A Nonconformist Compound

A material that shrinks when heated may keep thermal problems in check

By CORINNA WU

Wild temperature swings can crack a plate as surely as dropping it on a hard kitchen floor. A ceramic dish taken from the freezer and thrust into a hot oven splits apart because some parts heat up and expand faster than others.

This problem isn't unique to dishes. Computer chips, fiber optic cables, and dental fillings, for example, all risk failure when they expand differently from the materials around them.

An unusual compound called zirconium tungstate, however, might make these annoyances a thing of the past. Although most materials grow when they get hot, zirconium tungstate does the exact opposite—it shrinks.

A few other compounds have this characteristic, but they tend to shrink in one direction while they stretch out in others in order to preserve an overall volume. Zirconium tungstate, a blend of zirconium, tungsten, and oxygen, stands out from its peers because it shrinks equally in all directions. Moreover, zirconium tungstate exhibits this behavior over a huge temperature range—from near absolute zero to 777°C.

Although scientists have known about zirconium tungstate's weird behavior for 30 years, they have only recently begun to explain why the material acts so contrarily. With this new understanding, researchers are also beginning to learn how to blend zirconium tungstate with other compounds so as to make new composite materials resistant to thermal shock.

A team of Australian researchers first synthesized zirconium tungstate in 1959. Although they determined that the atoms in the crystal were arranged symmetrically, they didn't know the details of its structure. Eight years later, researchers at the Pennsylvania State University took another look at the compound and described how it behaved at different temperatures and compositions.

"But even at that point, people didn't realize that this material had this incredibly unusual behavior," says David Johnson, head of the metallurgy and ceramics research department at Lucent Technologies' Bell Labs in Murray Hill, N.J.

Then in 1968, Penn State scientists Floyd A. Hummel and Charles Martinek discovered the compound's unusual property. They published their findings in the Journal of the American Ceramics Society, but chemists paid little attention. They were looking for materials that didn't shrink or expand at all.

Corning, for example, was selling cookware based on heat-stable Pyrex glass that could go from "freezer to oven."

"In that era, people were scrambling to find materials that you could use in the household or laboratory without worrying about breakage. That was what Floyd was looking for," says Johnson, who was Hummel's student at the time. Upon discovering zirconium tungstate's behavior, the researchers "must have said to themselves, 'This is really weird, but it doesn't help our cause.'" Zirconium tungstate shrinks as much as other ceramics expand, so it would be just as susceptible to thermal shock.

Not until the early 1990s did interest in the compound pick up. At that time, researchers found a new reason to pay attention to the thermal expansion of materials: Heat generated by electronic circuit boards in computers was causing them to self-destruct. During use, silicon chips get hot and expand. If the chips are mounted on material that can't match the expansion, the silicon cracks and peels away from its foundation.

The heat problem becomes worse as computer chips get smaller and more densely packed with circuits. To achieve higher data-processing speeds, the next generation of microchips will require more effective ways to handle heat.

Chemist Arthur W. Sleight knew of this circuit board problem from his years spent at DuPont Co. He and his group at Oregon State University in Corvallis began looking for materials that could match the thermal properties of silicon. When they learned of zirconium tungstate, they suspected that the compound, if blended with materials that expand, could match silicon's thermal expansion.

"We found that the thermal-expansion properties were much more unusual than had been previously appreciated," says Sleight. By examining how the compound scatters X rays and neutrons at various temperatures, his team in 1996 pinpointed the atoms in the compound and thereby deduced its detailed structure.

Its structure revealed how the compound could be staging its incredible shrinking act. The atoms form a framework in which each zirconium is surrounded by six oxygens, and each tungsten is surrounded by four oxygens. Most of the oxygen atoms, in turn, share contact with one zirconium and one tungsten.

To understand what happens to the structure when the material is heated, says Arthur P. Ramirez, a physicist at Bell Labs, imagine a guitar string threaded through a ball and stretched between two posts. Plucking the string causes the ball to vibrate, and the string pulls on the posts. The more the ball vibrates, the harder the string tugs the posts toward each other.

Similarly, heat causes the atoms in zirconium tungstate to vibrate. The zirconium and tungsten atoms, bonded on all sides, don't move much, but the oxygens, like the balls in the middle of the guitar strings, jiggle up and down and side to side, yanking on the zirconium and tungsten posts.

The secret to the compound's shrinking is that one out of the four oxygens that surround a tungsten atom is unshared. In other words, it bonds only to one tungsten post, so "it's more free to wobble about," says Ramirez.

This free oxygen allows the crystal to move in unusual ways. The clusters of oxygens around each tungsten atom form a four-sided pyramid shape called a tetrahedron. When zirconium tungstate is heated, these tetrahedra twist, moving the tungsten and zirconium atoms closer together and collapsing the crystal in on itself. If all the oxygen were fixed rigidly, the tetrahedra couldn't rotate.

This understanding of the structure of the compound provides a good qualitative picture, says Sleight, but it doesn't allow researchers to predict how much zirconium tungstate will shrink. From experiments, they know the compound shrinks a minuscule one-thousandth of 1 percent per degree. Over a large temperature range, that slight change can be significant, especially for exquisitely sensitive electronic and optical applications.

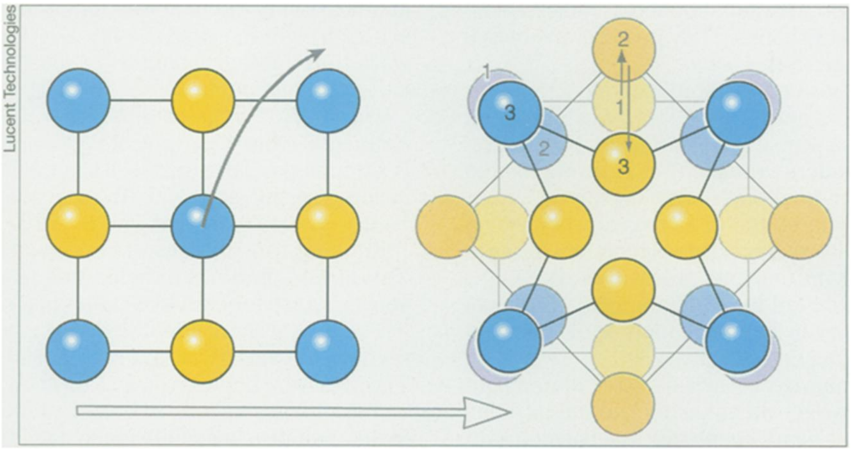
In the next step toward fully understanding the shrinking, the Bell Labs team is trying to mathematically describe the different ways the crystal can vibrate.

"What controls thermal expansion are the vibrational modes in a structure," Ramirez says. Vibrational modes can be thought of as waves of defined energy that move through the crystal. Zirconium tungstate has 132 different vibrational modes, and the Bell Labs team has set out to determine their energies.

By shooting beams of neutrons into zirconium tungstate and measuring how the material scatters the beam, the group has measured the range of energies in which most of these vibrational waves fall. Zirconium tungstate appears to have "many low-energy vibrational modes compared to other systems with similar constituents bonded in a similar way," Ramirez says. He and his colleagues believe that these low-energy waves are responsible for the compound's unusual property.

Because the unbonded oxygens move with relative ease, atoms in the structure as a whole jiggle more freely. This looseness shows up in zirconium tungstate's abundance of low-energy modes.

The big mystery is why zirconium tungstate assumes its unusual atomic arrangement. "This is an incredibly deep problem—part of a class of problems that hasn't been discussed much in solid-state physics," says Ramirez. "There is no good theoretical tool to deal with this."



When the oxygen atoms (yellow) in zirconium tungstate vibrate, they pull the surrounding metal atoms (blue) closer together.

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However, the Bell Lab researchers and their collaborator Collin Broholm at Johns Hopkins University in Baltimore are giving the problem a try by writing out the quantum mechanical descriptions of each of the 132 vibrational modes. These should lay the foundation for better models.

In addition to probing the physical properties of the compound, researchers have been working to make it easier to synthesize. The original method involved heating a mixture of zirconium oxide and tungsten oxide for several days at 1,200°C. A lower processing temperature and quicker synthesis would make the compound much more practical to produce on a commercial scale. Sleight has developed a way to make it at half that temperature and in just a couple of hours.

Glen R. Kowach, a chemist at Bell Labs, and his colleagues have taken the synthesis further by growing pure, large, single crystals of zirconium tungstate instead of a powder. With their new technique, Kowach can make thumbnail-size samples roughly half a centimeter thick. The solid is transparent and shatters when struck.

To grow the single crystals, the researchers put a mixture of zirconium oxide and tungsten oxide powders in a crucible and cover it with a layer of pure tungsten oxide. They heat the crucible to about 1,300°C to melt the powders, then slowly cool it to room temperature. Large pieces of zirconium tungstate end up sandwiched between two layers of excess ingredients.

Most practical applications of zirconium tungstate require it to be blended with other materials. David C. Dunand at Northwestern University in Evanston, Ill., has developed a way to combine zirconium tungstate with copper to form a composite material that could match the thermal expansion of silicon computer chips.

Currently, circuit boards consist of copper and molybdenum sheets laminated together like a layer cake, says Dunand. The copper conducts heat away from the silicon chip, and the molybdenum, a metal that has a low thermal expansion, prevents the copper from swelling too much.

By mixing zirconium tungstate into copper, "you can tailor [the thermal expansion of the composite produced] from negative to zero to positive," says Dunand.

At first, he pressed copper and zirconium tungstate powders at a high temperature, a process used to make other metal-ceramic composites. Unfortunately, the zirconium tungstate decomposed and reacted with the copper.

Dunand has found several ways to make the composite material at temperatures as low as 250°C. He and his colleague Hermann Holzer, currently at Electrovac in Klosterneuburg, Austria, will describe them in the March Journal of Materials Research.

"The challenge is to find conditions that will prevent decomposition and reaction while still being sufficient to give you compaction," Dunand explains. "If you go very low in temperature, you don't destroy the material, but you end up with loose powder."

One of the tricks to be revealed in the March publication is to coat the zirconium tungstate particles with a thin layer of copper before the actual compaction. The copper then welds together when pressure is applied to the powder particles. Like melting chocolate-covered raisins into a single lump, Dunand explains, "it's easier to compact chocolate with chocolate than raisins with raisins."

After Sleight and his colleagues announced their findings on zirconium tungstate in 1996, about 70 groups requested samples so they could conduct their own studies. A company called Oremet-Wah Chang in Albany, Ore., now manufactures it and sends out the test samples.

Dunand imagines that materials with zero thermal expansion could find uses in high-precision equipment. For example, orbiting telescopes undergo large temperature fluctuations as they move into and out of sunlight, so materials that don't shrink or swell could help in keeping the optics true. Precise measuring instruments on Earth, too, can't afford to have their components changing size.

Bell Labs is looking at zirconium tungstate for fiber Bragg gratings—filters that pick out particular wavelengths of light from signals that travel down fiber-optic cables. If the cable expands when heated, its optical properties change and scramble the signals. Packaging the cable with zirconium tungstate could solve the problem.

One day, people might even carry around a little bit of zirconium tungstate. "The one [proposed] application that took us by complete surprise was in teeth restoration," says Sleight.

In recent years, the cavity fillings of choice have been polymer-silica composites that match the color of teeth. Unfortunately, dentists are now finding that, because of expansion-contraction differences between the composite and tooth enamel, temperature fluctuations "from coffee to ice cream are enough to cause problems," says Sleight. He concludes that zirconium tungstate could play an important role.

Overall, interest is expanding for this shrinking material. □