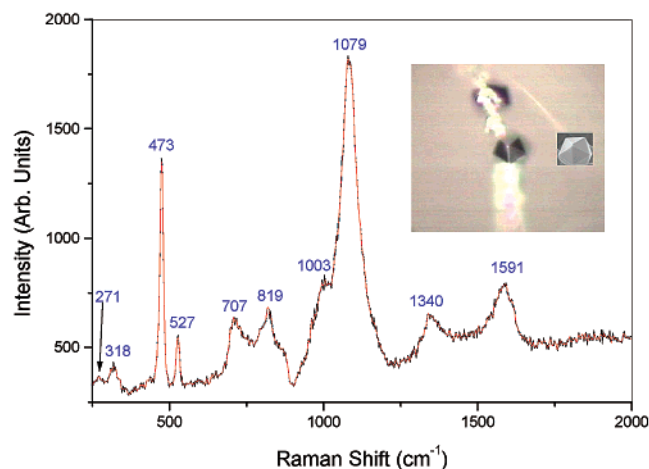


Figure 3. (a) Micro-Raman spectrum of an isolated icosahedral crystal obtained with a $1\ \mu\text{m}$ probe beam. Note the probe beam is smaller than the crystal size, so the Raman measurements are well located. The inset shows an optical micrograph of the appropriate 5-fold symmetry structure (emphasized with an SEM part). (b) An X-ray spectrum taken from the as-synthesized powder materials shows the existence of boron carbide and also some carbonaceous materials.

B_4C , known as “technical boron carbide”, shows the highest stability during most production methods. The most widely accepted crystal structure model for B_4C is rhombohedral, consisting of 12-atom $B_{11}C$ distorted icosahedra located at the corners of the unit cell, connected by linear $C-B-C$ or $C-B-B$

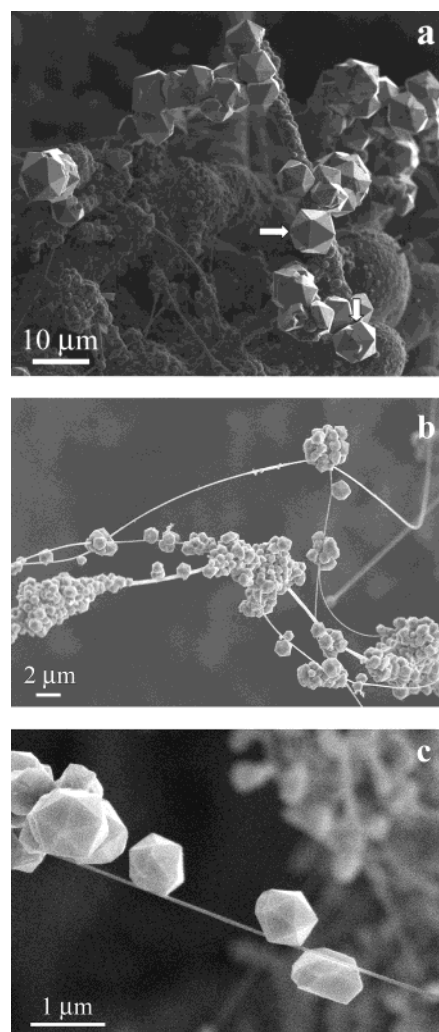


Figure 4. Morphologies of icosahedra of boron carbide. (a) Low magnification view of the aggregation of the icosahedra located on the surface of the deposited materials. Arrows indicate the presence of reentrant edges (horizontal arrow) indicative of twinning and growth of fused multiple MTPs (vertical arrow). (b–c) Fascinating images showing the 5-fold symmetrical units attached to carbon nanotubes and carbon fiber.

chains^{8,9} (Figure 2). However, the basic icosahedral units of B_4C structure could act as nuclei to build up large micrometer scale MTPs with 5-fold symmetry. The icosahedral building blocks of boron carbides exhibit centrosymmetric interactions resulting in enhanced mechanical properties for the crystals, such as hardness.

The experimental procedure used is a modified version of the arc-discharge technique used in the synthesis of fullerenes and nanotubes.^{10,11} A graphite anode rod, containing a small hole filled with boron/magnesium powder mixtures (pure B; atomic ratios of B/Mg at 3:1, 2:1, and 1:1), is arced against a pure graphite cathode in an atmosphere of He (~ 500 Torr) at a voltage difference of 20 V and a current level of 100 amperes. The deposit materials formed on the face of the cathode is collected and characterized by optical microscopy, field-emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction, and micro-Raman spectroscopy.

Crystals showing 5-fold symmetry, characteristic of icosahedral MTP crystals, are observed quite readily in the deposit formed on the cathode. The typical size of these crystals ranges from 1 to 10 microns. Figure 1a–d shows FE-SEM images of

typical icosahedral crystals obtained. A schematic of an icosahedron corresponding to the morphology and orientation of the real crystal in Figure 1a is shown as an inset. The widely accepted model of the B_4C crystal built from the icosahedral units is recalled in Figure 2. Figure 3a shows a micro-Raman spectrum obtained from an isolated crystal via measurement carried out with 1 μm probe beam diameter to provide the maximal lateral resolution (inset shows optical picture of the actual crystal taken by the Raman microscope). The spectrum shows excellent fitting to the literature details of boron carbide based on the local symmetry built from icosahedral units and bridges^{8,9} providing unambiguous evidence for that the crystals are boron-carbide with 20% carbon content. X-ray spectra taken from the bulk, as-synthesized powder confirm further the existence of boron carbide in the samples (Figure 3b). The X-ray spectrum also reveals that the boron carbide is mostly B_4C . Some efforts were made to obtain direct electron diffraction patterns and high-resolution TEM images of these crystals along the 5-fold axes; this proved to be impossible because of the large size of the crystals and the difficulty in obtaining diffraction from the entire crystal oriented along the 5-fold axes. Images and diffraction patterns obtained from the edges of crystals along the 3-fold axis corroborate that the crystal lattice corresponds to that of B_4C .

Figure 4a shows a collection of the crystals deposited on the surface of the soot that consist of amorphous carbon and some graphitic structures including carbon nanotubes. The large B_4C crystals show morphologies corresponding to MTP structures found in many materials such as fcc metals and diamond. Some of these crystals have perfect icosahedral morphology, and some have defects such as reentrant surfaces, which are indicative of twinning, and partially developed facets (see the arrows in the figure and the related figure captions). Some of the crystals are fused along their facets resulting in complex morphologies but retaining the local 5-fold symmetry of individual crystals.

The yield of the icosahedral crystals increases with increasing the B/Mg ratio used in the electrode (carbon always in excess), although there seems to be no dependence of this on the sizes of the crystals formed. Another interesting observation is that

the crystals, either isolated or aggregated, tend to grow on the surface and mainly attach to the carbon nanofiber structures (Figure 4b,c). The role of Mg in the process of formation of the crystals is unclear, and no Mg could be detected in the crystals; without Mg, however, no crystals were formed in the deposit.

In summary, we have observed the ready formation of large crystals of icosahedral multiply twinned particles of boron carbide during the arc evaporation of carbon and boron in the presence of magnesium. The icosahedral structural unit that builds up the rhombohedral crystal structure of bulk B_4C provides the nucleus to the formation of these large 5-fold symmetry crystals. The properties of these centrosymmetric crystals with close packing could improve the physical properties of boron carbide, which is a commonly used material for high hardness applications. For example, one could think of utilizing a properly oriented MTP crystal as a tip of a micro/nanoindenter.

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References and Notes

- (1) Klug, A.; Caspar, D. L. D. *Adv. Vir. Res.* **1960**, 7, 225.
- (2) Wals, J.; Tamura, T.; Tamura, N.; Grimm, R.; Baumeister, W.; Koster, A. J. *Mol. Cell.* **1997**, 1, 59.
- (3) Dubois, M.; Deme, B.; Gulik-Krzywicki, T.; Dedieu, J. C.; Vautrin, C.; Desert, S.; Perez, E.; Zemb, T. *Nature* **2001**, 411, 672.
- (4) Bühler, J.; Prior, Y. *J. Crystal Growth* **2000**, 209, 779.
- (5) Marks, L. D. *J. Crystal Growth* **1983**, 61, 556.
- (6) Mackay, A. L. *Acta Cryst.* **1962**, 15, 916.
- (7) Hubert, H.; Devouard, B.; Garvie, L. A. J.; O'Keeffe, M.; Buseck, P. R.; Petuskey, W. T.; McMillan, P. F. *Nature* **1998**, 391, 376.
- (8) Tallant, D. R.; Aselage, T. L.; Campbell, A. N.; Emin, D. *Phys. Rev. B* **1989**, 40, 5649.
- (9) Lazzari, R.; Vast, N.; Besson, J. M.; Baroni, S.; Dal Corso, A. *Phys. Rev. Lett.* **1999**, 83, 3230.
- (10) Ebbesen, T. W.; Ajayan, P. M. *Nature* **1992**, 358, 220.
- (11) Iijima, S.; Ichihashi, T. *Nature* **1993**, 363, 603.