Making the Hard Stuff

BY DENNIS DURBAND

"This substance may make possible an entirely new class of hardfacing and wear materials."

LIKE MUSICIANS mixing vocal and instrumental sounds into the tapestry of a song, teams of scientists at Arizona State University are working together to create and classify strange, new substances. Research conducted at ASU's Materials Research Science & Engineering Center (MRSEC) is focused toward the creation of super hard variations on the diamond theme. ☆ In the laboratory, researchers prepare materials under the extreme conditions of high pressure and high temperature. They work to form materials that possess special semiconductor capabilities, or materials which can be used in thin films for both the semiconductor and optoelectronics industries.

ASU scientists know how to make the hard stuff. In 1998, they took an indirect route to create the world's third hardest material. The researchers synthesized a low-density compound of boron suboxide (B_6O). The only harder materials known are diamond and cubic boron nitride.

Paul McMillan is the director of ASU's Center for Solid State Science. He says that an American research group had previously reported a boron oxide material with a graphite structure. A research group from Japan prepared a similar substance, but found a different result.

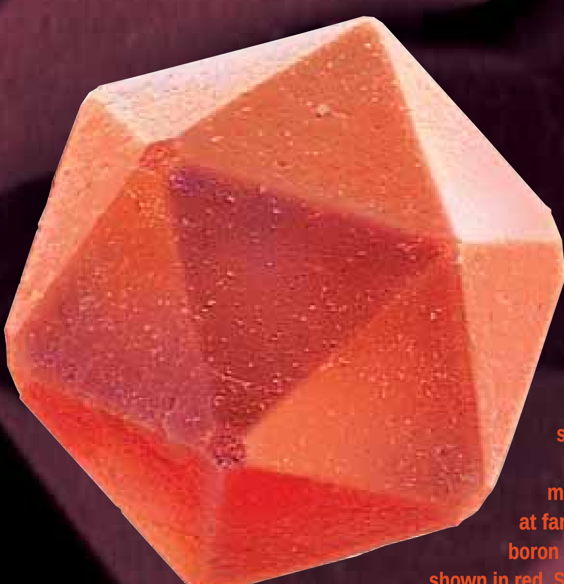
"The Japanese group that patented the finding suggested that the same material had the diamond atomic structure," McMillan explains. "We did some calculations and found that the atomic ordering scheme proposed by the Japanese was not the best one. We tried to repeat their synthesis to further refine their data according to our own proposed ordering scheme."

Postdoctoral researcher Hervé Hubert took on the task of repeating the synthesis reported by the Japanese group.

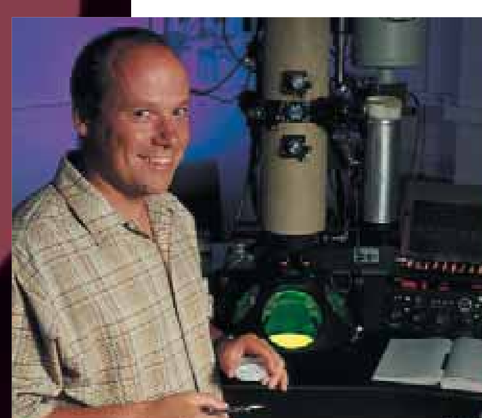
"Hervé could never repeat the Japanese findings," McMillan says. "Instead, he showed that their experiments were contaminated with gold from the sample capsule."

This finding should put an end to the Japanese patent.

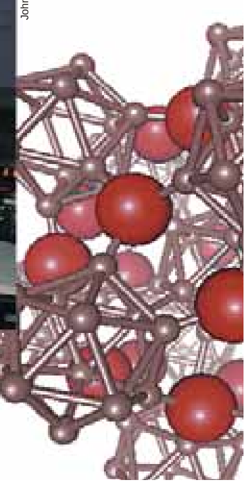
Hervé then started mixing boron and boron oxide and heating them at high pressure—up to 1,700 degrees Celsius and at 40,000 times the atmospheric pressure at sea level. During the heating and pressurization, orange-red particles formed.



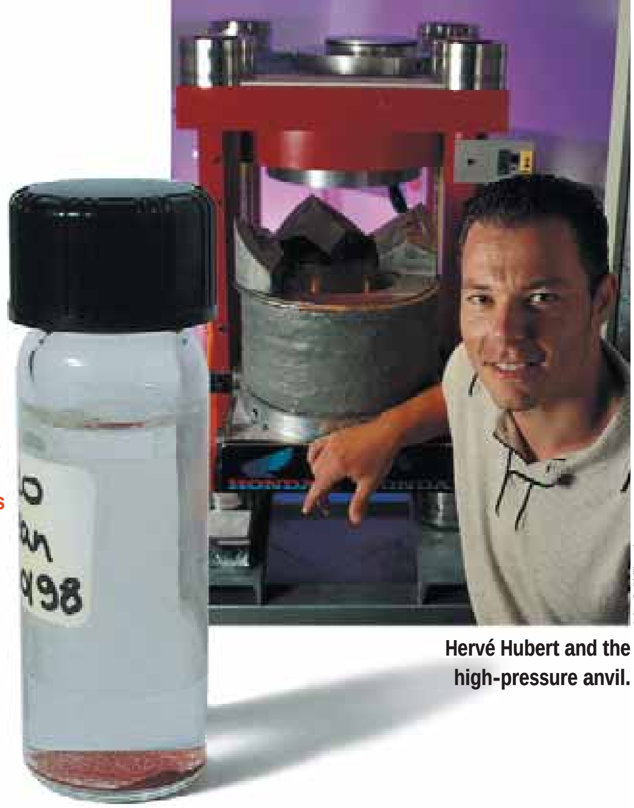
Courtesy Lawrence Garvie



John C. Phillips photo



Lawrence Garvie used a scanning electron microscope to obtain images of B_6O. The molecular structure is modeled at far right. Small knobs represent boron with the larger oxygen atoms shown in red. SEM pseudocolor image at left shows a single 20-sided symmetrical icosahedra.



Inside the high-pressure anvil, interlocking steel jaws compress a small crucible containing experimental mixtures. Scientists recover a small silica pellet the size of three aspirin tablets after each run. They break apart the pellet to wash out particles of boron suboxide with distilled water. Pictured is the result of a typical run—half a gram of fine red dust in a vial of water.

John C. Phillips photo

Hervé Hubert and the high-pressure anvil.

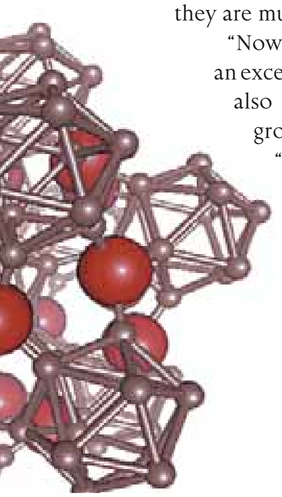
The research project took on a commuter-train nature as additional scientists got on board at subsequent experimental stops.

Postdoctoral researcher Laurence Garvie, an electron microscopist working with Peter Buseck, Regents Professor of Chemistry and Biochemistry, was the first to join in. Garvie had been refining a technique called electron energy-loss spectroscopy (EELS). Scientists use the technique to analyze low weight atoms such as boron and oxygen. Garvie's EELS work was essential because it provided detailed chemical analyses of the materials synthesized by Hubert.

A few weeks passed before Hubert and Garvie observed during electron microscope examination that the orange-red "crystals" were not single crystals at all. They had a perfect icosahedral shape—a particle, with 20 triangular faces and 12 corners, displaying five-fold symmetry.

A crystal, which contains atoms packed in a regular repeating pattern, cannot have five-fold symmetry. Icosahedral particles in nature are rare. Some viruses pack in this way, but they are much smaller in size.

"Now enter Bertrand Devouard, an excellent electron microscopist also from Buseck's research group," McMillan continues. "Bertrand had worked on minerals with five-fold symmetry before. Bertrand and Laurence took the most beautiful electron micrographs, and that really helped identify the substance."



Michael O'Keeffe is a Regents Professor of Chemistry and Biochemistry and an expert in crystallography, the study of crystal form and structure. O'Keeffe confirmed that the material was not a single crystal, but multiple-twinned particles.

Twenty tetrahedra, a solid with four faces—each a perfect crystal—came together at a point to form a radiating pattern away from the center. This substance displayed a new way of packing atoms together to make a solid.

The boron suboxide material ranks as the third-hardest substance in the world. Only diamonds and cubic boron nitride are harder than boron suboxide, which appears to have promising potential.

"This is more than a laboratory curiosity," says Paul Gray of the DuPont Company. "This substance may make possible an entirely new class of hardfacing and wear materials. The implications are enormous."

Since boron suboxide is extremely hard, it can be used as an abrasive, or as a cutting or polishing tool. Its mechanical characteristics and low chemical reactivity make it a candidate to replace tungsten carbide in high-wear applications. Boron suboxide may possess special semiconductor applications as well.

"The project was not planned in advance to come out the way it did," Buseck explains. "It took shape as the project grew. We certainly were not all working together in the lab at one time."

After Hubert's initial synthesis work, he spoke to Buseck's group about the aspect of electron microscopy.

"Hervé, Bertrand, and Laurence carried the bulk of the burden," Buseck says. "The faculty members provided input for various aspects of the problem." The ASU group's work was reported as a paper in the January 1998 issue of *Nature*, a major international science journal.

Hubert says that he and his colleagues were surprised with the initial results of the synthesis.

"We did not expect the boron suboxide particles to crystallize in the shape of an icosahedron," he says. "The primary objective of this project was to synthesize new superhard materials. The experiments were designed to obtain a detailed understanding of the growth conditions in order to prepare high-quality material, and to attempt the growth of single boron suboxide crystals. We stumbled on this finding by accident. We were startled. We did not understand how these icosahedra could form."

During their work, the ASU scientists created the largest-known icosahedra. It is larger than most viruses, and ranges in size up to 35 micrometers in diameter. That is about as wide as a single strand of human hair.

McMillan says that the experiment is remarkable. "The work involved the high pressure synthesis of beautiful icosahedral particles of boron which contain a low percentage of oxygen. The icosahedra themselves are constructed from boron icosahedra packed at the atomic scale. The oxygen atoms are bonded between them and arranged in a pattern that radiates from the central icosahedron."

University of London crystallographer Alan Mackay first suggested this method of packing matter in 1962. Mackay commented on the ASU findings. He wrote in *Nature* ("News and Views," January 1998) that "the [ASU] particles are very hard, promising technical applications."

"This was a case of people with overlapping interests becoming interested in a project. It grew mainly through the efforts of student and postdoctoral researchers," Buseck says.

Modern materials science is all about collaboration between scientists with different skills and expertise. That is one reason why the National Science Foundation created the MRSECs.

Boron suboxide is not yet totally understood. Currently, Otto Sankey, an ASU physicist, and Andrew Chizmeshya, a researcher at the Center for Solid State Science, are conducting studies to explore the electronic structure of the material. They want to learn how it forms a nucleus and grows under conditions of such enormous pressure.

The ASU Materials Research Science and Engineering Center is one of 24 American centers funded by the National Science Foundation. For information, contact Paul McMillan, Ph.D., Center for Solid State Science, College of Liberal Arts and Sciences, 480.965.6645. Send E-mail to pmcmillan@asu.edu Visit the Center's website at http://www.asu.edu/clas/csss