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JANUARY/FEBRUARY 2018



New facets for the role of
defects in ceramics



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January/February 2018 • Vol. 97 No.1

feature articles



Meet ACerS president Mike Alexander

During his presidential year, Alexander will pick up the mantle of humanitarian involvement that began last year with Bill Lee.

by Eileen De Guire



New facets for the role of defects in ceramics

Armed with advances in our ability to synthesize, characterize, and model materials, it may be time to redefine the negative connotation surrounding defects in ceramic materials. But can defects really shine as the “good guys” in materials science?

by S. Saremi, R. Gao, A. Dasgupta, and L.W. Martin



Innovative concretes provide the ultimate solution for rising construction costs and environmental footprint

Additive methods, nanostructure control, computational modelling, self-healing additives, and renewable byproduct raw materials will help cement scientists engineer stronger and more durable concretes—with less global societal cost.

by Rouzbeh Shahsavari and Sung Hoon Hwang



National Science Foundation CAREER awardees in Ceramics: Class of 2017

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by Lynnette D. Madsen

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As seen on Ceramic Tech Today...



One flash spark plasma sintering to rule them all: Technique can densify most materials in mere seconds

Researchers at San Diego State University have developed a flash spark plasma sintering technique that can densify all kinds of materials, regardless of their electrical conductivity, in a matter of just seconds.

Read more at
www.ceramics.org/flashsps

As seen in the December 2017 ACerS Bulletin...



What's in and on that car? The role of ceramics and glass in the \$4 trillion auto industry

Global automotive manufacturing industry revenues are worth an estimated \$4 trillion—and ceramic and glass materials play a significant role in this evolving industry.

Read more at
www.ceramics.org/carfeature

American Ceramic Society Bulletin covers news and activities of the Society and its members, includes items of interest to the ceramics community, and provides the most current information concerning all aspects of ceramic technology, including R&D, manufacturing, engineering, and marketing. American Ceramic Society Bulletin (ISSN No. 0002-7812). ©2015. Printed in the United States of America. ACerS Bulletin is published monthly, except for February, July, and November, as a "dual-media" magazine in print and electronic formats (www.ceramics.org). Editorial and Subscription Offices: 600 North Cleveland Avenue, Suite 210, Westerville, OH 43082-6920. Subscription included with The American Ceramic Society membership. Nonmember print subscription rates, including online access: United States and Canada, 1 year \$135; international, 1 year \$150.* Rates include shipping charges. International Remail Service is standard outside of the United States and Canada. *International nonmembers also may elect to receive an electronic-only, email delivery subscription for \$100. Single issues, January-October/November: member \$6 per issue; nonmember \$15 per issue. December issue (ceramicSOURCE): member \$20, nonmember \$40. Postage/handling for single issues: United States and Canada, \$3 per item; United States and Canada Expedited (UPS 2nd day air), \$8 per item; International Standard, \$6 per item.

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ACSBA7, Vol. 97, No. 1, pp 1 - 48. All feature articles are covered in Current Contents.

DOE projects could revive domestic rare-earth element production

Although they are not really rare, only eight countries currently mine and produce rare-earth elements—with China as the dominant producer. The last North American mine, United States-based Molycorp, which went bankrupt in 2015, was sold this past summer, leaving the U.S. without a domestic supplier of rare earths.

However, a new project funded by the U.S. Department of Energy could be a shot in the arm for domestic rare earth production and the coal industry. It has identified nine projects that will receive nearly \$4 million in cost-shared federal funding to “improve the technical, environmental, and economic performance of new and existing technologies that extract, separate, and recover rare-earth elements from domestic U.S. coal and coal by-products,” according to a DOE news release. The National Energy Technology Laboratory will oversee and manage the projects.

One of those projects is getting nearly \$875,000 to convert coal fly ash to rare-earth oxides. In a collaboration between Battelle and Rare Earth Salts (RES) (Beatrice, Neb.), researchers will use proprietary processes to separate rare-earth elements from coal fly ash and then purify them to make a marketable product, according to a Battelle news release.



Rare-earth elements, like this sample of yttrium, are valuable materials for many high-tech products.

Credit: Museum für Naturkunde Berlin, Y. Yitram, BY-NC-ND 2.0
hp, Wikimedia Commons; Flickr, CC BY-NC-ND 2.0

“This is an important project to prove the viability of this approach,” Battelle research scientist Rick Peterson explains in the release. “The need to recover rare-

earth elements in the U.S. is of national importance, since so much of the capacity to produce these critical materials lies outside the U.S.”



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Coal fly ash is a by-product of coal combustion in coal-fired power plants that generate electricity. Because of its pozzolanic properties and environmental advantages, it has been used to make concrete, and as a filler in multiple applications.

Battelle's acid digestion process extracts rare earths from coal fly ash while recycling the chemicals used in the process. RES also uses an environmentally friendly process to separate and purify rare-earth elements.

"We are particularly interested in recovering and purifying the magnetic rare-earth elements (such as praseodymium, neodymium, and dysprosium), but we'll be doing

work in recovery of all the naturally occurring rare-earth elements plus yttrium and scandium," Peterson writes in an email.

With demand for coal declining due to industry regulations, the DOE projects could also benefit the coal industry. "Our technology positions us to be a primary producer of consistent, low-cost, rare-earth oxides to Western economies," RES CEO Cameron Davies says in the release. "As we seek additional sources of domestic rare earth feedstock, coal fly ash presents a promising opportunity."

Peterson explains that coal-based sources have a higher proportion of heavy rare-earth elements, which tend to be more scarce, making them more valuable than light rare earths.

"This project is important to ensure that we have an accessible and recoverable supply of all the rare-earth elements, which are vital to industries from ceramics to energy, electronics, and defense," he writes.

Revitalizing the coal industry and lessening U.S. dependence on rare earth imports might be considered two positive "by-products" of the DOE's rare-earth element projects. ■

Fisker sets sights on solid-state battery tech

Electric car maker Fisker plans to use a new solid-state battery technology drivetrain in its electric vehicles to vastly improve driving range, charging time, energy density, and battery cost.

The company recently filed patents for its "flexible solid state technology," which can provide its Emotion model vehicles with a reported 500-mile range. Tesla's best, the Model S 100D, gets an estimated 335 miles in its range.

But the even bigger perk is that the company says it can be charged in just minutes. Tesla's best rate, at its Supercharger stations, is a half-hour to fully charged.

Of course, details about the seemingly revolutionary materials and workings behind this technology are scant. So is it all smoke and mirrors?

The company does say that it has developed a working prototype of the battery, designed with 3-D electrodes that provide 2.5-times the energy density of lithium-ion batteries, according to a *Designboom* article.

And in an interview with *Fox Business*, Fisker owner Henrik Fisker says his company's solid-state battery uses less cobalt than conventional batteries, allowing the company to reduce manufacturing costs to one-third that of conventional (presumably lithium-ion) batteries.

But there are a lot of steps in between a lab prototype and a commercial product, which Fisker predicts could be ready for the automotive industry in the next 4-5 years.

The company is marching forward with bringing its technology to market, however. It is already accepting pre-orders for its \$130,000 Emotion vehicle. And to enable such blistering fast charging times, Fisker also says that his company is next developing a commercial "ultra charger" to charge the battery in the minutes that it says is possible.

Fisker plans to debut the car prototype at the Consumer Electronics Show in January 2018. Although it says that the technology will not be ready for mass automotive production until after 2023, it could find its way into smaller electronic devices sooner. ■



Fisker's prototype electric vehicle, Emotion, which will reportedly be powered by novel solid-state battery tech.

Business news

Kyocera breaks ground on new structural ceramic manufacturing plant in Japan (www.global.kyocera.com)...

Armor Ceramics sets out to build self-sustainable refractory market in Ukraine (www.armorceramics.com)... RAK

Ceramics plans capacity expansion in India (www.reuters.com)... Saint-Gobain reinforces its strategic positioning in insulation in central Europe (www.saint-gobain.com)...

Energy Department announces \$25M for combined heat and power technologies (www.energy.gov)... Latest cost study stacks brick homes against competitors (www.gobrick.com)...

Bangkok Glass aims for top spot as new plant for float panels kicks off (www.nationmultimedia.com)... Owens Corning mineral wool insulation earns safety designation (www.owenscorning.com)...

AGC Flat Glass Italia officially inaugurates new float line at its Cuneo plant (www.agc-glass.eu)... Guardian Glass Europe installs emissions control system in Luxembourg (www.guardianglass.com)...

Asahi India Glass to start commercial production at Taloja float glass plant (www.aisglass.com)... Henkel invests in advanced materials start-up NBD Nanotechnologies (www.henkel.com)...

PGW's oldest auto glass plant will shut down in June 2018 (www.buygwautoglass.com) ■

ceramitec 2018 is a hot spot for the ceramics industry

ceramitec 2018—the European trade show for the complete ceramics industry, ranging from the manufacturer to science—will open its gates April 10–13 in Messe München, Germany.

Igor Palka, exhibition director of ceramitec and Indian Ceramics, is extremely satisfied with the application status: “A great number of key accounts have signed up. Almost half of the applications come from abroad. Newcomers are, among others, XJet from Israel, Toto from Japan, Gabbrielli from Italy, Kexing Special Ceramics Co., LTD from Canada, REF Minerals from Latvia, or Arcillas from Spain. As in earlier years, the trade show will be able to welcome international market leaders as exhibitors, such as Amberger Kaolinwerke, Bongioanni, Ceramifor, Dorst, Gustav Eirich, Händle, Keller HCW, Imerys,

ceramitec 2018 will welcome an international audience to Germany for the ceramic industry exhibition and trade show, complete with a full conference program.

Lingl, MOTA, Netzsch, Sabo, Schunk, Stephan Schmidt, and Tecnofiliere. In addition, six large joint pavilions have already signed up, among others from France, Hungary, and China.”

Just like previous editions, ceramitec 2018 will be accompanied by a top-class conference program. The ceramitec Forum constitutes the platform for knowledge and know-how transfer for research and development.

Both the trade show and conference program will feature focal topics of relevance for the future in 2018, including



technical ceramics and additive manufacturing. The aim is to make ceramics and their fields of application even more visible for all representatives from the industry.

In 2018, analytica—the marketplace for products and services along the entire value-added chain of state-of-the-art laboratory processes—will be held parallel to ceramitec. Exhibitors can tap new visitor target groups and expand their business networks. In doing so, synergies arise particularly in the fields of analytics, quality control, and laboratory technology. ■

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3-D printed technical ceramics market forecast to reach \$544 million by 2022

By Margareth Gagliardi

The global 3-D printing industry is currently valued at over \$7 billion and is expanding at a very healthy rate, with a compound annual growth rate (CAGR) greater than 20% through 2022.

Ceramic 3-D printing represents almost 11% of this market and is dominated by printing of consumer products, primarily pottery. However, there is growing interest in the development and commercialization of 3-D printed technical ceramics for various applications in the healthcare, mechanical, chemical, and electrical sectors, among others.

The global market for 3-D printing of technical ceramics, which includes equipment, materials, and services, increased from \$118 million in 2015 to \$142 million in 2016 and is estimated to reach \$174 million by the end of 2017, corresponding to a very strong CAGR of 21.4% during the two-year period (Table 1).

Applications within the mechanical/chemical sector currently account for the largest share of the market at an estimated 44.8% of the total in 2017, corresponding to \$174 million in sales. Within this segment, 3-D printed ceramics are primarily used for fabrication of structural components for aerospace and defense, filters and membranes, and catalysts and catalyst supports.

Ceramic 3-D printing for life science also represents a relevant share of the market, with estimated total revenues of \$74 million in 2017, equal to 42.5% of the total market. Within this segment, 3-D printed ceramics find use primarily in the fabrication of implantable devices, dental products, and tissue engineering scaffolds. Electrical and electronics are expected to generate global revenues of \$14 million in 2017, or 8.0% of the total market, whereas the remaining sectors will account for a combined 4.6% share.

Demand for 3-D printed technical ceramics is projected to continue growing at a rapid pace over the next five years, due to a variety of factors, including the following.

- Increased penetration in different sectors, particularly life science, mechanical/chemical, and electronics;
- Healthy growth of certain types of products that can be produced by applying ceramic 3-D printing (such as tissue engineering scaffolds, microelectromechanical systems, and fuel cells);
- Introduction of new processes that allow for high-throughput manufacturing of 3-D printed ceramics and lower production costs; and
- Rising levels of related R&D activities.

As a result, the total market for 3-D printing of technical ceramics is forecast to grow at a CAGR of 25.6% from 2017 to 2022, reaching global revenues of \$544 million by 2022.

The 3-D printed technical ceramics market is driven primarily by five types of materials: alumina and zirconia among the oxide ceramics, silicon-based (e.g., silicon carbide and silicon nitride) among the non-oxide ceramics, and two popular biomaterials (hydroxyapatite and calcium phosphate).

Alumina-based products account for the largest share of the market at 24.1% of the total (Table 2). The market for equipment, materials and services used to 3-D print alumina-based products is estimated to reach \$42 million by the end of 2017, growing at a CAGR of 24.7% since 2015.

Zirconia-based ceramics are projected to generate global revenues of \$14 million in 2017, or 8.1% of the total, corresponding to a CAGR of 18.3% during the two-year period. Expanding at a CAGR of 19.5% since 2015, nonoxide silicon-based technical ceramics are expected to contribute 17.2% of global revenues with estimated sales of \$30 million in 2017.

Table 1. Global market for 3-D printing of technical ceramics by application, through 2022 (\$ millions)

Application	2015	2016	2017	2022	CAGR%, 2017-2022
Mechanical/chemical	53	64	78	239	25.1
Life science	49	60	74	256	28.2
Electrical and electronics	10	12	14	34	19.4
Optical and optoelectronics	4	4	5	10	14.9
Energy	2	2	3	5	10.8
Total	118	142	174	544	25.6

Table 2. Global market for 3-D printing of technical ceramics by material, through 2017 (\$ millions)

Material	2015	2016	2017	CAGR%, 2015-2017
Oxide/alumina-based	27	33	42	24.7
Oxide/zirconia-based	10	12	14	18.3
Nonoxide/silicon-based	21	24	30	19.5
Hydroxyapatite-based	25	32	39	24.9
Calcium phosphate-based	19	23	28	21.4
Others	16	18	21	14.6
Total	118	142	174	21.4

The market for equipment, materials, and services used to 3-D print hydroxyapatite-based biomedical products is projected to reach \$39 million by the end of 2017, or 22.4% of the total, increasing at a CAGR of 24.9% since 2015. Calcium phosphate-based products, which consist primarily of tricalcium phosphate, are expected to generate revenues of \$28 million in 2017 (a 16.1% share), corresponding to a CAGR of 21.4% during the two-year period.

About the author

Margareth Gagliardi is a project analyst for BCC Research. Contact Gagliardi at analysts@bccresearch.com.

Resource

M. Gagliardi, "3D Printed Technical Ceramics: Technologies and Global Markets" BCC Research Report AVM141A, June 2017. www.bccresearch.com. ■

ACerS announces new Bioceramics Division!

ACerS Board of Directors recently approved the creation of the Bioceramics Division. This new division was formed out of the ~90-member Bioceramic Technical Interest Group to build relationships among members with strong ties to bioceramics and biomaterials-related industries. Division leaders include Steve Jung (Mo-Sci), chair; Roger Narayan (North Carolina State University), chair-elect; Julian Jones (Imperial College of London), vice chair; and Ashutosh Goel (Rutgers University), secretary. To join this exciting new ACerS division at no additional cost, complete a division affiliation form and choose "Bioceramics Division" at www.ceramics.org/join-a-division. ■

St. Louis Section/RCD 54th Annual Symposium on Refractories set for March 21–22

The 54th Annual Symposium on Refractories will take place in St. Louis, Mo., at the Hilton St. Louis Airport Hotel on March 21–22, with the theme "Refractories for the Cement, Glass, and Minerals Manufacturing Industry." A kickoff event (TBD) will be held the evening of March 20. Program co-chairs are Andrew Domann (Bucher Emhart Glass) and Steven Ashlock (Kyanite Mining Corporation).

For details about the event, including vendor information, registration fees, and hotel reservations, visit www.bit.ly/54thRCDSymposium. Hotel reservation deadline is **February 17, 2018**. ■

Names in the news

Boccaccini elected chair of the Department of Materials Science and Engineering, Erlangen, Germany

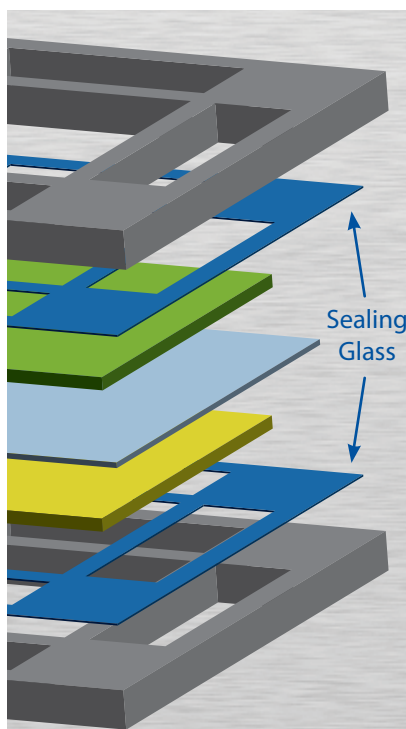


ACerS Fellow Aldo Boccaccini has been elected chair of the Department of Materials Science and Engineering at University of Erlangen-Nuremberg (FAU), Germany for a two-year period. He is a member of the Basic Science Division. ■

Huang receives Lifetime Achievement Award



ACerS member Jow Lay Huang received the Albert Nelson Marquis Lifetime Achievement Award, presented by Marquis Who's Who. Recipients are selected based on leadership qualities, achievements, noteworthy accomplishments, and success in their respective fields. Huang is dean of the Office of Research and Development and chair professor of the Department of Materials Science and Engineering at National Cheng Kung University in Taiwan. ■



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Society and Division news (continued)

Warm up to EAM and ICACC with free journal articles

Before you head to EAM 2018 and/or ICACC18, check out the special compilation of articles authored by the meetings' plenary speakers, conference organizers, and session chairs on the Wiley website. Through January 31 you can access 30 articles from fellow ACerS members, many of whom you may already know! Visit www.bit.ly/FreeJournalArticles to start reading. ■

In memoriam

Telesphore Charland

Some detailed obituaries can also be found at www.ceramics.org/in-memoriam.

Awards and deadlines

ACerS Global Distinguished Doctoral Dissertation Award deadline is January 15

The award recognizes a distinguished doctoral dissertation in the ceramics and glass discipline. Nominees must have been a member of the Global Graduate Researcher Network and have completed a doctoral dissertation as well as all other graduation requirements set by their institution for a doctoral degree within 12 months prior to the application deadline. Nomination deadline is **January 15, 2018**. Visit www.bit.ly/GDDDAward for nomination instructions. ■

Congrats to ICACC17 award winners!

The Engineering Ceramics Division has announced the Best Paper and Best Poster winners from ICACC17, held last January in Daytona Beach, Fla. The awards will be presented during the plenary session at ICACC18. Congratulations to the authors of these award-winning papers and posters!

Awards and deadlines (continued)

Best Papers

First place

Numerical Analysis of Inhomogeneous Behavior in Friction Stir Processing by Using a New Coupled Method of MPS and FEM, **Hisashi Serizawa** and **Fumikazu Miyasaka**, Osaka University

Second place

Influence of Temperature and Steam Content on Degradation of Metallic Interconnects in Reducing Atmosphere, **Christoph Folgner**, **Viktar Sauchuk**, **Mihails Kusnezoff**, and **Alexander Michaelis**, Fraunhofer IKTS

Third place

Three-Dimensional Printing of Si_3N_4 Bioceramics by Robocasting, **Mohamed N. Rahaman** and **Wei Xiao**, Missouri University of Science and Technology

Best Posters

First place

Light Gated Zinc-Tin Oxide (ZTO) Thin Film Transistor Fabricated via Solution Process, **I. Wang**, **J. Li**, and **J. Chen**, National Cheng Kung University

Second place

Mechanical and Tribological Properties of Boron Carbide/Graphene Platelets Ceramic Composites, **A. Kovalcikova**, **R. Sedlak**, **J. Balko**, **E. Mudra**, **J. Dusza**, Institute of Materials Research Slovak Academy of Sciences; **V. Girman**, Pavol Jozef Šafárik University, Faculty of Science; and **P. Rutkowski**, AGH University of Science and Technology

Joint third place

Processing of Doped Hafnia Ceramics for Fundamental Structure Studies, **M. Kasper**, **B. Johnson**, **S. Jones**, **C. Chung**, and **J. Jones**, North Carolina State University

Effect of Ion Irradiation on Bioactivity of Hydroxyapatite Ceramics,

S. Kobayashi, **T. Izawa**, Tokyo Metropolitan University and **Y. Teranishi**, Tokyo Metropolitan Industrial Research Institute ■

Congratulations to the Global Ambassador Award recipients

The Global Ambassador Program recognizes dedicated ACerS volunteers worldwide who demonstrate exceptional leadership and/or service that benefits the Society, its members, and the global ceramics and glass community.

ACerS 2016–2017 President William Lee selected the following 15 volunteers for the Global Ambassador Award:

- **Jingyang Wang**, Shenyang National Laboratory for Materials Science
- **Manabu Fukushima**, AIST
- **Tatsuki Ohji**, AIST
- **William Fahrenholtz**, Missouri University of Science & Technology
- **Ivar Reimanis**, Colorado School of Mines
- **Eugenio Zapata-Solvas**, Imperial College of London
- **Mrityunjay Singh**, Ohio Aerospace Institute
- **Theresa Davey**, Tohoku University
- **Lisa Rueschhoff**, Air Force Research Laboratory
- **Kevin Fox**, Savannah River National Laboratory
- **Surojit Gupta**, University of North Dakota
- **Darryl Butt**, University of Utah
- **Edgar Zanotto**, Federal University of Sao Carlos
- **John Hewitt**, Interstate Brick Company
- **Tyler Ley**, Oklahoma State University ■

Last call for 2018 award nominations!

Nominations for most ACerS Society awards, including Distinguished Life Member, Global Distinguished Doctoral Dissertation, Kingery, Du-Co Ceramics Young Professional, Jeppson, Coble, Corporate Technical Achievement, Spriggs Phase Equilibria, Friedberg, and Fulrath, are due **January 15, 2018**.

For more information, visit www.ceramics.org/awards or contact Erica Zimmerman at ezimmerman@ceramics.org. Please note that the 2018 Purdy Award is for papers published in 2016. ■

Nomination deadline for GOMD awards is January 21

The Glass & Optical Materials Division seeks nominations for its awards:

The Stookey Lecture of Discovery Award recognizes an individual's lifetime of innovative exploratory work or noteworthy contributions of outstanding research on new materials, phenomena, or processes involving glass that have commercial significance or the potential for commercial impact.

The George W. Morey Award recognizes an individual for new and original work in the field of glass science and technology and excellence in publication of work, either experimental or theoretical.

The Norbert J. Kreidl Award for Young Scholars recognizes research excellence in glass science and is open to all graduate students (M.S. or Ph.D.) or those who have graduated within twelve months of the GOMD meeting in San Antonio, Texas, May 20–24, 2018.

Visit www.ceramics.org/awards for more details. ■

Member spotlight

Share good news about your division

Help spread good news about your division by educating potential members with our new giveaways. ACerS introduced promotional materials at MS&T17 (division-specific calendars and pocket-sized cards with the periodic table of elements) specifically designed and branded for each of ACerS 10 divisions. These items include division-specific content, such as meeting dates and contact information. Use these tools to personally invite potential members to join ACerS and your division. Contact Erica Zimmerman, ezimmerman@ceramics.org to request your supply. ■

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Students and outreach



Credit: HarbisonWalker International Advanced Technology and Research Center

Jeff Bogan, technology manager monolithics, demonstrates the effectiveness of a rapid dryout monolithic.

Students learn about refractory research at HarbisonWalker tour at MS&T17

Approximately 25 students attending MS&T17 were treated to a tour of the Advanced Technology and Research Center (ATRC) of HarbisonWalker International, a global producer of refractory products and services. Students learned about HWI's challenges and opportunities in the industries it serves, along with various refractory types, uses, and property tests.

Highlights included demonstrations on modular and monolithic refractories production, lifecycle testing, failure analysis, imaging methods and processes, and a test that illustrated the need for pathways for off-gassing in green refractories on heat treating. The tour concluded with pizza cooked in HWI's brick oven and a social hour with ATRC engineers and scientists. ACerS would like to thank HWI for hosting this year's student tour! ■

Students and young professionals—ACerS Winter Workshop offers professional development sessions

The Ceramic and Glass Industry Foundation will host ACerS 3rd annual Winter Workshop January 19–23, 2018, at ICACC18 in Daytona Beach, Fla. The Winter Workshop provides a combination of technical and professional development sessions created specifically for students and young professionals. To register, visit www.ceramics.org/winter-workshop-2018. ■

Identify ceramic failures in Student and Industry Failure Trials at ICACC18

Are you sharp enough to identify a ceramic failure mechanism in an industrial setting? The Student and Industry Failure Trials (SIFT) is a new competition at ICACC18 that challenges teams of students, industry professionals, and academics to analyze a ceramic material that has failed in an industrial setting and identify the failure mechanism. Each team is provided physical specimens of the failed material and additional characterization data, such as X-ray diffraction plots or micrographs as needed. Organized by ACerS President's Council of Student Advisors, SIFT is open to students, industry professionals, researchers, and student advisors. If you are attending ICACC18 this year, stay tuned for more details!

Check out other student events at ICACC18

Network with your peers at the Global Graduate Researcher Network student and young professional networking mixer, Monday, January 22, 7:30–9 p.m. at the hotel.

Show off your design skills in the SCHOTT glass competition, organized by PCSA and sponsored by SCHOTT on Tuesday, January 23, 6:45–8 p.m., in the Ocean Center exhibit hall.

Student and young professional talk: "Publishing in American Ceramic Society journals: Writing for search engine optimization and self marketing," Wednesday, January 24, noon–1:15 p.m. Lunch is included on a first come, first served basis.

For more details, contact Kevin Thompson, ACerS membership director, at kthompson@ceramics.org. ■

Ceramic and glass grad students: GGRN benefits include leadership development, networking

Are you looking to get involved in an international community of your peers within the ceramic and glass community? ACerS Global Graduate Researcher Network is an ACerS membership that addresses the professional and career development needs of graduate-level research students who have a primary interest in ceramics and glass.

GGRN members receive all ACerS individual member benefits plus special events at meetings and free webinars on targeted topics relevant to the ceramic and glass graduate student community.

Membership is only \$30 per year. Visit www.ceramics.org/ggrn to learn how GGRN can help your career and join today! ■

CERAMIC AND GLASS INDUSTRY FOUNDATION



Rick Beuttel of Air Products (left) presents a check to Marcus Fish (center) of The Ceramic and Glass Industry Foundation and Robert Lipetz of the Glass Manufacturing Industry Council.

CGIF receives \$15,000 donation from Air Products

The Ceramic and Glass Industry Foundation (CGIF) and the Glass Manufacturing Industry Council recently received a \$15,000 grant from Air Products of Allentown, Pa., to foster innovation by the next generation of ceramic and glass professionals.

The Air Products Foundation presented a check to both organizations at the 78th Conference on Glass Problems (GPC), November 6–9, 2017, in Columbus, Ohio.

“For more than 50 years, Air Products has been committed to helping glass producers improve their operations with innovative combustion and industrial gas technologies,” Air Products director of business development–Americas Rick Beuttel says. “We are excited to share our passion for innovation with the next generation of glass professionals through this donation to the CGIF.”

The money goes toward student travel grants to attend GPC, as well as CGIF initiatives to help with its mission to attract and train ceramic and glass professionals.

“We are extremely grateful to Air Products for championing our efforts in student outreach,” CGIF director of development Marcus Fish says of the donation. “This gift will support our mission to attract and train the highest quality talent available to work with engineered systems and products that utilize glass and ceramic materials.”

“This donation demonstrates how everyone benefits when progressive organizations like Air Products commit to investing in the future of their industry,” GMIC executive director Robert Lipetz comments. “It will allow us to provide student travel grants to the GPC, which will afford students the valuable opportunity to interact with industry leaders.”

For more information on the CGIF’s donation, visit the news page on its website at www.foundation.ceramics.org. ■

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Meet ACerS president Mike Alexander

By Eileen De Guire

Could you imagine your dentist ever saying, “It’s been a career that I’d love students to have?”

That is what Mike Alexander, who went to college to become a dentist, says about his actual career as a ceramic engineer working in the refractories industry.

Alexander grew up in Victor, N.Y., a small town in the Finger Lakes region of upstate New York. The aspiring dentist went to Alfred University (Alfred, N.Y.) with only one problem—cost. “My dad, as a union plumber, was on strike off and on. I was like a lot of kids at Alfred from a blue-collar life, doing what we needed to get by.”

The Ceramics School at Alfred is state supported, and students enrolled in ceramic engineering could take advantage of a dual degree program. By the end of his second year, Alexander jettisoned all thoughts of dentistry and focused entirely on ceramic engineering. “We had a great freshman lab situation. We made the St. Patrick’s celebration favors—beer mugs, cups, and bowls. You could get dirty and not worry about it!”

Working summers at Victor Insulator in his hometown pointed him toward an industrial career. On graduation, Alexander and two other Lambda Chi Alpha fraternity brothers took jobs with a refractory manufacturer, Quigley Company, in New Jersey.

He recalls the excitement of those early days at Quigley, saying “I remember going to steel mills, seeing ladles flying overhead, molten metal being cast, and thinking ‘this is cool.’ It was big, hot, dirty, sweaty, and smelly—but that was awesome. That comes from playing in the mud, right?”

“I started traveling the world when I worked for Quigley.” Subsequent jobs at Ferro, Riverside Refractories, and now Allied Minerals have taken Alexander “pretty darn near everywhere” in the world. “I can’t imagine not travelling, now. Who knew?”

Alexander first joined The American

Ceramic Society as a student. As a professional, he says the Society has afforded him a network, especially within the refractories community. He recalls that James Bennett first tapped him to get involved in the Refractory Ceramics Division and give a talk at the St. Louis Symposium, and to eventually organize a symposium.

“Once you got to be the symposium chair, the next thing you knew you were on a committee,” he says. With that entrée, he rotated up the ranks of division leadership and was asked to serve on the ACerS board of directors, leading to his election as ACerS president.

Alexander would like fellow Society members to benefit as much from the Society as he has. “I’d like to see more volunteers. Never turn anybody down—if somebody shows up at a breakfast meeting [such as at the RCD meeting in St. Louis], I always thought, give them something to do, because they’re here at 6:30 in the morning because they want to be involved,” he says.

During his presidential year, Alexander will pick up the mantle of humanitarian involvement that began last year with Bill Lee. He sees humanitarian outreach as an extension of the engineering mindset, which is “... applying science to the benefit of humanity. It can be as noble as that, because it needs to be as noble as that.”

A similar philosophy guides his evangelization of the ceramic engineering career that he has found so rewarding. “The thing about ceramic engineering is ... we’ve got our niche. If you’re specialized, like a ceramic engineer, you’re really going to have a lot of opportunities.”

He participates regularly at RCD’s Materials Camp demonstration at MS&T to introduce middle and high students to the field. “We need to approach undergraduates and younger kids, because the world’s changed. Today you have to apply the science. Whose lot are you going to improve?” He emphasizes,



“Curiosity and creativity are two things engineers have to have.”

Asked what surprises him most about his career, he says, “The whole trajectory, the whole path. I could not have imagined it. I tell students—become an engineer. I can’t tell you what you’re going to do or what you’re going to be. But if you don’t become an engineer, I know it isn’t going to happen for you!”

Alexander and his wife of 25 years, Cathy, live in Alabama, where their son’s family and four granddaughters also live. He plays guitar, mandolin, and ukulele in his free time, and dabbles a bit in songwriting, crediting Waylon Jennings and Willie Nelson as influences.

He invites Society members to be in touch. “Call me or email me anytime. I’ll gladly talk to anyone!” ■

advances in nanomaterials

Nanometer-tall cones provide antireflective properties, eliminate glare

Researchers at the Center for Functional Nanomaterials at Brookhaven National Laboratory (Upton, N.Y.) have found a way to reduce the reflection of sunlight on glass by etching tiny nanometer-sized cones onto the glass's surface—making the glass virtually invisible. The cones “have the effect of making the refractive index change gradually from that of air to that of glass, thereby avoiding reflections,” according to a description in a BNL news release.

The conventional way of reducing reflection is to coat a surface with an antireflective coating. But adding an additional layer only works for a single wavelength and a single incident light angle, according to the research team's paper. The nanometer cones are more efficient at eliminating reflection without adding additional layers of material.

“We're excited about the possibilities,” CFN director Charles Black says in the release. “Not only is the performance of these nanostructured materials extremely high, but we're also implementing ideas from nanoscience in a manner that we believe is conducive to large-scale manufacturing.”

The researchers used a block copolymer as a template for the self-assembly process, where nanoscale cones with sharp tips were etched onto the surface of the glass 52 nm apart. The resulting surface glare was nearly eliminated.

In subsequent experiments to measure light reflection, the scientists noted that taller cones reflect less light. They also found that when covered with a nanotextured glass cover, a commercial silicon solar cell can generate as much electric current as one without a cover. The textured glass can also withstand three times as much optical energy from laser pulses than antireflective coatings currently on the market.

“This simple technique can be used to nanotexture almost any material with precise control over the size and shape of



Glass surfaces with etched nanotextures reflect so little light that they become essentially invisible. This effect is seen in the above image, which compares glare from a conventional piece of glass (right) to that from nanotextured glass (left).

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the nanostructures,” Aitkur Rahman, assistant professor in the Department of Physics at the Indian Institute of Science Education and Research and research team member, says in the release. “The best thing is that you don’t need a separate coating layer to reduce glare, and the nanotextured surfaces outperform any coating material available today.”

Black believes the research is scalable and mentions that the research team is looking for a partner “to help advance these remarkable materials toward technology.”

And that could be good news for the solar panel industry’s efficiency challenges.

The paper, published in *Applied Physics Letters*, is “Self-assembled nanotextures impart broadband transparency to glass windows and solar cell encapsulants” (DOI: 10.1063/1.5000965). ■

Silver nanowires and graphene offer touchscreen alternative to indium tin oxide, could build less breakable screens

Researchers at the University of Sussex (Brighton, U.K.) have unveiled a new touchscreen material that offers several improvements over the industry standard, indium tin oxide, and could enable less breakable future smartphone screens.

The material, a layered combination of silver nanowires and graphene, is more inexpensive, flexible, and robust than indium tin oxide—which altogether could enable smartphone screens that are not composed entirely of glass.

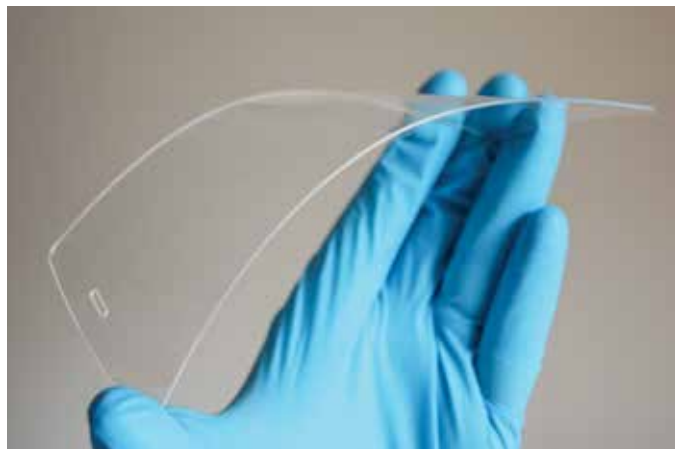
Indium tin oxide is transparent and conductive, making it well suited for touchscreen technology. But the problem with indium tin oxide is the indium—a rare earth in scarce supply and consequently high in cost. So researchers and manufacturers have been searching for a replacement material.

Graphene is a viable option, although it is not perfect. Several other materials have been considered and investigated as well, including carbon nanotubes, silver nanowires, and gallium-doped zinc oxide—but so far, none of the options have been just right.

Now, a team of researchers at the University of Sussex may have developed a Goldilocks touchscreen material that is just right—a combination of silver nanowires and graphene.

To fabricate the new touchscreen, the team patterned graphene over a film of silver nanowires. In a method similar to using a potato stamp, the researchers used a polydimethylsiloxane (a simple silicone polymer) stamp to grab a single layer of graphene floating on the surface of water and transfer it onto a silver nanowire film.

The graphene layer serves several purposes—for one, it protects the silver nanowires from tarnishing. But graphene also links the silver nanowires together, according to an *IEEE Spectrum* article, and boosts their electrical conductivity, allowing just a small amount of silver to be sufficient for the touchscreen. The resulting layered material, which has considerably lower cost than indium tin oxide, is flexible and main-



Credit: University of Sussex

A new touchscreen material could enable flexible smartphone screens that are less likely to break.

tains its electrical properties even after repeated bending.

“The addition of graphene to the silver nanowire network also increases its ability to conduct electricity by around a factor of ten thousand,” Alan Dalton, Sussex professor of experimental physics and senior author of the research, says in a University of Sussex press release. “This means we can use a fraction of the amount of silver to get the same, or better, performance. As a result, screens will be more responsive and use less power.”

In addition to enhanced performance and reduced cost, the touchscreens could enable entire smartphone screens that are less likely to break. Because the silver nanowire touchscreen is more robust, it could allow smartphone manufacturers to reduce the glass substrate of smartphone screens—which support the thin touchscreen material—to a thin layer.

“What we are envisaging is that the typical glass top surface of the device would be replaced by plastic with a thin, scratch-resistant glass protective layer,” Matt Large, first author and lead researcher on the project, explains via email. “The whole device would then be far more robust as the thinner glass and plastic could flex to absorb impact energy when dropped. Even if the glass layer does get cracked, it would be far cheaper to peel off and replace than having to replace the whole touch sensor.”

Large also adds that the new touchscreen can be deposited on top of glass, too.

Plus, the new touchscreen material seems to have major commercial potential when it comes to manufacturing as well. In addition to lower material costs than indium tin oxide, the fabrication technique is scalable, too.

“It would be relatively simple to combine silver nanowires and graphene in this way on a large scale using spraying machines and patterned rollers,” Dalton adds in the release.

The paper, published in *Langmuir*, is “Selective mechanical transfer deposition of Langmuir graphene films for high-performance silver nanowire hybrid electrodes” (DOI: 10.1021/acs.langmuir.7b02799). ■

Can hydrogen fuel our future? With this ceramic membrane, maybe

A team of scientists from CoorsTek Membrane Sciences (Golden, Colo.), the University of Oslo (Norway), and the Institute of Chemical Technology (Spain) has developed a promising new ceramic membrane that could reduce the cost and enhance the feasibility of hydrogen generation far enough to bring the technology to the forefront of clean energy solutions.

The new ceramic membrane—made from oxides of barium, zirconium, and yttrium—can separate hydrogen from natural gas in a one-step process with extremely high efficiency. Incorporated into a protonic ceramic fuel cell, the membrane can generate high-purity compressed hydrogen using just natural gas and electricity.

“By combining an endothermic chemical reaction with an electrically operated gas separation membrane, we can create energy conversions with near zero energy loss,” Jose Serra, co-author of the paper and professor at the Institute of Chemical Technology, says in a CoorsTek press release.

The membrane consists of a dense film of a BaZrO₃-based proton-conducting electrolyte on a porous nickel composite electrode, a combination that has high proton conductivity at 400°C–900°C—allowing it to separate primarily hydrogen protons out of methane, the primary component of natural gas, with incredibly high efficiency. According to the paper’s abstract, the scientists report that the membrane removes 99% of formed hydrogen from methane at 800°C.

In addition to industrial-scale and smaller-scale hydrogen generation, one potentially promising application for protonic ceramic fuel cells is to power low-emission vehicles. Natural gas is so abundant and low-cost and the separation process is so efficient that the ceramic membrane could make hydrogen the best all-around option to fuel future automobiles in terms of emissions and cost.

The paper, published in *Nature Energy*, is “Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss” (DOI: 10.1038/s41560-017-0029-4). ■



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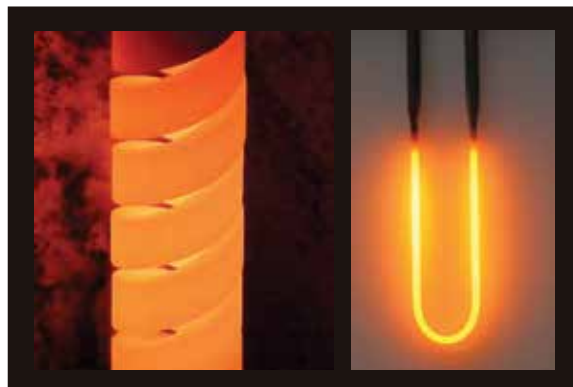
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New facets for the role of defects in ceramics

By S. Saremi, R. Gao, A. Dasgupta, and L. W. Martin

Armed with advances in our ability to synthesize, characterize, and model materials, it may be time to redefine the negative connotation surrounding defects in ceramic materials. But can defects really shine as the “good guys” in materials science?

Defects have a public relations problem—for too long, they have been regarded as the “bad guys.” Defects generally have been dismissed as deleterious to properties and performance of ceramic materials and devices, and, in turn, considerable efforts have attempted to either minimize their concentration or to counterbalance their detrimental impact.

We know, however, that defects can generate value. For example, defects and impurities cause highly desirable color in gem-quality diamonds (see sidebar). Today, advances in synthesis, characterization, and theoretical modeling of ceramics are beginning to challenge the “bad guy” reputation of defects.

The intentional and purposeful introduction of defects, with control over type, concentration, and location, presents an opportunity to make use of “good guy” defects. In this new role, defects are a tool for tuning and enhancing properties and even enabling new functionalities. This perspective focuses on current work and future potential for this role redefinition by highlighting advances in methodologies and scientific examples where defects have been embraced and applied to improve material function.

Defects and their role in materials

One role for modern materials science is to provide a foundation upon which scientists and engineers in diverse fields can address the needs of current and future societal challenges through the realization of next-generation technologies. Key to such advances is not only the development of advanced materials with novel or enhanced properties and performance,

Impurities or point defects in diamond are responsible for colored stones. Despite the imperfections, colored diamonds are often more valuable than colorless varieties.

Diamond color	Color-causing defect
Brown	Clusters of ~60 carbon vacancies; rarer causes are defects associated with hydrogen or isolated nitrogen atoms, or presence of “amber centers” or CO ₂
Yellow	Nitrogen atoms adjacent to carbon vacancies; saturated yellow caused by isolated nitrogen atom defect; other defects are hydrogen-related
Pink, red, purple	Mostly unknown, but likely involves nitrogen atoms associated with vacancies in twin planes; other rarer pink diamonds get color from one nitrogen atom associated with one vacancy
Blue	Boron substitution for carbon
Gray to blue to violet	Hydrogen defects; more violet color may be related to nickel-related defects
Green	Vacancies from natural irradiation from elements such as uranium or thorium; may also be due to hydrogen defects
Chameleon (changes color from olive-green to yellow depending on light and heat exposure)	Not fully understood, but may be related to interaction between hydrogen atoms and nitrogen atom aggregates
Orange	Defect unknown

*From E. Gaillou, G.R. Rossman, “Color in natural diamonds: The beauty of defects,” *Rocks & Minerals*, 89, 66–75 (2014).

Capsule summary

'BAD GUY' REPUTATION

Material defects generally are considered to contribute negatively to the properties and performance of ceramic materials. As such, considerable efforts have attempted to either minimize their concentration or to counterbalance their detrimental impact.

but also the know-how to synthesize and process such materials in a deterministic manner so that their properties can be effectively and efficiently utilized.

Materials science was founded upon the concept that structure, processing, properties, and, ultimately, performance of materials are intimately interconnected. And, as the field has evolved, materials scientists and engineers have increasingly realized that even our best efforts to control these tenets can be remarkably hampered if we do not account for and address the role of material imperfections. In all fields of materials science, the importance of defects is ever present; from critical flaws in a material that can dramatically reduce its strength to careful introduction of desired defects required for production of modern electronic materials, defects play an important role in the evolution of materials properties.

Underlying all this is the fact that defects are unavoidable. Even in the most "perfect" materials, there are always finite concentrations of various structural and compositional defects. In this spirit, the general opinion of defects is not a good one—defects are thought to be (uniformly) deleterious to material performance. In turn, immense efforts have been invested in understanding how to limit defect concentrations, identify defects and their locations, and even fix defects after the fact. Even the name itself, defect, carries a distinctly negative connotation. Defects are generally considered to be "bad guys" to avoid in the world of materials science.

But, armed with advances in our ability to synthesize, characterize, and model materials, this negative connotation stands poised to be redefined. So can defects really be "good guys" in materials science?

Today, even in ceramics, defects

CLEANING UP THE ACT

Advances in synthesis, characterization, and theoretical modeling of ceramics are beginning to redefine the "bad guy" reputation of defects. Instead of avoiding defects, intentional and purposeful introduction of defects offers novel opportunities for materials engineering.

are viewed in a new light—a positive one—that casts them as another tool to design better materials and emergent properties. Such an idea is not new, and some fields have already embraced the power of defects to improve material performance over "ideal" materials. For example, in the semiconductor industry, "defects"—lovingly called dopants in a successful rebranding effort—underpin the modern electronic materials we all rely upon. There, years of development have gone into production of large-scale, high-purity crystals with extremely low concentrations of defects that have limited utility in their pristine state. Instead, once wiped clean of defects, engineers rely on their ability to deliberately "dope" defects back to precisely control properties such as conductivity.

Such an approach in ceramics has not yet been thoroughly embraced. This is not to say that there are not ceramists (in both research laboratories and industry) that do not understand, control, and utilize defects in some shape or form, but that this approach to deterministically use defects to improve material function and performance is not pervasive in ceramics. However, opportunities exist because, like group IV and III-V semiconductor systems, even small concentrations of defects can dramatically impact structural, chemical, electronic, dielectric, thermal, and other properties of ceramics.

Defect engineering in ceramics lags behind that in classic semiconductor systems for a number of reasons. First, compared to elemental/binary semiconductors, ceramics have many constituent elements and possess more diversified crystal structures. In turn, they can accommodate a wider variety of defects, including intrinsic (related to the constituent elements) and extrinsic (related to the impurities and/or dopants) point

WHAT'S BAD IS GOOD

A new understanding is emerging that defects in and of themselves are not bad—they possess a set of properties and influences that, when understood and controlled, provide a depth of control and utility that could rival any other factor.

defects, point defect complexes and clusters, line defects, and planar and volume defects. Second, ceramics have a strong penchant for defects because of the relatively low energy barrier of formation and because they are readily formed to maintain charge neutrality (to compensate for impurities that are often present in the source materials and/or non-stoichiometry) due to the ionic nature of these systems. Finally, there has not been a need or strong driving force to accomplish the same level of control in ceramics, where properties can be robust even in the presence of large defect densities or one can simply "swamp-out" deleterious effects by introducing large numbers of different defects. Even source materials are generally many orders of magnitude less pure than semiconductor sources because there has not been the same driving force or need for exacting chemical control to date.

As a result, state-of-the-art defect and composition control is limited to ~1 atomic percent in many ceramics—far from the parts-per-billion control in semiconductors. This is exacerbated by the fact that there are few characterization methods that reliably measure these complex defect structures, and those that do exist are not (generally) widely applied within the ceramics community. Researchers have used theoretical, modeling, and computational approaches to study defects in ceramics, but they require considerable computational resources and have been limited to a few model systems where the approaches, potentials, and parameters are fairly well known.

As a result, a complete description of defect structures and prediction of their impact on materials behavior remains a challenging and time-consuming task. All told, these challenges have limited the

New facets for the role of defects in ceramics

advance of defect engineering in ceramics. Instead, the community typically either works to limit defect introduction in processing in the first place or to counteract deleterious effects through brute-force approaches, such as chemical alloying.

More recently, however, simultaneous advances in synthesis, characterization, and modeling of ceramics have enabled researchers to address and potentially overcome these challenges and consequently explore new ways to control and

use defects as tools to manipulate material properties and function. Interest has surged in recent years, particularly in transition-metal oxides where there are intrinsically strong couplings between defects and the lattice, orbital, charge, and spin degrees of freedom that drive property evolution. It is this strong coupling, which can be manipulated with deliberate introduction of certain defect types at controlled concentrations and locations, that can provide new path-

ways to novel or enhanced properties and function.

From old to new school—Defects in ceramics today

The most familiar and traditional example of using defects for property control and enhancement in ceramics is chemical alloying. This approach has generally been used to enhance properties by counterbalancing undesirable effects of other defects. In electroceramics, for example, chemical alloying has long been used to reduce electronic leakage by compensating charges introduced to the lattice (in part) by off-stoichiometry and/or impurities. Chemical dopants also have been used directly to achieve desired responses, including aliovalent substitution of A- and B-site cations in perovskite (ABO_3) materials to enhance ionic conduction.

Despite its long history, chemical alloying has been mainly driven by empirical observations and chemical intuition, and the “better” performance that is achieved is either only post-rationalized or poorly understood in many cases.

Synthesis and on-demand production of defects

In addition to conventional doping, advances in material synthesis techniques, such as molecular-beam epitaxy, now enable production of materials with low concentrations of grown-in defects and precise control over doping concentrations and locations. This has manifested in researchers doping wide band-gap oxides similar to traditional semiconductors and achieving high carrier mobilities, such as La-doped $SrTiO_3$ ($\sim 10^4$ cm^2/Vs at 4K) and $BaSnO_3$ (~ 150 cm^2/Vs at 300K).

In addition to point defects, controlled introduction of planar defects, such as interfaces between two different materials or crystal structures, also can improve properties. Spurred by widespread access to reflection high-energy electron diffraction (RHEED)-assisted growth, researchers now use interfaces to induce new physics (e.g., observation of new topologies of polarization, such as polar vortices in ferroelectrics)¹ and to improve material properties for critical applications (e.g., periodically introduc-

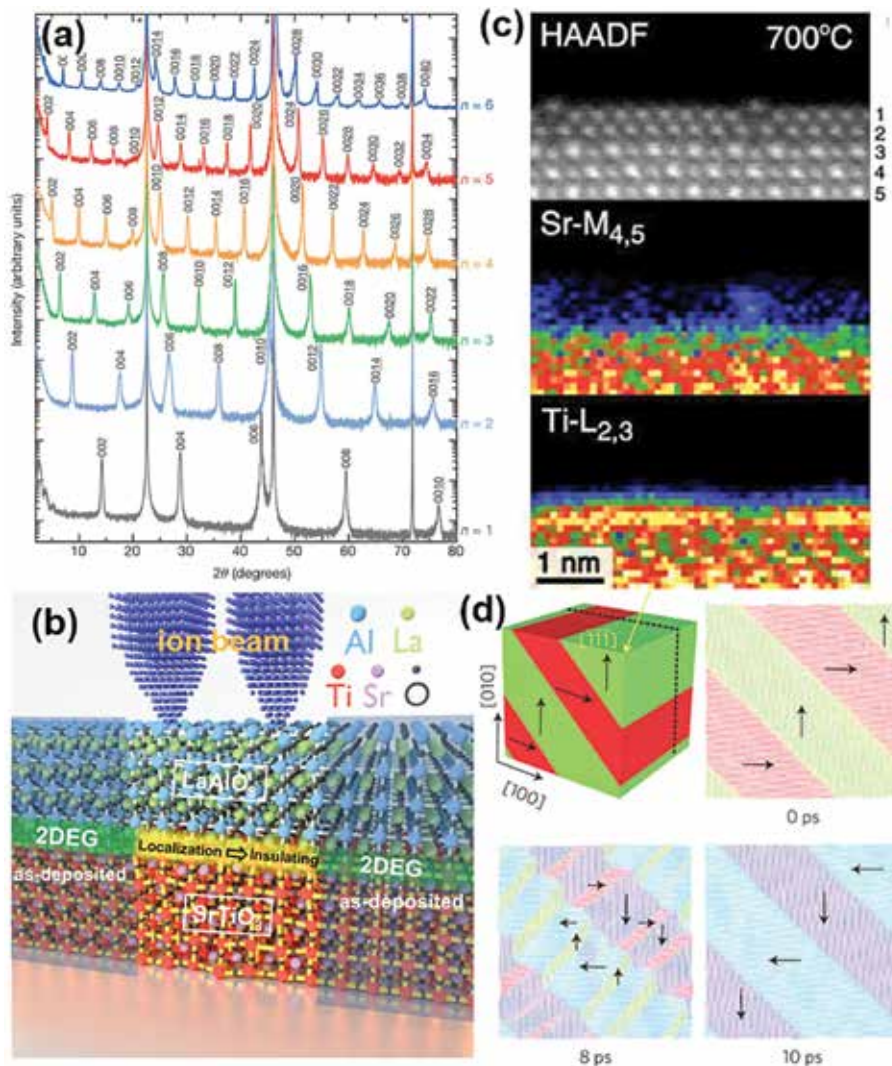


Figure 1. (a) θ - 2θ X-ray diffraction scans of various molecular beam epitaxy-grown epitaxial $Sr_{n+1}Ti_nO_{3n+1}$ ($n = 1-6$) films, showing the deterministic ability to produce planar defects in a designer fashion. Adapted from Lee et al., 2013.² (b) Schematic illustration of patterning of 2-D electron gas formed at the interface of two band insulators, such as $LaAlO_3/SrTiO_3$, using an energetic proton beam. Adapted from Mathew et al., 2013.⁵ (c) STEM-based analysis of surface reconstruction in $SrTiO_3$ (110), including a HAADF-STEM image (top), corresponding EELS elemental maps of the same region at the Sr-M edge (middle), and Ti L-edge (bottom) at $700^\circ C$. Adapted from W. Xu et al., 2016.⁷ (d) MD simulation of a polydomain $PbTiO_3$ sample with electric field applied along [111], revealing a complex domain switching process as a function of time. Adapted from R. Xu et al., 2016.⁸

ing “defect” rock-salt layers in perovskite $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ materials—in essence making artificial Ruddlesden-Popper phases—to improve losses and quality factor for microwave applications) (Figure 1a).²

Apart from in situ defect control during synthesis, there is also growing interest in controlled ex situ introduction of defects—including controlling the type, concentration, and spatial distribution of defects—to produce new functionalities. Researchers have used *knock-on damage*, where materials are exposed to an energetic ion or electron beam that displaces atoms from their ideal lattice positions;^{3, 4} *ion implantation*, where materials are exposed to relatively low-energy ion beams to implant foreign species and create interstitial doping and local strain fields; *nanopatterning of defects by focused-ion beams* to control spatial distribution of defects, and creation of “active” and “dead” regions that can enable patterning of circuits [as in the $\text{LaAlO}_3/\text{SrTiO}_3$ system (Figure 1b)]⁵ and magnetic domains.⁶

Characterization of defects

Characterization is a foundational tenet of materials science, and progress in this regard is providing unprecedented insights into macroscopic defect responses, local/microscopic defect structures, in situ defect kinetics under stimuli, and more. Many advances have come from application of both old and new techniques developed outside ceramics. The following are a few examples of state-of-the-art defect characterization techniques now impacting ceramics.

Electrical characterization

Apart from traditional fitting of current-voltage curves for characterizing transport mechanisms in electroceramics, research has explored various characterization techniques based on macroscopic defect response under applied fields. Techniques making a resurgence or emergence include: *thermally-stimulated depolarization current spectroscopy*, wherein, especially for wide band-gap materials, depolarization currents are measured while heating at a constant rate to provide information about carrier trap energies, densities, etc; *deep level transient spectroscopy*, which is a transient capacitance

technique that monitors capacitance of a depletion region under a voltage pulse and measures carrier trap energies, densities, and captures cross-sections; and *impedance spectroscopy*, wherein AC impedance is measured as a function of frequency and is modeled with circuit elements to differentiate grain boundary versus bulk conduction, ionic versus electronic conduction, and other dielectric information.

Optical and magnetic characterization

Traditional optical methods, including photoluminescence and cathodoluminescence, where excited carriers release light during recombination and give information about band gap and intra-gap states, have been used for years. Other current techniques include: *photoinduced current transient spectroscopy*, which, especially for wide band-gap materials, uses light to excite carriers into trap states and measures current transients, thus providing information about intra-gap traps; *ellipsometry*, which measures changes in polarization of light as it is reflected from the material, allowing extraction of the dielectric constant along with information about surface defects; *electron paramagnetic resonance*, which measures the g factor of a paramagnetic ion using microwaves to move electrons between spin states split by the Zeeman effect under a magnetic field and is particularly efficient at detecting the type and orientation of defect dipoles (i.e., complexes of charged point defects).

Direct imaging and mapping

Methods today provide not only macroscopic or average probes of defects, but also local, atomic-level characterization. Advances in scanning transmission electron microscopy (STEM) together with in situ electron energy loss spectroscopy (EELS) are now a pervasive and powerful tool to directly study (and potentially produce) local defect structures and chemistry. For example, defect migration and surface reconstruction of SrTiO_3 single crystals at high temperature have been directly mapped at the atomic level (Figure 1c).⁷ Likewise, X-ray diffraction-based techniques (typically done at a synchrotron) also are an important method

to determine atomic arrangement, crystal symmetry, and chemical environment of surface and local areas of materials and can also provide insights into the presence and type of defects. Due to the extreme sensitivity to surface layers and the nondestructive nature of probing material properties, synchrotron-based X-ray diffraction has, for instance, been used to reveal the effects of defects on chemical reactions at interfaces.

Theory, modeling, and computational approaches to defects

Beyond studies of traditional metallic compounds or single/binary semiconductor materials, recent computing infrastructure developments have also led to new discoveries and understanding of functional materials with more complicated crystal structures and chemistries. From atomic- to mesoscopic-level structures, multiscale and modal techniques can predict and understand material behaviors like never before. Increased computational power and accessibility, together with better methods and more efficient approaches, today enable study of large-scale simulated cells—which resemble more realistic defect structures—at finite temperatures and allow for time-resolved studies of defect evolution under external perturbation.

Specifically in oxide materials, understanding of static/dynamic defect structures has been bolstered by application of density functional theory (DFT), Monte Carlo simulations, phase-field modeling, and molecular dynamics (MD) simulations. At the unit-cell level, DFT calculations can provide information on the stability of defect structures, kinetics, defect-induced electronic/magnetic properties, phase competition, etc. At the mesoscopic level, especially regarding defect kinetics, Monte Carlo and MD simulations building from advances in pseudopotentials are now widely used. For instance, in electrochemical applications of ceramics, understanding of ionic migration pathways and lattice interactions in materials with different structures (fluorites, perovskites, etc.) has become critical in designing next-generation solid-oxide fuel cells. Similarly, studies on gas reactions at the solid-vapor

New facets for the role of defects in ceramics

interface and kinetic incorporation of protons or ions in oxide lattices have drawn significant attention for engineering electrochemical electrode materials with high stability and efficiency. MD simulations are also used to understand dynamic lattice response of ferroelectric materials under optical excitation or electric bias (Figure 1d).⁸ Research is underway to explore similar approaches to understand defect dynamics.

Showing the way forward—“Good guy” defects

Armed with these techniques, researchers are beginning to reap the rewards of defect control in ceramics. Here we highlight some examples—primarily in the realm of functional electroceramics, including conducting, dielectric, ferroelectric, and magnetic properties—wherein defects are used for good today.

Functional materials and properties

As mentioned earlier, chemical alloying has long been used in ceramics to

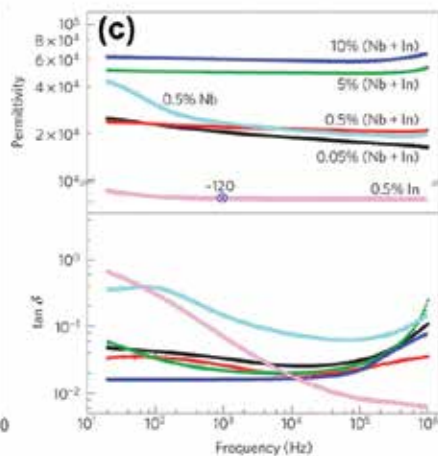
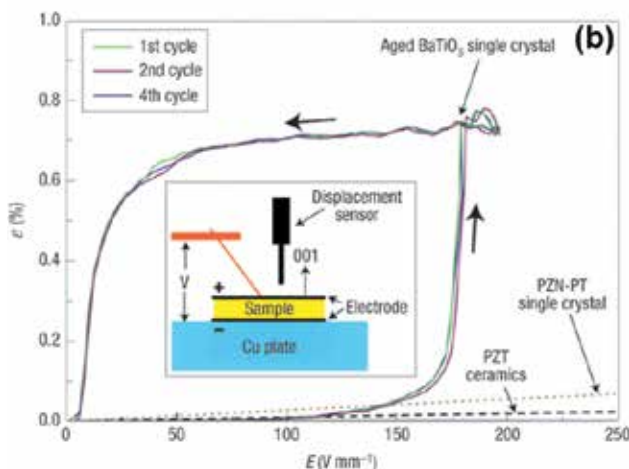
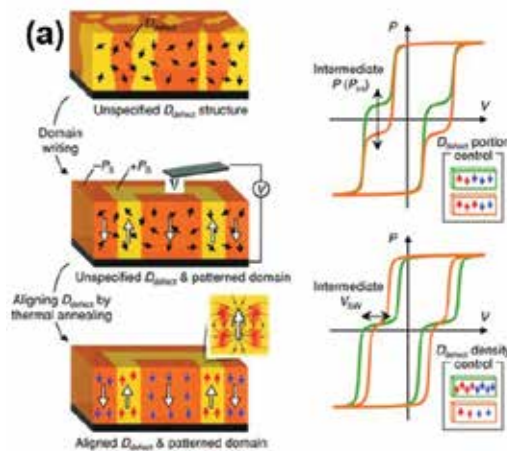
tailor properties, but such approaches have at times been guided by empirical observations and trial-and-error alone. Advances in our understanding and control of how dopants occupy the lattice and affect properties now allow us to do much better even with alloying. For example, amphoteric dopants, or “magic dopants,” choose their site according to nonstoichiometry of the lattice. These dopants are very effective in maximizing the lifetime of base-metal multilayer capacitors.⁹

More recent investigations have focused on controlling the type and concentration of defects beyond chemical dopants and beyond thermodynamic limits. For example, researchers have highlighted unexpected benefits of specific defect types, such as charged point defect complexes (so-called defect dipoles), due to strong coupling of electrical and elastic dipoles of such defects to the lattice and polarization. For instance, defect dipoles in BaTiO₃,

films enhance ferroelectric ordering by inducing additional anisotropic lattice deformation.¹⁰ Energetically preferred alignment of defect dipoles parallel to the polarization direction has also been demonstrated and used to control local polarization switching and to achieve macroscopic double-polarization switching and tri-state memory effects in BiFeO₃ (Figure 2a).¹¹

Defect dipoles have also been used to enhance piezoresponse and achieve large reversible nonlinear electro-strains in BaTiO₃ single crystals by providing a restoring force for reversible domain switching (Figure 2b).¹² Finally, strong correlations between different defect dipoles in systems such as Nb and In co-doped TiO₂ rutile can give rise to large defect-dipole clusters containing highly-localized electrons. These can, in turn, lead to colossal permittivity (Figure 2c),¹³ opening up promising routes to systematic development of new high-performance materials via defect engineering.

Figure 2. (a) Schematic illustration of active control of defect dipoles and associated ferroelectric switching and the resulting double-polarization switching. Adapted from Damodaran et al., 2014.¹¹ (b) Large, recoverable electric-field-induced strain (ϵ) in BaTiO₃ single crystals containing defect dipoles, shown compared to the piezoelectric effect of soft PZT ceramics and PZN-PT single crystals. Adapted from Lee et al., 2012.¹² (c) Dielectric permittivity and loss tangent ($\tan \delta$) of Nb and In co-doped rutile TiO₂ at room temperature. Corresponding properties of 0.5% Nb-only and In-only doped rutile TiO₂ are also given for comparison. Adapted from Ren et al., 2004.¹³



Off-stoichiometric defects also are effective in controlling and enhancing materials response if introduced in a deliberate and controlled fashion. For example, in pulsed-laser deposition of complex-oxide films, changing energetics of the growth process can be used to systematically tune defects. This growth-induced tuning of chemistry can enable fine-tuning and control of structure, dielectric response, and thermal and electrical conductivity, for example in SrTiO₃, LaAlO₃, NdNiO₃, and BiFeO₃ films.¹⁴ Off-stoichiometric defects also play a major role in ionic conduction. For example, manipulating oxygen stoichiometry has been suggested as an effective approach to manipulate the type and magnitude of ionic conduction in La₂NiO_{4+δ}. In addition, because specific cation dopants can interact with

oxygen vacancies/interstitials, they have been thoroughly studied to produce better ionic materials.¹⁵

Ion-bombardment-induced defects, extensively used in semiconductors, have recently been used for property control in ceramics. This includes both intrinsic point defects (formed as a result of collision events and atomic displacements) and extrinsic point defects (formed as a result of implantation of incoming species), as well as their complexes and clusters created beyond thermodynamically defined levels. For example, recent investigations have shown the potential of bombardment-induced defects for order-of-magnitude tuning and control of resistivity, systematic tuning of ferroelectric switching dynamics, enhancement of ferroelectric and piezoelectric responses, and engineering of rewritable domain patterns in ferroelectrics (Figure 3a,b).³⁻⁵ Similar approaches have also created local structural distortions and complex nanostructured magnetic phases in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films (Figure 3c).⁶

Further, extended defects have been used for property control and enhancement. On-demand introduction of planar defects—effectively rock-salt layers in a perovskite matrix (derived from the Ruddlesden-Popper (RP) series)—accommodates nonstoichiometry without the formation of point defects that would otherwise deleteriously dope the lattice with charge that exacerbates electrical losses.² These same RP-type defects can also yield dramatic changes in thermal conductivity and magnetic properties.

Extended defects, along with charged point defects, also play a central role in resistive switching (i.e., electric-field-induced switching between high- and low-resistance states) for memristors. Local modulations and redistribution of defects under the switching field is considered a main mechanism for resistive switching. For instance, extended defects, such as dislocations, could act as short-circuit paths for oxygen transport and drive the material into a macroscopically detectable metallic state. Likewise, domain boundaries wherein defects such as vacancies can accumulate could also give rise to interesting transport properties.

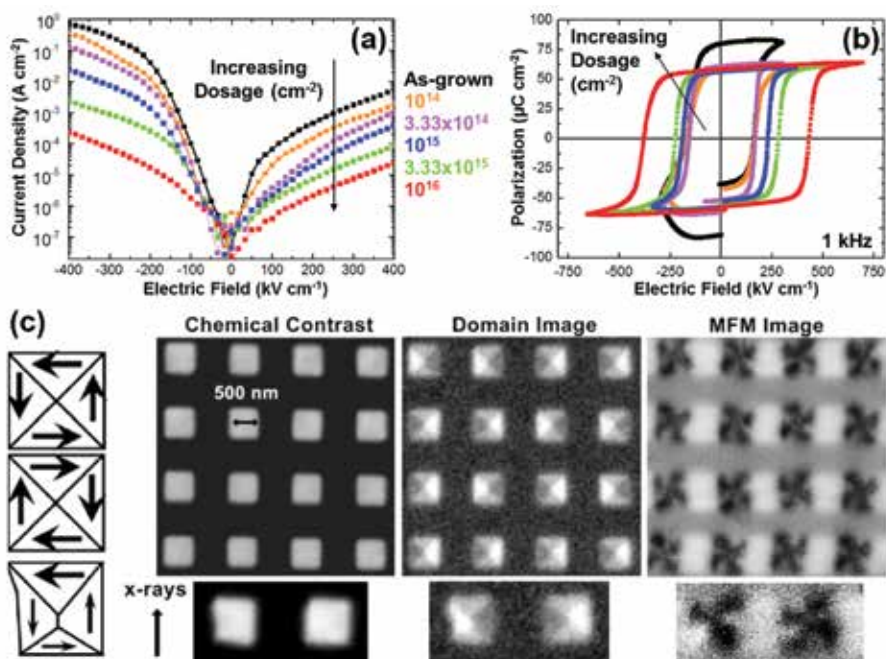


Figure 3. (a) Leakage current density as a function of DC electric field and (b) ferroelectric polarization-electric field hysteresis loops measured at 1 kHz after ion-bombardment with various He²⁺ dosages for BiFeO₃ thin films, showing that purposeful introduction of defects can have marked impact on device properties in a positive manner. Adapted from Saremi et al., 2017.⁴ (c) Schematic of the domain pattern (left), together with X-ray photoemission electron microscopy-based, chemically-resolved (as the Mn-L3 edge, chemical contrast) magnetic domain structure (domain image), as well as magnetic-force microscopy-based imaging (MFM image) of 500-nm-diameter square $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ islands on SrTiO₃ (001) substrates. The lower panel to each image shows effect of distortions of shape of the island. Adapted from Takamura et al., 2006.⁶

Emergent functionalities

Purposely induced defect structures can give rise to physical properties that do not exist in a pristine version of the material. For example, oxygen vacancies are often seen as detrimental to a ferroelectric material, adversely affecting its transport and fatigue properties. In the case of SrMnO₃, however, epitaxial tensile strain is accommodated by oxygen vacancies and leads to formation of a polar state in a non-*d*⁰ system.¹⁶ Similarly, oxygen vacancies have been used to engineer polar displacements in Fe in (LaFeO₃)₂/SrFeO₃ superlattices (Figure 4a).¹⁷ In the case of magnetic materials, there are reports of oxygen-vacancy-driven ferromagnetism in TiO₂, CeO₂, HfO₂, and a host of other oxides. Oxygen vacancies are believed to play an important role in charge redistribution as well as the exchange mechanism, though there is ongoing research and debate into the specifics of this process.

Surfaces and interfaces where periodicity of the crystal lattice terminates are examples of planar defects and have

been the focus of much research. The most celebrated interface in recent years has been the LaAlO₃/SrTiO₃ system, where a 2-D electron liquid arises at the interface between two insulators. The properties of this emergent state are strongly influenced by stoichiometry and point defects.¹⁴ Superlattices also allow creation of a large number of interfaces and novel boundary conditions, allowing us to study new phenomena. Interleaving polar PbTiO₃ with non-polar SrTiO₃ leads to the formation of new polar states, namely improper ferroelectricity driven by octahedral rotations at short periodicities, and polar vortices with continuously rotating polarization at intermediate periodicities (Figure 4b-e).¹ Superlattices of ferroelectric LuFeO₃ and ferromagnetic LuFe₂O₄ give rise to room-temperature multiferroicity with coupling between the two-order parameters (Figure 4f).¹⁸

Functional oxides possess strong coupling among various degrees of freedom, and the resulting complexity provides a veritable playground for exploration of

New facets for the role of defects in ceramics

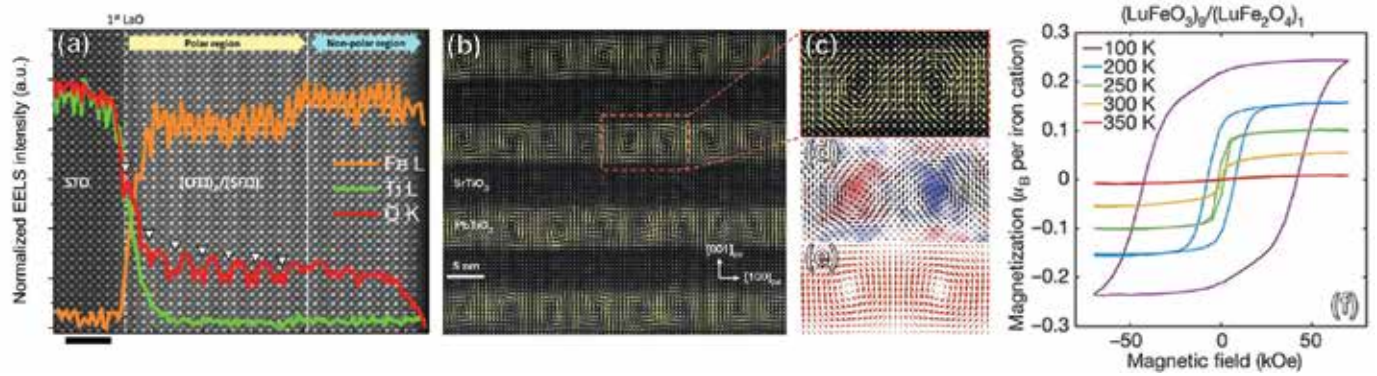


Figure 4. (a) Core-loss EELS of $(\text{LaFeO}_3)_2/(\text{SrFeO}_3)$ superlattice showing oxygen-vacancy ordering (denoted by arrows) in the polar region. Adapted from Mishra et al., 2014.¹⁷ (b) Atomic-displacement mapping from a STEM image of a $(\text{SrTiO}_3)_{10}/(\text{PbTiO}_3)_{10}$ superlattice, wherein polar vortex structures are produced. Zoomed-in view of a pair of left- and right-handed vortices in (c) atomic-displacement maps from STEM; (d) experimentally extracted polarization gradient, wherein red and blue have opposite senses or signs; and (e) phase-field simulations that recover the same structures. Adapted from Yadav et al., 2016.¹ (f) Magnetization versus magnetic field loops for $(\text{LuFeO}_3)_0/(\text{LuFe}_2\text{O}_4)_1$ superlattices at various temperatures, showing that production of interfaces between different materials can drive emergent magnetic effects. Adapted from Mundy et al., 2016.¹⁸

effects driven by competition between various energetic terms affected by defects. For example, SrTiO_3 is an incipient ferroelectric material where the ferroelectric order is quenched by quantum fluctuation. However, ferroelectricity can be induced if Sr-deficient centers are pro-

duced during synthesis (Figure 5a,b).¹⁹ Similar ideas have also been applied to antiferroelectrics such as PbZrO_3 , where a nonpolar phase (antiferroelectric ordering) is only slightly energetically favorable compared to a polar phase (ferroelectric ordering). Under external

electrical fields, phase-competition can be perturbed such that the ferroelectric phase is stabilized. Alternatively, purposely introduced point defects can also tip the energetic balance between two competing phases. In particular, antisite defects (lead atoms occupying B-site positions) can stabilize a polar (ferroelectric) ground state (Figure 5c,d).²⁰

Looking to the future

As we look to the future—and in particular to the role of defects in ceramics—the near-term seems poised for dramatic advances. The work of recent decades in synthesis, characterization, and modeling are now providing unprecedented access to precisely controlled and understood materials. In turn, this opens the door for innovations. As it pertains to defects, we expect advances in several key areas.

Driven by concepts of the Materials Genome Initiative, there is strong interest in high-throughput discovery and design of next-generation materials (see, for example, PyCDT). Methodological advances that now enable the prediction and rapid assessment of complex properties are, in turn, poised to incorporate lessons of defect interactions into the design lexicon. This will enable rapid expansion of functional materials whereby designer defect structures produce new effects. At the same time, this will drive further advances in the control and study of defects. Driven by the desire to produce ever more precise structures with both atoms and a lack thereof placed in deterministic and exact-

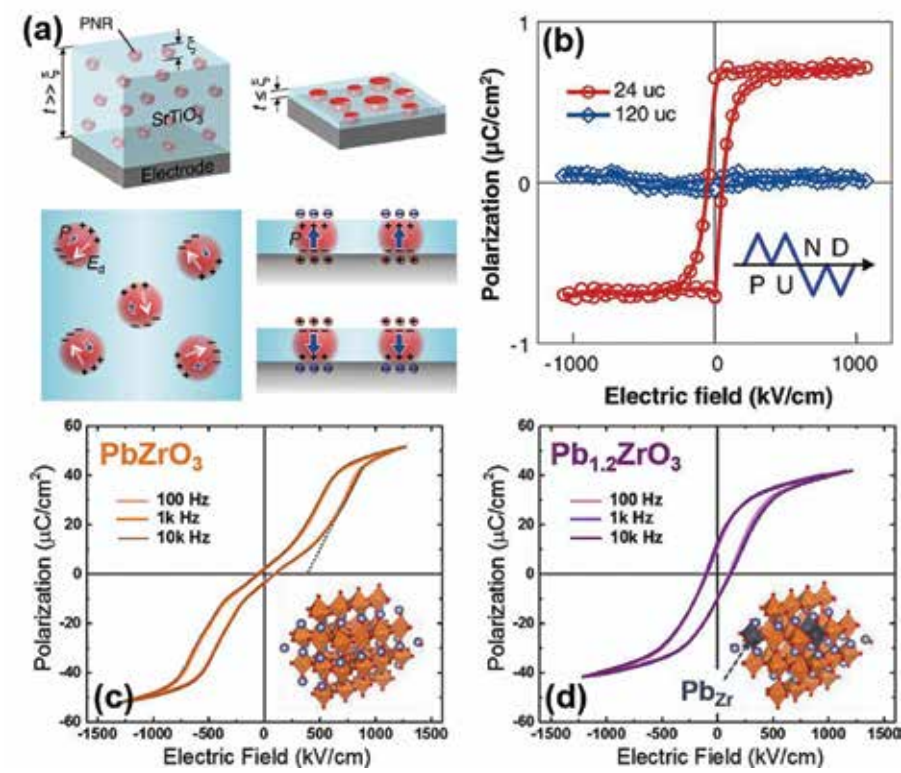


Figure 5. (a) Schematic illustration of the effect of size confinement on polar nanoregions induced by non-stoichiometry in SrTiO_3 . (b) Polarization hysteresis of thin (24-unit cell) and thick (120-unit cell) SrTiO_3 measured using the positive-up, negative-down method. Adapted from Lee et al., 2015.¹⁹ Polarization versus electric field hysteresis loops for (c) PbZrO_3 and (d) $\text{Pb}_{1.2}\text{ZrO}_3$ thin films show classic antiferroelectric double hysteresis loops and a ferroelectric hysteresis loop, respectively. The latter results from presence of lead-antisite defects in the lattice. Adapted from Gao et al., 2017.²⁰

ing manners, experimentalists will continue to strive for ways to create, destroy, place, and move individual defects or groups of defects. Methodologies that leverage advances in aberration-corrected microscopes, scanning-probe microscopy, and coherent light sources all have the potential to provide this control. As a result, we will uncover a new era of materials engineering.

If anything has held true in science and engineering, it is that things that have sounded like science fiction in the past at some point become reality. For decades, defects have been a bad word in materials science—with entire subfields built around controlling and limiting their impact. But as our abilities to interact with materials evolve, such relationships must be reexamined.

Defects in and of themselves are not bad—they possess a set of properties and influences that, when understood and controlled, provide a depth of control and utility that could rival any other factor. Materials science has evolved from controlling materials microstructure to nanostructure to mesostructure. Perhaps the horizon that approaches us now is the era of complete control—placing atoms and using their presence and absence to create structures outside of equilibrium that have properties we have yet to imagine. In the end, defects are already showing their power for good. Further attention to them and to the power they provide scientists and engineers will only open doors for more exciting endeavors. ■

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Innovative concretes provide the ultimate solution for rising construction costs and environmental footprint

By Rouzbeh Shahsavari and Sung Hoon Hwang

Additive methods, nanostructure control, computational modelling, self-healing additives, and renewable byproduct raw materials will help cement scientists engineer stronger and more durable concretes—with less global societal cost.

The global construction industry is expected to grow to \$15.5 trillion by 2030. This rapid growth is boosted by numerous ongoing major construction projects, such as Al Maktoum airport in the United Arab Emirates and Grand Paris Express in France, which each have costs exceeding \$30 billion.¹ The “One belt, one road” initiative proposed by China, which plans to connect more than 60 countries via new infrastructures, is expected to receive a total investment of \$1 trillion.² Further, the American Society of Civil Engineers in 2014 reported a renewal program worth \$3.6 trillion for infrastructure in the United States.³

Worldwide cement consumption has drastically increased since 1926 (Figure 1). Overall, owing largely to the aforesaid high-cost construction activities, initial construction costs as well as maintenance and repair costs for infrastructures are rapidly rising. This is now adding unprecedented pressure on the construction industry to take active yet appropriate measures and make significant changes. Another key concern is energy and environmental footprints—current concrete manufacturing is responsible for 8–9% of global anthropogenic CO₂ emissions and 2–3% of global primary energy use.

Because concrete is the most common building block of today’s infrastructure, cost issues are highly linked with processing and overall properties of concretes. If concrete structures can be placed in large scale without manual labor and in a timely fashion, significant portions of current construction costs, such as labor, can be negated. Further, stronger and more durable concretes under different types of mechanical stresses that ultimately possess a longer service life will significantly reduce the economic cost as well as CO₂ and energy footprint stemming from cement production, in accordance with a “do more with less” approach. Also, incorporating industrial byproducts, such as fly ash, ferrous slag, and silica fume in a concrete design can also help mitigate CO₂ footprint, which arises largely from cement production.

All of the aforementioned approaches, which can relieve the rising cost of global construction activities and related environmental issues, are now receiving a significant boost from technological innovations and recent nanotechnology advances. Self-healing concretes, which may have sounded like surreal science fiction only a few years ago, have recently been tested in construction sites with promising success. CeraTech USA (Baltimore, Md.) has commercialized CO₂-free concretes with zero cement by using industrial byproducts. Now it is undeniable that the construction industry is undergoing a major paradigm shift, and concrete, the most widely used synthetic material in the world, is at the center of the ongoing shift.

Additive manufacturing offers unique opportunities

Additive manufacturing, or 3-D printing, is a key state-of-the-art technology that will revolutionize the construction industry during the next industrial revolution. Additive manufacturing will negate the need for basic construction tools, including molds and physical framework, thereby drastically reducing material costs. This in turn enhances the degree of design freedom to ensure greater creativity during construction. Further, computer-controlled automation can significantly reduce labor costs, as the number of qualified construction workers has been decreasing over the past years. Automation also guarantees a decreased amount of material waste.⁴

The first attempt to apply additive manufacturing on construction sites was made by Shimizu Corporation in the 1980s,

Capsule summary

RISING COSTS

Worldwide cement consumption has increased drastically in the past century, and construction costs, as well as maintenance and repair costs, are rising rapidly. In addition, energy and environmental costs are high—current concrete manufacturing generates 8–9% of global anthropogenic CO₂ emissions and consumes 2–3% of global primary energy.

EMERGING SOLUTIONS

Engineering stronger and more durable concretes with longer service life will significantly reduce economic, energy, and environmental costs of cement production. In addition, incorporating industrial byproducts in concrete designs can also help mitigate the CO₂ footprint of cement production.

SHIFTING PATHS FORWARD

Concrete—the most widely used synthetic material in the world—is at the center of an ongoing paradigm shift. Field testing on construction sites will demonstrate the utility of new approaches to engineering cements. Adoption of new formulations and building techniques could revolutionize the construction industry.

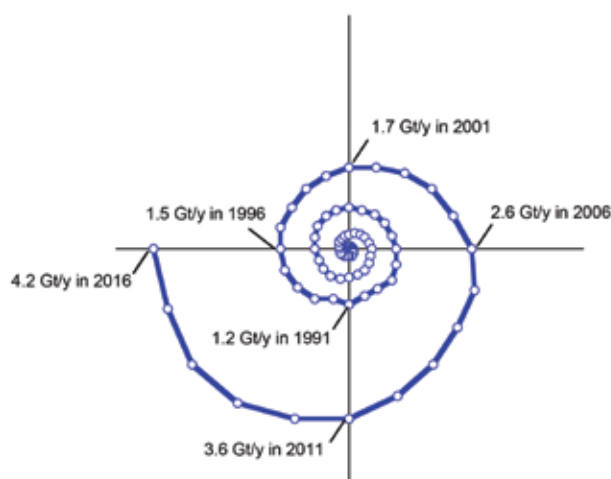
implying that the demand for automation in construction is not something new but existed more than 30 years ago.⁵ In 1997, Pegna implemented laboratory-scale additive manufacturing using sand and Portland cement, illustrating for the first time the prospect of applying automated layer-by-layer fabrication in the construction industry.⁶ The technique alternatively deposited uniform layers of sand and a patterned layer of Portland cement, using steam to cure the cement. The as-created structure with controlled cavities exhibited promising mechanical properties compared to conventional concretes.

Since then, there have been myriad successful efforts to create small-scale, individual building elements via additive manufacturing. Nevertheless, we have yet to observe ubiquitous on-site application of 3-D printing to construct large-scale houses or high-rise buildings. Contour crafting is one of the major 3-D printing techniques that has been developed for large-scale construction.⁷ A nozzle attached to an automated crane extrudes cement paste layer-by-layer, with top and side trowels on the crane finishing the surface with unprecedented quality. Owing to its advantages, such as ease of transport and preparation of building materials on-site, contour crafting is expected to provide shelters at natural disaster sites within the next couple of years.⁸

Concrete printing is also an automated technique that carries out extrusion-induced layer-by-layer fabrication using concrete. The technique has been developed and applied at Loughborough University in the United Kingdom to create various architectural pieces with large complexities, such as a wall-like artifact that features 128 total layers and 12 voids for reinforcement.⁹ A major advantage of concrete printing lies in the significantly enhanced degree of design freedom.

Owing to consistent efforts to apply automated additive manufacturing to large-scale construction, 3-D printing in construction is now entering a new era of practical applications. For example, researchers now have employed extrusion-based 3-D printing to create a 512 ft² concrete-based barrack for the U.S. Army.¹⁰ As in contour crafting described earlier, the work involved in situ preparation of concrete materials, thereby confirming the prospect of using the technique to create a protective hut during military operations. Also, Construction Robotics (Victor, N.Y.) recently developed a brick-laying robot, the Semi-Automated Mason, which can lay 3,000 bricks per day—a rate six-times higher than a human worker.¹¹ This robot is expected to replace manual labor within the next couple of years.

World Cement Production from 1926 to 2016 (Gt/y)



Credit: Dr. Paulo Monteiro, University of California, Berkeley

Figure 1. World cement consumption since 1926.

Enhancing concrete by improving material properties

Additive manufacturing aims to reduce time and cost and endow construction designs with greater creativity. In other words, it is about improving the “processing” stage of concretes, but it is not linked to improving their intrinsic material properties. To achieve the latter, advances in nanofabrication techniques and nanomaterial characterizations come into play. One definitive strategy to mitigate the environmental footprint and economic cost associated with use of concretes is simply enhancing their mechanical properties, which will in turn extend service life. The question is if modern science, typically known as nanoengineering, can play a critical role in improving the mechanical properties of concretes.

Nanofabrication techniques are typically divided into “top-down” or “bottom-up” approaches depending on reaction pathways. For improving concrete mechanics, bottom-up fabrication, where nanoscale building blocks are assembled to synthesize a larger product, is more relevant. The fundamental, strength-giving building blocks of concretes are calcium-silicate-hydrate (C-S-H), which is present as nanoscale particle aggregations.¹² C-S-H is semi-crystalline, lacking long-range order, and occupies 60% of total mass of cement paste.¹³ It also is nonstoichiometric with varying proportions of calcium, silicon, and hydrate ions. No universal structure exists for C-S-H up

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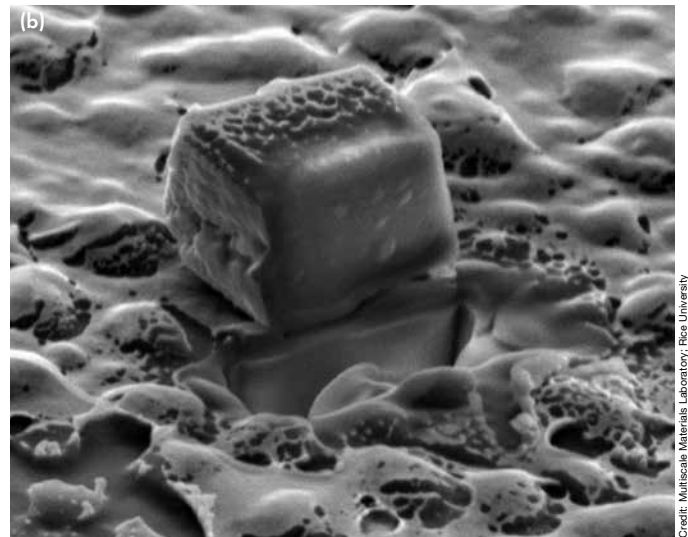
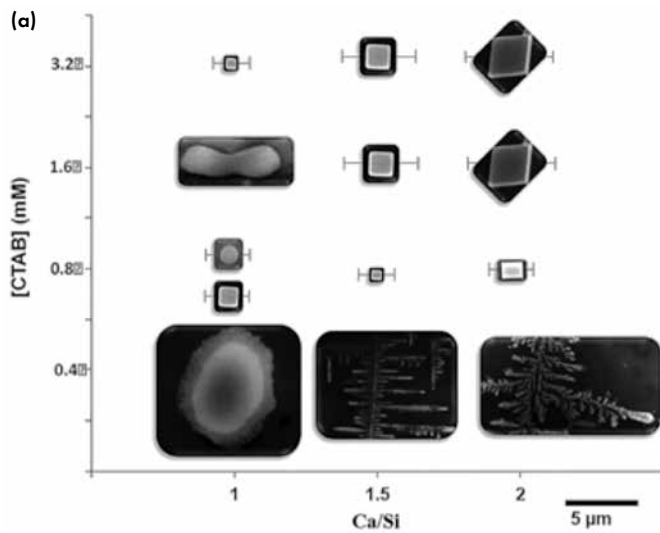


Figure 2. (a) Morphogenesis of cement hydrate. (b) Rectangular C-S-H produced via an ultrasonication-assisted method.

to this point, but several different models based on crystalline analogs have been proposed.^{12,14}

The general notion is that the C-S-H structure resembles that of the layered mineral tobermorite, which comprises parallel silicate chains with calcium ions between them. Considering that C-S-H is the major strength provider for concretes, there are ongoing efforts to synthesize C-S-H in the laboratory, tune its properties at a microscopic scale, and assemble it via bottom-up engineering to ultimately develop mechanically-enhanced concretes.

For example, Ca/Si molar ratio is an important chemical property that defines C-S-H. Pelisser et al.¹⁵ synthesized C-S-H with different Ca/Si molar ratios and performed nanoindentation, a technique often employed to probe mechanical behavior of nanomaterials. The authors concluded that a lower Ca/Si molar ratio enhances nanoscale and microscale mechanical properties.

In addition to chemical properties, structural morphologies of C-S-H can be fine-tuned to improve mechanics at multiple length scales. Our group recently attained comprehensive morphological control of C-S-H, whose shapes can be systematically varied from irregular to dendritic and, finally, to well-defined cubic (Figure 2).¹⁶ Naturally-formed calcite particles form cubic seeds, providing facile routes for nucleation and semi-epitaxial growth of C-S-H. Subsequent mechanical testing proved that the well-defined cubic morphology benefits mechanical properties at multiple length scales from a single particle to assembled states. This suggests that controlling the morphology of concrete nanoparticles can ultimately induce enhanced mechanical properties of concretes.

Because the major shortcoming in mechanical properties of concretes is high brittleness, research has also applied biomimetic approaches based on the structural ensemble of organic and inorganic components to C-S-H. Inspired by natural materials such as nacre, where a small fraction of organic components remarkably enhances mechanical toughness,¹⁷ a significant number of efforts have been directed towards combining inorganic C-S-H with soft, organic polymers.¹⁸ In fact, adding polymer-based plasticizers during concrete mixing is a common practice to enhance workability.

Orozco et al.¹⁹ identified the nature of interaction between

C-S-H and polycarboxylate-based superplasticizers with silyl functionalities and found that the two components interact via combination of ligand-type interactions and covalent bonding. Nevertheless, such C-S-H-polymer composites naturally created by adding polymer-based plasticizers to wet concrete mixtures do not contain an ordered microstructure, where C-S-H and polymer are structurally coordinated with each other in an orderly manner.

The first successful attempt to intercalate polymer within the basal spacing of synthetic C-S-H was made by Matsuyama, who successfully incorporated polyvinyl alcohol during the precipitation process.²⁰

Power of modelling

So far, only experimental techniques for fine-tuning properties of C-S-H have been discussed. In fact, theoretical simulations have played immense roles in decoding the relationship between structure, composition, and mechanical properties of C-S-H over the past decade. Our group performed atomistic simulations on tobermorite and jennite, two mineral analogs of C-S-H, to ascertain their anisotropic mechanical properties.²¹ We found that unlike the common intuition that a layered direction serves as the weakest link in layered crystals, such as tobermorite and jennite, inclined regions forming a hinge mechanism are the softest parts.

Later we employed a combination of three distinct types of modelling techniques—atomistic simulations, Monte Carlo, and molecular dynamics (MD) techniques—to propose for the first time a realistic structural model for C-S-H.¹² The authors started by applying a Ca/Si ratio (1.7) and density (2.6 g/cm³) of C-S-H acquired from experiments as compositional constraints for modelling. This solved potential accuracy issues associated with using perfectly crystalline tobermorite or jennite as a model system for C-S-H, since their Ca/Si ratios deviate from experimental values. Qomi et al.²² created an impressive database of atomic configurations for C-S-H with specific defect attributes, each of which results in distinct mechanical properties. This in turn allows selection of structural configurations with optimum mechanical properties.

MD methodology is particularly useful for simulating an ensemble of thousands of atoms, a scale that cannot be modelled using first principles quantum simulations. Therefore, MD has been particularly useful for simulating the macroscale response of C-S-H to a variety of mechanical stresses.²³⁻²⁵ Tao et al.²⁶ recently employed tobermorite as a model system for C-S-H and studied its global deformation under tension, compression, and shear loading as well as local deformation under nanoindentation. The authors found that mechanisms for global deformation are governed by displacive and diffusive mechanisms, while local deformation under nanoindentation exhibits size-dependent mechanical behavior.

Further, Zhang et al.²⁷ performed more than 600 MD simulations using C-S-H-FF potential²⁸ and found that the inclusion of portlandite particles or nanoscale voids induces higher toughness for C-S-H, thereby proposing useful experimental strategies to enhance concrete toughness. The same groups of authors performed several simulations on dislocations within cement crystals²⁹⁻³¹ and found that screw dislocations within the layered structure of C-S-H can serve as a bottleneck during shear loading, thereby impeding interlaminar gliding (Figure 3).³² This relieves stress and increases toughness in contrast to the conventional, logical perception that a defect is detrimental to mechanical properties of a material.³³

Cracking down on concrete with self-healing strategies

All above strategies are important recipes to improve the mechanics of concrete and “to do more with less”—thereby reducing concrete’s environmental and energy footprints. Another way is to reduce maintenance costs. This can be achieved by developing self-healing concretes. Since microcracks are the major culprit for increased water and chloride penetration, they exert detrimental effects on concrete integrity. Further, small-scale cracks, if left untreated, can rapidly propagate and coalesce together, ultimately leading to catastrophic failure of the entire structure.

Due to inherent high brittleness, concretes are highly susceptible to microcrack formation, which favors ingress of water and other harmful ions, including chloride and sulfates. Penetration of the aforesaid chemicals can be a major cause of corrosion of reinforcing bars within concrete structures. In light of potential dangers brought upon by microcracks, researchers have proposed a variety of self-healing strategies that enable concretes to self-detect and independently undergo healing processes.

The concept of self-healing concretes can be divided into two types of mechanisms at large. One mechanism is autogenous healing, which relies on natural healing of concrete in the presence of water.³⁴ Examples include hydration of unreacted cement particles and carbonation of calcium hydroxide to produce calcium carbonate minerals. Also, partial replacement of cement with fly ash can trigger similar healing processes, as unreacted fly ash particles can react with water at late ages.³⁵ The other type of mechanism is autonomous healing, where external agents are incorporated into concretes and actively participate in the healing process.

Since autogenous healing is often constrained to cracks with

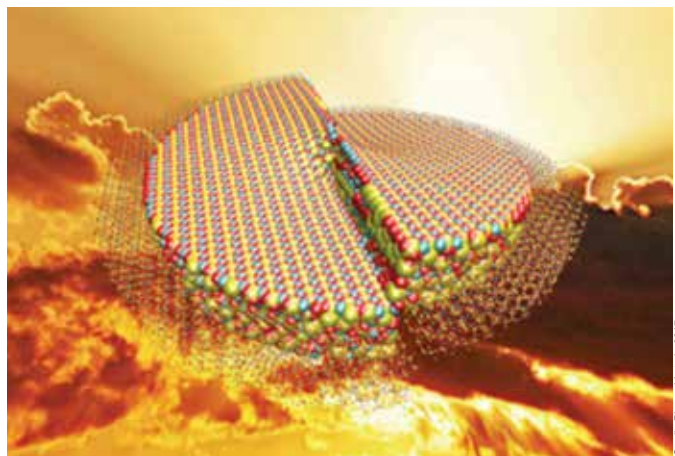


Figure 3. Illustration of a screw dislocation created in a computational model of tobermorite.³²

limited widths (<100 μm) and is only effective when sufficient moisture is present, a greater proportion of recent research efforts has been devoted to autonomous healing.³⁴ The idea of autonomous self-healing for concretes was initiated more than 20 years ago, when Dry et al.³⁶ employed hollow glass tubes filled with healing agents as extrinsic agents. The design ensured that formation of a crack fractured the glass tubes, mimicking self-healing of human skin where a complex network of blood vessels exists underneath the skin.

Since then, one of the most classical and most-attempted approaches has been a capsule-based approach, where nanocapsules or microcapsules containing organic self-healing agents are incorporated into concrete. Capsules in pathways of crack propagation rupture, triggering release of the capsules’ inner contents and initiating self-healing processes. Outer shells of the capsules are typically composed of polymer-based materials, including silica, poly(urea-formaldehyde), poly(melamine-formaldehyde), and poly(urethane). Self-healing agents, including sodium silicate solution, epoxy resin, and methylmethacrylate, occupy core regions.³⁷

Nevertheless, this capsule-based strategy suffers from critical shortcomings, such as intrinsic properties of matrix materials compromised upon the addition of large volumes of capsules and low survival rate due to vigorous mixing and highly alkaline conditions.

Some researchers have avoided those challenges by developing self-healing coatings for concrete surfaces or steel rebar. Chen et al.³⁸ developed a self-healing epoxy coating for concrete rebar by encapsulating tung oil in poly(urea-formaldehyde) microcapsules, because tung oil polymerizes simply upon exposure to air. The coating not only provides enhanced resistance against corrosion, but also induces better bond strength between the rebar and concrete. Song et al.³⁹ also developed a similar protective, self-healing coating for the surface of concrete by encapsulating photoresponsive monomers and initiators in urea-formaldehyde capsules. The capsules successfully incorporate into an epoxy coating matrix and polymerize after induction with natural UV light from the sun, opening the door toward new opportunities for self-healing capsules in concretes.

In addition to capsule-based strategies, bacteria-based self-healing concretes are another proposed approach. Jonkers and colleagues⁴⁰ mixed alkaline-resistant bacterial spores along with

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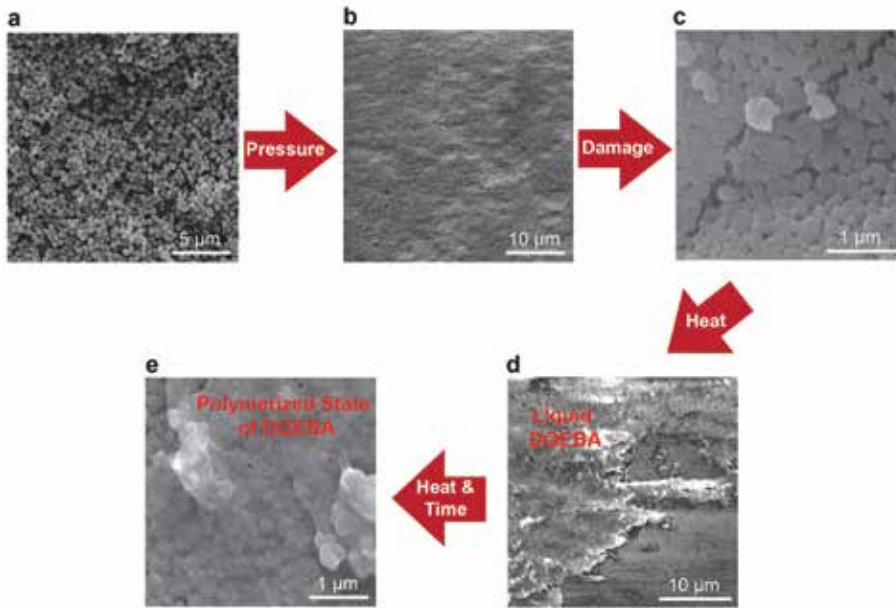


Figure 4. Sequential mechanism of self-healing. (a) Mixture of sealant-loaded calcium-silicate porous nanoparticles. (b) Top-most surface of the sealant-loaded tablet, created using pressure-induced assembly. (c) Nanocrack created under flexural mechanical loading. (d) Release of liquid epoxy resin DGEBA onto top-most surface at the initial stage of heating. (e) Polymerized DGEBA on the top-most surface.⁴³

calcium lactate into cement pastes and showed that the bacteria can catalyze formation of calcium carbonate minerals, which can plug cracks. Calcium carbonate is first formed from the metabolic conversion of calcium lactate catalyzed by bacteria. This conversion produces carbon dioxide as a byproduct, which further reacts with portlandite to generate more calcium carbonate minerals.

Despite novelty of a concept that exploits the chemical environment of concrete rich in portlandite, this bacteria-based approach faces similar problems as polymer-based capsules. A large proportion of bacterial spores are destroyed by rigorous mixing and high alkalinity. Consequently, numerous follow-up investigations have focused on immobilizing bacterial spores in a protective medium prior to addition to cement paste. For example, Wiktor et al.⁴¹ immobilized bacterial spores in porous expanded clay and showed that the self-healing system can heal up to 0.46-mm-wide cracks in concrete, while normal concrete can only heal 0.18-mm-wide cracks. Since then, bacterial spores have been encapsulated in a variety of core-shell type capsules, including silica gel, polyurethane, and microcapsules, to enhance their viability inside concretes.⁴²

A myriad of other unique self-healing

approaches has been proposed and tested. Very recently, our group devised a novel strategy to synthesize strong, tough, and self-healing cement⁴³ integrating soft and hard components within scaffolded universal porous building blocks, mimicking naturally strong and tough materials.⁴⁴ The composite system is comprised of calcium-silicate porous nanoparticles with unprecedented monodispersity over particle size, particle shape, and pore size, which facilitate effective loading and unloading with organic sealants—resulting in a 258% and 307% increase in indentation hardness and elastic modulus of the composite, respectively. Further, heating the damaged composite triggers controlled release of nanoconfined sealant into the surrounding area, enabling recovery in strength and toughness (Figure 4).

Prompted by the advent of novel strategies, self-healing concretes have recently begun taking major steps towards applications on actual construction sites. In 2015, one site integrated three distinct self-healing strategies—adding shape memory polymers, embedding a blood vessel-like network of healing agents, and incorporating extrinsic carriers containing organic healing agents or bacteria—into a single system and tested its on-site viability.⁴⁵ Initial successful on-site trials have

led to a more recent project that received an investment of £4.7 million.⁴⁶

New recipe: Adding recycled industrial waste

Another approach to reduce production of Portland cement is addition of recycled industrial wastes, including fly ash, iron and steel slag, rice husk, and silica fume. Since they are byproducts of the world's biggest manufacturing, food, and energy industries, these industrial waste products have large availability and resultant low costs.

U.S. production of ferrous slag, a major byproduct of the iron and steel manufacturing industry, reached 20–50 million tons in 2016.⁴⁷ During the same time, worldwide production reached 460–600 million tons. Ferrous slag is rich in calcium oxide and silica and can be used as an aggregate or partial replacement of cement.⁴⁸ Further, Osborne et al.⁴⁹ found that replacement of 70% (by mass) conventional Portland cement with blast-furnace slag enhances chemical resistance of the resultant concrete against sulfates, chlorides, and water. Slag also reduces heat release as well as rate of temperature increase, thereby decreasing the chance of detrimental thermal cracking.

In addition to use as an alternative binder, its exploitation as a new type of aggregate offers additional benefits compared to conventional counterparts, such as limestone aggregates. Slag-based aggregates are particularly effective in enhancing fracture toughness of concretes and reducing occurrence of alkali-silica reactions, which degrade mechanical integrity of concretes.⁴⁹ Slag can also serve as useful aggregates for stone mastic asphalt mixtures, thereby improving high-temperature properties and enhancing resistance to low-temperature cracking.⁵⁰

Fly ash is another coal combustion byproduct with proven capabilities as a binder material. As with slag, its annual production exceeds 100 million tons in India and China, offering opportunities for use as a low-cost, environmentally friendly binder.⁵¹ It is already highly established in construction markets as a supplementary cementitious material, which partially replaces Portland cement and offers a plethora of benefits, such as improved

Credit: Hwang et al., 2017

durability, enhanced late-age strength, and reduced bleeding.⁵² Because the current replacement level is ~20–30% by mass in a typical concrete design, there are active ongoing research efforts to achieve 100% replacement to completely solve environmental concerns associated with cement production.⁵³ CeraTech USA received an Environmental Production Declaration for its trademarked product ekkomaxx in 2014 for achieving virtually zero carbon footprint with 95% fly ash and 5% liquid binder.⁵⁴

The future of concrete

Owing to global construction activities with high capital costs and rapidly rising construction markets, including China and India, rising construction costs and CO₂ footprint have evolved into societal concerns. Scientists now realize that the major key to solving those problems lies in enhancing properties of concretes, the most commonly used infrastructure material. In this context, decade-long efforts are finally reaping fruits, with 3-D printing successfully constructing large-scale houses and self-healing concretes being tested on actual construction sites.

Nevertheless, there remain limitations that need to be overcome to ensure those successes eventually evolve into ubiquitous future applications. For example, there exists a large knowledge gap between properties of C-S-H produced on a laboratory scale and macroscale behavior of hydrated cement. C-S-H is indeed the major product of cement hydration, ultimately responsible for mechanical strength of concretes. However, the overall properties of concretes do not rely solely on the behavior of C-S-H, but arise from a complex interplay between multiple hydration products, including but not limited to portlandite, C-S-H, and calcite. Therefore, there should be constant efforts to apply state-of-art nanomaterial characterization techniques to decode the link between microscopic behavior of C-S-H and real phenomena observed at a macroscale of cement hydration.

This also signals the importance of inventing new simulation techniques to correctly describe the interplay

between various hydration products at a larger scale than is possible with the likes of atomistic simulations or MD. In this context, current global trends in big data, computational materials science, and artificial intelligence (e.g., machine learning), when combined with advanced experiments, can perhaps provide the most promising strategy to streamline the processing–structure–property design landscape. Broadly, mimicking the promises of emerging hybrid nanomaterials,^{55–57} other strategies such as creating hybrid cementitious materials,^{58–61} also will be important to create innovative multifunctional construction materials (e.g., with high thermal, electrical, and mechanical properties), offsetting cost and environmental footprint of secondary materials, thereby making innovative concretes an ultimate solution to rising construction costs and environmental concerns.

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National Science Foundation CAREER awardees in Ceramics: Class of 2017

By Lynnette D. Madsen

Three junior faculty showcase the research and engagement activities that make them exemplary teachers–scholars.

The National Science Foundation's Faculty Early Career Development (CAREER) program supports junior faculty who exemplify the role of teachers–scholars through excellent research and education. The purpose of this NSF CAREER award series is to give these junior professors and their work better visibility in the ceramics and glass community and to inspire academic careers of ceramic researchers and educators.^{1–8} Incoming junior faculty sustain and grow the field—they are indeed the future as well as the guardians of the future. Therefore, it is my honor to present the three 2017 CAREER awardees from the Ceramics Program of the Division of Materials Research at NSF.

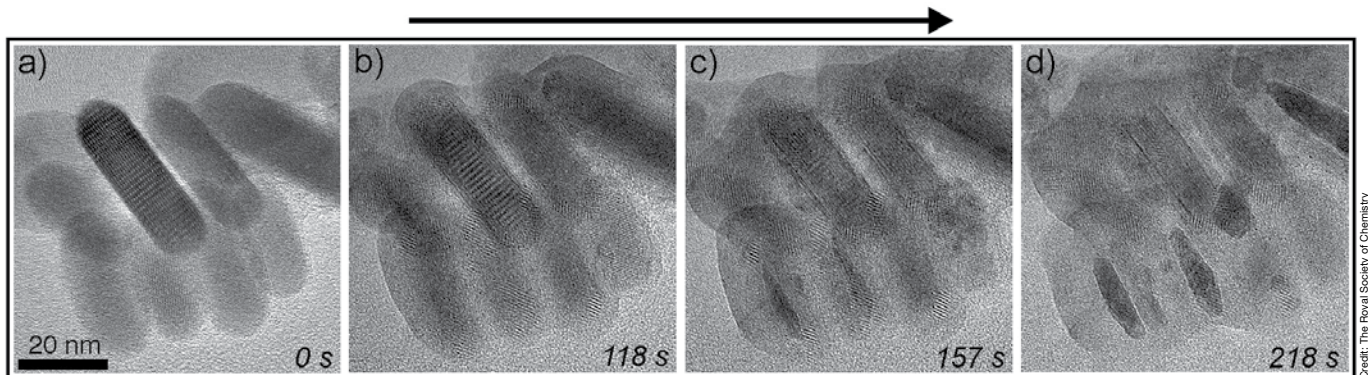
MATTHEW MCDOWELL, Georgia Tech Research Corporation — Award 1652471

Matthew McDowell's CAREER project focuses on interfacial transformations in ceramic ion conductors for solid-state batteries. Interfacial transformations and instabilities at ceramic electrolyte interfaces in alkali metal-based solid-state batteries often increase impedance and reduce cycle life. The goal of this project is to understand the spatiotemporal evolution of structure, chemistry, and morphology of ceramic electrolyte interfaces within solid-state batteries and to determine how these factors influence ionic conductivity and stability of ceramic electrolytes.



Matthew McDowell in his laboratory at Georgia Tech.

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This series of *in situ* transmission electron microscopy images show the reaction process of Cu_2S nanocrystals with sodium. These nanoscale images reveal the phase transformation process that occurs when these materials are used in batteries. a) A group of pristine Cu_2S nanocrystals. b-c) The reaction proceeds via growth of Na_2S shells with lighter contrast at particle edges. d) Fully reacted particles feature Cu metal cores surrounded by a Na_2S network. Adapted from article M. G. Boebinger, M. Xu, X. Ma, H. Chen, R. R. Unocic, M. T. McDowell *J. Mater. Chem A*, 5, 11701-11709 (2017) with permission from The Royal Society of Chemistry.

To improve lifetime and stability, this research uses novel experimental techniques to understand interface degradation processes in real time and to determine how to protect these interfaces from degradation. Multiple *in situ* experimental techniques probe nanoscale transformations at ceramic electrolyte/alkali metal interfaces before and during battery operation and examine the influence of tailored protection layers on interfacial transformations.

Broader impacts include:

- A fundamental understanding is critical for creation of reliable, long-lasting solid-state batteries. Rechargeable solid-state batteries could be used in electric vehicles and mobile applications that demand improved safety (in comparison to lithium-ion batteries). By directly revealing nanoscale transformations at ceramic electrolyte interfaces for the first time, this research helps create a scientific foundation for stabilizing critical interfaces in next-generation solid-state batteries, thereby enabling superior energy storage technologies.
- Graduate and undergraduate students will receive training in the science of materials for energy applications.
- Collaboration with a high school teacher to develop a new high school curriculum focused on integrating materials and energy sciences in ways that are relevant to high school students' daily lives. These new learning tools will better prepare high school students

from underrepresented groups for careers in science and engineering.

LUIZ JACOBSON, Clemson University – Award 1653016

Luiz Jacobsohn's CAREER project targets engineering of electronic defects in inorganic luminescent materials. The performance of scintillators and dosimeters is related to, among other things, the presence of electronic traps that correspond to localized energy levels

within the band gap that are generated by defects, such as vacancies, interstitials, and impurities. This project is the first comprehensive investigation to relate characteristics of luminescent materials, such as chemical composition and crystallographic structure, to specific characteristics of electronic traps. Within this context, the goals of this project include investigating relationships between the structure of families of materials and dopants with characteristics of their



Luiz Jacobsohn prepares a custom-designed spectrofluorometer for a round of measurements at his laboratory, The Light Factory, at Clemson University.

electronic traps and their luminescent/scintillating properties, as well as guided discovery of new compositions and development of luminescent materials in diverse forms to address scintillating and dosimetric needs. Given the serendipitous nature of the discovery of scintillators and dosimeters to date, this project offers an innovative and transformative approach toward engineering electronic traps in luminescent materials to guide discovery, create functionality, and enhance performance of dosimeters and scintillators.

Broader impacts include:

- Discovery and development of more efficient sensors for ionizing radiation. In addition, advances in luminescence affect applications such as electronic screens, lighting, and medical imaging.
- Undergraduate and graduate students will receive training in cutting-edge research methods and techniques related to synthesis, processing, and characterization of inorganic luminescent materials.
- A cooperation among high school, undergraduate, and graduate students, including the Luminescence Across Borders (LAB) summer program at Clemson University, will integrate research, training, and education.
- Developing resources and strategies to incorporate fundamental materials science and engineering concepts into science classes will enhance the educational infrastructure of high schools in South Carolina. In addition, these activities will increase students' visibility of materials science and engineering careers.

JESSICA KROGSTAD, University of Illinois at Urbana-Champaign – Award 1654182

Jessica Krogstad's CAREER project focuses on achieving enhanced ferroelastic toughening in electroceramic composites through microstructural coupling. Experimentation is establishing a fundamental relationship between otherwise stochastic morphological features and intrinsic toughening mechanisms to systematically design highly durable, ferroelastic/ferroelectric functional composites. Ferroelastic switching is one of



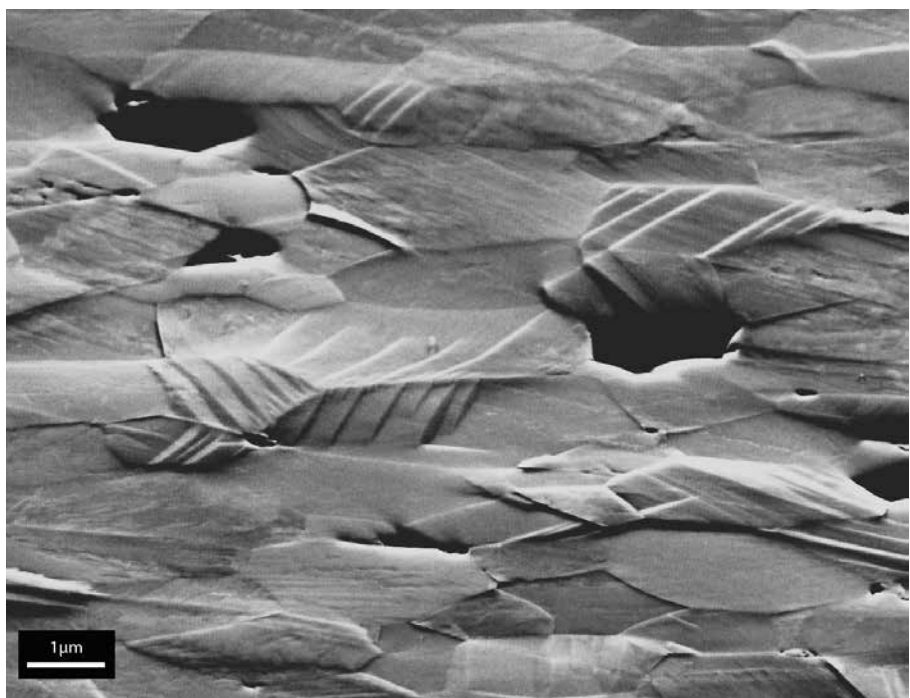
Credit: Caitlin McCoy, University of Illinois Urbana-Champaign

Jessica Krogstad in her lab in the Frederick Seitz Materials Research Laboratory in Urbana, Ill.

a limited number of intrinsic toughening mechanisms available for advanced ceramics, yet it is not fully utilized due to a largely uncharacterized relationship among localized morphological features, efficient activation of domain nucleation and motion, and resultant improvements in toughness. By bridging this gap using in situ microscopy and targeted micromechanical probes, this research provides the foundation for accelerated physics-based design of more durable ceramic composite systems.

Broader impacts include:

- Better functionality in a wide range of advanced applications, including superconductive wires in supercomputers, precise gas sensors in automotive exhaust, and tilt sensors in consumer electronics. New perspectives are being generated on fundamental mechanical responses within a class of electrical ceramics necessary to enhance durability without sacrificing electrical performance. Accelerating development of new electroceramic materials and



Credit: Krogstad group, unpublished data

Twining is one of few mechanisms capable of accommodating permanent deformation in ceramics. In this example of a polycrystalline tetragonal zirconia ceramic, the bands are twins induced by a nearby crack that contribute to enhanced toughness.

National Science Foundation CAREER awardees in Ceramics: Class of 2017

material systems could dramatically expand the existing limits of performance and durability.

- Training to prepare graduate students for a more digitally-reliant materials science industry, with state-of-the-art characterization and processing methods in combination with data-driven integrated computational materials engineering.

- Cross-curriculum integration of industrially relevant computational tools into undergraduate material science and engineering courses.

- Exploration of mentoring as an approach to increase work force diversity and appreciation of diversity by working with the week-long summer camp for high school students, Girls Learning about Materials (GLAM).

Closing remarks

A CAREER award is a defining step for these researchers, and it identifies them as emerging world leaders in their respective fields. The junior faculty supported through these NSF awards in this Class of 2017 hope to:

- Provide valuable contributions to their research fields;
- Consolidate and increase visibility of their research groups;
- Establish a reputation for impactful research disseminated through publications, presentations, and new collaborations;
- Transform the community's understanding of dynamic processes in ceramic materials, thereby enabling development of material systems;
- Reach out to schools and attract young students to a professional career in science and technology;
- Engage and develop thoughtful and creative students who are excited about ceramics and materials science; and
- Educate, train, and prepare the next generation of engineers and scientists to tackle important societal challenges in connection with energy and the environment.

Ceramic and glass research is in an exciting era. To realize the full potential of these unique materials, we celebrate rising professors who are undertaking fundamental research and educating the next generation.



Attendees of the 2017 Professional Development Workshop in Ceramics.

Professional Development Workshop Series

Geoff Brenneka (Colorado School of Mines), Hui (Claire) Xiong (Boise State University), and Liping Huang (Rensselaer Polytechnic Institute) organized a 2017 Professional Development Workshop in Ceramics (1734055), which took place in conjunction with the 12th Pacific Rim Conference on Ceramic and Glass Technology in Hawaii. Similar workshops were held annually from 2011 to 2014. In all cases, NSF provided support so that participants were not charged registration fees for the workshop. Early-career faculty, post-doctoral associates, senior graduate students, and senior faculty interested in mentoring were encouraged to attend these open workshops. The goal of the workshops is to enhance career development of the next generation of future leaders in ceramic materials research and education.

This 2017 workshop focused on early-career faculty who were awarded NSF CAREER grants in 2015 or 2016 from the Ceramics Program in the Division of Materials Research. The intensive two-day workshop brought together targeted technical panels of international experts from the awardees' chosen research specialties in a forum that promoted professional discussions, mentoring, and networking. The panel's feedback impacted research and training, broadened exchange of best practices for training and teaching, and forged new relationships for collaborative research and mentoring. In addition, there were sessions on mentoring success stories, avoiding common pitfalls of junior faculty, navigating the tenure track, work-life balance, and the future of ceramics research and education. The workshop series provides a strong basis for all attendees to better succeed as outstanding researchers and educators, and thereby it strengthens the broader ceramic materials research community.

Planning is underway for the next workshop in the series by Candace Chan of Arizona State University. Expressions of interest or ideas can be sent to Chan at candace.chan@asu.edu.

About the author

Lynnette D. Madsen has served as program director, Ceramics Program, at NSF since 2000. Contact her at lmadsen@nsf.gov.

Acknowledgements

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Does your company export? U.S. Commercial Service can help

Looking at boosting your bottom line by making new sales abroad? The United States Commercial Service of the Department of Commerce's International Trade Administration can assist. With 108 offices across the U.S. and in U.S. embassies and consulates in more than 75 countries, the U.S. Commercial Service helps U.S. companies export and looks out for American business interests abroad.

With more than 95% of the world's consumers outside of the United States, businesses cannot afford to miss out on international opportunities. How about your firm—are you leaving money on the table by not exporting? In today's competitive global economy, if a company is not exporting, it is highly likely its competitors are or will be selling internationally. Don't be left behind.

As thousands of exporters can attest, selling internationally is important because it enables them to diversify their portfolios and weather changes in both the domestic and world economies. So, by spreading risk, it boosts competitiveness and bottom line.

Contrary to what many people think, it is not just the big companies that export. By far, the vast majority of exporters—some 98%—are small- and medium-sized businesses (with fewer than 500 employees). Yet we know that only a very small share of businesses export. Moreover, nearly 60% of all current exporters only sell to one foreign market, so many of these firms could boost exports by expanding the number of countries they target.

Many smaller businesses do not export because they believe it is too burdensome, are not sure how they will get paid, or are unaware of available export assistance. However, exporting does not have to be burdensome. The internet, improved transportation logistics, free trade agreements, and an array of export assistance from the U.S. government and its partners have greatly streamlined the export process.

Are you export ready?

To become export ready, companies should have a long-term perspective and top management commitment. Exporting can be rewarding but challenging, and businesses need to be in it for the long haul. Also, a track record of successful selling in the domestic market is very helpful. Companies also need to assess their internal resources for doing business abroad.

International trade specialists with the U.S. Commercial Service can help because the value of assistance is tailored to individual needs of the company. Basic export counseling is our bread and butter, but the scope can vary greatly. Becoming export-ready also includes developing a solid export plan, and our trade experts can assist.

Services tailored for exporters

As noted earlier, there is no “one-size-fits-all” when it comes to export assistance—each company has unique needs. So whether a business is new-to-export or looking to hone an existing export plan, U.S. Commercial Service can help.

For example, one company may need market-entry strategies for multiple markets, while others may be dealing with regulatory, documentation, and customs issues for certain countries. Sometimes our business clients need help understanding U.S. export laws for high-technology products or how to use free trade agreements. We do market research on economic and industry

trends in key sectors for many markets, much of which is available through our “Country Commercial Guides.”

Our trade experts also help U.S. exporters find qualified business partners, distributors, agents, representatives, or end-users in foreign countries. For example, through our Gold Key Service, U.S. embassies and consulates provide customized matchmaking by lining up prescreened agents and distributors for U.S. business in those countries.

For example, prior to ceramitec in Germany (www.ceramitec.com), our local German industry expert will promote U.S. exhibitors to local buyers and distributors, provide counseling to U.S. businesses at the show, discuss business strategies, and explain Commercial Service programs through the worldwide network available to U.S. exporters. This is also a unique opportunity to explore opportunities in other countries rather than just one market.

Colleagues may work together on industry “teams” to help U.S. businesses or tap into industry expertise through the International Trade Administration's Industry & Analysis division. Our Enforcement & Compliance division helps U.S. companies with trade barriers or advocacy issues. All of these services save businesses valuable time and resources when competing in world markets.

No time to travel? We can help

It is always best to meet potential customers face-to-face, but many small companies do not have the time or budget for extensive travel. Commercial Service offers products and services for those companies depending on the market. For instance, we offer a report called an Initial Market Check, which is a combination of market research and four or five qualified contacts.

With the International Partner Search, we compile a list of qualified contacts, all of whom have received the

U.S. client's market literature. We interview each foreign firm to gauge interest and include in a report for the U.S. company. International Company Profiles offer in-depth background reports that also can help you assess a potential foreign buyer's financial viability. The financial aspects of a foreign firm's background may be of particular interest before agreeing to a deal. The foreign company is interviewed for this report, and the foreign Commercial Service office is often able to render an opinion. These are some inexpensive ways smaller companies can pursue international sales opportunities.

Protect your intellectual property

Violation of intellectual property (IP) laws is a reality and always a potential risk for companies that export. U.S. Commercial Service international specialists can put you in touch with law firms to mitigate IP risks in a market, which help U.S. companies take preventive steps and know how to be aware.

The U.S. Patent and Trademark Office points out that 85% of small- and medium-sized businesses that export do not realize their U.S. patents and trademarks do not protect them overseas. The U.S. Commercial Service has also initiated a STOP! program in partnership with the U.S. government, the private sector, our trading partners, and law enforcement.

The International Trade Administration provides aggressive outreach to educate U.S. companies on how to register and enforce their IP rights in foreign markets, such as China. More information can be found at www.stopfakes.gov. U.S. exporters should also seek legal counsel to find out what steps they need to take to prevent IP violations and what their legal recourse might be in a country if IP theft is discovered.

Strategic approaches to exporting

Many companies are beginning to take a more strategic approach to doing business internationally. Savvy business owners often understand the dynamics of the global marketplace. Also, companies are increasingly taking a regional rather than country-by-country approach. For example, firms are selling not just to Mexico, but also expanding into Latin American countries, such as those covered by free trade agreements, including Chile and the Central America Free Trade Agreement (CAFTA). Many minority-owned firms start their export sales by first selling to their home countries, where they have a cultural familiarity with the market.

Key online resources

Whether you are a new-to-export company or looking to boost your existing international sales, visit export.gov, the U.S. federal government's export assistance portal. On the site, you can:

- View a short video on U.S. Commercial Service resources and locate our domestic and international offices;
- Learn more about selling internationally through the Export Basics video series; and
- Read our Country Commercial Guides with the latest market intelligence from U.S. embassies abroad on more than 140 countries.

About the author

Deborah Dirr is international trade specialist with U.S. Commercial Service within the U.S. Department of Commerce (International Trade Administration). Contact Dirr at Deborah.Dirr@trade.gov. ■



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Thousands of materials scientists converge on Pittsburgh for ACerS Annual Meeting and MS&T17

MS&T17

(Credit all images: ACerS)

The 2017 edition of the Materials Science and Technology Technical Meeting took place October 8–12. The conference welcomed 3,206 attendees from 46 countries to Pittsburgh, Pa. to participate in 82 symposia.

Symposia topics demonstrated the leading-edge nature of the conference:

- Eight symposia were dedicated to additive manufacturing;
- Nine symposia had ‘advanced materials’ or ‘advancements’ in their titles;
- Symposia addressed materials for energy, electronics, health care, and aerospace;
- Dedicated symposia on data informatics and tools, along with modeling and simulation, showed the rising importance of computational methods in materials R&D; and
- Career development and education symposia focused on attracting young materials scientists and helping them find their niche in the field.

Save the dates: MS&T18 in Columbus, Ohio—October 14–18, 2018

ACerS 120th Annual Meeting—October 15, 2018

MS&T17 attendees included 872 students, many of whom presented their research in poster sessions on the expo floor.

The American Ceramic Society also held its Annual Meeting and awards banquet at MS&T17. During the Annual Meeting, President Bill Lee and other officers reported on the State of the Society, recognized outgoing board members and officers, and inducted new board members and officers.

Lee reviewed his year and reported on achievements regarding his top three priorities, which were strengthening ACerS international outreach, supporting young members, and engaging industry. On the international outreach front, Lee reported the start-up of ACerS first international chapter in the U.K. Other international chapters will soon be established in Italy, India, and Canada.

Treasurer Dan Lease reported the Society’s finances continue to maintain a strong position. Executive director Charlie Spahr updated the membership on changes to MS&T starting in 2020 with ASM leaving the partnership, and the opportunity to strengthen ACerS presence in a “new MS&T.”

Incoming president Mike Alexander shared his goals for the coming year, which include focusing on volunteerism, working toward the betterment of humanity through the Advocacy Committee and the Humanitarian subcommittee, and promoting a holistic view of engineering as applying the science while engaging the arts. “We need to reenergize curiosity and creativity,” he says, “and recreate

the wonder of ceramics—the best materials out there.”

ACerS presented awards at the annual Honors and Awards Banquet during MS&T17. President Bill Lee elevated 15 members to Fellow and awarded ACerS highest honor of Distinguished Life Member to Richard Bradt, Marina Pascucci, and Masahiro Yoshimura. Other distinguished members and corporations were also recognized.



Incoming president Mike Alexander (left) accepts the official president's ceramic gavel from president Bill Lee.

SINTERING 2017 SPARKS RECORD ATTENDANCE IN SAN DIEGO



(Credit all images: ACerS)

The International Conference on Sintering 2017, held November 12–16, welcomed a record attendance of 239 participants to the Hyatt Regency Mission Bay Spa and Marina in sunny San Diego, Calif.

The international conference and worldwide forum on sintering science and technology addressed latest developments in sintering and microstructural evolution processes for the fabrication of powder-based materials, with a focus on the increasing ability to design complex and multifunctional materials with specific microstructures and properties.

Conference attendees hailed from 29 countries to provide global perspectives on sintering in more than 200 oral presentations and 45 posters. In addition to three plenary presentations and six concurrent sessions focused on fundamental understanding, technological issues, and industrial applications of sintering, the conference included an honorary symposium, industry reception, and city tour, including a visit of San Diego Old Town, boat trip along the harbor, and visit of the Aircraft Carrier Museum.

United States cochairs Rajendra Bordia (Clemson University) and Eugene Olevsky



Martin Harmer delivers his plenary lecture on grain boundaries.



Gary Messing (left) presents glass appreciation pieces to 2017 U.S. conference cochairs Eugene Olevsky (center) and Rajendra Bordia.

(San Diego State University) organized the conference, supported by international cochairs Suk-Joong Kang (Korea Institute of Ceramic Engineering and Technology, Korea Advanced Institute of Science and Technology, Korea), Didier Bouvard (University of Grenoble, France), and Bernd Kieback (Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Germany). ■



Sintering 2017 attendees presented 45 posters on various aspects of sintering science and technology.



The meeting program was thoughtfully designed to facilitate discussion and knowledge-sharing among participants.



The San Diego harbor provided a nautical backdrop for the meeting.



Meeting attendees take a quick break for a photo-op between presentations.

new products



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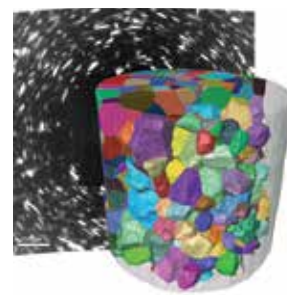
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PLENARY SPEAKERS



Roger de Souza

Institute of Physical Chemistry, RWTH, Aachen University, Germany

Using transport studies to reveal the myriad secrets of SrTiO₃

Abstract: There is renewed interest in electrical conduction in the perovskite oxide SrTiO₃, driven by the material's possible application in devices for all-oxide electronics and resistive switching. In my talk, I will briefly review, first, the defect chemistry of SrTiO₃, and then, the thermodynamics of space-charge formation at extended defects. The main part of the talk will concentrate on understanding the electrical conductivity of single crystal, bicrystal, and thin film samples of this prototypical perovskite-type oxide. In particular, I will focus on the conductivity behavior of the bulk phase as a function of temperature (from room temperature up to ca. 700°C), of bicrystal samples as a function of misorientation angle, and of thin-film samples as a function of film thickness. For all three cases, I will demonstrate that it is possible to predict the electrical conductivity using thermodynamic models. Finally, I will describe the consequences for memristive devices, and I will draw attention to current challenges and outstanding problems.



Judith MacManus-Driscoll

Department of Materials Science and Metals, University of Cambridge

New materials paradigm in oxide epitaxial nanocomposite thin films and the realization of enhanced functionalities

Abstract: Since the discovery of high-temperature superconductivity in perovskite oxides in 1986, the unearthing of a huge range of physical phenomena in transition metal oxides has been nothing short of remarkable (e.g., new magnetics, ferroelectrics, multiferroics, semiconductors, transparent conductors, calorics, plasmonics, catalysts, and ionic conductors.) However, for a variety of reasons ranging from lack of perfection to complexity of processing, to the functional effect being too weak, there are few applications of complex oxide films today. This talk will discuss new insight into overcoming these challenges by using epitaxial nanocomposite films. Examples of our recent work on unprecedented functional property enhancements in ferroelectrics, ferromagnetics, magnetoelectrics, and ionics will be given.

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- S9 Substitution and sustainability in functional materials and devices
- S10 Synthesis and processing of science of thin films and single crystals —The details of engineering structure–property relationships
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BASIC SCIENCE DIVISION TUTORIAL

Defect chemistry in perovskite ceramics and its impact on materials processing and properties

In functional ceramics, defect chemistry is of outstanding importance for materials properties. For example, electric or ionic conductivity of ceramics is governed by point defects. But, other effects—ferroelectricity and optical properties—are impacted by defects, and microstructural evolution is closely linked to defect chemistry. However, because many applications of functional ceramics involve polycrystalline materials, a deep understanding of bulk defect chemistry needs to be extended to the existence of charged interfaces and space charge at interfaces.

This tutorial gives a comprehensive introduction to defect chemistry of functional ceramics in general and perovskites in particular. Reasons for the existence of charged interfaces and space charge and its interplay with defect chemistry are reviewed. Finally, the impact of these concepts on materials properties and processing is highlighted. Talks illustrate the most important tools in this field and give examples for their application.

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TENTATIVE SCHEDULE Current as of December 14, 2017

Tuesday, January 16, 2018

Conference registration 5 – 6:30 p.m.

Wednesday, January 17, 2018

Conference registration 7:30 a.m. – 6 p.m.

Plenary session I –
Roger de Souza, Aachen University 8:30 – 9:30 a.m.

Coffee break 9:30 – 10 a.m.

Concurrent technical sessions 10 a.m. – 12:30 p.m.

Poster session set up Noon – 5 p.m.

Lunch on own 12:30 – 2 p.m.

Concurrent technical sessions 2 – 5:30 p.m.

Coffee break 3:30 – 4 p.m.

Poster session and reception 5:30 – 7:30 p.m.

Basic Science Division tutorial 7:45 – 9:45 p.m.

Thursday, January 18, 2018

Conference registration 7:30 a.m. – 6 p.m.

Plenary session II –
Judith Driscoll, University of Cambridge 8:30 – 9:30 a.m.

Coffee break 9:30 – 10 a.m.

Concurrent technical sessions 10 a.m. – 12:30 p.m.

Lunch on own 12:30 – 2 p.m.

New member welcome break 1:30 – 2 p.m.

Concurrent technical sessions 2 – 5:30 p.m.

Coffee break 3:30 – 4 p.m.

Young Professionals reception 5:30 – 6:30 p.m.

Conference dinner 7 – 9 p.m.

Friday, January 19, 2018

Conference registration 7:30 a.m. – 5:30 p.m.

Concurrent technical sessions 8:30 a.m. – 12:30 p.m.

Coffee break 9:30 – 10 a.m.

Lunch on own 12:30 – 2 p.m.

Concurrent technical sessions 2 – 5:30 p.m.

Coffee break 3:30 – 4 p.m.

Failure: The greatest teacher 5:15 – 6:25 p.m.



42ND INTERNATIONAL CONFERENCE AND EXPOSITION ON ADVANCED CERAMICS AND COMPOSITES



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JAMES I. MUELLER AWARD



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George G. Wicks, CTO, Applied Research Center, S.C.; VP/CTO, SpheroFill LLC; Wicks Consulting Services LLC; adjunct professor, Medical College of Georgia, Georgia Regents University; consulting scientist (retired), Savannah River National Laboratory

Title: *Tiny Bubbles: An innovative ceramic opens new opportunities in medicine, security, energy, and environmental remediation*

BRIDGE BUILDING AWARD



Zhou

Yanchun Zhou, professor and deputy director of science and technology of Advanced Functional Composite Laboratory at the Aerospace Research Institute of Materials and Processing Technology of China

Title: *Strategies for searching for damage tolerant ceramics: from MAX phases to MAB phases*

PLENARY SPEAKER



Brook

Richard Brook, emeritus professor, Dept. of Materials, University of Oxford, United Kingdom

Title: *Research. Why? For whom? How?*

PLENARY SPEAKER



Mücklich

Frank Mücklich, Univ.-Prof. Dr.-Ing., head, Institute for Functional Materials, Dept. Mat. Science & Engineering, Saarland University, Germany

Title: *3D microstructure is the "know-it-all"—Advanced classification and quantitative analysis including data mining and deep learning methods*

ECD GLOBAL YOUNG INVESTIGATOR AWARD



Fischer

Thomas Fischer, Institute of Inorganic Chemistry, University of Cologne, Germany

Title: *Electrospun metal oxide fiber meshes for improved sensing of toxic analytes in the gas phase*

EXHIBITION INFORMATION

Connect with decision makers and influencers in government labs, industry, and research and development fields. ICACC18 is your destination to collaborate with business partners, cultivate prospects, and explore new business opportunities.

Exhibit Hours:

Tuesday, January 23, 2018, 5 – 8 p.m. | Wednesday, January 24, 2018, 5 – 7:30 p.m.

Exposition Location: Ocean Center Arena, 101 North Atlantic Avenue, Daytona Beach, FL

Exhibit space is filling up fast. To reserve your booth, visit www.ceramics.org/icacc2018 or contact **Mona Thiel** at mthiel@ceramics.org or 614-794-5834.

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Alfred University	315	Netzsch Instruments	300
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AVS	307	Praxair Surface Technologies Inc.	217
B3 Systems Inc.	317	Reserved	216
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Second prize

ICACC 2019 free registration (\$730 value)

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Turn your raffle tickets in during exhibit hours at the ACerS booth (109) in the Exhibit Hall. You may turn in as many tickets as you gather from exhibitors, so the more you visit with our vendors, the better your odds to win! Prizes will be drawn at 6:30 p.m., Wednesday, January 24, at the ACerS booth. You need not be present to win. This is a great opportunity to collaborate with potential business partners and walk away with something useful for your business or career—it can be a win-win, literally!

2018 MECHANICAL PROPERTIES OF CERAMICS AND GLASS SHORT COURSE*

JANUARY 25, 2018 | 8:30 a.m. – 4:30 p.m.

JANUARY 26, 2018 | 8:30 a.m. – 4 p.m.

LOCATION: HILTON DAYTONA BEACH RESORT AND OCEAN CENTER

INSTRUCTORS: George D. Quinn, NIST, and Richard C. Bradt, University of Alabama

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* Additional fee required. To sign up, please visit www.ceramics.org/acers-courses or the registration booth at ICACC.

OFFICIAL NEWS SOURCES

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Calendar of events

January 2018

17–19 EAM 2018: ACerS Conference on Electronic and Advanced Materials – DoubleTree by Hilton Orlando Sea World, Orlando, Fla.; www.ceramics.org/eam2018

21–26 ICACC18: 42nd Int'l Conference and Expo on Advanced Ceramics and Composites – Hilton Daytona Beach Resort/Ocean Walk Village, Daytona Beach, Fla.; www.ceramics.org/icacc2018

March 2018

21–22 54th Annual St. Louis Section/Refractory Ceramics Division Symposium on Refractories – Hilton St. Louis Airport Hotel, St. Louis, Mo.; www.bit.ly/54thRCDSymposium

April 2018

10–13 ➤ ceramitec 2018 – Munich Germany; www.ceramitec.com

18–20 ➤ CICMT 2018: IMAPS/ACerS 14th Int'l Conference and Exhibition on Ceramic Interconnect and Ceramic Microsystems Technologies, University of Aveiro, Aveiro, Portugal; www.imaps.org

May 2018

1–3 ➤ 4th Ceramics Expo – I-X Center, Cleveland, Ohio; www.ceramicsexpousa.com

20–24 GOMD 2018: Glass and Optical Materials Division Meeting – Hilton Palacio de Rio, San Antonio, Texas; www.ceramics.org/gomd18

June 2018

4–14 14th Int'l Ceramics Congress and the 8th Forum on New Materials – Perugia, Italy; www.2018.cimtec-congress.org/14th_ceramics_congress

5–8 ACerS Structural Clay Products Division & Southwest Section Meeting in conjunction with the National Brick Research Center Meeting – Columbia, S.C.; www.bit.ly/2018SCPDmeeting

11–12 9th Advances in Cement-Based Materials – Pennsylvania State University, University Park, Pa.; www.ceramics.org

17–21 ICC7: 7th Int'l Congress on Ceramics – Hotel Recanto Cataratas, Foz do Iguaçu, Brazil; www.icc7.com.br

July 2018

9–12 6th Int'l Conference on the Characterization and Control of Interfaces for High Quality Advanced Materials and the 54th Summer Symposium on Powder Technology – Kurashiki, Japan; www.ceramics.ynu.ac.jp/iccci2018/index.html

9–13 ➤ 15th Int'l Conference on the Physics of Non-Crystalline Solids & 14th European Society of Glass Conference – Le Grand Large, Saint-Malo, France; www.ustverre.fr

22–27 ➤ CMCEE-12: 12th Int'l Conference on Ceramic Materials and Components for Energy and Environmental Applications – Singapore; www.cmcee2018.org

August 2018

11–12 ➤ Gordon Research Seminar: Solid State Studies in Ceramics – Defects and Interfaces for New Functionalities in Ceramics – Mount Holyoke College, South Hadley, Mass.; www.grc.org/programs.aspx?id=17148

12–17 ➤ Gordon Research Conference: Solid State Studies in Ceramics – Mount Holyoke College, South Hadley, Mass.; www.grc.org/programs.aspx?id=11085

20–23 MCARE2018: Materials Challenges in Alternative & Renewable Energy – Vancouver, BC, Canada; www.ceramics.org/mcare2018

October 2018

14–18 MS&T18, combined with ACerS 120th Annual Meeting – Greater Columbus Convention Center, Columbus, Ohio; www.matscitech.org

November 2018

5–8 ➤ 79th Conference on Glass Problems – Greater Columbus Convention Center, Columbus, Ohio; www.glassproblemsconference.org

January 2019

23–25 EAM2019: 2019 Conference on Electronic and Advanced Materials, Organized by ACerS Electronics and Basic Science Divisions – DoubleTree by Hilton Orlando at Sea World Conference Hotel, Orlando, Fla.; www.ceramics.org

27–Feb. 1 ICACC19: 43rd Int'l Conference and Expo on Advanced Ceramics and Composites – Daytona Beach, Fla.; www.ceramics.org

April 2019

30–May 2 ➤ 5th Ceramics Expo – I-X Center, Cleveland, Ohio; www.ceramicsexpousa.com

June 2019

9–14 ➤ 25th Int'l Congress on Glass, Boston, Mass.; www.ceramics.org/icg2019

Dates in **RED** denote new entry in this issue.

Entries in **BLUE** denote ACerS events.

➤ denotes meetings that ACerS cosponsors, endorses, or otherwise cooperates in organizing.



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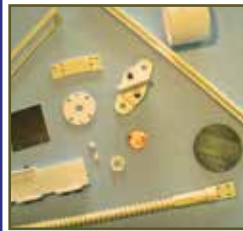


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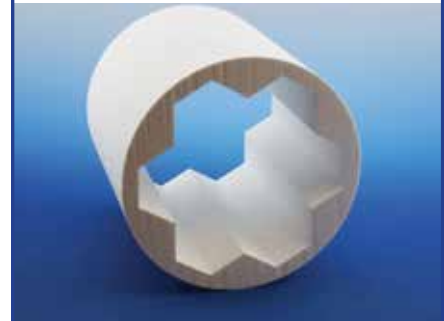


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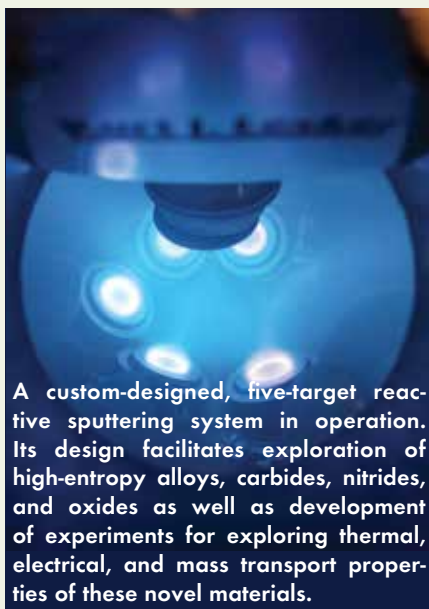
What is a defect? A missing atom here, an extra atom there, an impurity, a stacking fault, a dislocation? Traditionally defects are considered exceptions to perfection—individual, relatively easily identifiable abnormalities in an otherwise pristine crystal structure.

However, each type of defect can star in opposing roles, as friends to some and foes to others. Depending on who you ask, one materials scientist might speak highly of a particular defect and its benefits, while another may avoid it at all costs—such as dislocations in metals versus semiconductors.

However, no field appears to embrace the role of defects as strongly as the fields of high-entropy solid solutions. Whether metal alloys, oxides (some of which are proven to be stabilized by the $-T\Delta S$ term),¹ or refractory carbides, nitrides, and borides, these materials are made up almost entirely of atomic defects on one or more crystal sublattices. This raises the question: If you cannot predict which atom will occupy a site, are all atoms considered defects or are none?

Regardless of which side of this philosophical debate you stand on, the fact remains that random distribution of atoms across all lattice sites—like their more traditional defect counterparts—contributes to configurational entropy of the system. Further, unlike their more conventional counterparts (vacancies, impurities, dopants, and small alloying additions), there is an equal probability (with equimolar compositions) of finding each atom on the same lattice site—providing significantly larger configurational entropies than those achievable with conventional defects.

This begs the question: What are the benefits of such a defective structure,



A custom-designed, five-target reactive sputtering system in operation. Its design facilitates exploration of high-entropy alloys, carbides, nitrides, and oxides as well as development of experiments for exploring thermal, electrical, and mass transport properties of these novel materials.

Credit: Trent Borman

and why would you create such a thing?

Some key benefits of such a structure can be discerned just by looking at Gibb's free energy: $\Delta G = \Delta H - T\Delta S$.

By substantially increasing entropy (as a byproduct of including five metal cations in a solid solution), the positive enthalpy term associated with elements that do not traditionally form the desired structure (e.g., rocksalt) can be overcome. This creates a negative ΔG for the solid solution as a whole, as unambiguously first demonstrated by Rost et al.¹ with (MgNiZnCuCo)O. This can, in principle, provide pathways for incorporation of functional elements (such as magnetic or phosphorescent elements) into structures that are desirable but otherwise difficult to incorporate with such elements.

In addition to enhancing the spectrum of elements that can be incorporated into structures, the thermal properties and stability of high-entropy ceramics can be altered relative to their constituents. In principle, increasing entropy of the solid solution structure can decrease ΔS of melting, requiring high temperatures to overcome the large ΔH of melting associated with solid solutions of refractory compounds, such as transition metal carbides.

While the field of high-entropy alloys has existed for quite some time, the field

of high-entropy and entropy-stabilized ceramics is comparatively in its infancy. Since Rost et al.¹ first demonstrated entropy stabilization, numerous other published papers have reproduced as well as expanded the work to new elemental and structural systems. Thus far, reports include colossal dielectric constants,² room-temperature superionic conductivities,³ and enhanced exchange coupling⁴ in high-entropy and entropy-stabilized oxides, as well as improved hardness and oxidation resistance in high-entropy transition metal diborides.⁵ Now the race is on amongst the research community to continue embracing these extreme defect concentrations to discover and perfect the next great materials for a broad range of applications.

¹C.M. Rost, E. Sachet, T. Borman, A. Mobballegh, E.C. Dickey, D. Hou, J.L. Jones, S. Curtarolo, et al., "Entropy-stabilized oxides," *Nat. Commun.*, 6 8485 (2015).

²D. Bérardan, S. Franger, D. Dragoë, A.K. Meena, and N. Dragoë, "Colossal dielectric constant in high entropy oxides," *Phys. Status Solidi - Rapid Res. Lett.*, 10 [4] 328–333 (2016).

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⁴P.B. Meisenheimer, T.J. Kratoofil, and J.T. Heron, "Giant enhancement of exchange coupling in entropy-stabilized oxide heterostructures," 25 [July] 1–17 (2017).

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