

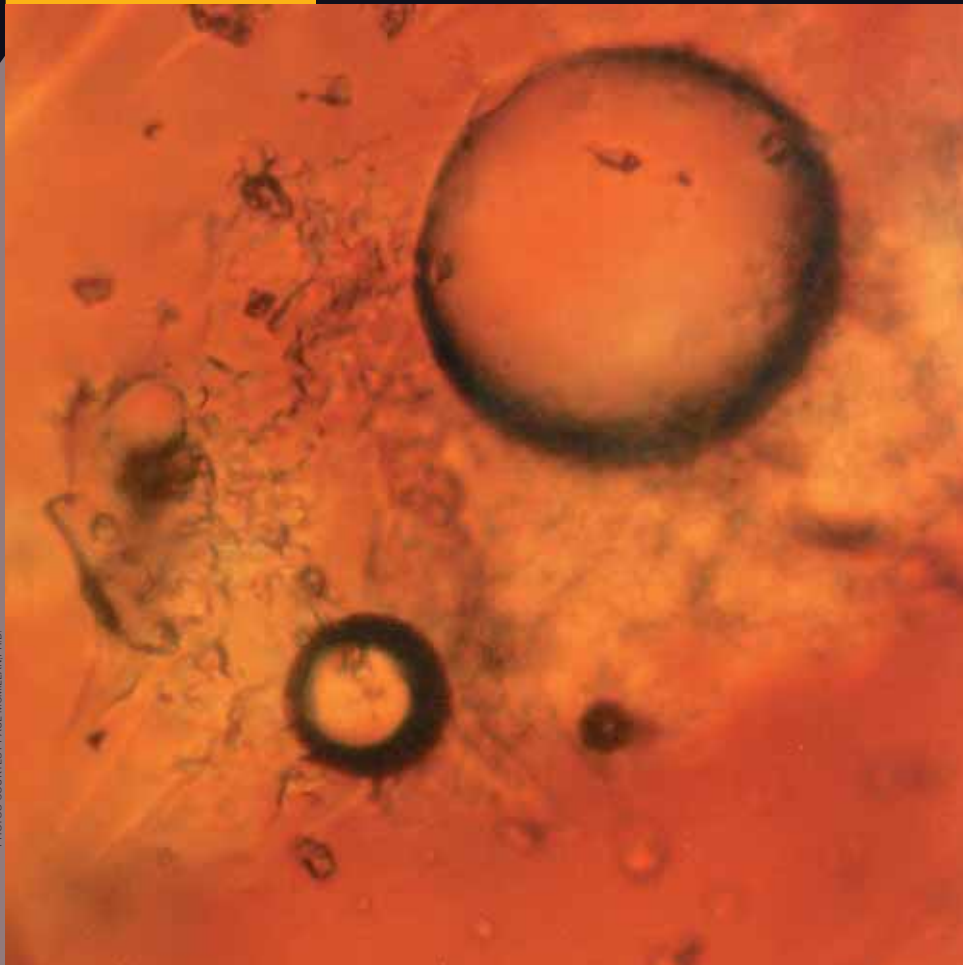


So you think you know
about pressure on the job?
Think again.

Members of ASU's
Materials Science
Research Group
have a whole new definition
for high pressure
in the workplace.

by Grant E. Smith
and
Steve Koppes

P R E S S U R E G R O U P



PHOTOS COURTESY PAUL McMILLAN, PH.D.

Above, crystals formed during cooling within a sample of exotic nitride glass. Right, nitrogen bubbles solidified within another sample. Results are influenced by cooling rates and variations in composition.

PAUL MCMILLAN and his colleagues are familiar with working under pressure. In fact, their work involves more pressure than most people could ever imagine.

McMillan and members of Arizona State University's Materials Research Group labor at the leading edge of a new chemistry that uses immense amounts of pressure to compress materials and alter their molecular structure. The processes are similar to those which occur to rocks and minerals deep within the Earth and other planets.

Work in the ASU laboratories is selective. The scientists don't work with any old rock or mineral. Their focus is on chemical compositions that might provide new types of useful materials. The hope is that such new materials will find a place in emerging technologies.

"We are trying to develop a new way of doing chemistry," says McMillan, a professor of chemistry. "Most processes for making new materials use temperatures and chemical composition as the variables. Pressure is the great unknown. New materials are waiting to be discovered."

SCIENTIFIC ALL-STAR TEAM Funded by the National Science Foundation's Division of Materials Research, the ASU group is a bit more than two years old. The human expertise was already in place on campus. The group represents a merging of existing faculty strengths and interests in high pressure geochemistry and solid state science.

"We're one of only 16 materials research groups in the country," says McMillan, an inorganic chemist and geochemist responsible for pulling together the scientific talent. "To get the grant, we not only had to demonstrate the advantage to doing high pressure materials research, but that we would work well as an interdisciplinary team."

The team consists of seven faculty members in the departments of chemistry, physics, and geology. Together, they are a veritable "Who's Who?" of materials research expertise.

John Holloway is an expert in high pressure synthesis techniques. He also designs experiments to mimic the processes which occur deep within the Earth.

Originally a geophysicist from the University of California, Berkeley, team member George Wolf uses laser spectroscopy to study the properties of materials while they are held at high pressure. He uses a tiny reaction chamber called a diamond anvil cell to do the work.

Other team members include Michael O'Keeffe, C. Austen Angell, Otto Sankey, and William Petuskey. O'Keeffe is a

Regents' professor of chemistry widely known for his work designing new materials and in solid state chemistry. Chemist C. Austen Angell is internationally recognized for his pioneering studies of liquids and glasses under high pressure, and for his work on battery materials.

Sankey is a physics professor. He develops new theoretical techniques to calculate the structures and properties of materials held under enormous pressures. Chemist William Petuskey pursues wide interests in materials science ranging from structural ceramics to novel semiconductors and superconductors.

TOUGH, NEW GLASS One of the group's first accomplishments has been to produce a new, tougher, high-tech family of glasses. The group has applied for a patent on these materials, which have several possible technological applications.

"Instead of glass based on oxygen, we've made the first glass based solely on nitrogen," McMillan says. Members of the discovery team included Angell, Holloway, McMillan, and chemist Tor Grande.

Nitride glass is harder than normal glass, which is based on silica. Nitride glass is less likely to scratch or melt. It also has unusual optical characteristics. As light passes through the new glass, it is slowed to half the speed it moves through air. This makes the refractive index large, which means that light is bent abruptly when it enters or leaves the glass at an angle.

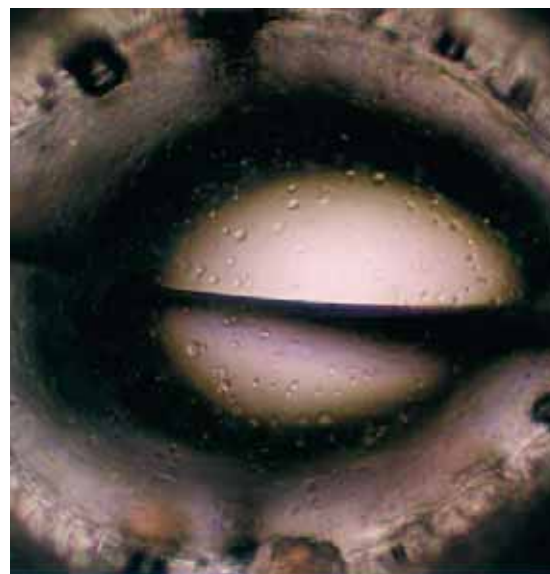
"Nitride glasses could have a wide range of application," McMillan says. "They could become important in designing new, miniaturized lenses and prisms."

All properties of nitride glasses are not unique. Other glasses have been made with high refractive index values. But nitride glasses boast other useful traits. They can withstand temperatures nearly twice as high as that of many conventional glasses. They can be heated to 1,400 degrees Fahrenheit or more without softening. They also are more resistant to scratching and chemical damage. Until now, glasses based solely on nitrogen were considered impossible to make or work with.

"Glass is usually made by melting a mixture of components and then cooling them to form the finished substance," McMillan explains. "If you heat a mixture of nitrides, it usually decomposes to give nitrogen gas."

The technique developed by the ASU group involves melting the nitrides under high pressure to keep the nitrogen in the molten material.

Austen Angell had wanted to develop nitride glasses for about eight years. While



ASU scientists use tiny, hollow iridium wires as reaction vessels for materials research. The wires are only one millimeter in diameter. Yttrium aluminum garnet has been melted and cooled to a tiny glassy drop that reveals how the same molten material can solidify in two ways.

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working at Purdue University, his first attempt ended unhappily.

“The only thing I succeeded in doing was melting a hole in one of our platinum crucibles,” Angell says. “It’s been very satisfying to find that you can make them.”

Angell praised Tor Grande’s persistence in conducting the difficult experiments. One of the first postdoctoral researchers working with the group, Grande has since returned to his native Norway to become a professor there.

The scientists formed nitride glasses by subjecting the ingredients to pressures 5,000 to 10,000 times greater than normal atmospheric pressure, conditions equivalent to those found several miles below the Earth’s crust.

“You need high-pressure conditions to make these materials from the melt,” McMillan explains. Otherwise, the nitrogen will escape.

The group used a high-pressure, high temperature piston-cylinder device to make samples of the new glass. Holloway originally built the piston-cylinder to simulate conditions within the Earth’s molten core. Each sample measures less than a tenth-inch square, but the group has plans to make larger pieces.

The Asu scientists also are exploring other ways to make the new glasses using techniques that avoid high pressures and temperatures entirely. If successful, such new materials could have applications in the semiconductor industry. They would be useful as coatings and substrates for electronic components.

PRESSING FOR OTHER ANSWERS

The nitride glasses are the first major success story for the group. But other projects are giving results as well. Led by Petuskey and Sankey, one effort involves the search for new semiconductors and structural materials.

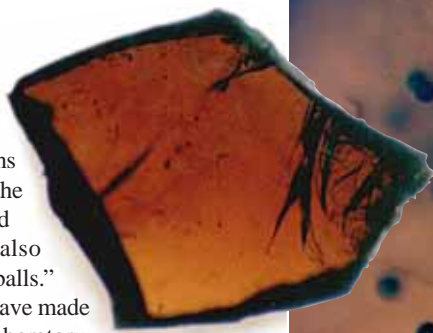
These materials are formed of elements such as germanium, silicon, carbon, boron, and oxygen. They give rise to the known families of semiconductors used in that multibillion dollar industry. They also contain the superhard materials used in cutting tools and for grinding applications.

“If we can produce new materials and show how they can be made in large enough quantities, they could provide the base for new industrial developments,” McMillan says.

To date, several new materials have been “synthesized” inside Sankey’s computers. Many have beautiful structures and interesting properties. These findings please Michael O’Keeffe, who has spent much of his scientific career exploring the symmetry of solid state compounds.

Some of the materials predicted by graduate student Alex Demkov include substances

called silicon clathrates. These are chemical cousins of the fullerenes, the soccer-ball-shaped forms of carbon also known as “buckyballs.” Asu researchers have made clathrates in the laboratory.



SQUEEZING TO RELIEVE TENSION

Asu researchers also are studying the behavior of a class of materials called perovskite. One form, magnesium silicate perovskite, is stable only at extremely high pressures. It forms most of the Earth’s deep hot interior.

Perovskite is a natural mineral based on calcium, titanium, and oxygen. It includes a whole family of compounds with interesting and useful properties.

“We are trying to make new perovskites by replacing oxygen with sulfur at high pressure,” McMillan says. The results should include materials with interesting electronic properties.

The work is done using a multi-anvil high pressure device which is capable of pressing up to 200,000 times atmospheric pressure. Holloway, McMillan, and former scientific associate Alison Pawley assembled the device which was built in the Asu machine shop.

Wolf and Angell are interested in what happens when perovskite’s molecular structure collapses to form a glass. They use the diamond anvil cell and computer simulations to study the process.

FERTILE WORKING ENVIRONMENT

McMillan credits Asu with providing the interdisciplinary environment that led to formation of the Materials Research Group.

“I came here in 1977 as a graduate student in chemistry,” McMillan says. “I did my doctoral work with John Holloway. He had established a laboratory to simulate conditions found deep inside the Earth to help geologists understand the inner workings of volcanoes.

“This is one of the few places where a scientist can productively combine expertise in chemistry, physics, and geology, and work between those disciplines,” McMillan says. “That’s why I decided to stay.”

High pressure materials research is supported by the National Science Foundation.

For more information about specific projects, call Paul F. McMillan, Ph.D., Department of Chemistry and Biochemistry, College of Liberal Arts and Sciences, 602.965.3461 or 965.1021.

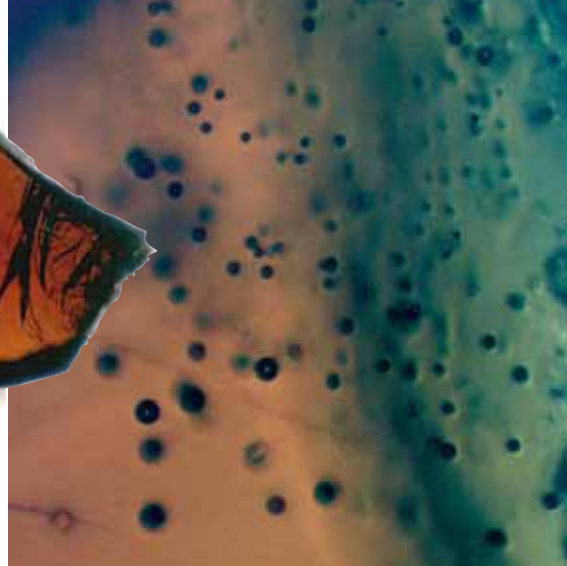
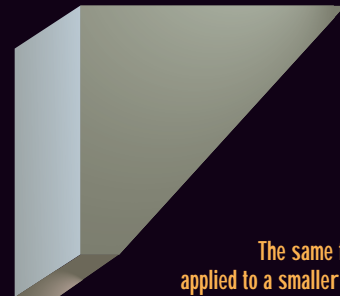


PHOTO COURTESY PAUL MCMILLAN, PH.D.

Actual size of the shard of nitride glass pictured above is less than a millimeter across. The material interests scientists because it has a very high refractive index, or ability to bend light, as indicated by the dark appearance of the edges. This useful property has applications in many optical devices. Also shown is a highly magnified view of nitrogen bubbles formed during cooling in a separate sample.

PRIMER ON PRESSURE

Pressure is the result of force applied to a given area.



The same force applied to a smaller area geometrically increases pressure.



MICHAEL HAGEBERG ILLUSTRATION

DESIGNING AND DEVELOPING devices that exert immense amounts of pressure is a major preoccupation of scientists who make up ASU's Materials Research Group. As is true in all experimental work, the key to scientific credibility is that each device they develop must be able to exert pressure in a reproducible manner.

"We've had to build our laboratories from scratch," says project leader Paul McMillan, an ASU professor of chemistry. Regardless, the group has enjoyed considerable success in the two years since initial grant support was received from the National Science Foundation.

In that time, the ASU researchers have built a pair of multi-anvil devices. Each device is capable of exerting more than 200 kilobars of pressure at temperatures up to almost 2,000 degrees Centigrade. The 200 kilobar total is equal to 200,000 times the normal atmospheric pressure found at sea level. A third multi-anvil device is nearing completion.

Each multi-anvil device consists of a series of containers within containers. The outer containers are made of machined steel or carbide wedges. When assembled, the wedges form an octahedral space in the center.

Researchers place samples inside a drilled ceramic holder which fits inside the octahedral hole. Force exerted on the outer container moves the wedges to constrict the volume of the hole. The reduction in surface area between each successive layer serves to multiply the pressure applied to the sample. Some multi-anvil devices can generate more than 300 kilobars of pressure.

McMillan credits group member John Holloway, a professor of chemistry and geology, with the new design. "John is a master at designing compact high-pressure equipment," he says. ASU researchers use the multi-anvil press to produce sample materials in amounts of only tens of milligrams, which is much too little for industrial purposes. But the experiment can be scaled to larger size. McMillan says that Japanese laboratories have huge devices capable of making a liter of material at 100 kilobars of pressure.

Holloway also designed and built a piston-cylinder machine that exerts up to 25 kilobars of pressure. The machine is used to produce larger samples for study.

The new devices are used to complement research conducted by George Wolf at ASU's first high pressure

laboratory. Wolf, an associate professor of chemistry, uses diamond anvil cell technology in his work.

With less torque than is needed to tighten a spark plug, a scientist using diamond anvil cell technology can create pressures that exceed that found at the center of the Earth. "In fact, you can exert pressure that is roughly equal to that found a third of the way through Jupiter," McMillan says.

The diamond anvil fits easily within the palm of one hand. The device is just what its name implies. At the center of the cell are two flawless, gem-cut diamonds, each about a third of a carat in weight. The points of the diamonds are ground off to small, flat surfaces set in opposition to each other.

Tiny slivers of sample material are placed between the diamond faces. The thrust generated by hand-cranking a pressure bolt is transmitted to the sample. The diamond anvil cell multiplies that pressure by 500 to 1,000 times.

Wolf uses the diamond anvil to test materials under pressures in excess of one megabar. A megabar is one million times the atmospheric pressure at sea level. Think of it as a pressure roughly equivalent to the weight of six full-grown elephants concentrated on an area of four square millimeters, an area the size of a matchstick's base. One megabar also represents the pressure found at about 2,000 kilometers beneath the Earth's crust.

An added advantage to using the diamond anvil cell is that Wolf and other scientists can directly observe samples through a microscope while they are being squashed. Scientists also can use spectroscopy to study samples by beaming lasers or x-rays through the diamond anvils. They can even measure electrical conductivity or magnetic properties of the sample.

The major disadvantage of diamond anvil research is that only a minuscule amount of material can be studied at any one time—less than a microgram.

Other group members use powerful computer work stations to do theoretical calculations of materials under pressure. The combination of experimental and theoretical techniques sets ASU apart from other research groups.

"Other laboratories have decided to follow one approach or another," McMillan explains. "We have married experimental technologies with theoretical methods."

In the past, most high pressure research was conducted by geochemists or geophysicists. Intense interest in new materials that might be technologically important is changing the scene.

"There is increased interest in new materials that might be produced using high pressure techniques," McMillan says. "We need to work out ways of producing these materials commercially in large batches."

Some might say that the pressure is on.

—Grant E. Smith

John Holloway (left) and Paul McMillan display the innards of a multi-anvil press.

