Welcome to the meeting

We are very pleased to welcome all of you to the 9th Annual CCAC Student Conference. I hope you will enjoy our variety of scientific research and speakers.

We would like to begin by thanking our industry sponsors FEI and Corning, as well as the organizations affiliated with Colorado School of Mines which have sponsored this conference: the Colorado Fuel Cell Center (CFCC), the office of the Vice President for Research and Technology Transfer (VPRTT), and the Colorado Center for Advanced Ceramics (CCAC).

We would also like to thank our keynote speakers: Dr. Jacob Jones from North Carolina State University and Dr. Richard Brow from Missouri S&T. Additionally, we would also like to thank our CCAC Faculty presenters: Dr. Brian Gorman and Dr. Geoff Brennecka. We are grateful to all of them for making room in their busy schedule to accept our invitation.

Last but not least, we would like to thank all of you for your hard work and active contribution to the conference.

Best Regards,

Debora Barcellos  
Brian C. Davis  
Valerie Jacobson  
John Mangum

2017 CCAC Student Conference Committee

*Cover Image Courtesy of Dr. Geoff Brennecka*
2017 CCAC Student Conference
Colorado Center for Advanced Ceramics

Program & Proceedings

August 16\textsuperscript{th}-17\textsuperscript{th}, 2017
American Mountaineering Center
Golden, CO

Organized By
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## Conference Schedule

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In situ Scattering Experiments on Dielectrics and Ferroelectrics:
New Methods, Analysis, and Physical Insight

Jacob L. Jones
Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC

Figure: Shown on the left are some sections of representative diffraction patterns during application of electric field to a ferroelectric. Profile fitting, like that shown at the right, provides information about the domain wall behavior in ferroelectrics. Advanced analysis of the profiles using Bayesian statistics will be presented in this talk.

Abstract: Dielectric and piezoelectric materials are used to store and convert electrical and mechanical energy, making them essential to a broad range of applications and devices including impact and displacement sensors, actuators, capacitors, microelectromechanical systems, vibrational energy harvesting, diesel fuel injectors, sonar, and ultrasound. In these applications, the dielectric and piezoelectric coefficients define the performance and the limits of device operation. However, the true origin of the material response, and thus the property coefficients, are not well understood because of the numerous and complex microstructural and crystallographic contributions to these properties (e.g., ionic and dipolar polarizability, ferroelastic domain wall motion, interphase boundary motion, the intrinsic piezoelectric effect, etc.)

This talk will first demonstrate the use of advanced in situ X-ray and neutron scattering methods (including diffraction and pair distribution functions from total scattering) to discern the underlying mechanics and physics at play in electro-active materials such as dielectrics and piezoelectrics, ultimately revealing the contribution of these various mechanisms to the property coefficients. In all cases, direct measurements of the contribution from lattice deformation (e.g., piezoelectric) and the motion of intragranular interfaces (e.g., ferroelectric domain walls, interphase boundaries) are quantitatively related to the property coefficients using micromechanics-based formulations.

The second part of this talk will include an introduction to an alternative statistical framework for analysis of diffraction data, that of Bayesian statistics in conjunction with a Markov Chain Monte Carlo (MCMC) algorithm. This analysis approach is applied to modeling doublets from ferroelastic degenerate reflections and quantifying the extent of domain wall motion in ferroelectrics on a probability basis. We have also applied these approaches to full-pattern profile fitting. The parameters in the new models represent structure using probability distributions, treating solutions probabilistically with improved uncertainty quantification.
Dissolution and Precipitation Reactions of Borate Glasses for Biomedical Applications

Richard K. Brow
Department of Materials Science, Missouri University of Science & Technology, Rolla, MO, USA

Abstract: Borate glasses rapidly convert to hydroxyapatite (HAp) in physiological environments and have been developed as scaffolds for tissue engineering applications [Rahaman et al., 2011] and as treatments for surface wounds [Zhao, et al., 2015]. For example, the figure below shows an electron microscopic image of borate glass fibers after a week in a cell culture medium, with x-ray diffraction evidence for the formation of HAp (from Chen, 2017). To study the related dissolution and precipitation processes, we use a micro-Raman spectrometer as a non-contact probe of the interfacial regions between a borate glass surface and the surrounding solution, and show that two borate species, B(OH)$_3$ and B(OH)$_4$-, are released to solution and that their relative concentrations reveal local pH gradients [George and Brow, 2015]. Dissolution rates based on these borate release measurements are related to glass composition, particularly the O/B ratio which determines the relative fraction of tetrahedral borate sites in the glass structure, and on the type of metal oxide used to modify the glass. The effects of borate glass fibers on the vitality of human fibroblast cells were determined by a series of in vitro tests, including the detection of vascular endothelial growth factor, a protein secreted from the cells and an important agent in the wound healing process [Chen, et al. 2017].

Abstract: Solar Thermochemical Hydrogen Production (STCH) is an emerging technology that uses concentrated solar heat to split water and produce hydrogen. STCH leverages the ability of some transition metal oxides to reversibly change their oxygen stoichiometry with changes in temperature and oxygen partial pressure. The potential impact of this technique is significant because it enables the use of a carbon-free energy source (solar radiation) to produce industrial scale quantities of hydrogen, which is widely used in the production of steel, ammonia for fertilizers, and as an alternative renewable fuel.

In the water splitting perovskite niche, our recently discovered BaCe$_{0.25}$Mn$_{0.75}$O$_3$ compound has been demonstrated to have an exceptional water splitting performance under more realistic reactor process conditions (lower reduction temperatures and higher hydrogen-from-steam conversion). The investigation of the thermodynamic properties of the reduction/reoxidation reaction is key for understanding this material’s outstanding behavior and ultimately to give insight for the design of new water splitting perovskites.

BaCe$_{0.25}$Mn$_{0.75}$O$_3$ has a phase transition between polytypes of the same composition between the reduction and oxidation temperatures of interest. Understanding the thermodynamic differences between the two polytypes will be critical in ascertaining whether, ultimately, the transition is harmful or beneficial to the performance of this material. In this study, we measure the enthalpy and entropy of formation of oxygen vacancies using Thermogravimetric Analysis, compare the water splitting water reaction favorability versus the material’s further reduction and, finally, investigate the phase transition impact on the change in reaction favorability.
Understanding Space Charge Regions in a Dual Phase Ceramic Hydrogen Separation Membrane via Atom Probe Tomography

George L. Burton¹, David R. Diercks¹ and Brian P. Gorman¹

¹Colorado School of Mines, Department of Metallurgical and Materials Engineering, Golden, CO, USA

Abstract: Ceramic hydrogen separation membranes could offer a low cost, energy efficient alternative to current energy intensive hydrogen separation techniques. The 50/50 wt.% dense composite ceramic, BaCe₀.₈Y₀.₂O₃₋δ–Ce₀.₈Y₀.₂O₃₋δ (BCY-YDC), can be synthesized via solid state reactive sintering [1] and has functioned at high hydrogen fluxes [2]. Under a reducing atmosphere, YDC acts as an electron conductor and BCY as an ion conductor. Hydrogen disassociates into H⁺ ions and electrons and the charges travel through their respective phases and recombine on the opposite side of the membrane to form pure hydrogen gas. Like a number of other technologically relevant conducting oxides, electron and ion conductivity in BCY-YDC is impeded by the formation of space charge regions at grain and phase boundaries [3]. To quantify these regions, laser-assisted APT was employed to measure nanoscale composition variations in 3D, particularly oxygen vacancies and cationic species. A BCY grain boundary was examined in the figure below. The APT reconstruction in (b) shows the GB highlighted by an Al isoconcentration surface. Segregation of oxygen vacancies, Ba cations and Al impurities and a depletion of Ce cations were found at the interface, depicted by the proxigram in part (c) of the figure. YDC GB as well as phase boundary chemistry and their effects on device performance will also be discussed.

Model Predictions of Chemo-Thermal-Mechanical Stress Coupling in BZY10/BCZY27 Protonic Ceramic Membranes

Alexis Dubois, Sandrine Ricote, John R. Berger, Huayang Zhu, Robert J. Kee, Robert J. Braun

Figure 1: Comparison of measured and modeled BZY10 lattice parameters moist and dry reducing atmospheres.

Abstract: Proton-conducting ceramic materials, such as yttrium-doped barium cerates and zirconates, are being developed as membranes for a range of potential applications that include fuel cells and membrane reactors. Although these materials have been demonstrated at the laboratory scale and have the potential to deliver effective performance, the practical development is still in early stages. In addition to electrochemical performance, understanding and controlling mechanical robustness and reliability will be important in scaling to commercially viable technologies. The primary objective of the present study is to predict quantitatively the complex relationships between charged-defect transport, lattice-scale strain, and macroscopic stress.

The present computational study is based on a Nernst-Planck-Poisson (NPP) formulation that represents charge-defect transport within dense mixed ionic-electronic conducting (MIEC) materials [1]. The particular focus is on BaZr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ (BZY10). Although the theoretical foundations and modelling approaches are reasonably well developed [2], establishing the physical and chemical parameters needed to predict chemo-thermal-mechanical coupling remains challenging. The present study uses X-ray-diffraction measurements [3] to determine the needed thermal and chemical expansion coefficients. As illustrated in Fig. 1, the model accurately represents lattice expansion in dry, moist, reducing, and oxidizing environments. These results establish the basis for developing models of entire membrane-electrode assemblies.

[3] G. Hudish, S. Ricote, A. Manerbino, W.G. Coors, Chemical expansion in BaZr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ and BaZr$_{0.7}$Ce$_{0.2}$Y$_{0.1}$O$_{3-\delta}$ upon hydration determined by high temperature X-ray diffraction, submitted, 2017.
Catalysis Studies of Reduced Yttrium Doped Barium Zirconate (BZY) with Nickel Additions

Dylan Jennings\textsuperscript{1}, Canan Karakaya\textsuperscript{2}, and Ivar Reimanis\textsuperscript{1}

\textsuperscript{1}Department of Materials and Metallurgical Engineering, Colorado School of Mines, Golden, CO, USA
\textsuperscript{2}Department of Mechanical Engineering, Colorado School of Mines, Golden, CO, USA

Abstract: Barium zirconate was synthesized using a chemical synthesis process with nitrate precursors, and dopants of 15\% yttrium and 0-8\% nickel incorporated in the material. This material was then tested with a packed bed catalysis testing set-up. The BZY particles were reduced in-situ, resulting in the appearance of nickel nanoparticles on the surface of the BZY particles. Performance of the composite for water-gas shift and methane reforming reactions was evaluated. It is hypothesized that the improved coking resistance reported for this system is related to a barium nickelate monolayer that forms on the BZY surface.
In-situ Raman spectroscopy of pressure-induced phase transformations in DyPO$_4$ and Gd$_x$Dy$_{(1-x)}$PO$_4$

M A Musselman$^1$, T M Wilkinson$^1$, B Haberl$^2$, C E Packard$^1$

$^1$Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, CO, USA
$^2$Chemical and Engineering Materials Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Abstract: Rare-earth orthophosphates (REPO$_4$s) have shown potential as fiber coatings in oxide-oxide ceramic-matrix-composites (CMCs). Phase transformations were observed in xenotime coatings that demonstrated reduced fiber push-out stresses, easing fiber sliding within the matrix. The phase transformation behavior of these coating materials had not yet been characterized in isolation. Xenotime DyPO$_4$ and Gd$_x$Dy$_{(1-x)}$PO$_4$ ($x = 0.4, 0.5, 0.6$) (tetragonal $I_{41}$/amd zircon structure) have been studied at ambient temperature under high pressures inside a diamond anvil cell with in situ Raman spectroscopy. The typical Raman-active modes of the xenotime structure were observed at low pressures and the appearance of new Raman peaks at higher pressures indicated a phase transformation to a lower symmetry structure – likely monoclinic. Raman mode softening was observed, resulting in a line crossing at approximately 7-8 GPa for each material and preceding the phase transformation. The onset of phase transformation for DyPO$_4$ occurred at a pressure of 15.3 GPa. DyPO$_4$ underwent a reversible phase transformation and returned to the xenotime phase after decompression. The transformation pressures of the solid solutions (Gd$_x$Dy$_{(1-x)}$PO$_4$) were in the range of 10 – 12 GPa. The Gd$_x$Dy$_{(1-x)}$PO$_4$ solid solutions yielded partially reversible phase transformations, retaining some of the high-pressure phase spectrum while reforming xenotime peaks during decompression. The substitution of Gd into DyPO$_4$ decreased the transformation pressure relative to pure DyPO$_4$. The ability to modify the phase transformation pressures of xenotime rare-earth orthophosphates by chemical variations of solid solutions may provide additional methods to improve the performance of ceramic matrix composites.
High-Throughput Study of Structural and Compositional Effects on Conduction Mechanisms in Triple Conducting Oxides

Meagan C. Papac¹, Andriy Zakutayev², Ryan O’Hayre¹

¹Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, CO, USA
²National Renewable Energy Laboratory, Golden CO

Figure: High-throughput methods allow rapid screening of composition-based trends, such as the effect of average B-site cation size on lattice constant, illustrated here.

Abstract: Protonic ceramic fuel cells (PCFCs) offer intermediate temperature operation (400-600°C), promising increased durability and efficiency compared to more traditional solid oxide fuel cells. This is due to the higher diffusivity of protons (versus oxygen ions) through the electrolyte. However, novel electrode materials are needed to maximize potential efficiency. Triple conducting oxides (TCOs), such as $\text{BaZr}_{0.1}\text{Y}_{0.1}\text{Co}_{0.1}\text{Fe}_{0.2}\text{O}_{3-\delta}$, are promising materials for PCFC cathodes. Their ability to simultaneously conduct electron holes, protons, and oxygen ions eliminates the need for triple phase boundaries to facilitate the cathode reaction. The present work seeks to optimize triple conduction within the $\text{Ba(Zr, Y, Co, Fe)}\text{O}_{3-\delta}$ system by manipulating composition. This material has a perovskite ($\text{ABO}_3$) structure and demonstrates significant flexibility in B-site occupation. Previous work suggests that transport properties are tunable according to composition and environmental conditions. To rapidly explore this complex system, high-throughput methods are used, including thin film synthesis by pulsed laser deposition (PLD) and combinatorial characterization. Studies of PLD deposition parameters, results of compositional and structural characterization, as well as current and future development of combinatorial measurement capabilities will be discussed.
Heterostructural alloying of piezoelectric nitrides materials using combinatorial synthesis and characterization.

Kevin Talley\textsuperscript{1}, Andriy Zakutayev\textsuperscript{2}, and Geoff Brennecka\textsuperscript{1}

\textsuperscript{1}Colorado School of Mines, Golden CO
\textsuperscript{2}National Renewable Energy Laboratory, Golden CO

**Figure**: Experimental X-ray diffraction profiles for a majority of the alloying space compared to the end member peak positions. All films shown were deposited on p-type (100) silicon with a substrate temperature of approximately 400°C.

**Abstract**: Aluminum nitride (AlN) is an important piezoelectric material utilized in applications such as bandpass filter resonator devices for wireless communications. This work investigates heterostructural alloying as a route to improved device performance for more efficient use of the electromagnetic spectrum and increased battery life. Combinatorial thin film synthesis and characterization approaches were developed and utilized to understand the effects of alloy composition on material properties. The results of alloying scandium, boron, and/or chromium nitride with aluminum nitride are presented with a focus on properties relevant to wireless applications such as crystal structure, film texture, electrical, mechanical, and piezoelectric properties.
Investigating the Morphology and Reformation of Electrochemically Etched Mesoporous Ge

N Alkurd\textsuperscript{1}, R Mathiesen\textsuperscript{1}, X Murugappan\textsuperscript{1}, D Young\textsuperscript{2}, A Ptak\textsuperscript{2}, C E Packard\textsuperscript{1}

\textsuperscript{1}Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, CO, USA
\textsuperscript{2}National Renewable Energy Laboratory, Golden, Colorado, USA

Abstract: In the growth of III-V photovoltaic cells, the highest cost component is typically the substrate used as a lattice-matched seed crystal to facilitate high quality growth of the active semiconductor. With such a comparatively high cost, reusing the Ge seed crystal would be a good strategy to reduce the overall cost of the final photovoltaic device.

In our study, we attempt a Ge substrate reuse strategy based on electrochemically etching the Ge in an HF-based electrolyte and subsequently reforming the surface by annealing in H\textsubscript{2}-containing atmospheres. Ideally, the reformation process would leave a surface suitable for III-V growth and the pores near the pore-bulk interface would coarsen, creating an embedded weak layer to facilitate device removal. Bipolar electrochemical etching, where the forward and reverse bias are alternately applied in fast succession, was applied to avoid excessive electropolishing. We achieved mesoporous Ge layers by controlling the electrolyte composition, forward/reverse biased current densities and duty cycle. To study the reformation kinetics of porous Ge, we annealed various pore morphologies in ultra high vacuum conditions including the use of H/H\textsubscript{2}, H\textsubscript{2}, and N\textsubscript{2}/H\textsubscript{2}. The morphology of mesoporous Ge layers was characterized with Field Emission Electron Microscopy and ImageJ image analysis software. We hope to gain a fundamental understanding of the etching, reformation and device-removal process to determine the viability of this technology, for future industrial processes.
Reversible Protonic Ceramic Electrochemical Cells for power generation and green fuel production

Chuancheng Duan, Neal P Sullivan, Robert J Braun, Robert J Kee, Hanping Ding, Long Le, Alexis Dubois, Ryan O’Hayre

Abstract: A Reversible Protonic Ceramic Electrochemical Cell (RPCEC) is a device based on proton-conducting ceramics that can operate in both fuel cell and electrolysis cell modes. Compared to reversible electrochemical devices based on oxygen-ion conducting ceramics, RPCECs offer several potential advantages including lower temperature operation, improved coking resistance, and broad fuel flexibility. In fuel cell mode, RPCECs can efficiently convert the chemical energy contained within a wide variety of fuels (including hydrogen, various hydrocarbons, methanol, ethanol and ammonia) to electricity at intermediate temperatures (300 °C-600 °C). In electrolysis mode, RPCECs can operate with applied power from a renewable source (e.g. solar) to produce a number of versatile chemical fuels including hydrogen (via water electrolysis), ammonia (via solid-state electrochemical ammonia synthesis), and even certain hydrocarbon and/or liquid fuels. In this work, we will overview our progress towards fuel-flexible, intermediate-temperature RPCEC devices with promising performance, stability, and efficiency in both electricity-production and fuel-production modes.

Alexis Dubois, Sandrine Ricote, Kevin J. Albrecht, Chuancheng Duan, Ryan P. O’Hayre, Robert J. Braun

Abstract: Conventional solid oxide fuel cells (SOFCs) are showing increasing interest in distributed power applications, particularly for small-scale power capacity systems in the 1-100 kW range. Distributed generation technologies, such as SOFCs, continue to face challenges due in part to their presently high installed capital cost and high temperature degradation. Intermediate temperature protonic ceramic fuel cells (PCFCs) offer the potential for significant capital cost reductions and potential lower degradation rates, relative to their SOFC counterparts. Indeed PCFCs operate in the temperature range 400-600°C allowing for lower installed capital costs, while keeping equal system LHV efficiency above 50%. Then cheaper metallic components can be used at both stack- and system-levels, as a result of the lower operating temperature. Finally proton conduction triggers significant design and operating differences. Equipment downsizing opportunities are demonstrated for the PCFC in the balance-of-plant as compared to conventional SOFC systems due to different flow rates, heat flows and cathode water production.

Current research efforts in the protonic ceramic cell field have focused primarily on high cell performance and potential cell manufacturing cost reduction at a button-cell level. In this work, we estimate both PCFC and SOFC stack and system techno-economic performance for equivalent output net power at small-range 1-25 kW. Electrochemical, thermodynamic and cost models are combined to provide a quantitative comparison between PCFC (500 and 550°C) and SOFC (800°C) systems [1–3] for combined heat and power. Comparative sub-system analyses identify where cost advantages for PCFC technology are likely to be superior to SOFCs.

SQUID magnetometry of transition metal doped ceramics

M. Knight, I. Reimanis

Colorado School of Mines, Golden, CO, USA

Figure: A SQUID is the most sensitive device available for measuring magnetic fields, however it does not directly detect the magnetic field from the sample in the magnetometer. Instead, the sample moves through a system of superconducting detection coils connected to the SQUID by superconducting wires, allowing the current from the detection coils to inductively couple to the SQUID sensor. As the sample moves through the coils, the current in the detection circuit varies the SQUID output voltage proportionally with the magnetic moment of the sample.

Abstract: Many current ceramic materials of interest contain transition metals to impart some desired processing or performance characteristic. The valence states and valence transitions of metals such as Mn(IV)/Mn(III), Fe(III)/Fe(II), Ni(II)/Ni and Co(III)/Co(II), are of great interest due to their impact on the electrical, optical or magnetic properties of many ceramic materials. Unique magnetic responses are observed between undoped ceramics, metal particles in a second phase, metal ions in solution with the doped ceramic, or metal ions in an oxide phase with nanoscale features influencing the total electronic spin state of the metal. The magnetic behavior of the material can be measured with the highly sensitive technique called Superconducting Quantum Interference Device (SQUID) magnetometry. This characterization technique provides a non-destructive method to investigate magnetic moments of powders or sintered compacts with high accuracy. Interpreting the magnetic response of a material typically requires varying temperature and magnetic field of the instrument and determining the individual magnetic contributions to deconvolve the mixed magnetic response. Analysis of the magnetic behavior provides useful information on the electronic spin state of the metal and may be used to identify potentially interesting nanoscale features in the ceramic system. This underutilized characterization technique is expected to offer new insight into the beneficial properties imparted by transition metals on various ceramic systems of interest.
Investigating Metastability of Titania Polymorphs via Nanoscale Characterization

John S. Mangum\(^1\), Lauren M. Garten\(^2\), Lisa H. Chan\(^1\), David S. Ginley\(^2\), Brian P. Gorman\(^1\)

\(^1\)Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO, USA
\(^2\)National Renewable Energy Laboratory, Golden, Colorado, USA
\(^3\)TESCAN USA Inc., Warrendale, PA, USA

Abstract: Material properties, and therefore functionality, are inherently a product of both the chemical and structural makeup of the material systems we explore. Atomic level processes define many properties and therefore we often require the employment of nanoscale characterization techniques for accurate and reliable materials investigations. Such analytical tools include transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), and atom probe tomography (APT).

The goal of this research is to understand the mechanisms by which a particular metastable structure of TiO\(_2\), brookite, is synthesized and stabilized. Brookite has been shown to possess photocatalytic properties superior to its polymorphic counterparts.[1] Therefore, understanding formation pathways for this metastable polymorph could provide a breakthrough in the photocatalysis community. Several theories currently exist on why and how the brookite polymorph forms. Some propose topotactic transformation from more stable polymorphs via structural orientation relationships, while others suggest stabilization by incorporation of small concentrations of helper ions (e.g. Na\(^+\), Ca\(^+\)).[2,3] Nanoscale characterization offers the spatial and chemical resolution necessary for investigating both the crystallographic and chemical components of this elusive titania polymorph. High resolution TEM and selected area electron diffraction (SAED) were used to directly determine crystallographic structure of nanoscale grains of titania polymorphs. Dark field TEM imaging was combined with SAED to probe possible orientation relationships between the anatase and brookite polymorphs of TiO\(_2\). Nanoscale EDS and EELS, as well as APT, were utilized for chemical mapping, Ti valence state determination, and characterizing oxygen stoichiometry, respectively.

Identifying Reverse-bias Breakdown Sites in CuIn$_x$Ga$_{(1-x)}$Se$_2$ Photovoltaic Modules

Steve Johnston, Elizabeth Palmiotti, Andreas Gerber, Mowafak Al-Jassim, Angus Rockett

Abstract: Imaging techniques spatially resolve how defects develop and damage occurs when applied reverse-bias is used to resemble partial shading of CIGS modules. We use electroluminescence imaging and dark lock-in thermography (DLIT) to supplement current-voltage curves when reverse-bias breakdown occurs on CIGS mini-modules. For better understanding of how these defects originate and propagate, we are developing techniques where the current is limited during reverse-bias stressing. This allows for DLIT-based detection and detailed study of the region where breakdown initiates before thermal runaway leads to permanent damage and the formation of ‘wormlike’ defects, which are frequently observed after partial shading of CIGS modules. Under low current limitations, hotspots are noted on cells and correlation to where breakdown occurs. Figure 1 shows the reverse-bias stressing of two cells with varying degrees of current limitation until breakdown is achieved. Current-voltage analysis of the cells during stressing are studied to note effects on resistance prior to permanent breakdown. We are statistically analyzing where breakdown occurs to further investigate these regions by optical, chemical, and structural analysis.

Figure: Two CIGS cells by DLIT imaging. The first is undergoing 2V in forward bias. Thereafter, the cells are undergoing 20V in reverse bias with current limitations of 1mA, 1.5mA, 25mA, and 100mA, respectively.
The Densification of Bi$_2$Te$_3$ with Forming and Sintering Process

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Abstract: Bi$_2$Te$_3$ element which is the typical thermoelectric material is produced by growing and cutting the ingot of Bi$_2$Te$_3$ single crystal. Therefore, in this process, the material loss by sawing and slicing is so large and the occurrence of defective products is also large. Many studies have been reported on this point to reduce the material loss and the defective products. Until now, the typical approach is SPS(Spark Plasma Sintering) method which is one of the sintering process using Bi$_2$Te$_3$ powder. However, this method is high process cost relatively for the mass production and after treatment cost is also expensive. In this study, a regular sintering furnace was modified to combine rapid sintering and ambient sintering in order to obtain dense Bi$_2$Te$_3$ pellets. First, Bi$_2$Te$_3$ powder was synthesized mechanochemically and a wet-milling process was established so that densification can occur easily during the sintering process. Using the synthesized powder, dense Bi$_2$Te$_3$ pellets were obtained after 10 min sintering at 520°C after rapid heating at a rate of 120°C/sec in a H$_2$ and Te atmosphere. During the rapid sintering process, abnormalities were not produced from the oxidation reaction, and by preventing Te volatilization using Te atmosphere powder, no peculiar phenomena related to Te volatilization were observed in the pellets. Through this study, the feasibility of mass production of Bi$_2$Te$_3$ by the pressureless sintering process was investigated using rapid and ambient sintering.

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Environmental Mechanical Testing of Single Glass Fibers

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Figure: A cross sectional ESEM image of a single 50 um E-Glass fiber fractured in tension.

Abstract: The mechanical strength of industrially manufactured E-Glass used in fiberglass and fiber composites is significantly impacted by the degradation effect of moisture in the atmosphere through the static fatigue of stress corrosion. Single fibers were tested uniaxially in tension, and data were gathered to determine the strength-limiting flaws in these fibers. Variable relative humidities, strain rates and loads were used to determine the as-received strength of the glass and identify the moisture induced degradation. The results from this study show that a number of factors including relative humidity, age, and handling of the E-Glass fibers all influence the measured strength.
Utilizing Atom Probe Tomography for 3-D Quantification of Point Defects

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Abstract: Many properties of oxides are dependent upon non-stoichiometry and associated charge compensations. Properties such as electronic and ionic transport, dielectric constant, and electrical breakdown are dependent upon the accumulation of point defects at internal interfaces such as grain boundaries and heterojunctions. Quantification of these point defect accumulations using techniques such as EDS and EELS has been difficult previously, either due to light element sensitivity, detectability limits, or the 3-D nature of the internal interfaces.

Recent work has shown that Atom Probe Tomography (APT) has the requisite counting statistics, 3-dimensionality, detectability limits, and spatial resolution to quantify point defect accumulations at grain boundaries [1-3] and heterojunctions [4]. Utilizing the 3-D atom by atom nature of APT data has also enabled the conversion of analytical characterization data directly into space charge voltages and band alignments, ultimately enabling the direct relationship between materials characterization and materials or device properties.

Figure: (a) Slice of an APT reconstruction (doped CeO₂) and a 2-D projection of the Oxygen concentration illustrating the location of a grain boundary on the right side. (b) Ce and (c) O concentrations as determined from a proximity histogram from the center of the grain boundary. Oxygen vacancies and cations tend to accumulate at the grain boundary, resulting in a net charge and voltage.
The ability of APT to quantify point defect distributions in 3-D has limitations that are dependent upon the type of defect. Some examples include:

1. Individual vacancies on either oxygen or metal cation sites (\(V_{o}^{\ast\ast}\) or \(V_{m}^{\prime}\)). Both types of vacancies have been quantified with APT at grain boundaries (Figure 1) and at heterojunctions. Quantification of these are heavily dependent upon the detection efficiency of the APT experiment that can vary between 15 and 60% of all atoms based primarily upon the laser energy and resulting temperature rise in the specimen. Quantification is also dependent upon the volume being sampled, i.e., are the atomic counting statistics in the volume sufficient to be statistically accurate?

2. Interstitial oxygen or metal cations (\(O_{i}^{\ast\ast}\) or \(M_{i}^{\ast}\)). Similar to vacancies, a change in the number density of oxygen or cations can be observed but is limited to the counting statistics of the volume being analyzed. APT currently does not have the spatial resolution or 100% detection efficiency necessary to identify a single interstitial atom in 3-D.

3. Substitutional cations and defect pairs (\(M_{N}^{\prime}\)). As long as the cations are distinguishable in the mass spectrum (have different mass to charge ratios), then substitutional defects are able to be distinguished in a specific volume. As shown previously, substitutional defects coupled with vacancies are common ordered defect pairs and these are quantifiable using APT [4].

4. Schottky defects (\(V_{o}^{\ast\ast} + V_{m}^{\ast}\)) can be quantified using APT, as these defect pairs result in a change in atomic density. These defects are normally present only at internal or external interfaces or they tend to diffuse until they are nulled.

5. Frenkel pairs on either the oxygen or metal cation sites (\(V_{o}^{\ast\ast} + O_{i}^{\ast\ast}\)). These defect pairs do not result in a change in atomic density and are only dependent upon site occupancies. Similar to interstitials, APT does not have the spatial resolution or detection efficiency necessary to identify individual Frenkel pairs. Such analyses will have to wait for Atomic Scale Tomography, of which APT may play a part.

Ultimately, the combination of APT’s 3-D spatial and chemical resolution combined with analytical techniques such as EELS that allows for cation valence and free carrier energy levels to be determined will be the most complete solution to defect chemistry quantification.

Mines enters the first century BC!
Introducing our new hot glass shop.

Jake Ivy, Katie Gann, and Geoff Brennecka

Figure: (left to right) Bobby Puerling, Addison Wong, and Katie Gann showing off their hot glassworking skills and new forearm fashions.

Abstract: Thanks to the generosity of the MRS Foundation and the Mines Technology Fees and despite the dashpot tendencies of facilities personnel and associated contractors, Mines now has a functioning hot glass shop in the Hill Hall Foundry area. The purpose of this shop is to provide the Mines community with an opportunity to explore the artistic and hands-on aspects of materials science while also sneaking in some learning disguised as entertainment. While the combined glass shop and metal foundry facilities are being rebranded as a single integrated ‘Hill Hall Hot Shop’ (recommendations for a better name are welcome), the glass portion will eventually be managed by the Mines chapter of κεραμός. Our resident glass gurus will continue training additional gaffers through the fall 2017 semester in hopes of having sufficient expertise available to open the shop to all of campus (via an activity similar to Free Pour Friday—again, name suggestions are welcome) during the spring 2018 semester. The primary purpose of this CCAC presentation is to introduce the management/operation scheme to the audience and provide some show-and-tell about the capabilities of the shop.
CCAC News: 2016-17

Awards, Honors & Achievements

Prof. Angus Rockett joined the MME Department as Department Head in August 2016. He currently leads three projects on solar cell performance, characterization, and processing.

Drs. Geoff Brennecka, Corinne Packard, and Ivar Reimanis organized a visit of the National Academies of Science, Engineering and Medicine for their “Frontiers of Materials Research: A Decadal Survey” meeting held in Golden, CO July 27 & 29, 2017.

Drs. Dave Dierks and Brian Gorman were granted a patent with NIST: Norman A. Sanford, Ann N Chiaramonti-Debay, Brian P. Gorman, David R. Diercks, “Extreme-UV Atom Probe Tomography Instrumentation”, March 31, 2017.


Dr. Geoff Brennecka started serving as Editor of the Journal of the American Ceramic Society starting July 1, 2017

Dr. Geoff Brennecka was elevated to Fellow of the American Ceramic Society

Dr. Geoff Brennecka authored an APL paper on thermal conductivity of PZT which was one of the “editor’s picks”
Dr. Geoff Brennecka was asked to co-organize the 2018 National Academies of Engineering Frontiers of Engineering conference

Dr. Geoff Brennecka organized the NSF CAREER workshop with PacRim

Dr. Ryan O’Hayre lectured on fuel cells and electrochemical energy conversion at two international summer schools: The 6th International School on Materials for Energy and Sustainability at Caltech and the European Physics Society/Italian Physics Society International Physics Summer School on Basic Issues in Energy in Varenna, Italy

Dr. Corinne Packard received tenure & promotion to associate professor

Dr. Corinne Packard received AIME Robert Lansing Hardy award

Dr. Corinne Packard attended the National Academies of Engineering Frontiers of Engineering conference

Dr. Ivar Reimanis was elected to the World Academy of Ceramics.

Dr. Ivar Reimanis was awarded the Global Ambassador Award from the American Ceramic Society.

Dr. Ivar Reimanis was selected to chair the 2020 Gordon Research Conference on Ceramics. He is co-chairing the 2018 GRC meeting.

John Mangum was a recipient of the first ever Joe Goldstein Award.

John Mangum attended the 6th International School on Materials for Energy and Sustainability at Caltech.

Meagan Papac was awarded a full scholarship to attend the European Physics Society/Italian Physics Society International Physics Summer School on Basic Issues in Energy in Varenna, Italy

Brian C. Davis was awarded an ACerS scholarship to attend the ECerS summer school “Innovative technologies in the field of ceramic manufacturing” in Budapest, Hungary

Michaela Beuerlein earned her MS

Cassi Sweet became employed as an Engineer in Research & Process Development at Intel

Dustin Crouse earned his MS and is working as an Applications Engineer at 3D Systems

Aaron Miller earned his PhD and is employed in the R&D team at CoorsTek.

Taylor Wilkinson earned her PhD and is working as a Development Scientist at Corning