Lawrence Livermore National Laboratory

Science & Technology REVIEW

December 2023

Controlling Semiconductors with Light

Also in this issue:

Drone-Mounted Threat Detection

Carbon Capture at a Winery

Hydrogen Storage Evaluation

About the Cover

In parallel with the continuing demand to improve computing, optical, power distribution, and other technologies comes the need to advance semiconductor materials at the heart of high-power devices. As described in the article beginning on p. 4, a Lawrence Livermore research team working with a specific class of semiconductor materials—ultrawide bandgap materials—explored the use of light rather than chemical impurities for controlling material properties to suit higher-power applications. The cover image represents light as the source of improved semiconductor materials to meet future technology needs as well as the potential for the featured research project to enable more energetic shots at the National Ignition Facility.

Cover design: Mary J. Gines

About *S&TR*

At Lawrence Livermore National Laboratory, we focus on science and technology research to ensure our nation’s security. We also apply that expertise to solve other important national problems in energy, bioscience, and the environment. *Science & Technology Review* is published eight times a year to communicate, to a broad audience, the Laboratory’s scientific and technological accomplishments in fulfilling its primary missions. The publication’s goal is to help readers understand these accomplishments and appreciate their value to the individual citizen, the nation, and the world.

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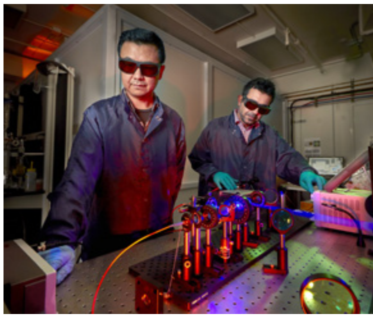
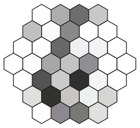
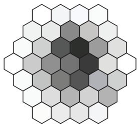
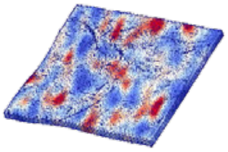


Research Highlights







Departments

Molecular Dynamics Cornerstone Breaks Down

For over a century, the Nernst-Einstein (NE) relation has linked charged particles' ability to diffuse through liquids (diffusion coefficient) to movement in the presence of an electric field (electrophoretic mobility). However, new research finds this correspondence is not universal but breaks down inside carbon nanotube porins (CNTPs). Appearing December 30, 2022, in *Nature Nanotechnology*, research by scientists at Lawrence Livermore and the Massachusetts Institute of Technology found that strongly confining ions inside CNTPs alters expected molecular behavior.

The study, involving experimentation and simulation, confined potassium ions (K^+) and water molecules inside straw-shaped nanotubes (0.8 nanometers in diameter) inserted into phospholipid membranes, forming transmembrane pores. K^+ ions could not freely diffuse due to obstruction from a water molecule chain filling the CNTP; but under an electric field, the chain broke down, allowing formation of individual ion-water clusters that migrated quickly. "The extreme spatial confinement in these pores hinders the diffusion of K^+ ions, reducing the diffusion coefficient by three orders of magnitude relative to its bulk value," says Livermore scientist Aleksandr Noy, the study's co-lead author. "Surprisingly, the same confinement has a negligible effect on the electrophoretic mobility, leading to a complete breakdown of the NE relation."

The study suggests that the NE relation does not hold universally as Nernst theorized in 1888. At the extreme nanoscale, diffusion and electrophoretic mobility values may not correlate at all when confinement forces a different electromigration mechanism. These new insights are especially relevant to cell physiology and drug discovery because the ion channels mimicked by CNTPs are critical to cellular functioning.

Contact: Aleksandr Noy (925) 423-3396 (noy1@llnl.gov).

Deep Learning Explains Photocatalyst Surface Chemistry

Interaction between liquid water and metal oxide surfaces is applicable to several technologies. In the presence of sunlight, surfaces of titanium oxide (TiO_2) can accelerate separation of water into the molecular species H_2 and O_2. This process, photocatalysis, drives hydrogen production and photooxidation of organic matter in self-cleaning devices. Predicting how these reactions may proceed requires understanding the chemical form of water at the material's surface—molecular or dissociated. Published January 3, 2023, in *Proceedings of the National Academy of Sciences*, a multi-institutional research team including Lawrence Livermore used deep learning-based simulations to characterize associated structures and interactions of water on TiO_2 surfaces.

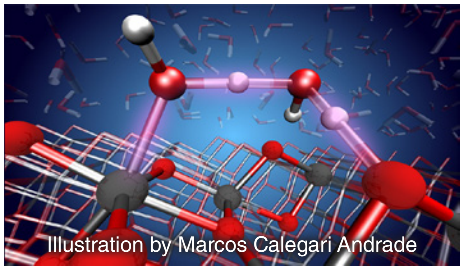


Illustration by Marcos Calegari Andrade

Using ab initio-based atomistic simulations with nanosecond timescale, the team assessed the dynamic equilibrium of molecular and dissociated water at the surface of rutile $TiO_2(110)$, the material's most common crystal polymorph. "Our simulations revealed how sensitive the surface chemistry of TiO_2 is relative to the thickness of thin TiO_2 films, and they provided atomic-level detail into the structure of water close to the TiO_2 surface," says co-author Marcos Felipe Calegari Andrade from the Quantum Simulations Group at Lawrence Livermore.

Researchers found a larger water dissociation fraction than previously estimated, supporting the greater photooxidative capacity of rutile TiO_2 over its other anatase phase. Greater understanding of surface interaction between water and TiO_2 could enable discovery of efficient, affordable materials for clean hydrogen production and medical uses.

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Turbulence-Measuring Telescope Sees Smooth Launch

For vehicles traveling at hypersonic speeds (above Mach 5, 6,174 kilometers per hour), slight variations in encountered air patterns have magnified effects on drag and heat factors. To better understand these impacts on hypersonic flight, the Stellar Occultation Hypertemporal Imaging Payload (SOHIP), a prototype telescope designed and built by Livermore researchers, was launched March 14, 2023, from Cape Canaveral, Florida, to the International Space Station (ISS).

"If we [can] accurately predict the conditions that trigger erratic gravity waves or hypersonic flows, we could inform better vehicle design, reduce costs, and improve overall hypersonic flight performance," says principal investigator Matthew Horsley. SOHIP employs Livermore's patented monolithic optics to investigate upper-atmosphere turbulence using starlight. Focusing on one star above the atmosphere and another in the wake of the ISS's trajectory, the telescope will monitor for minute fluctuations in air refractivity. Capturing roughly 1,000 images per second, it will work in concert with other ISS instruments to calculate encountered turbulence at the finest spatial resolution to date.

The shoebox-size design weighs only 13.6 kilograms and is constructed from off-the-shelf parts, making it readily integrable with existing ISS equipment. Data captured using specialized firmware will enhance development of algorithms for modeling turbulence. SOHIP represents the first Livermore instrument to operate on the ISS, and the project fulfilled strict NASA safety requirements while being completed on time and within budget.

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Commentary by Manyalibo (Ibo) Matthews

Supporting the Mission with Materials Excellence

THAT Lawrence Livermore excels in materials science is not news. The Laboratory has applied materials science expertise to national security (actinides, high explosives), clean energy (materials for hydrogen generation, carbon capture, and batteries), and additive manufacturing. Our capabilities in semiconductors and active optics for laser systems may be considered nascent compared to more established research at Livermore, but such expertise is critical in positioning ourselves to be responsive and meet future needs in our broader deterrence mission.

The feature article in this issue of *Science & Technology Review* delves into a three-year Laboratory Directed Research and Development (LDRD) project to optimize ultrawide bandgap (UWBG) materials—semiconductor materials tolerating higher power levels than silicon—and apply them to photoconductive devices for the National Ignition Facility's (NIF's) powerful laser system. These photoconductive devices are used as selectable, spatial light blockers capable of masking specific regions of the beam that may otherwise initiate optical damage or growth on downstream optics.

Along with spatially modifying NIF laser beams to control optical damage, the ability to shape the spatial distribution of laser energy—a goal of laser material processing—has been fundamentally constrained by limitations in the laser damage threshold of beam shaping optics for high-power applications. Evolving from the LDRD research team's work are potential improvements in laser welding, drilling, cutting, and shock peening as well as laser powder bed fusion and directed energy deposition through tailored laser beam shaping. Process science to enhance production of UWBG materials has also been addressed. While traditional approaches amount to trial-and-error experimentation, the UWBG LDRD team has harnessed the power of the Laboratory's competencies in computation and computational material science to predict viable materials for optimal performance.

Mission applications are always underpinned by science and technology innovation. The underlying UWBG materials innovation and research findings enable many applications: high-power radio frequency electronics supporting radar, communications, and national defense; inertial confinement fusion, high-power laser systems, and space optics for scientific discovery; and further improvements to speed and refine advanced manufacturing.

Research and technology advancing the Laboratory's diverse mission areas are further reflected in this issue's research highlights. The first highlight introduces MiRadar, a ground-penetrating radar (GPR) developed to identify buried threats in real time, protecting military personnel. MiRadar's drone-mounted technology builds on earlier, larger, and heavier GPR technologies and adds an array of antennas that both send penetrating pulses and receive data to be transmitted into high-resolution, 3D images. This technology demonstrates innovation to support the Laboratory's Multi-Domain Deterrence mission area, strengthening defensive capabilities.

The second research highlight, detailing the design and testing of a carbon capture system at a Napa Valley, California, winery, reflects Livermore's commitment to the Climate and Energy Security mission area. As the article describes, researchers identified ideal packing material for an absorber built to capture carbon dioxide at its source—in this case, fermenting wine in tanks. Expertise in industrial chemistry yielded a mineralization technique to sequester captured carbon dioxide gas into a mineral powder. With further development and refinement, a similar carbon capture system could remove hundreds of thousands of tons of greenhouse gas emissions in California alone for pennies per bottle in wine production costs.

The third highlight returns to the Climate and Energy Security mission area with a focus on a potential source of reliable, secure, low-carbon energy: hydrogen. The multilaboratory Subsurface Hydrogen Assessment, Storage, and Technology Acceleration (SHASTA) Project considers the potential for hydrogen storage in depleted oil and gas reservoirs, saline aquifers, and salt caverns throughout the nation. Key to assessing the behavior of hydrogen stored underground are diagnostic instruments in development at Lawrence Livermore as well as an open-source reservoir simulator designed specifically to model hydrogen flow. SHASTA also addresses the monitoring, technoeconomic factors, and safety communication elements underlying real-life application of underground hydrogen storage. As each of these articles demonstrate, the Laboratory's capabilities are put to work every day to enable national security, global stability, and resilience—in defense, in the environment, in energy security, in industry, and in accelerating the innovations that make the mission possible.

■ Manyalibo (Ibo) Matthews leads the Materials Science Division.

ULTRAWIDE BANDGAP Materials in the Spotlight

Lawrence Livermore researchers explore controlling semiconductors with light, rather than chemical impurities, to optimize for high-power and laser applications.

THE semiconductor materials at the heart of most electronic devices have shaped computing, power distribution, optical, and communication technologies. As demands for improved performance evolve, so must semiconductor materials evolve to support high-power applications. For example, silicon cannot efficiently control the voltage levels handled by switches that integrate alternative energy sources into the nation's electric grid. Electric vehicles demand materials that can bear high electric fields for improved charging efficiency.

Semiconductor materials such as silicon carbide and gallium nitride—wide bandgap (WBG) semiconductor materials—operate at higher temperatures, voltages, and frequencies, enabling smaller and more efficient components for lower cost, high-power applications. The bandgap of a semiconductor is the energy required for an electron to move from a lower energy state (the valence band) to a higher energy, free state (the conduction band). In making this jump, the electron leaves behind an empty space (hole) in the valence band that enables electron movement in that band as well.

The wider the bandgap, the higher the energy. Therefore, ultrawide bandgap (UWBG) semiconductor materials tolerate even higher voltages with lower power losses than WBG materials. UWBG materials promise to improve high-power devices for grid control along with laser applications and technologies such as diode-based additive manufacturing, in which an optically addressable light valve (OALV) shapes high-power laser light in programmed, layer-by-layer images to build parts.

The Right Time with the Right Tools

Understanding the growing need for high-power technology, Department of Energy (DOE) energy frontier research centers (EFRCs) have turned their attention to UWBG materials. The topic is not new to Livermore materials engineer Lars Voss. "High-power semiconductor research is a niche at Lawrence Livermore compared to other national laboratories," he says. "The Laboratory builds devices in different ways to meet different requirements than basic science centers. We've long realized the need to move beyond the last decade's state of the art."

No single UWBG material stands out as the best candidate for high-power devices. Diamond offers superior electron mobility and thermal conductivity but does not offer the large-area substrates required for additive manufacturing. Gallium oxide possesses the availability of low-defect, large substrates but represents a compromise in electron transport and thermal properties compared to diamond. Aluminum nitride registers closer to diamond's energy and thermal characteristics but at a higher cost and lower substrate area than gallium oxide.

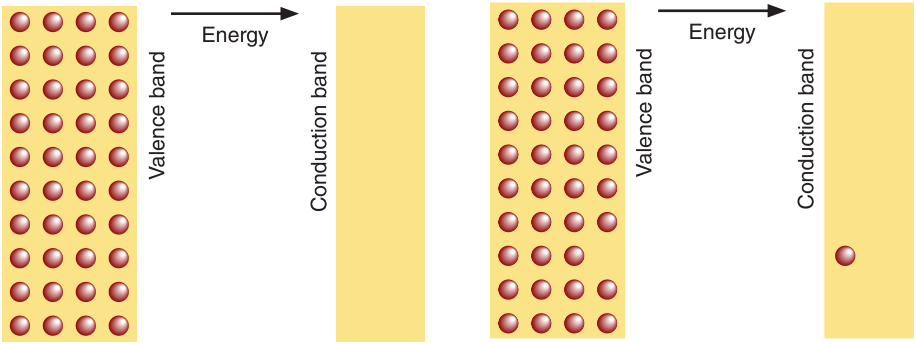
Dopants—impurities introduced to a semiconductor crystal—alter the number of charge carriers (electrons and holes) to tailor a semiconductor's electrical properties. However, UWBG materials cannot be doped with impurities that are able to achieve the broad conductivity control required for high-power applications.

An alternative approach to shape the properties of semiconductor materials is to use photons, rather than impurities, to generate electron carriers and control the conductivity of these materials, an approach Lawrence Livermore has used with great success in laser and other mission-focused programs. Photogenerated carriers are excited directly across the bandgap from the valence band to the conduction band, the way photons are converted to electrical current in solar cells. However, to generate free carriers, an exceptionally wide bandgap requires high-energy photons such as those from deep, ultraviolet (UV) light sources, which is an impractical requirement for deployable systems.

To overcome the challenge of controlling the UWBG materials' electrical properties, a team of Lawrence Livermore researchers led by Voss proposed to introduce un-ionized dopants, with energy levels deep within the materials' bandgap, that can be excited with lower energy light, generating free carriers. "Other institutions are focused on electronic approaches to build UWBG devices," says Voss. "However, they find themselves unable to achieve broad conductivity. Sub-bandgap, optical excitation provides a universal, material-agnostic approach to building devices to meet high-power needs. Livermore is the perfect place to do this because we have applied the same approach using other material systems for more than a decade."

Earlier Laboratory Directed Research and Development (LDRD) projects at Lawrence Livermore provided a foundation for a new proposal. Projects exploring silicon carbide and diamond photoconductive switches led to improved defect absorption of the materials and increased photo response, exciting higher current as voltages increased. Livermore research teams had also demonstrated significantly (100x) higher electrical fields across increasingly thinner switches. Voss and materials scientist Vincenzo Lordi saw an opportunity to expand on past LDRD projects by applying precise computational approaches to predict the electronic qualities of ideal dopants in UWBG materials and how the dopants would react to light. "We recognized that a new project could build quantitatively on earlier Livermore projects, which had only crudely predicted many of these properties," says Lordi. "With the more powerful supercomputers now at Livermore, we can advance the calculations to direct experimental doping efforts."

In 2021, Voss, Lordi, and a Livermore team of chemical, electrical, materials, and mechanical engineers embarked on a new LDRD project to generate mobile charge carriers in UWBG materials with sub-bandgap photons, synthesize optimal UWBG materials, and demonstrate devices using optimized materials. "This project came at the opportune time from a technology and a need standpoint to dive into these materials and solve the problems Livermore cares about," says Voss. "The LDRD project

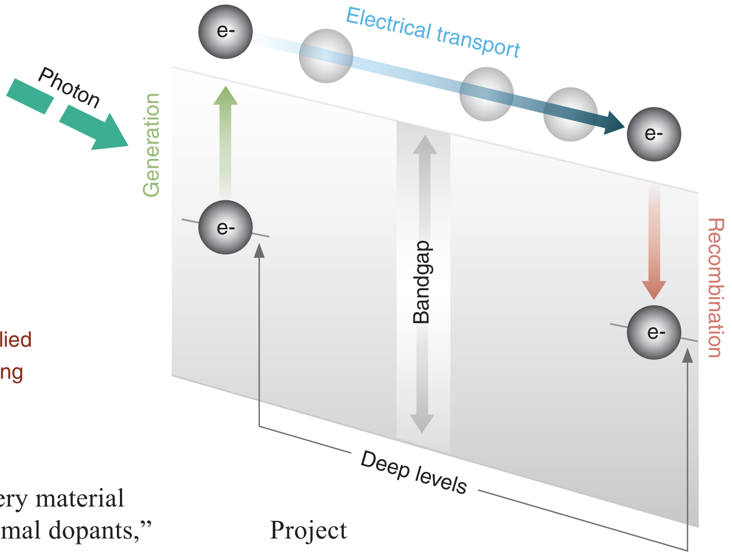


The bandgap of a semiconductor is the energy required for an electron to move from a lower energy state (the valence band, on the left side in each image) to a higher energy, free state (the conduction band). In making this jump, as indicated in the image on the right, the electron leaves behind an empty space (hole) in the valence band that enables electron movement in that band as well.

combines materials discovery with a demonstration of real devices that can ultimately be scaled to move up the technical readiness scale,” says Voss.

The research can enhance the Laboratory’s opportunities to support DOE’s Office of Energy Efficiency and Renewable Energy and the Advanced Research Projects Agency–Energy (ARPA–E) as well as future EFRC calls in the power electronics fields. Looking beyond the DOE enterprise, Lordi observes, “Power switching on the order of 10 times more efficient can lower energy use at data centers, which are a major consumer of energy and, hence, a notable contributor to greenhouse gas emissions. A pathway to radiation-tolerant electronics for use in extreme space environments may be another area of impact.”

Closer to home, the researchers saw an opportunity to apply their findings to fabricating OALVs with optimized materials to better withstand the high fluence of laser operations at the National Ignition Facility (NIF) and other advanced laser facilities. (See sidebar, “More Shots, More Potential for Success.”)



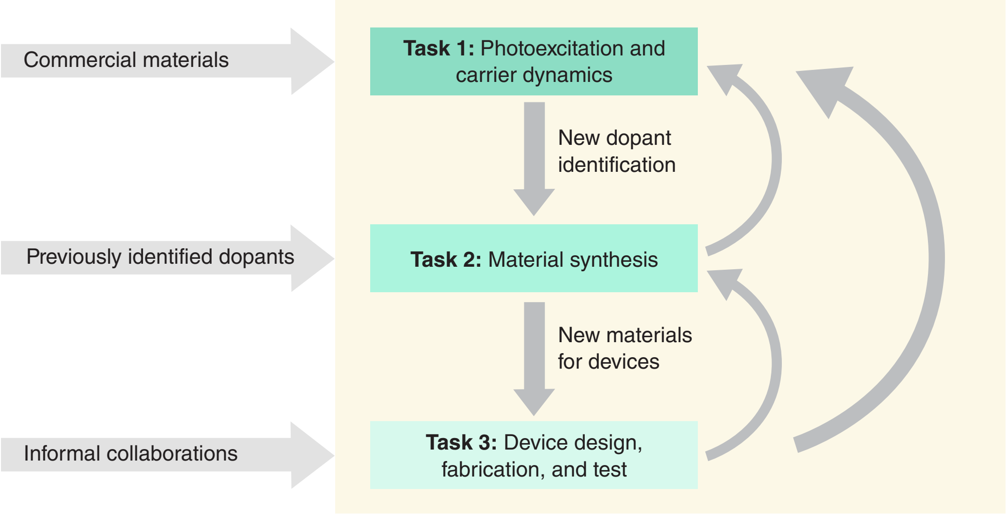
The properties of ultrawide bandgap (UWBG) materials can be enhanced by photoexcitation rather than doping—adding impurities to a semiconductor material. In photoexcitation, sub-bandgap light excites an electron from the deep, ultraviolet level, and the electron moves under an applied electric field before recombining back into the deep level.

Iterative Innovation

The LDRD project proposed three research tasks to be carried out simultaneously. In this way, each task would inform and refine the project overall, improving material candidates along the way to spur innovation more quickly.

In the first task, a group led by Livermore scientist Joel Varley investigated material choices and candidate dopant atoms to more favorably tune absorption and photoconductive response. Varley’s group performed predictive materials simulations using hybrid-functional density functional theory, which uses details of a material’s electronic structure to consider how it would respond to optically generated carriers, targeting the favorable combination of strong absorption and higher conductivity. “Every material has a potential set of optimal dopants,” says Varley. “The desired optical response in an OALV is largely dictated by fundamental properties of the photoconductive material as well as impurities or suitable defects that lead to photo absorption and generate the conductivity. Increasing computing automation enabled us to explore appropriate dopants more accurately and in less time than with earlier computing capabilities, and many years faster than trial and error.”

Project partners at the University of California at Santa Barbara (UCSB), Washington State University (WSU), and Vilnius University provided valuable insight and materials research data to Varley and his team. “When adding new dopant sources to the system, we consider theoretical findings and factors such as material purity, vapor pressure, and literature regarding whether the material will linger in the system after growth,” says UCSB researcher Steve Rebollo.



An iterative project plan enabled findings from each task to inform and improve outcomes over the three-year duration of the project rather than constrain research in later tasks to a limited number of dopant and material candidates.

“Following growth, we analyze a dopant’s effect on material growth using atomic force microscopy, x-ray diffraction, and other techniques to probe the surface morphology and crystalline quality, respectively. We shared this information with the Livermore team.”

The UCSB researchers have found gallium oxide films attractive due to the high purity of the epitaxial material and its ability to withstand high-power laser pulses. “Gallium oxide’s qualities translate into experimental demonstrations of the highest laser-induced damage threshold (LiDT) among UWBG semiconductors,” says UCSB’s Sriram Krishnamoorthy.

Researchers from WSU’s Institute of Materials Research discussed possible dopants that might have the desired optoelectronic properties with the Livermore team and gained valuable information in the exchange. “Working with Livermore enabled us to see the higher-level device side and participate in designing crystals to meet the end needs of those devices,” says WSU scientist John McCloy. His colleague Matt McCluskey adds, “To test the robustness of materials proposed for an OALV, candidate materials such as gallium oxide, aluminum nitride, and diamond are irradiated with intense laser pulses and then characterized using optical techniques. WSU uses a deep-UV photoluminescence system to investigate defects in UWBG semiconductors with a high level of detail. From the results of these fundamental studies, we aimed to develop a way to screen good versus bad crystals.”

To date, Varley’s team has computationally screened thousands of materials, investigating their intrinsic ability to generate a stronger response to photoexcitation. “Our results point to tailored materials with properties matched to end-use applications,” says Varley. A number of materials offer the promise of high photo response, provided that suitable dopants and defects can be introduced and lead to absorption

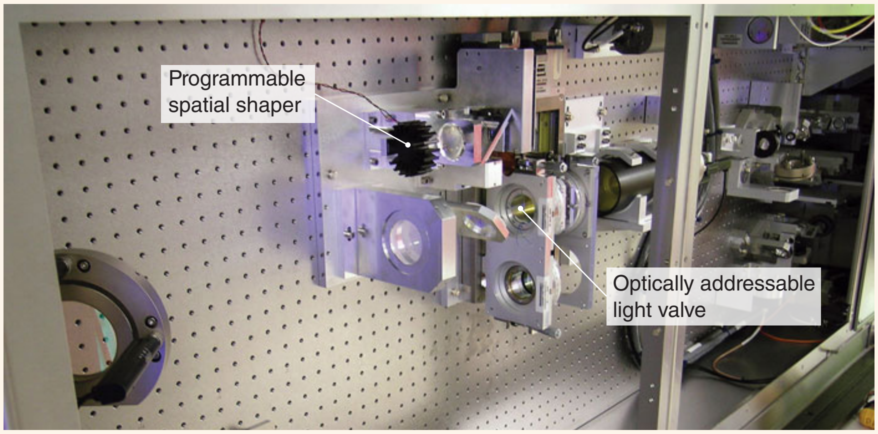
More Shots, More Potential for Success

Lawrence Livermore’s National Ignition Facility (NIF) stands to gain from the Laboratory Directed Research and Development (LDRD) project to explore ultrawide bandgap (UWBG) photoconductive devices. NIF, the world’s highest-energy laser system simulates extreme temperature and pressure conditions to advance understanding of fusion ignition and thermonuclear burn, relevant to stockpile stewardship. Programmable spatial shapers (PSSs) at NIF modulate laser intensity in the optical beam path to address laser-induced damage on optical components, which increases shots per year by reducing maintenance time and costs. Optically addressable light valves (OALVs) with wide bandgap bismuth silicon oxide (BSO) as a photoconductive layer enable drop-in retrofit of NIF’s PSS system.

“The PSS is a critical component for preventing degradation of downstream optical elements under laser illumination,” explains engineer Sara Harrison, a member of the LDRD project team. “The practice is to block light from shining in areas where flaws exist in the optics. While this protects the optics, light is thrown away unnecessarily with the present configuration. Therefore, NIF is eager to improve PSS specifications by exploring materials that enable the position of the OALVs to be shifted in the beam lines.”

Livermore scientist and LDRD project team member Joel Varley adds, “The current BSO device can only withstand so much laser fluence, and the technology cannot be scaled to a larger size to achieve the clear aperture areas required. Using more robust materials in light valves enables more energy per shot.” A new design incorporating an ultrawide bandgap (UWBG) photoconductor would enable higher power operation. A new OALV design will rely on photoconductive semiconductors that can be grown in large boules, heavily doped to form contact layers, and capable of withstanding fluences of 1 to 2 Joules/square centimeter area for adoption in high-power laser systems.

“The connection to NIF makes the UWBG materials research even more exciting,” says project advisor Vincenzo Lordi. “Applying the LDRD project’s findings at NIF will be impactful and improve performance dramatically.”



The programmable spatial shapers package incorporates optically addressible light valves to extend the operational lifetime of the National Ignition Facility’s high-energy laser optics by obscuring laser light where flaws exist in optical components, limiting further damage during subsequent shots.

at the desired energies. To that end, the team has leveraged atomistic-level simulations to continue refining dopant candidates that tune to optical response.

Taking the next step, the team, in concert with academic partners, synthesized materials with target dopants identified from theory to yield energy levels suitable for desired visible light excitation. WSU has synthesized single crystals while UCSB grew epilayers (thin films) onto crystals. These materials have been characterized and processed into OALVs, with promising optical responsivity. “We have focused on a beta composition of gallium oxide, a UWBG semiconductor commercially available in large-area substrates ideal for fabricating large-format OALVs,” says Varley.

Synthesis Success

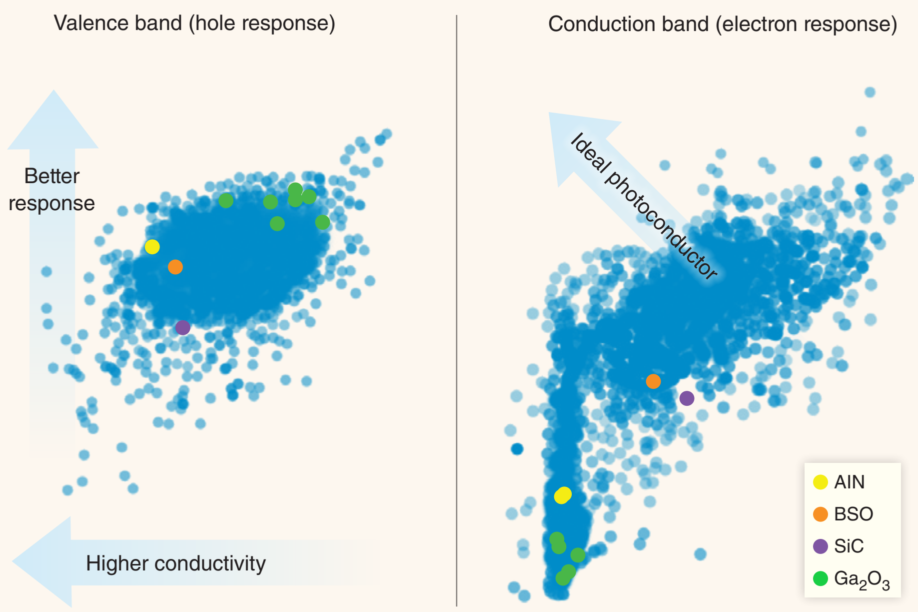
The second project task focused on procuring and synthesizing material candidates to identify materials with ideal properties such as carrier generation, recombination, and transport for high-power devices. The task team, led by engineer Clint Frye and former Livermore scientist Andrew Lange, started with the top contender: gallium oxide. Gallium oxide offers the advantage of providing large substrates. Other candidate materials—diamond crystals and aluminum nitride—were also grown or procured and then characterized and tested for photoconductive properties during this task.

Continuing the project’s iterative research format, the team worked with commercial vendors to source UWBG materials while candidate materials continued to undergo growth and custom doping for optimized outcomes. WSU’s unique capability for growing gallium oxide crystals combined with data informing custom dopants enabled the growth of bulk beta gallium oxide crystals. With repeated characterization and further computational modeling, the team learned process improvements to incorporate the dopant and activate desired material qualities such as conductivity.

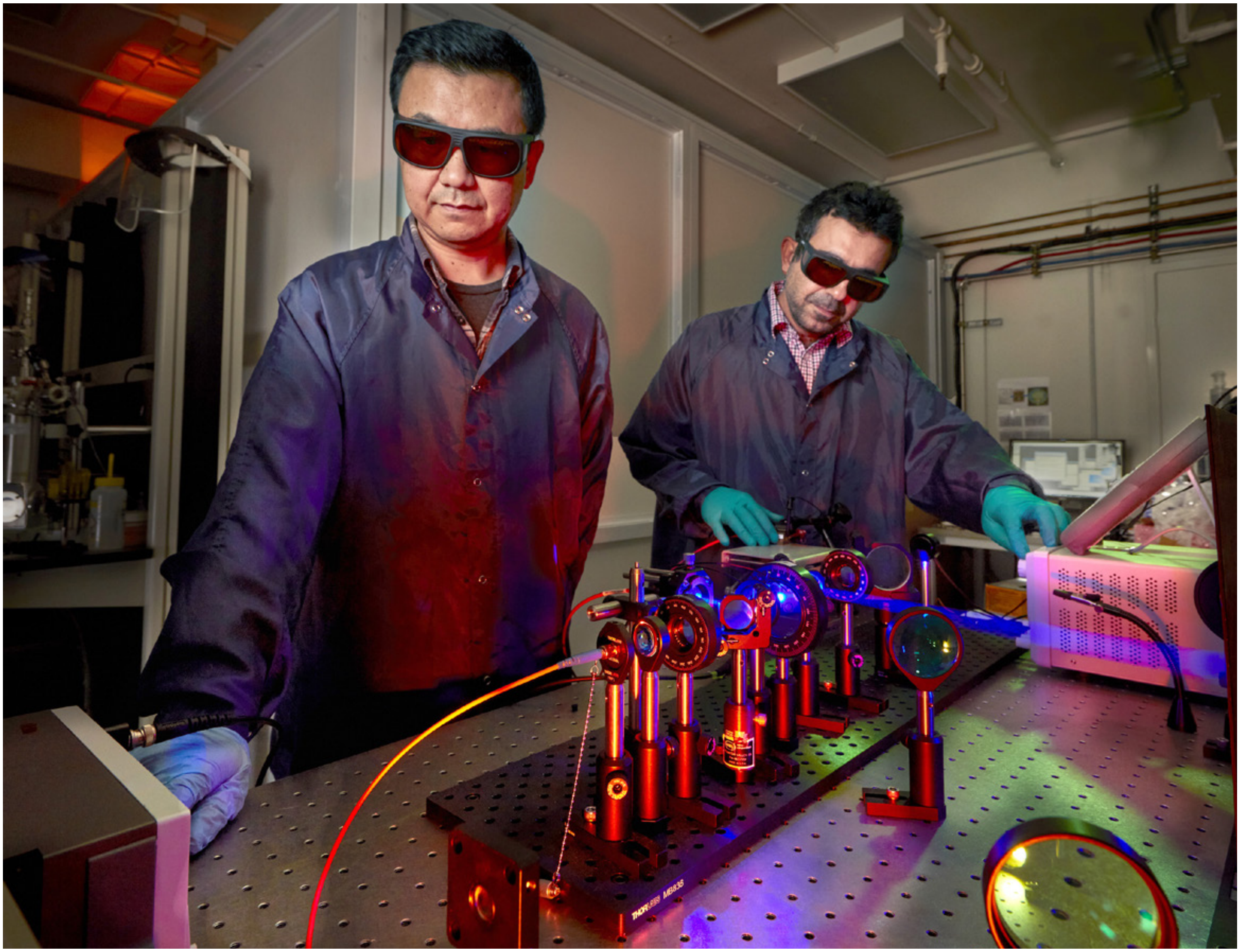
Frye, who came from a semiconductor background before joining the Laboratory, enjoys the interdisciplinary nature of the work that is part semiconductor, part microfluidics, and part optics. “Livermore has so much expertise in one place,” says Frye.

Since the project started, the team has characterized a range of commercially available and emerging–research-grade WBG and UWBG photoconductors for potential applicability to building both high-peak and high-average-power OALVs. Key material properties including photoresponsivity at different wavelengths, resistivity in total darkness, and available and potential wafer size were characterized and input into a technology computer-aided design model to evaluate their suitability. Further, materials were evaluated for LiDT with silicon carbide, aluminum nitride, and gallium oxide meeting a 1 Joule/centimeter-squared (J/cm^2) threshold and a 2 J/cm^2 goal.

Although gallium oxide possesses the most desirable LiDT, the required pump light wavelengths to achieve efficient operation for the material are in the UV and deep UV (DUV) range (280 nanometers), while silicon carbide and aluminum nitride can operate efficiently in the blue or near UV ranges. Long term, Voss’s team has targeted demonstration of a gallium oxide OALV pumped with DUV light for potential future use in high fluence applications. For near-term adoption for NIF’s programmable spatial shapers (PSSs), silicon carbide or aluminum nitride are more attractive options given the cost, availability, and



The project team has computationally screened thousands of materials, investigating their intrinsic ability to generate a stronger response to photoexcitation. Materials of particular interest to the team—aluminum nitride (AlN), bismuth silicon oxide (BSO), silicon carbide (SiC), and gallium oxide (Ga_2O_3)—are noted in the diagrams above.



Livermore's Qinghui Shao and Soroush Ghaniparsi (left to right) test the functionality of 50-millimeter optically addressable light valves (OALVs). Testing with the smaller wafer size enabled the team to get test results for more materials.

intensity of commercial, off-the-shelf components. Other materials, such as zinc gallium oxide may be even more attractive in the future, but their availability is limited to smaller (1 cm^2 or smaller) sizes available at only a few research institutions.

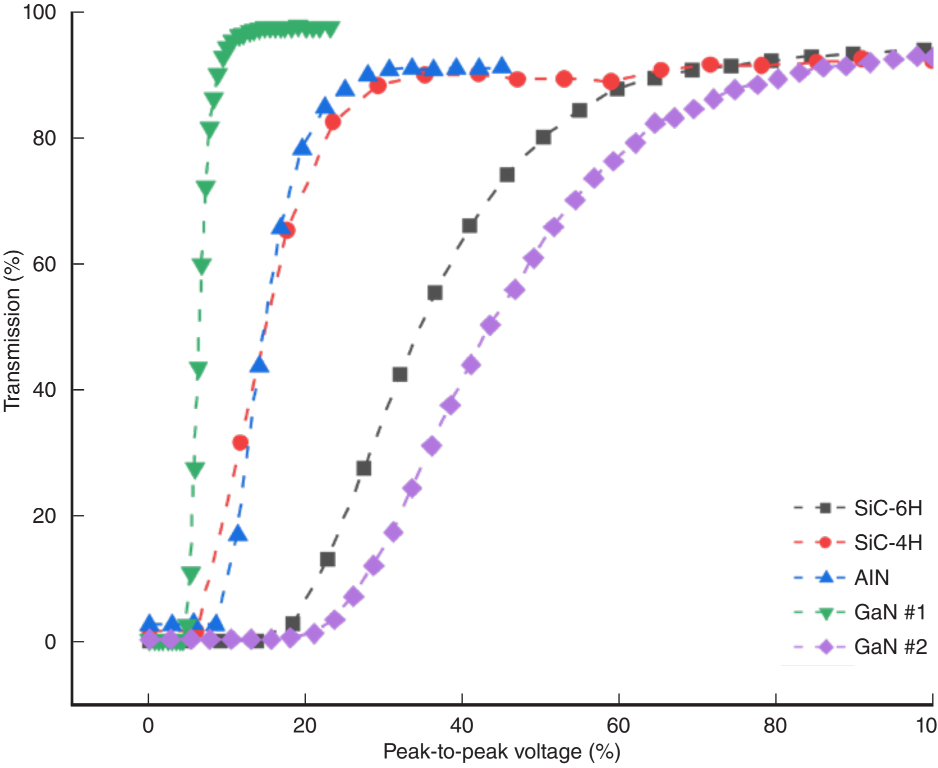
Optimizing OALVs

In the third task, a sub-group focused on building OALVs to maximize performance. Armed with knowledge gained by characterizing candidate dopants and materials, group lead Sara Harrison and device engineer Qinghui Shao used simulation software to design efficient devices, optimizing for different applications. "Our group studied the legacy process to fabricate and test NIF's PSS and adapted the process to our facility, where we address larger-size optics," says Harrison. A testbed was built to understand the performance of one device while others were fabricated.

As part of this task, Frye guided the team in fabricating OALVs using selected UWBG materials. "We've designed the building process and process controls to ensure consistency," says Frye. "Ensuring consistency—particularly when working with coatings in small volumes and 50 millimeter (mm) wafer sizes—is tricky. But the small size enabled us to use different materials.” The group has scaled its tooling and design process to achieve a larger, usable area for 100-mm diameter OALVs, increasing the area by a factor of four and increasing device thickness.

The team has already reviewed the performance of several different OALV designs in comparison to the legacy PSS at NIF. At low applied voltage, the fabricated OALVs block 99 percent or greater of the incident light. As voltage is increased, the OALVs operated in gray mode, which describes the case of light partially transmitting. At a high enough voltage or light intensity, the OALVs transition to greater than 90 percent transmissivity. The ratio of blocking to transmitting exceeds 450, well above the requirements for typical OALV applications. All in all, the fabricated OALVs meet performance requirements for NIF and other applications, although continued optimization and refinement of the design and fabrication processes are expected to increase performance further.

Next, the Task 3 sub-group designed OALVs for high average power applications such as diode-based additive manufacturing. In this case, an upper limit on temperature is set by the phase transition of the liquid crystal at around 60°C. At the high average power levels required (5 kilowatts), uncooled bismuth silicon oxide (BSO) OALVs stop functioning within seconds. BSO in particular has extremely low thermal conductivity, making thermal management challenging. By adopting WBG materials with excellent thermal conductivity, such as silicon carbide, heat sinking and active air cooling can be incorporated. The team’s designs have undergone further refinement as well as experimental validation of photoconductor heating, and a demonstration device is anticipated to be complete in the next year.



In testing the functionality of OALVs fabricated with a variety of wide bandgap and UWBG photoconductive materials, the team determined that, at low voltage, little to no light passes through the devices (low percentage transmission). As the voltage increases under illumination, they become increasing transmissive—reaching up to 99 percent transmissivity in some cases.

Although the LDRD project is winding down, several transition projects, with both internal and external programmatic customers, have already been launched and are progressing well. In addition to OALVs and other power devices, the team identified promising applications for optoelectronic WBG and UWBG materials. For example, a diamond junction field effect transistor, simulated extensively in the LDRD project, has been selected for negotiation by ARPA–E. Terahertz sources and fast x-ray detectors for NIF have been targeted for proof-of-concept demonstrations. Other possibilities include UWBG radio frequency transistors with no optical triggering.

“This project has broadened our understanding of UWBG materials,” says Voss. “Due to the hard work and exceptional progress of the team developing the science and devices initially targeted, we have been able to look into new, related areas. We hope to continue developing and spinning off ideas and technologies to meet Laboratory and broader national needs both now and for the future.”

— Suzanne Storar

Key Words: bandgap, dopant, Laboratory Directed Research and Development (LDRD), National Ignition Facility (NIF), optically addressable light valve (OALV), ultrawide bandgap (UWBG), wide bandgap (WBG).

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BENEATH THE SURFACE

HISTORICALLY, few field-ready methods have existed for detecting landmines or explosives that lay concealed underground, leaving military personnel to face potentially treacherous terrain. Today, Multistatic Imaging Radar (MiRadar), a ground-penetrating radar (GPR) technology developed at Lawrence Livermore, can search large areas for buried threats before military personnel are deployed. Designed for the U.S. military, MiRadar promises to significantly impact defense, transportation, emergency response, and mine clearance efforts, leading to a paradigm shift in the way subsurface and buried explosives are found.

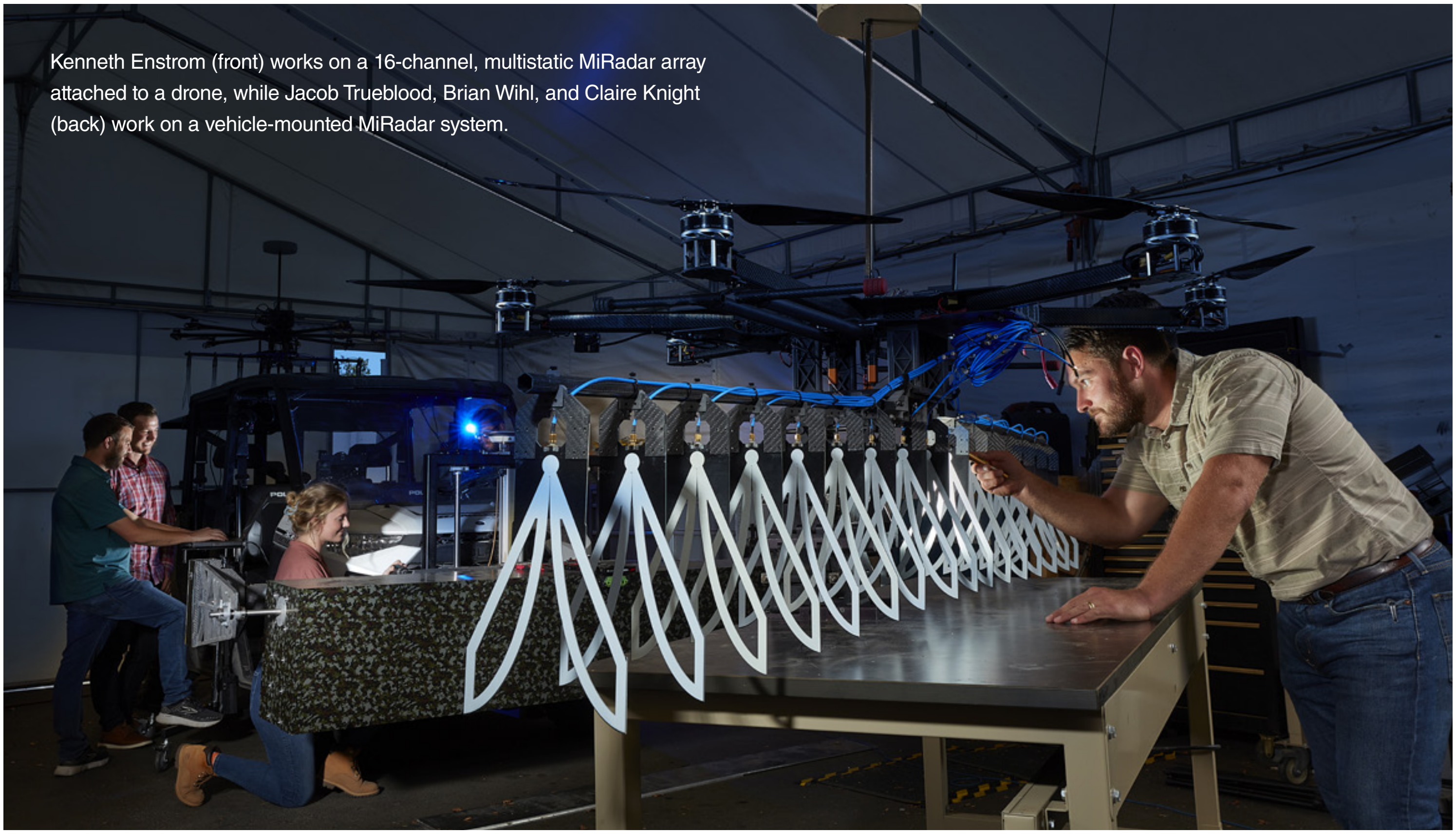
During operation, the MiRadar system transmits instantaneous wideband radio waves to penetrate substrates such as sand, soil, and concrete and then processes returned waves to detect buried objects and potential dangers in real time using 3D imaging. Lawrence Livermore's Defense Systems program leader Reg Beer says, "When we first started developing MiRadar, an American soldier using vehicle-mounted GPR had to hope that a sensor didn't trigger the very explosives that the GPR was trying to detect. We have since redesigned this technology and downsized it to fit on a small drone, helping to identify hazards ahead of time and keeping civilians and military personnel safe."

Building On the Past

MiRadar follows the theoretical principles used earlier in GPR technologies, such as micropower impulse radar (MIR), a patented Lawrence Livermore invention developed in 1993. The Federal Highway Administration applied MIR to bridge inspection in the 1990s. At that time, the technology used a two-dimensional array to collect data for subsequent processing, resulting in 2D images that required significant post-processing and made real-time results impossible.

Today, MiRadar uses a linear, one-dimensional array of transceiver antennas, aiding in faster and safer explosive detection. MiRadar combines advanced imaging techniques such as multistatic radar imaging to enable any combination of antennas to act as receivers or transmitters. In recent years, the team has extended MiRadar's array from 8 to 16 transceiver channels. Mechanical engineering generalist Kenneth Enstrom explains, "The 8 channel was a fixed design, but actuating the array made it possible to incorporate 16 channels. This way, when the drone is grounded the arrays collapse under it, and when the drone takes off, the arrays expand and swing out like butterfly wings."

As the transceiver antennas work together searching for buried threats, they rapidly emit wideband impulses that radiate and



Kenneth Enstrom (front) works on a 16-channel, multistatic MiRadar array attached to a drone, while Jacob Trueblood, Brian Wihl, and Claire Knight (back) work on a vehicle-mounted MiRadar system.

penetrate the ground. The antennas in receive mode then feed their returns, or findings, into reconstruction algorithms that apply machine-learning technology to the data to convert and interpret the raw data into high-resolution, 3D images of the subsurface area. Instead of producing raw data that require expert interpretation, as MIR did, MiRadar produces a colored image with spatial shape—displaying everything in its respective place, in real time. For this reason, MiRadar requires minimal user training as it automatically reconstructs acquired data into easy-to-interpret images.

The resulting images are similar to medical computerized tomography scans and ultrasound images used to generate a planar image of the body's interior. MiRadar project lead Brian Wihl explains, "We have taken an imaging approach, transforming raw data into real-time, easy-to-read 3D images that allow for automated detection of buried hazards with minimal false alarms or reports." The team's approach has aided in MiRadar's ability to quickly deploy and locate buried hazards, making it the first camera-style system to provide a 3D projection of underground objects—reporting their size, depth, and in some cases material composition.

From Design to Prototype

In addition to improving the imaging capabilities, MiRadar has been significantly reduced in size, weight, and power, enabling operation on compact drones. MiRadar currently weighs in at less than two kilograms, nearly 100 times less than earlier array systems. The process of shrinking GPR technology is comparable to that of cameras and cell phones—which have been made smaller over the years by combining functionality into ever more integrated packages—until the required components fit into a space small enough to, in this case, be attached to a small, uncrewed aircraft system.

Warfighters who have tested MiRadar firsthand report that it is an intuitive and powerful tool for military route clearance as well as humanitarian efforts underway to detect hidden or long-forgotten landmines and explosives in war-torn areas.

Prior to being redesigned, the original, vehicle-mounted MiRadar had to be manually moved up and down, allowing the system to be close to the ground during operation. The team automated this process so that MiRadar can move with the click of a button. Machine learning also plays a large role, taking in real-time information and automatically adjusting the drone's flight path without delay or the need for a human operator. Another part of the redesign included testing and integrating a new GPS solution into the system to more accurately track the radar's and other sensors' proximity to the ground. "One of the questions we had to answer was, 'How will we integrate the different sensors and tell each of them where they are and how far they are from the GPS?'" says electrical engineer Jacob Trueblood. "Ultimately, this work is about solving problems and building something that has never been done before."

The MiRadar team has been dedicated to building the whole system from scratch at Livermore, from the radar to the individual drone components, such as the propellers, to the imaging software code. The Laboratory's 3D printing capabilities and on-site machine shops have helped streamline

An eight-channel multistatic array MiRadar system mounted on a drone flies ahead of a traditional vehicle-mounted ground penetrating radar at Livermore's outdoor testing field.

the manufacturing process and rapidly prototype and test new designs. To date, the team has developed and tested a hybrid-electric drone that can run on battery power and gasoline, and they have confirmed the possibility to create a fully 3D-printed platform with the same flight time and payload capability as more costly off-the-shelf components.

"What makes this project unique is our ability to design, print, and test a part in the same day, make modifications, and repeat as needed," says mechanical engineer Claire Knight. "Everything must be designed with 'lightweight' in mind—finding a happy medium between making components robust but still light enough for a drone to carry."

Testing Makes Perfect

When evaluating new designs, the team uses Livermore's Robotics Integration Laboratory, an outdoor, 743-square-meter enclosure that serves as a testing field for autonomous drones, vehicles, and robots. "Teamwork is a huge part of this project," says Knight. "Having the opportunity to bring our cross-disciplinary team together on test days and interact with users is really important and motivating and makes the work we are doing more tangible."

A big piece of this project is doing field work and interacting with military personnel, who are the end-users of this technology, gaining their user insights and perspectives. In fact, warfighters who have tested MiRadar firsthand report that it is an intuitive and powerful tool for military route clearance as well as humanitarian efforts currently underway to detect hidden or long-forgotten landmines and explosives in war-torn areas.

Wihl says, "Most of our field-testing requests come from military bases and other government agencies. We see an amazing number of use cases and scenarios from beaches to deserts, flat to hilly terrain, and dry to humid conditions." Beer adds, "Testing in different regions shows us what works and what doesn't. This process is especially important since GPR radiates waves through the soil, and dielectric properties vary around the world."

Such a technology offers opportunities for commercial use in applications to understand subsurface structures, locate conduits and gas lines under concrete, and assist construction companies in mapping areas before digging, preventing workers from hitting buried pipelines or other objects. In some cases, multiple MiRadar systems can run at once to find objects even faster. "We try to consider every request to use MiRadar," says Beer. "Every test and every new application help us fine tune and assess the performance of this system."

Shelby Conn

Key Words: 3D imaging, drone, ground-penetrating radar (GPR), machine learning, micropower impulse radar (MIR), Multistatic Imaging Radar (MiRadar).

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BIG POTENTIAL with Small-Scale Carbon Capture

METRICS and certifications such as "organic," "sustainable," or "sustainability in practice" are key business drivers in the winemaking industry. To achieve sustainable, carbon neutral practices and reduce the industry's carbon footprint, some winemakers have considered renewable energy, such as solar and wind for their operations, along with organic agriculture and bioenergy production from solid wastes. However, for California wineries, the fermentation process alone generates between 400,000 and 450,000 tons of carbon dioxide (CO_2) per year. Methods for significantly reducing CO_2 emissions—a byproduct of microbial fermentation of the sugars in wine grapes—has been an area of great interest to the wine industry.

At Lawrence Livermore, researchers test, prove, and mature CO_2 emissions reduction and management technologies, honing a core capability to address climate challenges and their impacts on the nation's energy security. (See *S&TR*, January/February 2022, pp. 4–11.) When Continuum, a winery in California's Napa Valley, contacted the Laboratory in 2020 to discuss sustainable winemaking efforts, Livermore scientists recognized an opportunity of particular interest. The CO_2 emitted was biogenic—a byproduct of microbial fermentation of the carbohydrates in wine grapes—and thus neutral emissions from a carbon cycle perspective. Therefore, capture and sequestration of this CO_2 would be considered carbon dioxide removal, a way to draw down the amount of CO_2

in the atmosphere. In response, staff scientist Nathan Ellebracht and his team applied advanced manufacturing and industrial chemistry expertise to devise a technology that captures CO_2 from fermentation at the source and then safely and reliably sequesters the carbon from being released back into the atmosphere. This effort has opened a pathway for winemakers and other industries on a similar scale to achieve notable carbon emission reductions.

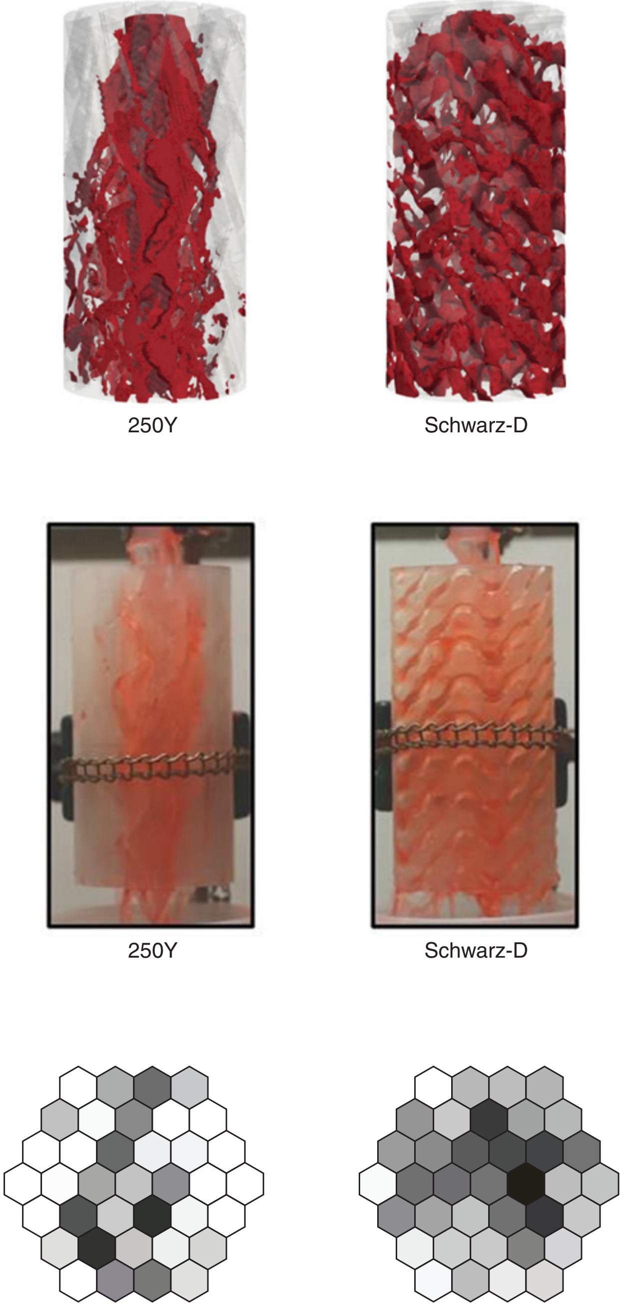
Point Source Carbon Capture

On an industrial scale, point source capture of CO_2 typically involves dissolving the gas into a liquid solvent inside an absorber—a massive cylindrical tower that enables the contact of CO_2 gas and the solvent. For the CO_2 and the liquid solvent to make effective contact in the tower, the liquid travels through a convoluted structure (called "packing") with a high surface area that increases the mass transfer efficiency of CO_2 gas into the solvent. Current packing materials—stacked sheets with a wavy surface similar in appearance to corrugated metal—have not changed much in the last several decades, leading to stalled improvements to the process.

Ellebracht and the Livermore team selected packing materials by simulating ideal flow and maldistribution—a measure of how unevenly flow is distributed across a horizontal cross-section of packing—and then verifying findings experimentally. The team—led initially by Josh Stolaroff and later by Du Nguyen—3D-printed selected geometries with tortuous bends and curves called triply periodic minimal surfaces (TPMS). These geometries were fabricated with the same physical surface area per volume as comparable conventional packing (250 square meters per cubic meter), but the improved geometry significantly increased CO_2 capture via mass transfer, one of the key metrics to determine packing structure effectiveness.

"With normal packing structures in which the liquid is perfectly spread out, we expect to see less than 250 square meters of liquid film because the liquid cannot touch every single centimeter of the packing," says Ellebracht. "With TPMS geometries, the effective area was larger than the geometric area. The liquid and gas were mixing so well, the effect was as if the structure had a much larger surface area." Unlike many absorber towers, which have dedicated sections to redistribute the solvent to improve CO_2 gas capture efficiency, the TPMS geometries also handle redistribution. For some packing configurations, mass transfer increased 50 to 60 percent, reducing the absorber space required and leading to absorber cost savings of more than 30 percent.

Also encouraging to the team was the lack of trade-offs observed for two aspects of fluid mechanics: pressure drop and flooding in the absorber tower. Pressure drop is the force needed to push gas through a column of liquid. Smaller channels in the packing provide a higher surface area but require more force.



250Y Schwarz-D

250Y Schwarz-D

250Y Schwarz-D

Results of simulated flow (top row) and experimentation (second row) for different packing materials such as industry-standard 250Y packing (left column) and Schwarz-D (right column) packing enabled the Livermore team to identify a packing material that maximizes solvent contact with CO_2 effluent gas in the absorber tower. The bottom images demonstrate how the packing materials can redistribute liquid introduced in a small area at the top of 15-centimeter packing sections.

Flooding results when too much liquid and gas flow through the tower and mix so vigorously that they foam over, similar to a covered pot of boiling water. The point of flooding determines the required height and width of the absorber tower. As pressure drop and tower size increase, so do the costs to build and operate the towers, as energy is required to push the gas through the column and overcome pressure drop.

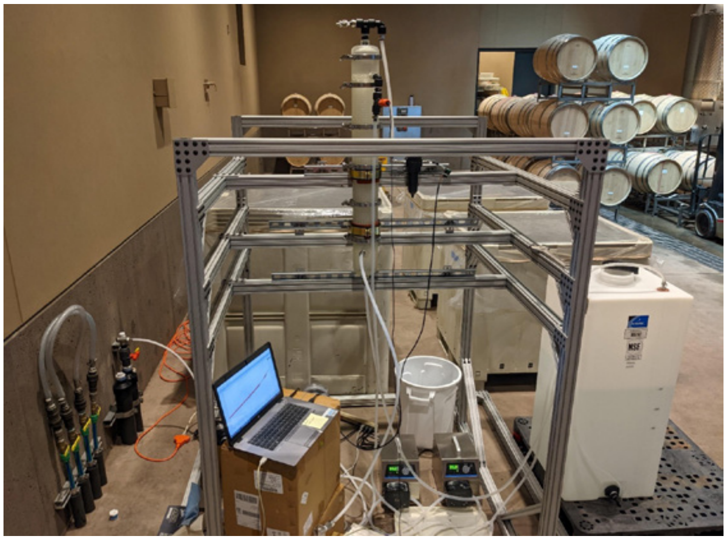
Two-phase flow pressure drop and flooding are challenging to elucidate through modeling, so Ellebracht and his team tested and identified two-phase flow pressure drop through experiments using differential pressure transducers and a custom-built apparatus to measure flooding. Ellebracht says, "We expected the better interaction between gas and liquid to lower the point of flooding as packings with improved surface geometries often experience more rapid flooding and higher pressure drops. Surprisingly, we saw no such trade-offs in our design, which is a good sign for its efficiency and cost-savings potential."

Mineralizing Carbon Dioxide

Although several liquid solvents can capture CO_2 in larger industrial applications, many do not scale down well for smaller industries. Typical solvents often require large, integrated systems to continuously heat the solvent in a parallel process to strip off and store the CO_2 as a purified gas and recycle the solvent to capture more CO_2. Alkaline caustic solvents such as potassium hydroxide may avoid the use of a heating unit to remove CO_2 as a gas. This strongly basic aqueous solution dissolves CO_2 as carbonate and bicarbonate, similar to the way CO_2 moves in and out of oceans and other natural systems. Harnessing this approach allowed Ellebracht and his team to sequester CO_2 through a process that mimics Earth's natural carbon cycle: mineralization.

In the mineralization process, the carbonate solution is mixed with another chemical solution that spontaneously converts CO_2 from the carbonate form to a solid form. Lime (calcium oxide) is commonly used to react with carbonates to form limestone. However, Ellebracht and his team wanted to find more effective and efficient options, as the production of lime releases a large amount of CO_2, negating the CO_2 being captured and sequestered.

Working with staff scientist Corey Myers, the team identified magnesium as a promising alternative. Magnesium chloride ($MgCl_2$), a low-value material and byproduct of desalination, was used as the cation source to turn the dissolved CO_2 into a mineral slurry. The team conducted experiments at different temperatures, reagent ratios, and additional conditions to determine how to sequester the most dissolved carbonate from the solution while using as little magnesium as possible. After many trials, mixing the $MgCl_2$ and carbonate at room temperature produced a mineral, nesquehonite, with the optimal one-to-one magnesium-to-carbonate ratio at high yields. By pumping and stirring the $MgCl_2$ solution into the carbonate solution, the contents changed to an opaque, milky solution. When the chemical reaction was complete, the team was left with salty water and a magnesium carbonate that had successfully sequestered the CO_2. Following a simple filtration process, the nesquehonite was isolated.



CO_2 off-gas from tanks of fermenting wine at Continuum, a Napa Valley winery, travels through plastic tubing and into the bottom of Livermore's absorber tower (center). Liquid solvent from the square container (right foreground) flows through the absorber packing.

Nesquehonite, a magnesium carbonate mineral containing the sequestered CO_2, is produced by mixing the saturated solvent with a magnesium chloride solution. Squeezing excess water from the nesquehonite results in a powdery substance safely containing the captured CO_2.

From Laboratory Setting to Winery Fermentation

In 2021, after demonstrating carbon capture methods at Livermore, the team set out to test them at Continuum. While there, Ellebracht and his team assessed Continuum's fermenters to determine total CO_2 production and release rates. With this information, the team then returned to the Laboratory to build the absorber and packings, test their carbon capture and mineralization process, and prepare to incorporate their setup at the winery during the 2022 fermentation season.

Unlike beer brewing, which uses dry grains and ferments year-round, wine fermentation takes place during a narrow window of a few weeks after each annual harvest. Timing was not anticipated to be a challenge for the Livermore team until a multiday heat wave across California in 2022 accelerated Continuum's picking and fermentation schedule. As a result, Ellebracht and colleagues set up their equipment sooner than initially planned.

Ellebracht and his team connected the absorber tower to off-gas from the fermentation tanks so CO_2 could be captured by the solvent as it flowed through the packing structure. Once the CO_2 was captured, the team deployed the mineralization process they had developed in a laboratory at the winery. "Continuum was extremely generous with its time, space, and equipment," says Ellebracht. Many of the tools used in winemaking also have utility in Livermore's carbon capture and sequestration efforts, including filters that could be repurposed for drying the magnesium carbonate holding the sequestered CO_2. In addition to scientific research, the project involved a fair bit of manual labor. Large-scale facilities typically have machinery that automates the filtering and drying process. For Ellebracht's smaller scale setup, he and the team had to do everything manually. Ellebracht says, "I spent a lot of time shoveling the mineral product into the filter and then using the shovel to press the water out."

Tackling CO_2 emissions at wineries offers opportunities for real environmental improvements with negligible impact on the cost of the product. With approximately 0.11 kilograms of CO_2 emissions produced through fermentation, per wine bottle, and a carbon capture cost between \$100 and \$1,000 per ton of CO_2 emissions, early cost estimates by Ellebracht's team indicate that implementing point source carbon capture technology such as Livermore's would add only \$0.01–\$0.11 in production costs per bottle.

Ellebracht's research and methods for carbon sequestration show great promise for reducing CO_2 emissions within smaller scale settings, but plenty of opportunity exists for growing the technological applications. Following their successful proof-of-concept testing at Continuum Winery, the team seeks to test their packing structures at the National Carbon Capture Center (NCCC) in Alabama. NCCC accesses the flue gas from a nearby power plant, which would allow the Livermore team to test their design with a CO_2 point source at a much larger scale. The unit tested at NCCC will measure about 0.3-meter (m) wide and just over 4.5-m tall, compared to the technology tested at Livermore and Continuum, which was 0.1-m in diameter and 0.6-m tall.

Team members (left to wright) Du Nguyen, Melinda Jue, and Nathan Ellebracht analyze absorber operation data in the lab.

"The NCCC work is the next logical step after the winery project," says Ellebracht. "Testing and proving our technology at this increased scale will be a significant technical validation of our packing technology." With that endorsement, Ellebracht's technology could assist other industrial CO_2 capture applications in agriculture, fertilizer development, power generation, and manufacturing, opening more doors for innovative and effective methods for promoting sustainable operations and combatting climate impacts.

— Sheridan Hyland

Key Words: absorber, carbonate, carbon dioxide removal, nesquehonite, packing, point source carbon capture, Triply Periodic Minimal Surface (TPMS).

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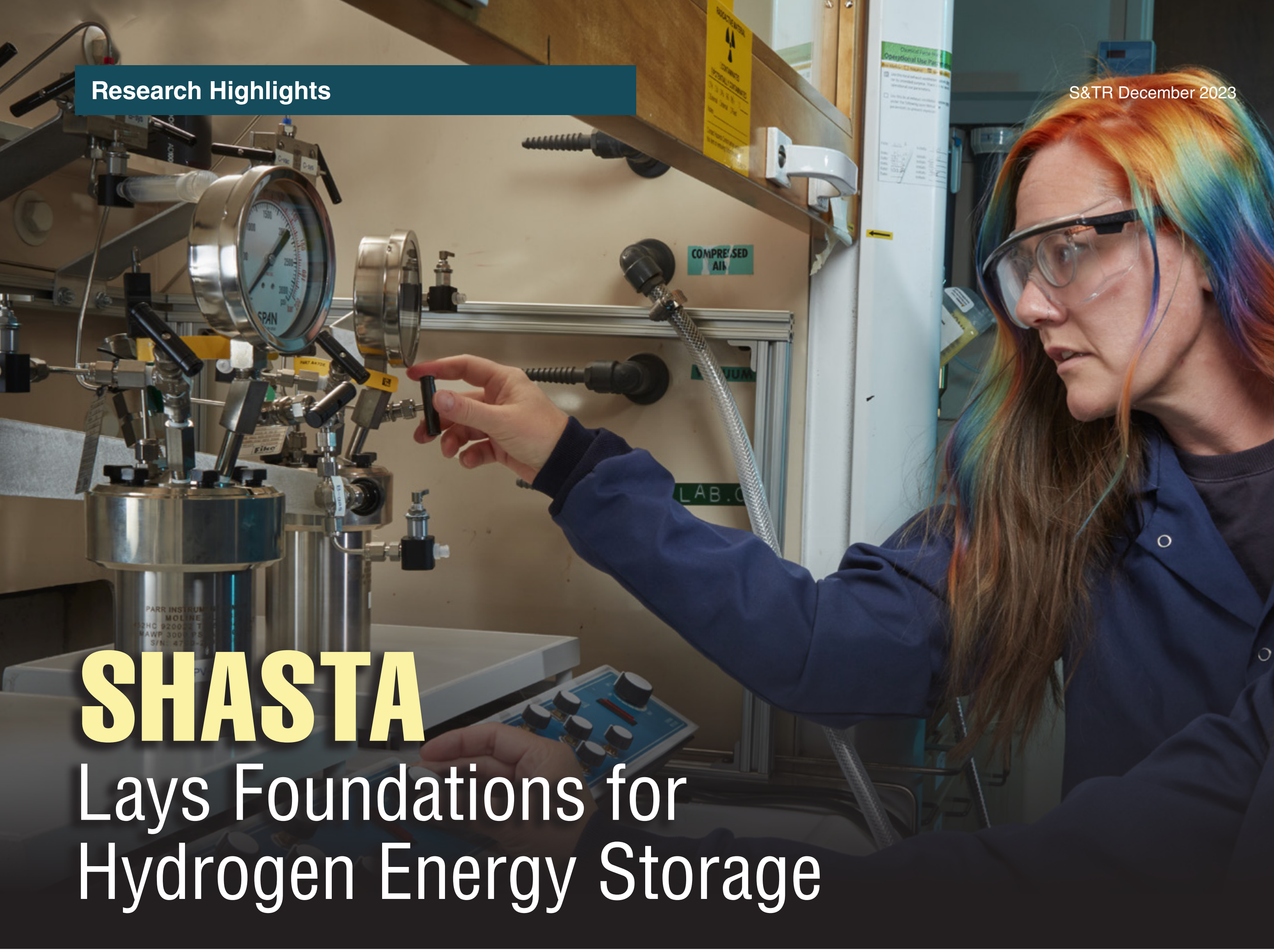


SHASTA Lays Foundations for Hydrogen Energy Storage

THE universe's lightest molecule may have massive implications for the nation's climate and energy security. Abundant and non-polluting, hydrogen gas could help meet growing domestic energy demand while spurring a low-carbon economy and reinforcing energy reliability, diversification, and independence. When renewable energy sources such as wind and solar generate more supply than demand requires, the surplus, stored as chemical energy in hydrogen, could ensure a retrievable electricity source decoupled from fluctuations in energy production and seasonal shifts in utilization.

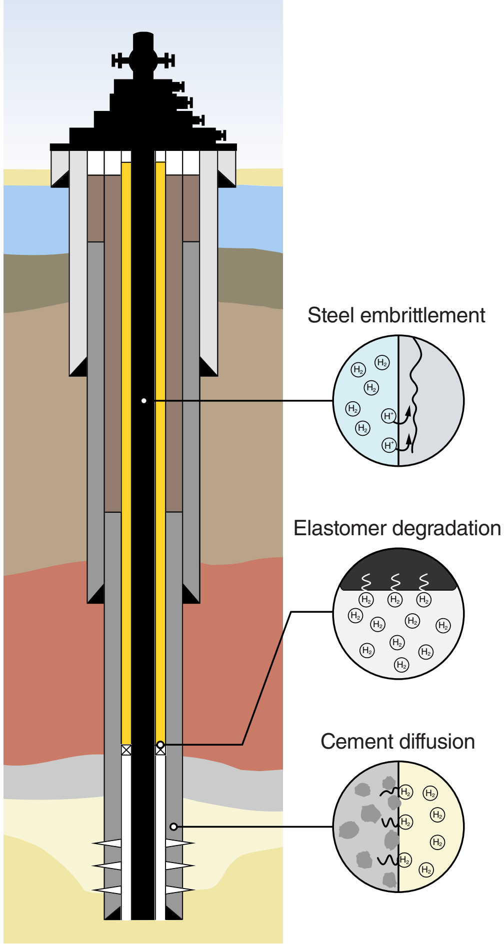
Adopting emerging technologies is easier said than done. Questions remain before hydrogen storage can be widely integrated with the energy grid. To tackle knowledge gaps, the Department of Energy (DOE) Office of Fossil Energy and Carbon Management launched the Subsurface Hydrogen Assessment, Storage, and Technology Acceleration (SHASTA) project in 2021. Carried out jointly by Lawrence Livermore, Sandia, and Pacific Northwest national laboratories and the National Energy Technology Laboratory, SHASTA addresses the intricacies of maintaining hydrogen fuel reserves.

Chemical Potential

Joshua White, deputy division leader for Science & Technology in the Atmospheric, Earth, and Energy Division and Livermore's technical lead for SHASTA, explains the growing interest in hydrogen energy: "The difficulty with electricity generation is that you must either use the energy immediately or store it. Typically, the term 'energy storage' brings to mind batteries in phones or electric vehicles that are drained and recharged daily. Hydrogen, by contrast, is meant to address industrial-scale energy storage on the order of months or years." Extensive research efforts underway address production, transport, and use of hydrogen fuel. SHASTA targets the foundation. "A crucial challenge is reliably storing hydrogen at scale in the first place," says White.

For solutions, researchers are digging deep. Naturally occurring, underground reservoirs make attractive locations thanks to their enormous volume and intrinsic layers of security. These vast subterranean voids could safeguard nearly 10 million metric tons of storage of pure hydrogen—an energy potential of more than 300 terawatt-hours. Depleted hydrocarbon fields are particularly promising candidates. These fields are abundant and

Researchers Megan Smith (left) and Maria Gabriela Davila-Ordonez (right) demonstrate the new experimental setup for testing the response of geologic and well infrastructure materials to heightened hydrogen concentration. Stainless steel vessels hold material coupons at representative pressure and temperature conditions for up to one month, and periodic fluid samples complement post-assay inspection to determine chemical or physical changes.



Injecting hydrogen into Earth's subsurface requires drilling a wellbore. Many reservoirs contain existing well infrastructure, but the full impact of hydrogen on the integrity of construction materials such as steel, elastomers, and cement still needs to be determined.

capable of holding fluid mixtures, as evidenced by existing well infrastructure from earlier oil and natural gas extraction. Other contenders such as salt caverns and saline aquifers offer unique advantages and challenges.

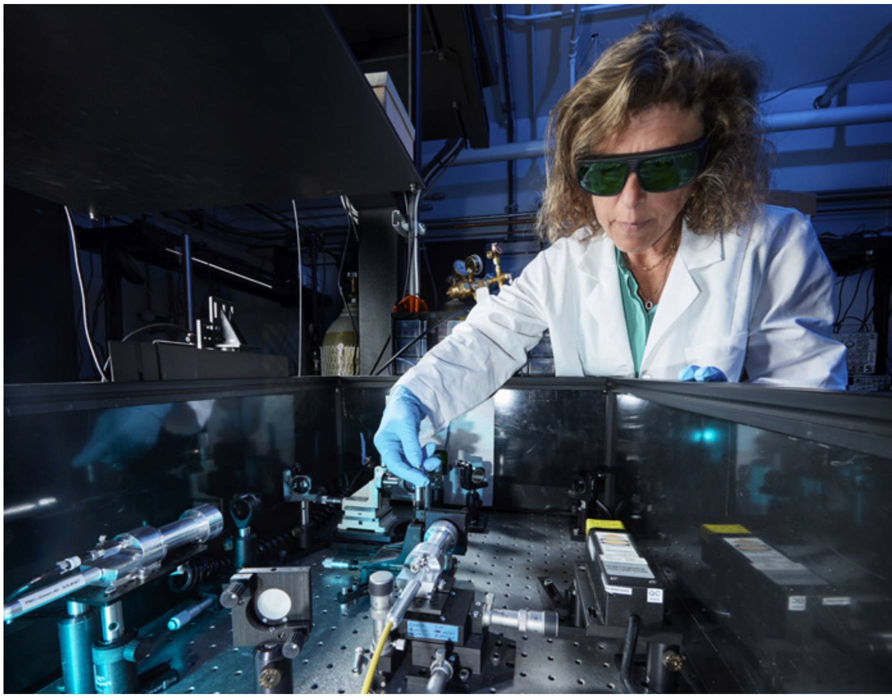
What remains unresolved is how best to maximize the safety and cost-effectiveness of underground hydrogen storage (UHS). In 2022, the program's State of Knowledge report detailed new findings and outstanding questions—notably, the numerous physical, chemical, and even biological interactions that could result from introducing hydrogen into reservoirs, possibly impacting storage efficiency and well integrity. Moreover, no two reservoirs are identical, nor are they distributed evenly across the continental United States, meaning SHASTA must address both scientific and technoeconomic aspects of UHS.

The Pressure Is On

Residing kilometers below Earth's surface, candidate reservoirs cannot be observed directly. Determining suitability for UHS demands scientific methods to recreate subterranean environments in the laboratory. Of primary concern is assessing the capability of caprock, the geologic layer that overlays reservoirs, to maintain a seal on hydrogen. Diatomic hydrogen is the smallest molecule in existence, capable of diffusing through materials that would contain any other gaseous substance; moreover, it is highly combustible. Even if a site's caprock proves impermeable, the injected hydrogen (usually mixed with natural gas and cushion gas) could meet water, brine, or other deposits, spurring a host of geochemical reactions whose implications are not fully understood.

"UHS is a bit like the Wild West at the moment, and we don't know which potential reactions will play an important role in determining overall viability of UHS," says staff scientist Megan Smith. "Where does the hydrogen go once we've injected it into the reservoir? Does it diffuse into fine formations, like clay-rich shales? Does it react with salt formations and corrode the steel of the well-line, causing embrittlement? How does the fluid behave when we back off of the injection pressure? So many questions need answering."

Smith's team is investigating how hydrogen-rich environments affect the integrity and compatibility of natural and artificial materials in reservoirs. Using instruments purpose-built at Livermore, her team exposes geologic samples (caprock, shale, sandstone, and salt cavern deposits) and construction materials (steel and cement) obtained from project sites to different concentrations of hydrogen and reservoir brine while replicating the elevated pressures and temperatures typical of depleted gas fields: 100–170 atmospheres and 50–80°C, respectively. Thin, coupon-shaped samples are inserted into a brine- and hydrogen-filled reaction vessel that heats and pressurizes the contents while liquid and gas samples are periodically siphoned off for analysis. Smith says, "Several reactions might occur. For instance, if water evaporates, the brine's salt content will increase. If hydrogen diffuses into the brine, we will detect specific chemical analytes released from the samples as well as concentration changes to its gas phase."



Optic engineer Tiziana Bond tests fiber-optic sensors that will detect temperature, pressure, and chemical signals to constantly monitor subsurface infrastructure.

After one month, samples are removed and examined using x-ray diffraction and electron microscopy. "Quantifying surface effects gives us insight into the permeability and microporous storage of each material," says experimental scientist Maria Gabriela Davila-Ordonez. "We can relate the ion concentrations measured in fluid samples to observed changes in porous structure and mineral formation. These measurements are key to determining which materials are ideal for UHS." The team also stresses the significance of constructing the experimental facility itself. "Typically, we would use titanium vessels, but hydrogen is a different beast, mainly because of its flammability," says Smith. Stainless steel, instead, is less reactive with hydrogen. "Putting together the necessary instrumentation required many consultations with safety engineers and countless inspections to safely work with hydrogen in the laboratory," recalls Davila-Ordonez.

From Simulation to Implementation

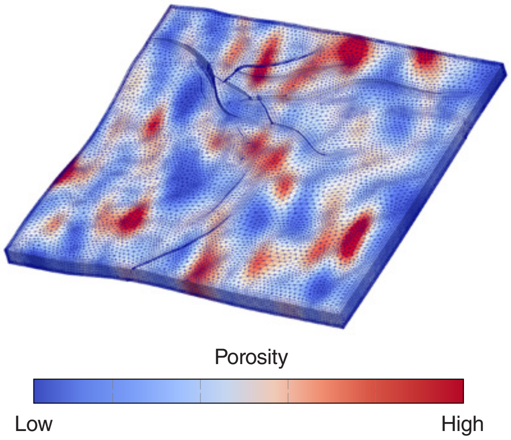
Understanding how hydrogen disperses and potentially reacts inside a reservoir is not possible without sophisticated modeling and simulation. UHS risk quantification unites benchwork and computational methods. Powering much of the digital work is GEOS, an open-source reservoir simulator developed at Livermore to understand fluid and mechanical flow of matter in Earth's subsurface. "Other commercial simulators are designed to model the movement of oil, natural gas, and carbon dioxide specifically. Hydrogen has different molecular properties and equations of state," says White. GEOS accounts for molecular differences that have pronounced macroscale effects on the movement of material mixtures. "Water, hydrogen, methane, and possibly other substances are distributed throughout the reservoir at different pressures, temperatures, and concentrations. We use compositional simulation to predict the state of each species at each timestep following hydrogen injection. Then, the 'flow step' predicts movement into neighboring cells." Crunching the numbers, researchers can identify ideal volume and timing of hydrogen injection to maximize energy storage potential at specific sites.

Beyond theoretical feasibility, SHASTA investigates practical factors for real-life implementation of UHS. For instance, ensuring the safe deployment and operation of UHS sites will demand reliable monitoring tools. Optic engineer Tiziana Bond is developing distributed fiber-optic sensors that function as the infrastructure's nervous system, detecting temperature, pressure, and chemical signals. Separated by kilometers of earth, operators must be able to detect transmission of a minuscule, transparent, odorless gas whose dispersal could cause energy resource loss and corrosion of the wellbore. "When used with imprinted gratings, fiber-optic sensors continuously emit and back-reflect specific wavelengths of light. If there were a fracture, then those vibrations will shift the associated wavelengths," says Bond. Knowing the length of the optical fiber and a signal's time of flight pinpoints anomalies in space, giving enhanced monitoring capabilities to well-drilling projects for carbon capture and sequestration.

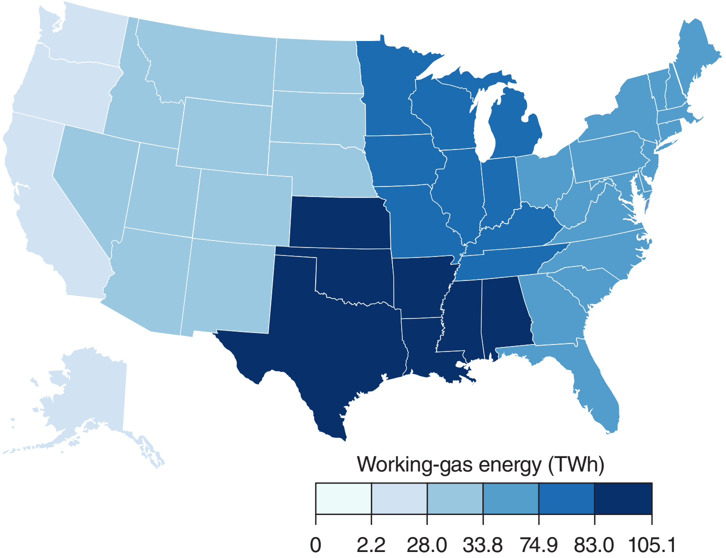
Fibers can also be used to perform chemical fingerprinting. Percolating through hollow fibers, different molecules produce unique Raman signals when intercepted by light, allowing differentiation between hydrogen, methane, and other gases. However, challenges remain. "We need to develop armor for the hollow fibers so they remain resilient during monitoring. These fibers then need to be spliced with the solid-core optical fiber." Cost is another factor, according to Bond. Lowering fiber production cost is critical because UHS sites would need kilometers upon kilometers of it to thoroughly monitor the subsurface.

The need for affordable materials underscores SHASTA's final focus: practicality and cost-effectiveness of UHS. The project's technoeconomic considerations include classifying the readiness and availability of associated technologies as well as determining the scenarios under which business would be most eager to take part in UHS projects. White explains, "We need to assess the volume and location of storage potential but also the costs associated with facility construction, material transport, energy conversion, etc., to establish a business case. As we consider deploying hydrogen technology in new areas, SHASTA will show whether our expectations are in the right ballpark."

The project's technoeconomic analysis involves classifying the readiness and availability of associated technologies as well as strategizing UHS project strategies that would most interest private businesses. In fact, UHS has already demonstrated commercial viability in salt caverns. Further study is underway to expand storage locations. Researchers must account for a spectrum of approaches to harnessing hydrogen that differ in targeted sources, methods of production or extraction, carbon intensity, and byproducts. As improved technologies and new experimental results continue to emerge, Livermore and its research partners regularly share data, inform stakeholders of revised scientific understanding, and recommend best practices for leveraging existing infrastructure.



GEOS software is a versatile tool for understanding underground fluid flow and stresses on well infrastructure. Structural permeability data, depicted here, is one input factor GEOS uses to simulate hydrogen dynamics in reservoirs as in this 2.4-kilometers-square, 300-meter-deep section.



If filled with hydrogen gas, existing underground resources such as depleted oil and gas reservoirs, saline aquifers, and salt caverns distributed throughout the United States could store more than 300 terawatt-hours (TWh) of energy, enough energy to light millions of homes for a year. The shades of blue represent regional energy storage capacity expressed as the working-gas energy in TWh that could be made available.

DOE aims to deploy pilot projects as soon as possible to evaluate injection, monitoring, and retrieval of hydrogen at scale in a hydrocarbon reservoir, but breaking ground first requires industry buy-in and approval from both regulators and the American public. "Going forward, we will articulate the safety and benefits of hydrogen technology to the public, yet we must also sincerely listen to and consider the sentiments of people who live where these projects might take place," says White. At the intersection of Livermore's climate and energy security missions, SHASTA's multifaceted approach to realizing UHS is vital to understanding the possibilities and challenges associated with clean energy transition.

— Elliot Jaffe

Key Words: corrosion; fiber optics; GEOS; hydrogen; material compatibility; renewable energy; reservoir; Subsurface Hydrogen Assessment, Storage, and Technology Acceleration project (SHASTA); technoeconomics; underground hydrogen storage (UHS); wellbore.

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Patents and Awards

In this section, we list recent patents issued to and awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory. For the full text of a patent, enter the seven- or eight-digit number in the search box at the U.S. Patent and Trademark Office's website (uspto.gov).

Patents

Electric Field Driven Assembly of Ordered Nanocrystal Superlattices
Yixuan Yu, Joshua D. Kuntz, Christine A. Orme, Andrew J. Pascall
U.S. Patent 11,499,248 B2
November 15, 2022

Multifaceted Radiation Detection and Classification System
Simon E. Labov, Karl E. Nelson, Brandon S. Seilhan
U.S. Patent 11,513,253 B2
November 29, 2022

Component-Wise Reduced-Order Model Design Optimization such as for Lattice Design Optimization
Youngsoo Choi, Sean Laughlin Mcbane
U.S. Patent 11,514,210 B2
November 29, 2022

Wide Bandgap Optical Switch Circuit Breaker
Lars F. Voss, Adam M. Conway
U.S. Patent 11,522,542 B2
December 6, 2022

Laser Pulse Shaping for Additive Manufacturing
James A. DeMuth, Andrew J. Bayramian, Eric B. Duoss, Joshua D. Kuntz, Christopher M. Spadaccini
U.S. Patent 11,524,458 B2
December 13, 2022

System and Method for Ablation Assisted Nanostructure Formation for Graded Index Surfaces for Optics
Jae Hyuck Yoo, Eyal Feigenbaum
U.S. Patent 11,525,945 B2
December 13, 2022

Systems and Methods for a Supra-Fusion Graph Attention Model for Multi-Layered Embedding and Deep Learning Applications
Uday Shanthamallu, Jayaraman Thiagarajan, Andreas Spanias, Huan Song
U.S. Patent 11,526,765 B2
December 13, 2022

Post Polymerization Cure Shape Memory Polymers
Thomas S. Wilson, Michael Keith Hearon, Jane P. Bearinger
U.S. Patent 11,530,291 B2
December 20, 2022

System and Method for High Power Diode Based Additive Manufacturing
Bassem S. El-Dasher, Andrew Bayramian, James A. Demuth, Joseph C. Farmer, Sharon G. Torres
U.S. Patent 11,534,865 B2
December 27, 2022

Large Scale Synthesis of Resorcinol-Formaldehyde Aerogel
Colin Loeb, Patrick Campbell, Jennifer Marie Knipe, Michael Stadermann
U.S. Patent 11,535,521 B2
December 27, 2022

Awards

Lawrence Livermore director **Kim Budil** was featured on the **"Power 100"** list published by the ***San Francisco Business Times***. 2023 marked the inaugural release of the list, which highlights exceptional business leaders in California's Bay Area. Budil was noted for supporting employees, customers, industries, and communities associated with Lawrence Livermore; propelling the Laboratory's vision for mission-driven science and technology development; and representing the Laboratory to affiliates and governing agencies.

William Evans, the Physics Division leader in Livermore's Physical and Life Sciences Directorate, was selected to serve on the **board of directors** for the **Fannie and John Hertz Foundation**. The foundation accelerates solutions to the world's most pressing challenges, from enhancing national security to improving human health, and it offers the highly competitive Hertz fellowship, which Evans completed earlier in his career. Evans's research into the physical and chemical effects of materials under extreme conditions furthers the organization's interest in solving complex problems of national security.

The American Chemical Society (ACS) selected **Annie Kersting** to a three-year term as **vice chair of the Division of Nuclear Chemistry and Technology,** graduating to program chair by the term's conclusion. Kersting's research focuses on geochemical mechanisms of actinide transport in the environment. At ACS, she will support the arrangement of national meetings and raise researchers' awareness of national laboratory career opportunities.

The publication **HPCWire** named **Terri Quinn** one of its **"People to Watch" in 2023**. Quinn is the Deputy Associate Director for High Performance Computing (HPC) where she oversees programs providing computing services to Livermore scientists. The distinction recognizes HPC professionals who play leading roles in driving innovation within their specialty and make significant contributions to society. Having previously served as a U.S. Navy lieutenant, Quinn's subsequent computing-focused role has spanned several programs with direct national security applications, including preparations for the exascale El Capitan system.

Abstract

Ultrawide Bandgap Materials in the Spotlight

Semiconductor materials are essential components for computing, power distribution, optical, and communication technologies. To improve performance of these technologies, researchers look to ultrawide bandgap (UWBG) semiconductor materials, which can withstand significantly higher power and energies than conventional semiconductor materials. However, unlike silicon, UWBG materials cannot be doped with chemical impurities to achieve the broad conductivity control required for high-power applications. A Lawrence Livermore Laboratory Directed Research and Development (LDRD) project aimed at overcoming key challenges in realizing the potential for UWBG semiconductor materials sought to dope semiconductors with light rather than chemical impurities to optimize the materials for high-power and laser applications. The LDRD team investigated materials and dopant atoms for favorable photoconductive response; synthesized material candidates; and fabricated and tested optically addressable light valves using selected UWBG materials. Immediate results of this research may be applied to retrofit National Ignition Facility systems designed to reduce degradation of optical instruments and enable more energy per laser shot.

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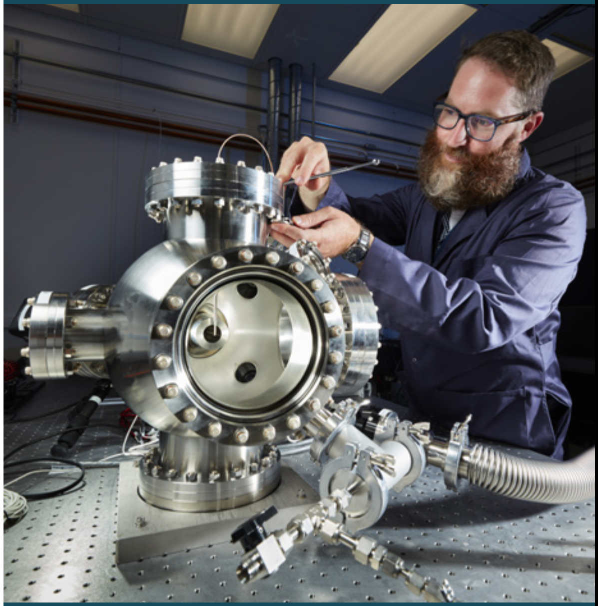
Coming Next Issue

Replicating Hypersonic Conditions



A Lawrence Livermore experimental facility will enable material integrity testing in a hypersonic flight environment to improve material discovery and fabrication plus related computer modeling.

Also in this upcoming issue...

- *Laboratory staff enhance policymaking skills through the Bush School of Government and Public Service's National Security Affairs Program at Texas A&M University.*
- *Upgrades at the Materials Science Division's headquarters building expand research capabilities and opportunities for collaboration.*
- *Research projects funded through the Academic Collaboration Team galvanize university relationships and attract new Laboratory staff.*

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