

# The Many Faces of Carbon Dioxide

**T**HE only solid carbon dioxide most of us know is the dry ice we use for cooling or in Halloween witch's brew. But researchers have known one other form of it for some time and recently isolated several more in the laboratory. One of the new-found forms is nearly as hard as diamond, and indications are that it will conduct heat just as well, too. Basic research in Livermore's mission-related work has led to yet another surprising and important scientific discovery.

Carbon dioxide (CO<sub>2</sub>) is a simple and nearly inert molecule. It is abundant in the atmosphere of Earth and other planets and is also a major byproduct of high-explosive detonations. Understanding how it and the other byproducts of high-explosive detonations—water, carbon, and nitrogen—behave at detonation pressures and temperatures is important for creating accurate models for codes that simulate nuclear weapons performance. Studying the optical, mechanical, and energetic properties of the individual reaction products at high pressures and temperatures provides important experimental data for improving Livermore's models to predict the performance of high explosives.

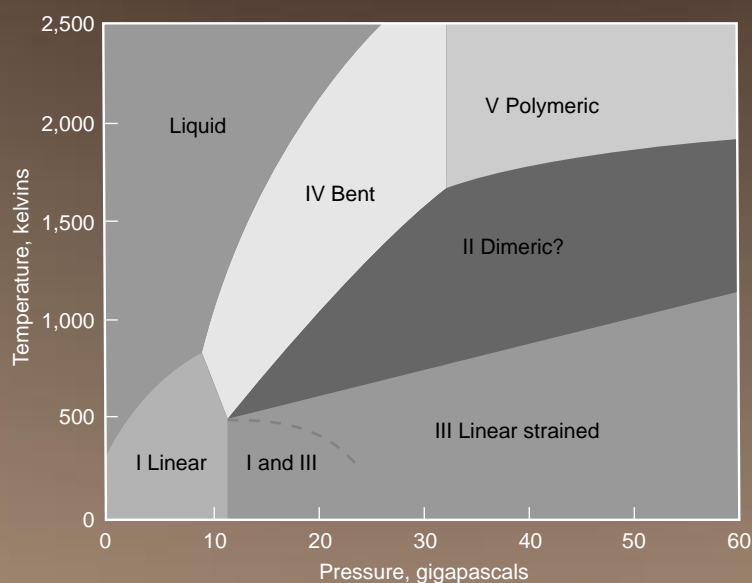
The split second of a high-explosive detonation may produce temperatures as high as 5,500 kelvin and pressures up to half a million times that of Earth's atmosphere. Chemists and material scientists have suggested a number of molecular phases for CO<sub>2</sub> at various high pressures and temperatures, but their structure and stability have not been fully characterized. That is changing, however.

In experiments using Livermore's diamond anvil cell to slowly increase pressures up to millions of Earth atmospheres, a team led by physicist Choong-Shik Yoo has verified two forms of solid CO<sub>2</sub> never before seen in the laboratory, known as CO<sub>2</sub>-IV and CO<sub>2</sub>-V. The team also has experiments under way on a third form, CO<sub>2</sub>-II, which has weaker chemical bonds. All three forms are very different from one another as well as from the two previously known molecular phases, CO<sub>2</sub>-I (dry ice) and CO<sub>2</sub>-III.

The phase diagram for carbon dioxide shows the pressures and temperatures at which changes in phase occur for CO<sub>2</sub> based on results to date. All five phases are solid in one form or another, but they differ greatly in their molecular configuration

and crystal structure and, more importantly, in the nature of their chemical bonding and the strength of intermolecular interactions. The intermolecular interactions change from weak quadrupolar interactions in the linear molecular phases (I and III), to relatively strong dipolar interactions in the bent-molecular phase IV, and eventually to strong covalent bonds in the polymeric phase V. (Results of the most recently discovered phase, CO<sub>2</sub>-II, are just beginning to be understood.)

The evolving intermolecular interactions are in line with recent theoretical and experimental results that suggest that many simple molecules will become polymeric and even metallic at high pressures and temperatures. These findings have important implications for the chemistry of high-explosive detonations, which entail similar temperatures and pressures.



Phase diagram for CO<sub>2</sub>, showing pressures and temperatures at which the phase changes.

Carbon dioxide crystallizes into CO<sub>2</sub>-I with a pressure of 1.5 gigapascals at room temperature. Increased pressure on CO<sub>2</sub>-I produces CO<sub>2</sub>-III, which becomes a highly strained, high-strength solid above 20 to 30 gigapascals. CO<sub>2</sub>-III is fairly stable at room temperature to about 70 gigapascals.

The Livermore team turned up both the pressure and temperature to isolate CO<sub>2</sub>-V, the polymeric solid, using the synchrotron facility at Grenoble, France. They found that CO<sub>2</sub>-V has extremely low compressibility, similar to that of cubic boron nitride. This suggests that the carbon dioxide polymer could be used as a superhard material just as cubic boron nitride and diamond are. What is especially interesting about CO<sub>2</sub>-V is that it shows nonlinear optical behavior. The frequency of light that passes through it doubles, which may lead to a new class of generating materials for high-power lasers.

More recently, Yoo's team discovered CO<sub>2</sub>-IV at pressures between 12 and 30 gigapascals. Its bent molecule is the precursor to polymeric CO<sub>2</sub>-V. Also, CO<sub>2</sub>-IV has proved to be optically nonlinear.

### Crystallizing a Liquid

To create CO<sub>2</sub>-V, the team placed a small amount of condensed, liquid CO<sub>2</sub> between the two tips of the diamond anvil cell and squeezed it to pressures of about 40 gigapascals, or 400,000 times the air pressure at Earth's surface. At the same

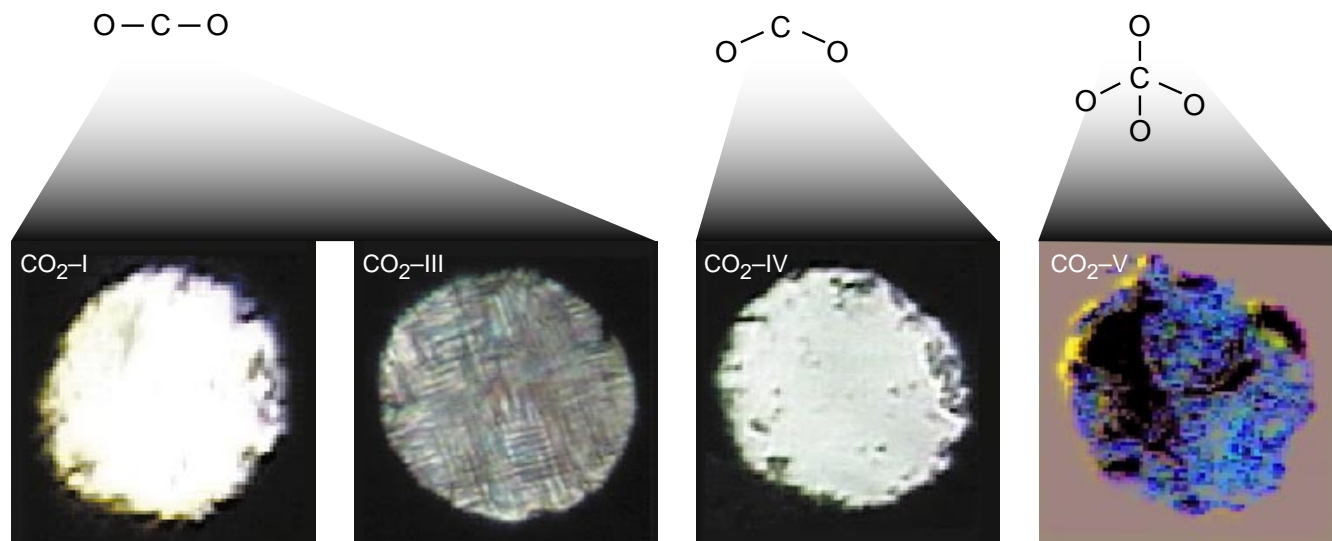
time, they used a neodymium-doped yttrium-lithium-fluoride (Nd:YLF) laser to indirectly heat the CO<sub>2</sub> to 1,800 kelvins.

When the compressed sample was heated, the team was surprised to see a visible emission of green light. The incoming laser light at the infrared wavelength of 1,054 nanometers had been frequency doubled to 527-nanometer light, which is green. The green light being emitted is the second harmonic of the laser light used to heat the sample.

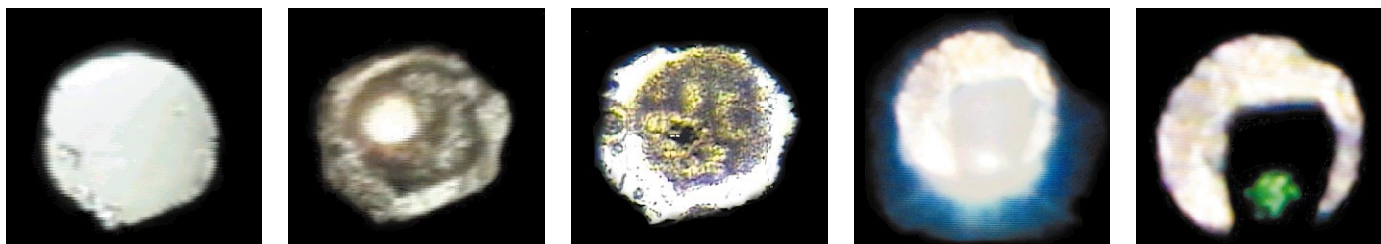
Because CO<sub>2</sub> absorbs the Nd:YLF light poorly, the team heated the sample indirectly by scattering micrometer-sized ruby chips in it and heating the chips with the laser. In other experiments, they used a platinum foil or a rhenium gasket for heating. The experiment was repeated 20 times and yielded the same results each time, regardless of the heating material used. "We wanted to verify that the frequency doubling we saw was not the result of contamination from the heating materials," says Yoo.

The sample, reduced to just a few micrograms, had become an extended solid phase of CO<sub>2</sub>. X-ray diffraction, Raman spectroscopy, and other forms of analysis showed that the carbon and oxygen atoms had rearranged themselves in chainlike patterns connected by single carbon-oxygen bonds, a structure similar to that of a high-temperature modification of quartz.

The team found CO<sub>2</sub>-IV by laser-heating CO<sub>2</sub>-III at pressures between 12 and 30 gigapascals to 1,000 kelvins



Phase changes in carbon dioxide result in changes in its molecular configuration. Phases I and III are linear structures, phase IV is a bent molecule, and phase V has covalent bonds. (Phase II was recently discovered and is still under study.)



Heated CO<sub>2</sub>-V emits green light, which is the second harmonic of the laser light used to heat the sample.

and quenching the sample to 300 kelvins. They found that with increasing pressure, the interactions weakened. At about 80 gigapascals, the quenched sample collapsed into an amorphous solid. If laser heating was continued with increasing pressure, the CO<sub>2</sub>-IV transformed into polymeric CO<sub>2</sub>-V above 30 gigapascals.

### Stabilizing CO<sub>2</sub>-V

If this new, very hard CO<sub>2</sub>-V can be stabilized at ambient temperatures and pressures, it will have many uses. New classes of high explosives, nonlinear optical materials with high thermal and mechanical stability, high-strength glass, and superhard materials for tools are all candidates. Crystals that can double the frequency of laser light from infrared to green would be valuable for Livermore's inertial confinement fusion energy program.

So far, once CO<sub>2</sub>-V has been created at high pressures and temperatures, it retains its structure at room temperature but only at pressures above 1 gigapascal. Below that pressure it collapses and is no longer a polymer. Nearly half a century ago, when scientists were trying to produce the first synthetic diamonds, the same problem arose. Diamond could be synthesized only at high temperatures and pressures until

scientists learned its growth mechanism. Then they were able to synthesize it at lower pressures and temperatures using catalysis. Now diamond is routinely manufactured at ambient pressure with very little heat. Says Yoo, "We'll be looking for something like that with this new carbon dioxide."

Other applications of the team's research are truly out of this world: the experimental temperatures and pressures used to create CO<sub>2</sub>-V are comparable to those inside giant gas planets like Uranus and Neptune. Who knows what lurks in their interiors?

—Katie Walter

**Key Words:** carbon dioxide, diamond anvil cell.

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# Award-Winning System Assays Radioactive Waste with Radiation

**M**ORE than half a million drums of radioactive waste are stored at 30 Department of Energy sites across the nation, with thousands more to come as additional facilities at weapons complex sites are dismantled. All of these drums must be assayed to determine and verify their contents and levels of radioactivity before they can be transported for permanent storage or disposal.

A system that assays containers of radioactive waste safely, accurately, and nonintrusively has garnered a prestigious

R&D 100 Award for Lawrence Livermore National Laboratory and its commercial partner, Bio-Imaging Research, Inc. (BIR) of Lincolnshire, Illinois. This award is presented annually by *R&D Magazine* to “the 100 most technologically significant new products and processes of the year.”

The award-winning Waste Inspection Tomography for Non-Destructive Assay (WIT-NDA) system was developed by a team of engineers and physicists headed by Livermore’s Patrick Roberson and Harry Martz. The system combines active and passive computed tomography and nuclear spectroscopy to accurately quantify all detectable gamma rays emitted from waste containers. The WIT-NDA is part of BIR’s Waste Inspection Tomography system, which provides nondestructive examination and assay of radioactive waste and has been commercially available since August 1999. “The WIT-NDA is an excellent example of successful technology transfer between a DOE national laboratory and a small private business,” says Richard Bernardi, WIT program manager for BIR.



Bio-Imaging Research, Inc. of Lincolnshire, Illinois, is collaborating with Livermore researchers in developing nondestructive evaluation technology. Here, BIR’s trailer is the site of an experiment using active and passive computed tomography to identify and quantify materials inside nuclear waste drums.

### Safe and Accurate

As recently as 10 years ago, researchers could accurately assay the contents of a waste drum only by sampling, and for that they had to break the container seals. Opening containers meant workers—and possibly the public—risked exposure to radiation and other hazardous materials. Beginning in 1990, physicists Harry Martz and David Camp headed a Livermore team to research ways to estimate the radioactivity of drum contents from the outside. Over the years, the team received funding for research and development from Livermore's Engineering Directorate, the Laboratory Directed Research and Development program, and DOE's Environmental Management program, as well as from BIR.

The Livermore team developed a process that pinpoints where radioactive materials rest inside the drum and accurately quantifies and identifies these isotopes, whether they are plutonium, uranium, or some other gamma-ray-emitting radioactive waste. "This system is unique in that to use it, we don't need to open the container, we don't need any prior knowledge of the radioactive waste inside, and we don't have to calibrate the system to a specific waste stream," explains Roberson.

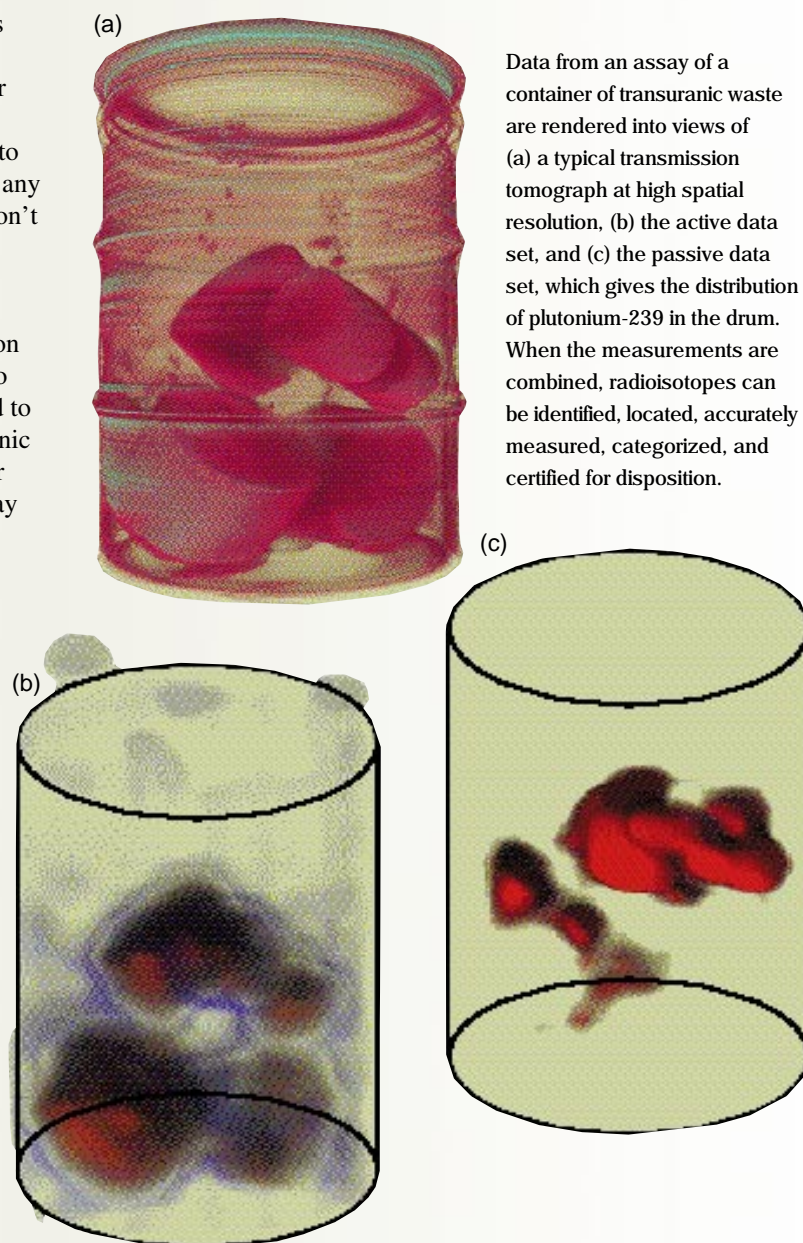
Determining the exact amount of radioactivity in each drum is essential to DOE's waste disposal efforts, Roberson notes. "DOE needs to characterize its radioactive wastes to verify that the waste drums meet criticality constraints and to differentiate transuranic from low-level wastes." Transuranic waste drums contain isotopes with atomic numbers greater than 92 (such as plutonium and uranium), radioactive decay half-lives greater than 20 years, and radioactivity levels greater than 100 nanocuries per gram of net waste weight.

Each class of waste is sent to a different disposal site. For example, the DOE Waste Isolation Pilot Plant (WIPP) in New Mexico accepts only transuranic wastes and, furthermore, has a limit on the total amount of radioactivity that can be placed within its underground repository. So waste drums must be nondestructively assayed to determine if they contain transuranic waste, and all radioisotopes in each drum must be inventoried to ensure that the WIPP limit is not exceeded. With NDA systems of lesser accuracy, waste regulators must err on the side of safety and designate waste disposal based on higher-end estimates of radioactivity.

### Two-Step Process

The WIT-NDA has a unique two-step process that provides an assay of greater accuracy than previously possible. It collects two tomographic measurements—one active and one passive—using six external radioactive sources collimated to shine through the waste drum into six opposing, high-purity germanium detectors.

The first step is active computed tomography, which, like radiographic techniques that produce medical x rays, measures the attenuation of radiation intensity that travels from an external source through an object to a detector. In this active measurement, the external radiation sources are aimed at the sealed drum. The sources emit gamma rays at discrete energy levels. As the rays pass through the drum and the various densities of material within, they are attenuated to varying degrees. On the other side of the drum, the gamma-ray spectrometer measures the resulting attenuated gamma radiation. Measurements are taken for 2.25-cubic-inch volumes



Data from an assay of a container of transuranic waste are rendered into views of (a) a typical transmission tomograph at high spatial resolution, (b) the active data set, and (c) the passive data set, which gives the distribution of plutonium-239 in the drum. When the measurements are combined, radioisotopes can be identified, located, accurately measured, categorized, and certified for disposition.

over the entire drum (a total of 2,304 volume elements for a standard 55-gallon drum). By detecting and measuring the attenuated gamma-ray intensity levels at specific energies, one can determine a map of the linear attenuation coefficient (a function of material density and atomic number) of the waste drum and its contents. These maps can be reconstructed to depict a drum's waste matrix attenuation per volume element and energy.

In the second step, called the passive measurement, the six transmission sources are shuttered. The six detectors measure the gamma-ray spectra emitted from inside the drum. Measurements are taken of all the volume elements. During the passive computed tomography reconstruction, the attenuation in these emission measurements, caused by material between the isotope and the detector, is corrected by using the active attenuation map. This correction leads to a far more accurate assay of radioactivity within the drum. The spectra

are also used to automatically identify the isotopes within the drum, because each isotope emits a unique signature within the energy spectrum.

### Unparalleled Accuracy

Other systems and techniques do not approach the accuracy of the WIT-NDA system. This was demonstrated by a DOE test that compared the performance of the WIT-NDA and fifteen other NDA systems. It was a blind test using a drum containing a simulated sludge with low levels of transuranic waste, one of the most challenging things to assay but typical of the types of wastes and drums the DOE must assay and dispose of. The WIT-NDA performed the best of all the systems by detecting the radioactivity within the sludge drum to within 1 percent of the known value. The nearest competing system detected only about 80 percent of the known radioactivity.

In the combined series of required DOE-sponsored tests for all NDA techniques that are proposed for certifying waste for disposal at WIPP, the WIT-NDA had a mean accuracy of 97.6 percent, with a precision within 4.1 percent. As Steven Cooke of DOE's Federal Energy Technology Center (now the National Energy Technology Laboratory in Morgantown, West Virginia) notes, "These results are truly exceptional in a difficult arena where par for the course is often plus or minus 50-percent accuracy."

### Other Applications

Roberson notes that since the WIT-NDA operates independently of whatever wastes are in the drum, it could also be used to measure the radioactivity in waste products from nuclear power plants or from industries that use radioactive tracers, such as the medical industry. "The system could also be used to quantify special nuclear materials in efforts to safeguard them and prevent their proliferation," he adds.

—Ann Parker

**Key Words:** active and passive computed tomography, nondestructive assay (NDA), nondestructive evaluation, R&D 100 Awards, waste disposal, waste inspection tomography, Waste Isolation Pilot Plant (WIPP).

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The WIT-NDA team (from left): DeLynn Clark, David Camp, Dennis Goodman, Harry Martz, Jr., Jessie Jackson, Dan Decman, Pat Roberson, Erik Johansson, Steve Azevedo, and BIR members (inset) Dave Nisius, Dick Bernardi, and Dave Entwistle.

# Nanoscale Chemistry Yields Better Explosives

**O**NE thousand years ago, black powder was prepared by grinding saltpeter, charcoal, and sulfur together into a coarse powder using a mortar and pestle. Since then, the equipment for making energetic materials—explosives, propellants, and pyrotechnics—has evolved considerably, but the basic process for making these materials has remained the same. That, however, is changing, thanks to an explosive combination of sol-gel chemistry and modern-day energetic materials research.

At Livermore Laboratory, sol-gel chemistry—the same process used to make aerogels or “frozen smoke” (see *S&TR*, November/December 1995)—has been the key to creating energetic materials with improved, exceptional, or entirely new properties. This energetic materials breakthrough was engineered by Randy Simpson, director of the Energetic Materials Center; synthetic chemists Tom Tillotson, Alex Gash, and Joe Satcher; and physicist Lawrence Hrubesh.

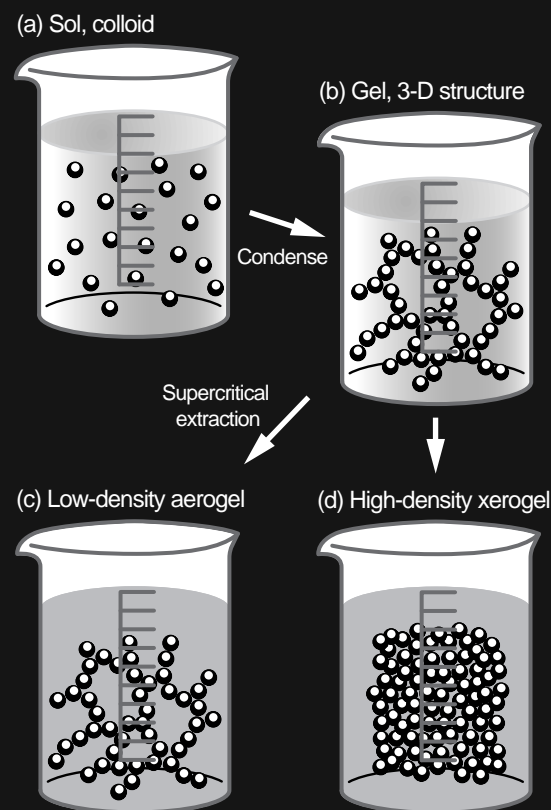
These new materials have structures that can be controlled on the nanometer (billionth-of-a-meter) scale. Simpson explains, “In general, the smaller the size of the materials being combined, the better the properties of energetic materials. Since these ‘nanostructures’ are formed with particles on the nanometer scale, the performance can be improved over materials with particles the size of grains of sand or of powdered sugar. In addition, these ‘nanocomposite’ materials can be easier and much safer to make than those made with traditional methods.”

## Energy Density vs Power, the Traditional Tradeoffs

Energetic materials are substances that store energy chemically. For instance, oxygen, by itself, is not an energetic material, and neither is fuel such as gasoline. But a combination of oxygen and fuel is.

Energetic materials are made in two ways. The first is by physically mixing solid oxidizers and fuels, a process that, in its basics, has remained virtually unchanged for centuries. Such a process results in a composite energetic material such as black powder. The second process involves creating a monomolecular energetic material, such as TNT, in which each molecule contains an oxidizing component and a fuel component. For the composites, the total energy can be much

greater than that of monomolecular materials. However, the rate at which this energy is released is relatively slow when compared to the release rate of monomolecular materials. Monomolecular materials such as TNT work fast and thus have greater power than composites, but they have only moderate energy densities—commonly half those of composites. “Greater energy densities versus greater power—that’s been the traditional trade-off,” says Simpson. “With our new process, however, we’re mixing at molecular scales, using grains the size of tens to hundreds of molecules. That can give us the best of both worlds—higher energy densities and high power as well.”

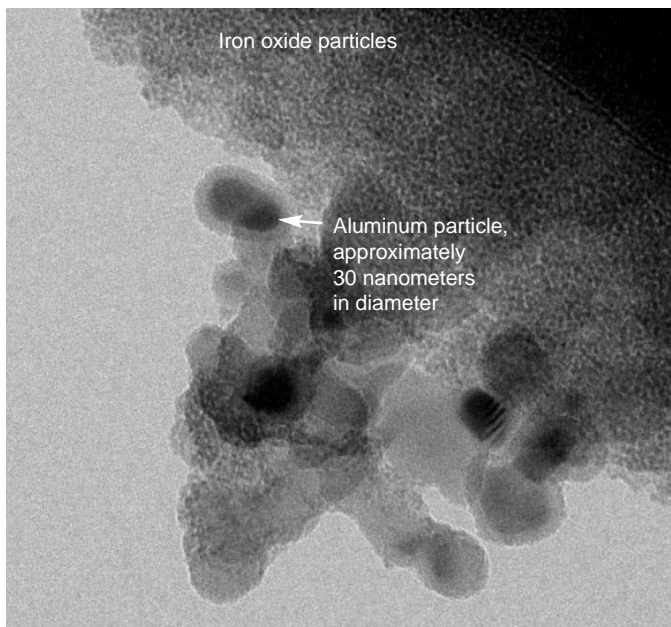


In sol-gel methodology, (a) chemicals in solution produce nanometer-size particles called sols. (b) These sols are linked into a three-dimensional solid network called a gel. (c) The solution can be supercritically extracted to produce aerogels, or (d) evaporated to create xerogels.

### Energetic Nanostructures in a Beaker

To control the mix of oxidizer and fuel in a given material at the nanometer scale, Livermore researchers turned to sol-gel methodologies. Sol-gel chemistry involves the reactions of chemicals in solution to produce nanometer-size particles called sols. These sols are linked together to form a three-dimensional solid network or skeleton called a gel, with the remaining solution residing in the open pores of the gel. The solution can then be supercritically extracted to produce aerogels (highly porous, lightweight solids) or evaporated to create xerogels (denser porous solids).

“A typical gel structure is extremely uniform because the particles and the pores between them are so small,” notes Tillotson. “Such homogeneity means that the material’s properties are also uniform. Our main interest in the sol-gel approach is that it will allow us to precisely control the composition and morphology of the solid at the nanometer scale so that the material’s properties stay uniform throughout—something that can’t be achieved with conventional techniques.”



Transmission electron micrograph of a thermite nanocomposite energetic material. The material is made up of an extremely fine iron oxide xerogel (approximately 2-nanometer particles) that has approximately 30-nanometer-diameter aluminum metal spheres (the larger globules) embedded in it.

Using these sol-gel-processing methods, the team derived four classes of energetic materials: energetic nanocomposites, energetic nanocrystalline materials, energetic powder-entrained materials, and energetic skeletal materials.

Energetic nanocomposites have a fuel component and an oxidizer component mixed together. One example is a gel made of an oxidizer with a fuel embedded in the pores of the gel. In one such material (termed a thermite pyrotechnic), iron oxide gel reacts with metallic aluminum particles to release an enormous amount of heat. “These reactions typically produce temperatures in excess of 3,500°C,” says Simpson. Thermites are used for many applications ranging from igniters in automobile airbags to welding. Such thermites have traditionally been produced by mixing fine powders of metal oxides and metal fuels. “Conventionally, mixing these fine powders can result in an extreme fire hazard. Sol-gel methods can reduce that hazard while dispersing extremely small particles in a uniform way not possible through normal processing methods,” adds Simpson. The Livermore team has successfully synthesized metal oxide gels from a myriad elements. At least in the case of metal oxides, sol-gel chemistry can be applied to a majority of elements in the periodic table.

In energetic nanocrystalline composites, the energetic material is grown within the pores of an inert gel rather than mixed into it. One way to initiate the growth is to dissolve the energetic material in the solvent used to control the density of the resulting gel. After the gel is formed, the energetic material in the pore fluid is induced to crystallize within the pores. The Livermore team synthesized nanocrystalline composites in a silica matrix with pores containing the high explosive RDX or PETN. The resulting structures contain crystals so small that they do not scatter visible light and are semitransparent.

In the powder-entraining method, a high concentration of energetic powders (90 percent by weight) is loaded within a support matrix (for example, silica) that takes up a correspondingly small mass. Highly loaded energetic materials are used in a variety of applications, including initiators and detonators. Manufacturing this type of energetic material using current processing technologies is often difficult. Producing detonators with pressed powders is a slow manufacturing process, mixing two or more powders homogeneously is difficult, and precise geometric shapes are not easy to produce. Also, pressing powders is a hazardous process.

Many of these problems may be overcome with the sol-gel process. One result is that the sol-gel explosives formed by adding energetic powders are much less sensitive than those



produced by conventional methods. “These results were surprising because conventionally mixed powders generally exhibit increased sensitivity when silica powders are added,” says Simpson. “We’re still exploring the reasons for this decreased sensitivity, but it appears to be generally true with sol-gel-derived energetic materials.”

The final class of energetic material produced by sol-gel methods is energetic skeletal materials. Basically, the sol-gel chemistry is used to create a skeletal matrix, which is itself energetic. Satcher thinks that it might also be possible to form a nanostructure made up of a fuel-oxidizer skeleton with precise stoichiometry (the numerical relationship of elements and compounds as reactants and products in a chemical reaction). “This is something we are still looking into,” he adds. In addition to providing materials that have high energy density and are extremely powerful, sol-gel methodologies offer more safe and stable processing. For instance, the materials can be cast to shape or do not require the hazardous machining techniques required by materials that cannot be cast.

### Future Looks Bright

Right now, making energetic materials using the sol-gel technique is in the basic research stage, but results look promising. “Many compositions depend on a simple, inexpensive procedure that we can basically do in an ordinary chemistry beaker,” says Tillotson. He notes that the practical advantages of these materials are encouraging. Some of the pluses are less sensitivity, safe mixing, low-temperature synthesis, safe handling, safe processing, and homogeneity leading to better performance.

“We’ve just begun to explore the possibilities for these new materials and the methodologies that produced them,” adds Simpson. “This approach is like a new baby—it has lots of potential. The ramifications are still largely unknown.”

—Ann Parker

**Key Words:** aerogel, energetic materials, explosives, nanocomposites, PETN, propellants, pyrotechnics, RDX, sol-gel, xerogel.

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In the laboratory, Alex Gash mixes a sol-gel to create an energetic material.