ADDITIVE MANUFACTURING BRINGS NEW POSSIBILITIES FOR TRANSPARENT CERAMICS

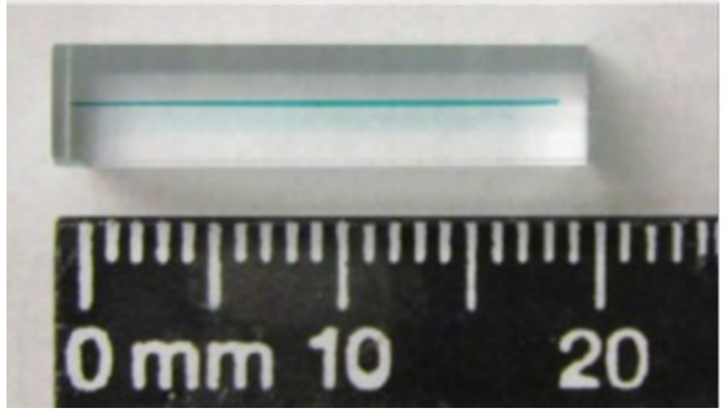
Optician Colby McNamee holds a piece of the R&D 100 Award–winning gadolinium–lutetium–oxide transparent ceramic scintillator, developed at Lawrence Livermore, which converts x rays to visible light seven times more efficiently than glass.

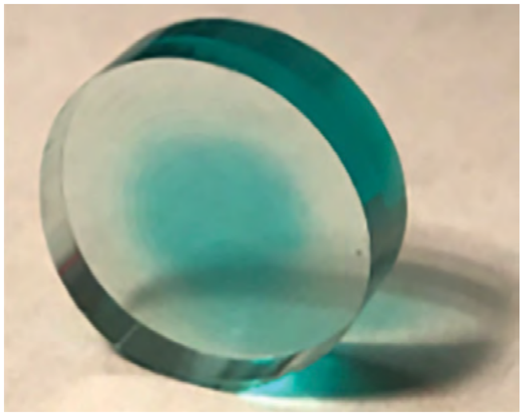
CONSIDER what makes a ceramic mug the perfect container for a morning cup of coffee: the material is durable and resists heat and corrosion. Due to strong interatomic crystalline bonds created when clay, earthen elements, and water are heated to between 1,200 and 1,800°C, a ceramic mug will last a long time—as long as no one drops it. The material also keeps the coffee hot and does not chemically react with it. Transparent ceramics exhibit similar desirable characteristics and are used in streetlamps and bullet-proof windows. Having developed several transparent ceramics for radiation detection applications for the Department of Homeland Security and the Stockpile Stewardship Program, Lawrence Livermore recently leveraged its unique additive manufacturing resources and capabilities to develop transparent ceramics with properties not previously available for use as laser materials.

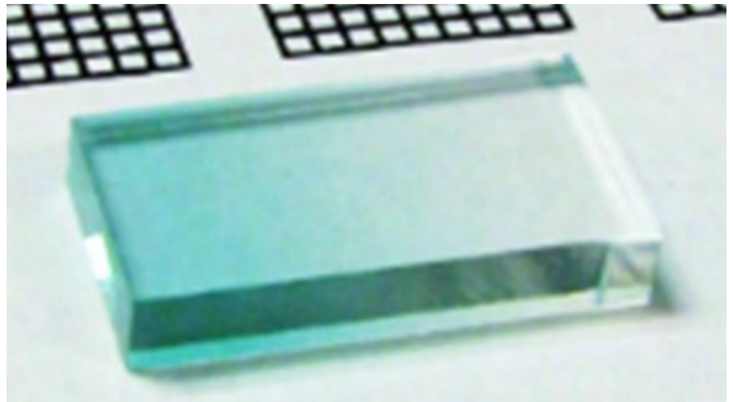
A Manufacturing Challenge

As Livermore researcher Zachary Seeley explains, the key difference between opaque and transparent ceramics is that transparent ceramics lack pores or holes. “In most common ceramics, microscopic pores or secondary structural crystal phases in the final product cause light to scatter, making them opaque,” says Seeley. Transparent ceramics are formed by using extreme heat and pressure to consolidate raw material nanopowder, an inorganic, polycrystalline material, into an initial “green body” of weakly bound material. The green body is then heated in a vacuum or controlled atmosphere to just below the material’s melting point in a process called sintering. To remove any remaining pores, the sintered ceramic is then subjected to very high temperatures and pressures in a process called hot isostatic pressing. The result is a fully dense nonporous ceramic object that is stronger and harder than glass and more resistant to corrosion, heat, or extreme environments than many other materials.

The ability to control the structure, composition, and properties of transparent ceramics makes them ideal for applications that demand a high degree of precision, particularly laser optics. (See *S&TR,* April 2006, pp. 10–17.) The Laboratory’s early work on transparent ceramics that could replace glass in various applications led to several breakthroughs, including a gadolinium–lutetium–oxide (GLO) transparent ceramic scintillator developed by a team led by Nerine Cherepy, which won an R&D 100 Award in 2016. The GLO scintillator converts x rays to visible light more efficiently than glass, allowing advanced computed tomography systems to produce detailed, 3D images of large, complex objects in less time. (See *S&TR*, January 2017, pp. 12–13.) Currently, Ian Phillips and Josh Smith, materials scientists in the Laboratory’s


Planar waveguide


Thin disk


Longitudinal doping gradient

Custom-tailored yttrium-aluminum-garnet, laser-gain media—with ytterbium doping gradients and integral, undoped regions—provide laser-mode control, mitigate thermal nonuniformities, and improve laser system performance.

Materials Science division, are working with vendors to commercialize GLO plates in sizes up to 1,300 square centimeters. Research and development also continues into transparent ceramics for scintillators, which have applications in x- and gamma-ray detection. Cherepy and colleagues are currently developing transparent polycrystalline gadolinium–garnet ceramic scintillators doped with cerium for use in gamma spectroscopy and radiation portal monitors.

Still, challenges remained. Applications of transparent ceramics, particularly in the laser science arena, were limited by residual microstructural defects. "With its exceptional expertise in additive manufacturing, chemistry, and laser science, and its multidisciplinary approach," says Seeley, "the Laboratory was uniquely positioned to tackle this problem." Seeley notes that transparent ceramics offer an advantage over traditional crystalline optics materials—spatially controlled doping with ions that absorb and emit light. Doping entails introducing low concentrations of elements such as chromium, erbium, neodymium, and ytterbium into a ceramic's microstructure to absorb and emit light. While some transparent ceramics employ undoped endcaps or exterior cladding to maintain optical and thermal stability, others require separately doped cores or dopant gradients to improve laser beam propagation. Because doping concentrations must be carefully optimized and executed, additive manufacturing, with its flexibility and precision, presents an innovative method to produce doping gradients. "For most printed ceramics, you're not worried about smooth interfaces to 500-nanometers of precision," says Seeley. "It only comes into play when you're crafting materials to control laser beams that have to be optically perfect with extremely small refractive index fluctuations."

A team of Laboratory researchers, including Seeley, Cherepy, and Stephen Payne, have developed processes that use both direct ink write (DIW) and material jetting to create green bodies that yield transparent ceramics with precisely tailored properties. "Choosing the right process for an application depends on the desired geometry of the end product," says Cherepy. "The DIW process is best for thicker, three-dimensional applications, whereas the jetting process is best for creating structures that require more precise, finer granularity in material deposition." In the DIW additive manufacturing process, the team has worked with colleague Timothy Yee to develop methods to extrude a ceramic slurry in precise configurations, similar to piping frosting onto a cake. Dopants can be introduced into the slurry to produce the desired concentration gradient or to integrate variably doped regions. Material jetting, on the other hand, applies droplets of ceramic slurry to build up thin layers of doped and undoped ceramic. Another technique, composite pressing, can yield three-dimensionally controlled chemical composition. As additive manufacturing advances, the customizable geometry of transparent ceramics offers enhanced mode stability, thermal management, efficiency, and power in laser gain media.

New Challenges, Applications Ahead

Laboratory researchers continue to explore how additive manufacturing can contribute to transparent ceramics in areas as diverse as laser materials, scintillators, and light-emitting diode (LED)-based lighting.

In laser optics, researchers are focusing on the doping challenges involved with laser-gain media—optics used to amplify the power of laser beams. Such optics usually take the shape of rods, slabs, thin disks, or waveguides. When a laser beam travels through the gain medium, its shape and doping profile affects the laser beam's power and geometry. To achieve optimal performance for various applications, different laser systems require different gain media. As additive manufacturing methods improve and evolve, increasingly complex optical structures will be possible, opening doors to novel laser designs. A new Laboratory Directed Research and Development (LDRD) project led by Thomas Rudzik is developing additively manufactured strontium–fluoride ceramics with neodymium-doping gradients for the next generation of laser materials for a futuristic design of a possible successor to the National Ignition Facility.

As LED lighting becomes standard in homes, workplaces, and public spaces, improving the color temperature of the light they emit to more closely match natural sunlight is crucial. LED color temperature is controlled through a thin layer of phosphor, a substance that absorbs the blue LED light, converting it to green and red to produce white light in the fixture. The Laboratory's Ross Osborne recently consolidated the narrow-emitting red phosphor, KSF:Mn ($K_2SiF_6:Mn^{4+}$), into a transparent ceramic for the first time under funding by the Critical Materials Institute, which seeks to develop technologies that avoid using rare-earth elements. The KSF ceramic has an ideal red emission spectrum and offers superior thermal conductivity compared to traditional phosphor powders, allowing efficient warm-white lighting.

A transparent phosphor ceramic KSF: Mn, developed and fabricated at Livermore, emits red light for solid-state, light-emitting diodes. The ceramic is not activated under normal room lights (left) but glows a brilliant pink-red when exposed to 450-nanometer-wavelength blue light (right).

These advancements and more can be traced back to the Laboratory's early and continued investment in materials science, which established the foundation for transparent ceramics research and rewarded multidisciplinary collaboration. Cherepy notes that her team "works with every part of the Laboratory that could possibly utilize optical ceramics." Payne adds, "We collaborate across the Laboratory, applying transparent ceramics to state-of-the-art science and technology in a variety of fields. We also collaborate with external partners, such as the United States Army, the Department of Homeland Security, and private industry. Internally, the LDRD program helps propel the transparent ceramics team to new heights with its focus on funding high-risk, potentially high-payoff projects." With so much going for it now, and the exciting challenges ahead, the future looks bright for transparent ceramics to find even more applications in the days ahead.

—Stephanie Turza

Key Words: Additive manufacturing, composite pressing, direct ink write (DIW), gadolinium–lutetium–oxide (GLO) transparent ceramic scintillator, KSF:Mn, Laboratory Directed Research and Development (LDRD), laser-gain media, laser optic, light-emitting diode (LED), scintillator, transparent ceramics.

For further information contact Nerine Cherepy (925) 424-3492 (cherepy1@llnl.gov).