

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-

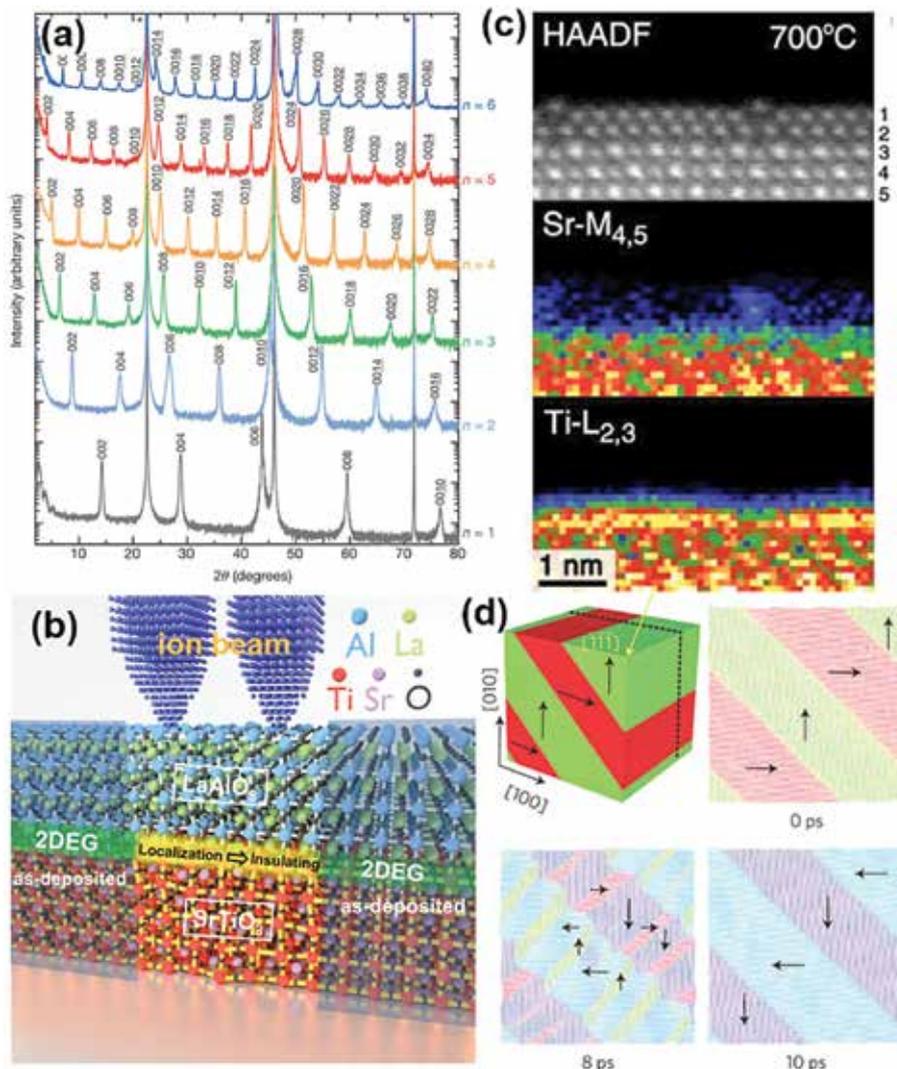


Figure 1. (a) θ - 2θ X-ray diffraction scans of various molecular beam epitaxy-grown epitaxial $Sr_{n+1}Ti_nO_{3n+1}$ ($n = 1-6$) films, showing the deterministic ability to produce planar defects in a designer fashion. Adapted from Lee et al., 2013.² (b) Schematic illustration of patterning of 2-D electron 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

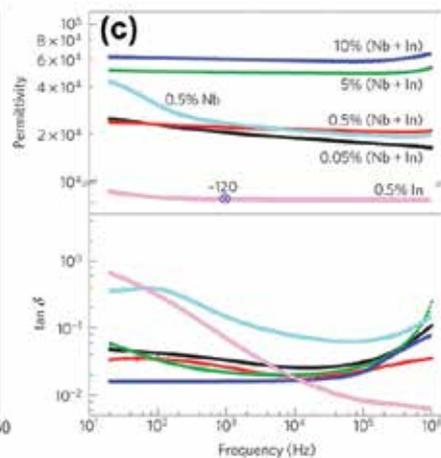
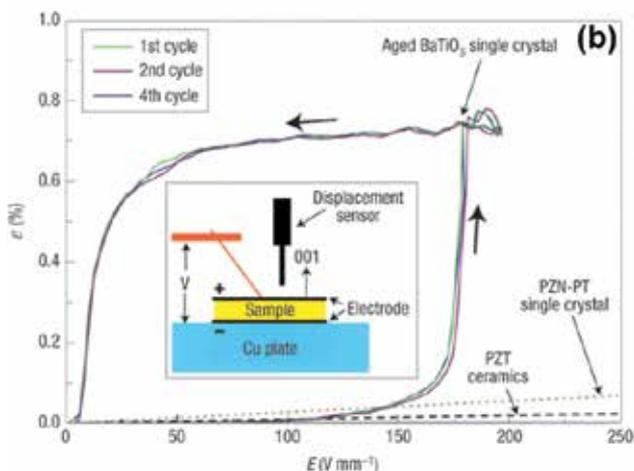
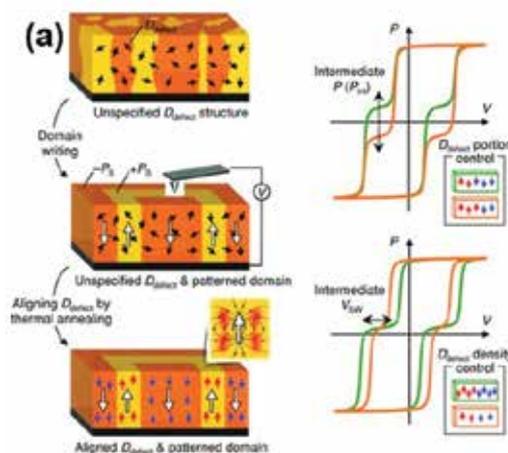
tailor properties, but such approaches have at times been guided by empirical observations and trial-and-error alone. Advances in our understanding and control of how dopants occupy the lattice and affect properties now allow us to do much better even with alloying. For example, amphoteric dopants, or “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.

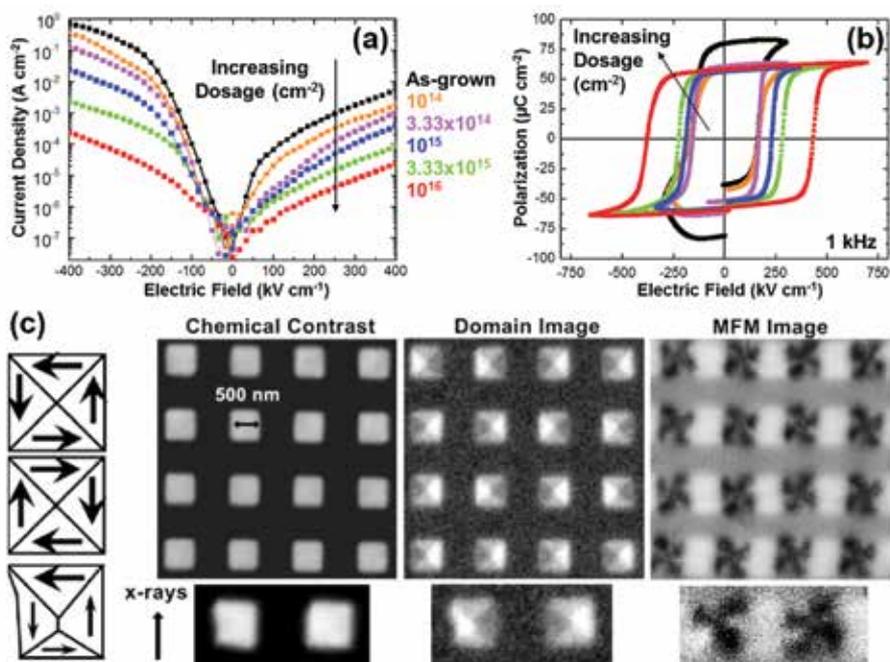


Figure 3. (a) Leakage current density as a function of DC electric field and (b) ferroelectric polarization-electric field hysteresis loops measured at 1 kHz after ion-bombardment with various He²⁺ dosages for BiFeO₃ thin films, showing that purposeful introduction of defects can have marked impact on 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 La_{0.7}Sr_{0.3}MnO₃ 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

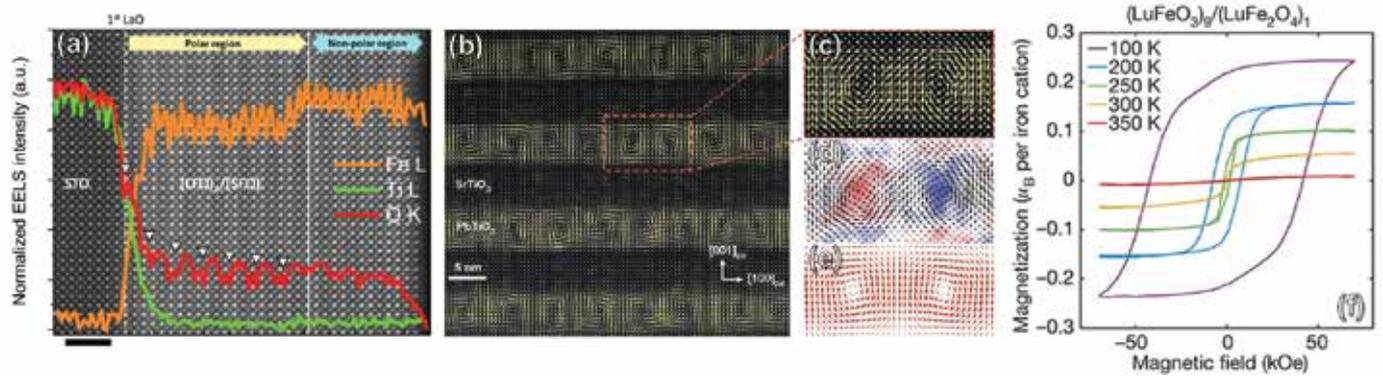


Figure 4. (a) Core-loss EELS of $(\text{LaFeO}_3)_2/(\text{SrFeO}_3)$ superlattice showing oxygen-vacancy ordering (denoted by arrows) in the polar region. Adapted from Mishra et al., 2014.¹⁷ (b) Atomic-displacement mapping from a STEM image of a $(\text{SrTiO}_3)_{10}/(\text{PbTiO}_3)_{10}$ superlattice, 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 $(\text{LuFeO}_3)_9/(\text{LuFe}_2\text{O}_4)_1$ 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-

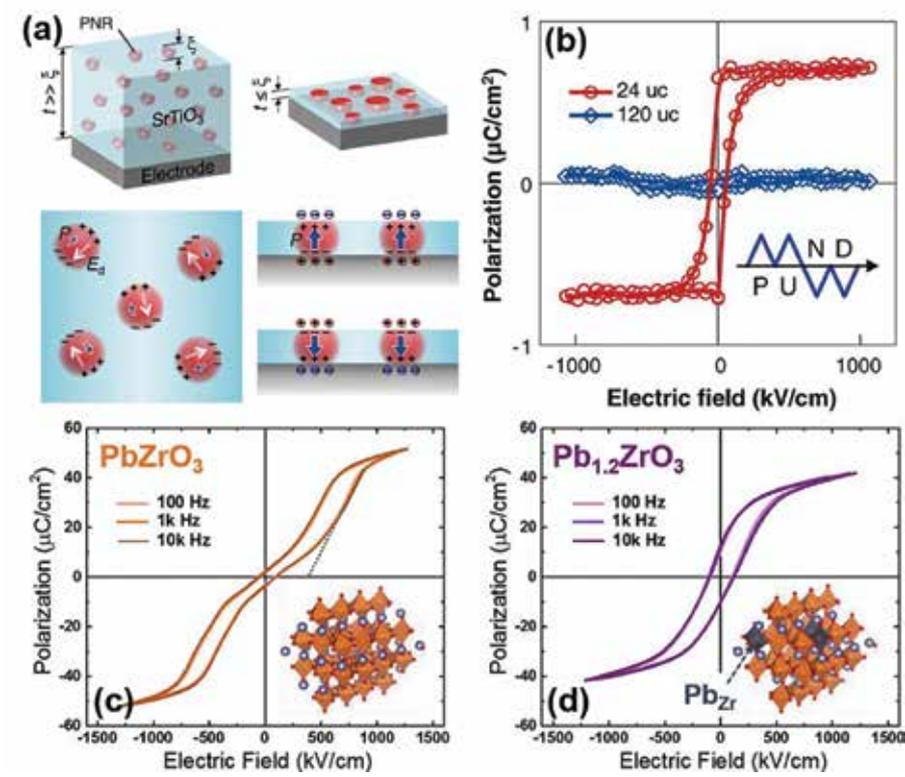


Figure 5. (a) Schematic illustration of the effect of size confinement on polar nanoregions induced by non-stoichiometry in SrTiO_3 . (b) Polarization hysteresis of thin (24-unit cell) and thick (120-unit cell) SrTiO_3 measured using the positive-up, negative-down method. Adapted from Lee et al., 2015.¹⁹ 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. ■

Acknowledgements

The authors acknowledge support from the Army Research Office under grant W911NF-14-1-0104, the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award DE-SC-0012375 and contract DE-AC02-05-CH11231: Materials Project program KC23MP, the National Science Foundation under grants DMR-1451219, CMMI-1434147, OISE-1545907, DMR-1608938, and DMR-1708615, and the Gordon and Betty Moore Foundation's EPIQS Initiative, under grant GBMF5307.

About the authors

S. Saremi, R. Gao, A. Dasgupta, and L. W. Martin are with the Department of Materials Science and Engineering, University of California, Berkeley. Martin is also with the Materials Sciences Division, Lawrence Berkeley National Laboratory. Contact Martin at lwmartin@berkeley.edu.

References

- ¹A.K. Yadav, et al., “Observation of polar vortices in oxide superlattices,” *Nature*, **530**, 198–201 (2016).
- ²C.-H. Lee, et al., “Exploiting dimensionality and defect mitigation to create tunable microwave dielectrics,” *Nature*, **502**, 532–536 (2013).
- ³S. Saremi, et al., “Enhanced electrical resistivity and properties via ion bombardment of ferroelectric thin films,” *Adv. Mater.*, **28**, 10750–10756 (2016).
- ⁴S. Saremi, et al., “Electronic transport and ferroelectric switching in ion-bombarded, defect-engineered BiFeO₃ thin films,” *Adv. Mater. Inter.*, accepted (2017).
- ⁵S. Mathew, et al., “Tuning the interface conductivity of LaAlO₃/SrTiO₃ using ion beams: Implications for patterning,” *ACS Nano*, **7**, 10572–10581 (2013).
- ⁶Y. Takamura, et al. “Tuning magnetic domain structure in nanoscale La_{0.7}Sr_{0.3}MnO₃ islands,” *Nano Lett.*, **6**, 1287–1291 (2006).
- ⁷W. Xu, et al., “In-situ real-space imaging of single crystal surface reconstructions via electron microscopy,” *Appl. Phys. Lett.*, **109**, 201601 (2016).
- ⁸R. Xu, et al., “Ferroelectric polarization reversal via successive ferroelastic transitions,” *Nature Mater.*, **14**, 79–86 (2016).
- ⁹Y. Tsur, et al., “Crystal and defect chemistry of rare earth cations in BaTiO₃,” *J. Electroceram.*, **7**, 25–34 (2001).
- ¹⁰A. R. Damodaran, et al., “Enhancement of ferroelectric Curie temperature in BaTiO₃ films via strain-induced defect dipole alignment,” *Adv. Mater.* **26**, 6341–6347 (2014).
- ¹¹D. Lee, et al., “Active control of ferroelectric switching using defect-dipole engineering,” *Adv. Mater.*, **24**, 6490–6495 (2012).

¹²X. Ren, “Large electric-field-induced strain in ferroelectric crystals by point-defect-mediated reversible domain switching,” *Nature Mater.*, **3**, 91–94 (2004).

¹³W. Hu, et al., “Electron-pinned defect-dipoles for high-performance colossal permittivity materials,” *Nature Mater.*, **12**, 821–826 (2013).

¹⁴E. Breckenfeld, et al., “Tunability of conduction at the LaAlO₃/SrTiO₃ heterointerface: thickness and compositional studies,” *Appl. Phys. Lett.*, **103**, 082901(2013).

¹⁵D. Lee, et al., “Controlling oxygen mobility in Ruddlesden-Popper oxides,” *Materials*, **10**, 368 (2017).

¹⁶C. Becher, et al., “Strain-induced coupling of electrical polarization and structural defects in SrMnO₃ films,” *Nature Nanotechnol.*, **10**, 661–665 (2015).

¹⁷R. Mishra, et al., “Oxygen-vacancy-induced polar behavior in (LaFeO₃)₂/(SrFeO₃) superlattices,” *Nano Lett.*, **14**, 2694–2701 (2014).

¹⁸J. A. Mundy, et al., “Atomically engineered ferroic layers yield a room-temperature magnetoelectric multiferroic,” *Nature*, **537**, 523–527 (2016).

¹⁹D. Lee, et al., “Emergence of room-temperature ferroelectricity at reduced dimensions,” *Science*, **349**, 1314–1317 (2015).

²⁰R. Gao, et al., “Ferroelectricity in Pb_{1-x}Zr_xO₃ thin films,” *Chem. Mater.*, **29**, 6544–6551 (2017). ■

bccResearch

SMART DECISIONS START HERE

3D Printed Technical Ceramics: Technologies and Global Markets
A BCC Research Report

**Our Members Agree:
BCC Research Knows Ceramics.**

LIMITED TIME: 15% OFF MEMBERSHIP

866-285-7215 | info@bccresearch.com | bccresearch.com