

# SYMPOSIUM PM05

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TUTORIAL: Field-Assisted Sintering—Microwaves, SPS and Flash Sintering  
November 25 - November 25, 2018

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\* Invited Paper

**TUTORIAL**  
**Field-Assisted Sintering—Microwaves, SPS and Flash Sintering**

Sunday Afternoon, November 25, 2018  
Hynes, Level 2, Room 208

**1:30 PM**

**Field Assisted Processing of Advanced Materials** Eugene Olevsky; Sand Diego State University

Sintering of powder materials is a widely used technological process, and, on the other hand, it is one of the most basic physical phenomena. The success of the industry in the development of computer-aided manufacturing made it possible to create a significant number of various devices for the processing of materials by the simultaneous action of heat, applied pressure, as well as electric current or electromagnetic field. These devices and processes belong to the area of so-called field-assisted sintering which offers fundamentally new materials processing conditions. Field-assisted sintering, which includes also the impact of electromagnetic factors, is, accordingly, a vivid example of a fundamental and multi-physics process. These sintering techniques enable materials and components with unique properties. Field-assisted sintering technologies thus represent an excellent experimental base for technologists engaged in the discovery of new materials. Simultaneously, field-assisted sintering opens up wide opportunities for modeling the processes of materials consolidation and synthesis taking into account numerous physical phenomena. The ninety minute tutorial will provide an introduction to sintering fundamentals as well as basics of field-assisted sintering techniques, including microwave and spark plasma sintering.

**3:00 PM BREAK**

**Flash Sintering** Rishi Raj; University of Colorado Boulder

In a 2010 paper it was shown that yttria-stabilized zirconia can be sintered in <5 s at a temperature of 850oC. (Conventional sintering requires several hours above 1400 oC – flash sintering is about four orders of magnitude faster.) Since then many different ceramics, including those that are semiconductors, electronic conductors, ionic conductors and high insulators, have been processed in this way. The flash phenomenon occurs in powder pressed samples, polycrystals and single crystals. An abnormal increase in electrical conductivity, and electroluminescence (in addition to rapid sintering) are characteristics of flash. Results from in-situ experiments at Synchrotrons are starting to provide fundamental insights. Molecular dynamics models are showing the significance of phonon-electron interactions. A roadmap for flash manufacturing is starting to develop. This emerging new field cuts across, materials science, ceramics science, engineering and solid state physics.

**4:30 PM**

**Open Discussion**

# SYMPOSIUM PM05

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Electromagnetic Fields in Materials Synthesis—Far from Equilibrium Effects  
November 26 - November 28, 2018

Symposium Organizers

B. Reeja Jayan, Carnegie Mellon University  
Woohong (Rick) Kim, U.S. Naval Research Laboratory  
Jian Luo, University of California, San Diego  
Eugene Olevsky, San Diego State University

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\* Invited Paper

**8:30 AM \*PM05.01.01**

**Reactive Flash Sintering** Rishi Raj<sup>1</sup> and Luis A. Maqueda<sup>2</sup>; <sup>1</sup>University of Colorado Boulder, Boulder, Colorado, United States; <sup>2</sup>Instituto de Ciencia de Materiales de Sevilla, Sevilla, Spain.

Conventional sintering of complex oxides is often fraught with undesirable phase transformations and, sometimes, loss of low melting and volatile constituents. Furthermore the synthesis of powders of these complex oxides also poses a challenge again for similar reasons. We show that reactive flash sintering where the powders of simple constituents, for example bismuth oxide and ferric oxide, can simultaneously react and sinter to form phase pure bismuth ferrite with highly insulating properties, which are elusive in conventionally sintered experiments. Results on other systems of technological significance will also be presented.

**9:00 AM PM05.01.02**

**Controllable Interface Approach in Field-Assisted Sintering** Eugene A. Olevisky; San Diego State University, San Diego, California, United States.

For the first time, by taking into account the explicit influence of the electric current effect on the SPS densification mechanism, the constitutive equations describing the electric current-assisted hot pressing of conductive powders are developed. The densification mechanism is determined by the inverse regression of the new SPS constitutive equations and by utilizing the experimental results on a conductive powder consolidation with and without the participation of the electric current effect. The developed model provides the theoretical basis of the new method of controllable interfaces which allows: extending flash sintering/SPS to nearly all materials, controlling sample shape, and an energy efficient mass production of small and intermediate size objects.

**9:15 AM \*PM05.01.03**

**Voltage-Dependent Electronic Conductivity in Yttria-Stabilised Zirconia Ceramics** Anthony R. West; University of Sheffield, Sheffield, United Kingdom.

Yttria-stabilised zirconia (YSZ) ceramics are used as the electrolyte in solid oxide cells since they have high oxide ion conductivity, negligible electronic conductivity and are stable in reducing atmospheres in contact with the fuel electrode. YSZ ceramics were the first materials in which the flash sintering technique was demonstrated, but there is still much debate concerning mechanistic details of flash sintering. It has been shown recently [1] that electronic conductivity can be introduced, reversibly, into YSZ by the application of a small dc bias. Further, with increasing Y content in cubic YSZ solid solutions [2], p-type electronic conduction can be introduced simply by increasing the oxygen partial pressure in the surrounding atmosphere. These results show that YSZ at atmospheric pressure is close to the upper limit of its electrolytic domain and the cross-over to p-type conduction. Results will be presented concerning the effects of composition, dc bias and oxygen partial pressure on the electrical properties of YSZ-related materials and their possible implications for the mechanism of flash sintering. The role of oxygen as a possible redox-active component of oxide lattices will be discussed as well as the conditions under which such redox activity may be observed.

1. N. Maso and A.R. West, *Chemistry of Materials* 2015, 27, 1552-1558

2. M. Jovani, H. Beltran, E. Cordoncillo and A.R. West, *Inorganic Chemistry* 2017, 56, 7081-7088

**9:45 AM BREAK**

**10:15 AM \*PM05.01.04**

**Flash Sintering and Related Field-Enhanced Processing for Oxide Ceramics** Hidehiro Yoshida<sup>1</sup>, Yamato Sasaki<sup>2</sup>, Koji Morita<sup>1</sup>, Byung-Nam Kim<sup>1</sup> and Takahisa Yamamoto<sup>3</sup>; <sup>1</sup>National Institute for Materials Science, Tsukuba, Ibaraki, Japan; <sup>2</sup>Tokyo University of Science, Tokyo, Japan; <sup>3</sup>Nagoya University, Aichi, Japan.

Electric field enhanced sintering is gaining interest in recent years owing to the accelerated consolidation compared to conventional, pressure-less sintering. In particular, flash sintering, where densification occurs almost immediately (typically <10 seconds) under high electric field, has attracted extensive attention as an innovative sintering technique. The flash sintering has been demonstrated in various ceramics, and almost full density has been achieved at relatively low furnace temperature for very short time. The non-equilibrium, drastic densification under strong electric field results from accelerated diffusional mass transport triggered by flash event; electric conductivity of material is highly increased, and excess anion vacancies are generated beyond threshold field strength and temperature. We should note that the flash event is rather a common phenomenon in oxide ceramics; it has been reported that flash event takes place not only in powder compact but also in dense, polycrystals even in single crystal. By employing flash event, for instance, superplastic flow at relatively furnace temperature can be attained in dense polycrystalline oxide ceramics such as tetragonal ZrO<sub>2</sub> polycrystal (TZP). For example, elongation to failure of more than 150% of nominal strain can be achieved in TZP at a furnace temperature of less than 1000°C and a strain rate of faster than  $1 \times 10^{-3} \text{ s}^{-1}$ . Flash sintering and field-enhanced sintering-related phenomena can be innovative processing techniques, i.e. consolidation and near-net shaping, of ceramic materials.

**10:45 AM PM05.01.05**

**Understanding and Controlling Flash Sintering—From a Case Study of ZnO to Other Ceramic Materials** Jiuyuan Nie, Yuanyao Zhang and Jian Luo; NanoEngineering, University of California, San Diego, La Jolla, California, United States.

This presentation will discuss a series of our recent studies of flash sintering. ZnO was used as our primary model system; TiO<sub>2</sub> and 8YSZ have also been studied. The effects of various doping, grain sizes (including single crystals) and sintering atmosphere have been systematically examined. A coupled thermal and electric runaway model has been developed to forecast the onset flash temperatures for ~ 20 cases with different materials, doping, particle sizes, and atmospheres [*Acta Mater.* 94:87 (2015) & 125:465 (2017)]. Further studies investigate the fast densification mechanisms of flash sintering [*Acta Mater.* 125:465 (2017)]. Using a new two-step flash sintering (TSFS) technology, fast densification with suppressed grain growth was achieved [*Scripta Mater.* 141: 6 (2017)]. Furthermore, various electric field/current effects on microstructural developments have been discovered and investigated. Interestingly, we recently demonstrated the feasibility of flashing ZnO at room temperature (without any furnace/external heating) to subsequently achieve ~98% densities in ~ 30 seconds with the adsorption of water vapor [*Scripta Mater.* 142: 79-82 (2018)]. This new water-assisted flash sintering (WAFS) technology represents an exciting opportunity for significant energy and cost savings.

The scientific questions and technological opportunities of flash sintering were discussed in a most recent Viewpoint article [*Scripta Mater.* 146: 260-266

(2018)].

**11:00 AM \*PM05.01.06**

**Insight into the Flash Sintering Process Mechanisms in Ceramics** Thomas Tsakalakos; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Flash Sintering (FS) utilizes the non-equilibrium rise in current under applied electric field to densify ceramic green body compacts in seconds. A new method, EDXRD Temperature Calibration, utilizes white energy dispersive x-ray diffraction (EDXRD) from a synchrotron source to track the lattice expansion of the ceramic during FS compared to the lattice expansion during conventional sintering (CS). The materials used in this study were ZnO, TiO<sub>2</sub>, CeO<sub>2</sub> and BiFeO<sub>3</sub> oxides and B<sub>4</sub>C, TiB<sub>2</sub>, ZrB<sub>2</sub> and BN nonoxides. This investigation analyzes the proposed mechanisms for the onset of the flash, the cause of the enhanced sintering kinetics during FS, and the temperature for each theory. The temperature has been measured directly as it causes a proportional lengthening of the bonds, which increases the unit cell volume. For all materials the temperature during FS is close to the CS.

New ways of performing FS experiments on ZnO by ramping the current linearly and by AC power supply, microstructural inhomogeneity, grain growth, and other physical properties will be also shown.

The FS of BiFeO<sub>3</sub> is a homogeneous process and since the FS takes place at quite low temperatures (350 °C < T<sub>c</sub>) it explains excellent dielectric properties. However, for CeO<sub>2</sub> and TiO<sub>2</sub> exhibited inhomogeneous lattice expansion from anode to cathode.

Acknowledgements

Thanks to my current group Harry Charalambous, Mary Anne Wassel, Dr. Shikhar Krishn Jha, & to ONR Dr. Antti Mäkinen ONR N00014-15-1-2492 & from Purdue ONR 4104-78982-820133 & to our collaborators: Dr. John Okasinski at Argonne N.L., Prof. Luis Perez Maqueda of University of Saville, Spain and his group, Dr. Haiyan Wang, Dr. Xinghang Zhang, Dr. R. Edwin Garcia, Xin Li Phuah, Han Wang, Jaehun Cho, Jin Li, and KSN Vikrant, at Purdue University, Dr. Amiyah Mukherjee at UC Davis, Dr. Steve Hellberg and Dr. Noam Bernstein at Naval RL

SESSION PM05.02: Field-Assisted Processing Techniques II

Session Chairs: Woohong (Rick) Kim and Eugene Olefsky

Monday Afternoon, November 26, 2018

Hynes, Level 1, Room 101

**1:30 PM \*PM05.02.01**

**Energy Coupled to Matter for Field-Enhanced Processing** Raymond Brennan, Victoria Blair, Michael Kornecki, Nicholas Ku, Selva V. Raju, Franklyn Kellogg, Michael Golt, Aubrey Fry and Carli Moorehead; U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

Energy Coupled to Matter (ECM) research at the U.S. Army Research Laboratory is focused on the study of material interactions with external fields to produce outcomes that are unattainable through conventional means, expanding materials-by-design and processing science capabilities beyond the current state-of-the-art. Research has been conducted to utilize these innovative technologies and material solutions for exploring structure-property relationships of ceramic materials based on their interactions with applied external fields (i.e. magnetic, electric, microwave, etc.). ECM research is focused on manipulation of microstructures, phase formation, and the overall behavior of materials subjected to controlled fields, which can enable rapid densification at reduced temperatures, grain and grain boundary modification, and crystallographic texturing. The ability to rapidly densify materials under less extreme processing conditions can allow for preservation of the nanoscale grain structure, providing the opportunity to improve mechanical properties including strength, hardness, and fracture toughness, which are vital to Army protection applications. Techniques for manipulating materials to make them more responsive to specific fields have also been investigated (ferromagnetic additives for magnetic fields, conductive second phases for electric fields, susceptor materials for microwave fields) to amplify these effects during processing. These strategies have combined experimental design, computational modeling, and in-situ characterization for development of unique ECM processes to enable field-enhanced production of improved components for protection, lethality, and energy-related (i.e. laser host, battery) Army applications.

**2:00 PM PM05.02.02**

**Low Temperature Ceramics Processing Under Electromagnetic Fields—Decoupling Thermal and Field Effects** B. Reeya Jayan; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Understanding the coupling between electromagnetic (EM) fields and matter can advance low temperature processing of several materials including ceramics. It is hypothesized that the EM field depending on frequency and polarization modifies energy barriers for chemical reactions. This talk will demonstrate experiments that use thin conducting films to selectively localize EM field interactions. We aim to delineate processing-structure relationships by creating and probing instances where there can be specific field driven effects that can be distinguished from conventional thermal phenomena. Specifically, our experiments will couple synthesis and characterization of binary ceramic oxide (e.g., ZrO<sub>2</sub>) films on conducting (metal) layers under 2.4-2.5 GHz microwave radiation. The solution bath in which the growth happens remains below 250 °C even during field exposure. We utilize synchrotron x-ray pair distribution function (PDF) analysis along with transmission electron microscopy (TEM) and Raman spectroscopy to study the crystallization and local atomic order in these thin films. By analyzing how EM field conditions (power, final temperature) influence the local atomic structure, we unlock potential mechanisms underlying field-assisted phase transformations and the role of defects in these field-induced structural changes.

Solving longstanding questions about the role of EM fields in processing advanced materials like ceramics has profound implications in diverse applications ranging from manufacturing to energy and healthcare. EM fields can offer a low temperature alternative to conventional thermal curing/sintering methods leading to energy-efficient manufacturing processes; even for materials like ceramics that conventionally requires high temperatures exceeding 500-2500 °C. Lower temperature processing can further be expanded to other delicate materials such as polymers and can even realize novel polymer-ceramic and metal-ceramic composites for biomedical use.

**2:15 PM PM05.02.03**

**Defects from Two Perspectives—Microstructure and Impedance Spectroscopy Comparison of Flash Sintered 8YSZ** Carolyn Grimley<sup>1</sup>, Andre Prette<sup>2</sup> and Elizabeth C. Dickey<sup>1</sup>; <sup>1</sup>North Carolina State University, Raleigh, North Carolina, United States; <sup>2</sup>Lucideon Limited, Stoke-on-Trent, United Kingdom.

Flash sintering, a technique for the rapid consolidation of ceramics under high electric fields, has been applied to a wide variety of materials with different

conduction mechanisms. The process is characterized by the application of an electric field to a heated ceramic, followed by increasing current, then rapid densification as the electric field decreases and the current hits an externally imposed steady-state limit. It is distinguished from similar field-based methods by the use of higher fields, relatively lower currents, and the exclusive application to materials with negative thermal resistivity coefficients. Given the basis of this specific material class and the observed electrical behavior, the onset of the electrical characteristics of flash are considered adequately explained by the thermal runaway model, which mathematically describes the feedback loop between the Joule heating of the ceramic and its increasing conductivity. It is tempting therefore to consider the entire technique as proceeding predominantly from the generalized conductivity trend of oxide ceramics, and independent of the specific conduction mechanisms or high field defect behavior that may be specific to different materials within the class.

Open questions remain, however, which may be greatly elucidated by considering these material-specific defect behaviors. For example, in samples processed under DC fields, inhomogeneous grain growth has been observed, with its relation to polarity changing based on the material processed. Furthermore, while the thermal runaway model explains the onset conditions of flash, no work has fully or conclusively proven a mechanism responsible for the rapid mass transport evidenced. Meanwhile, it is clear that the high electric fields in the process must simultaneously interact with the defects present in the material as well as add to the defect populations.

In the interest of exploring these defect contributions, we present a study comparing the final properties of flash sintered 8 mol% yttria-stabilized zirconia (YSZ) pellets using DC and AC fields. Microstructure is examined using scanning electron microscopy (SEM), and the final electrical characteristics are considered using impedance spectroscopy. While SEM gives direct microstructural observation, impedance spectroscopy fills in the picture with smaller scale defect and impurity implications specific to the grain boundary and bulk. A comparison between the two forms of characterization as well as conventionally sintered 8YSZ lends insight into fundamental reorganization and creation of defects produced in ionic conductors during flash sintering.

### 2:30 PM PM05.02.04

**Computational Insight for Field Assisted Sintering of TiO<sub>2</sub>** Jing Yang, Minh A. Dinh and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Field assisted sintering (FAST) has been demonstrated for multiple ceramic materials as a promising sintering technique in shortening consolidation time and lowering sintering temperatures. Mechanistically the interplay between electric field and the polycrystalline material is a complicated process and the governing factor for rapid densification during FAST is still under debate. In this work, we approached this problem from computational modeling in the model system of rutile TiO<sub>2</sub>. We separately quantified the effect of Joule heating and non-contact electric field on ion diffusion both in bulk and at grain boundaries. In bulk, we predicted the equilibrium defect concentrations at various pressures and temperatures from first-principles calculations. Berry phase calculation with electric field up to 8 MV/cm shows that electric field has negligible effect on both defect formation energy and migration barrier in bulk TiO<sub>2</sub>. For grain boundaries, we studied titanium diffusion by classical force field molecular dynamics. Ti diffusion is orders-of-magnitude faster close to the grain boundary. We also demonstrated the defect concentration change in space charge layer formed at grain boundaries with external bias. These results indicate that the local atomic structure and space charge layer profile of grain boundaries are important in understanding electric field effect on polycrystalline materials.

### 2:45 PM BREAK

### 3:15 PM \*PM05.02.05

**Laser Assisted Flash Sintering** Guillermo R. Villalobos<sup>1</sup>, Rafael R. Gattass<sup>1</sup>, Bryan M. Sadowski<sup>2</sup>, Robert E. Miklos<sup>2</sup>, Frederic H. Kung<sup>3</sup>, WooHong (Rick) Kim<sup>1</sup>, Shyam Bayya<sup>1</sup> and Jasbinder Sanghera<sup>1</sup>; <sup>1</sup>US Naval Research Laboratory, Washington, District of Columbia, United States; <sup>2</sup>KeyW, Hanover, Maryland, United States; <sup>3</sup>University Research Foundation, Greenbelt, Maryland, United States.

Flash sintering is an energy efficient sintering technique, which has been extensively researched, in recent years. Most of the work reported is on joule heating or the use of furnace as an additional heat source. This can pose a logistic challenge for quick repair or fabrication of a component in military challenging environment. We have successfully substituted laser energy for energy derived from joule heating and demonstrated flash sintering on Al<sub>2</sub>O<sub>3</sub> and B<sub>4</sub>C tapes at room temperature using an electrical potential of 100 - 1500V/cm and a 100W 975nm CW laser to heat the sample. No additional heat source, such as a furnace was used. We will show the effect of electrical potential on the degree of sintering. This furnaceless technique is very advantageous for various commercial and military applications due to its portability and the rapid processing time that leads to no or very small grain growth in the sintered product.

### 3:45 PM \*PM05.02.06

**Multi-Field Processing of Active Composites** Paris Vonlockette; The Pennsylvania State University, State College, Pennsylvania, United States.

Advances in materials science have seen the development and utilization of new classes of active materials including electroactive polymers and magneto-active elastomers. The sensitivity of these materials to electromagnetic fields allows them to generate actuation through magnetostrictive, electrostrictive, motive force, and other mechanisms. Engineers have used these responses to active suspensions, actuators, grippers, sensors, and morphing structures to name only a few of the myriad areas of application. While emphasis has been placed on development of materials for applications, researchers are also focusing on the process kinetics that drive formation of micro-architectures, architectures that ultimately determine material performance. Early work in magneto-active elastomers for example used DC field processing to generate alignment in embedded ferromagnetic particles. However, more recent work has shown that DC fields, are prone to produce agglomerations of particles especially at high volume fraction. Moreover research has shown that very low fields can produce strong alignment when the field is oscillated, e.g. when the system is not allowed to reach a static equilibrium state, but is instead forced into a steady state cycle with respect to its dynamic response. In this work, we explore the ability of coupled electric and magnetic field processing to develop a range of micro-architectures within a composite smart material. Our material system consists of micron-sized barium hexaferrite (BHF) particles, which have strong magnetic anisotropy, embedded in various polymers including a relaxor ferroelectric (RFE) polymer having nano-crystalline domains. Externally applied electric and magnetic fields act orthogonally on the embedded barium hexaferrite particles within the uncured composite due to the particles' planar shape and crystallographic c-axis magnetization, allowing multi-axis control of particle alignments. Furthermore, externally induced dielectrophoretic and magnetophoretic particle-particle interactions allow control of the arrangement of aggregates of particles, providing a second hierarchical level of control. Both levels have an inherent time dependence as well. The combination of BHF and the RFE polymer gives us, to varying degrees, the electrostrictive response of traditional electroactive polymers coupled with the magnetostrictive and magnetic-torque based response of magnetoactive elastomers. The microarchitectures formed, visualized using optical microscopy and SEM techniques, range from traditional chains of particles, to aligned clusters, to segregated agglomerations and are achieved within specific regimes of the processing parameter – constituent design space. The ability to tailor varying architectures is seen as a pathway to developing localized multi-material response, from a single set of constituents, through processing alone.

#### 4:15 PM \*PM05.02.07

**Non-Thermal Microwave Effects and the Role of Spin Entropy Configurations** Daryoosh Vashace, Amin Nozariasbmarz and Kelvin Dsouza; North Carolina State University, Raleigh, North Carolina, United States.

Today microwave radiation is quite often used to derive chemical reactions. Rapid and convenient heating, product selectivity, and better control over the product properties are some of the main advantages of using the microwave synthesis. In some cases, the reactions happened at rates several thousand times faster than what is achievable with conventional heating at similar average temperature. The observation of such extraordinary effects has been the subject of a fundamental question that whether there exist additional microwave specific effects. One of the main reasons that contradict the direct interaction of the microwave field is the significantly smaller energy of the microwave photons than the energy of the chemical bonds. Therefore, microwave excitations have been believed cannot dissociate the bonds and can merely heat the material by exciting the rotation or torsion of the dipoles a.k.a. dielectric absorption. As we will discuss this is not covering the whole story, and a fundamental study at the molecular level offers a better understanding of the energy transfers and the interaction of the material with the electromagnetic field.

In recent years, remarkable studies have been focused on understanding the microwave effects that cannot be explained by equilibrium thermodynamics. We will group some of these effects based on our experiments and the literature into (a) field-induced decrystallization, (b) enhanced solid-state reaction, (c) densification, (d) solid solution alloy decomposition, and (e) field-induced reduction. After a brief discussion of the existing theories or hypothesis associated with each group, we will present a detailed study that due to its molecular approach permits application to numerous experiments. In particular, we solved the master equation to describe the time evolution of the system under microwave radiation. Gillespie's exact stochastic method was used to model the chemical reactions occurring within the system considering the collisional energy transfers, spin degeneracy, microwave absorption/emission, and the chemical reaction. The vibrational and rotational states were evaluated while counting the densities of states. Notably, the energy split due to the Jahn-teller spin crossover lead to a change in the density of states and amplified absorption/emission of microwave radiation, which could not be explained otherwise. The outcomes demonstrated a noteworthy increment in the number of trajectories experiencing chemical dissociation contrasted with the system without the microwave. The resonance absorption and emission of the microwave photons inducing a transition between the states of different spin configurations increased especially the dissociation rate. These outcomes can clarify at least partially a number of the non-thermal influences of the electromagnetic interactions with materials.

SESSION PM05.03: Poster Session: Field-Assisted Processing—Techniques, Characterization, Modeling

Session Chairs: B. Reaja Jayan, Woohong (Rick) Kim and Eugene Olevsky

Monday Afternoon, November 26, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

#### PM05.03.01

**Electric Field-Induced Formation and Crumpling of Particle Shells Formed on Droplets** Alexander Mikkelsen and Zbigniew Rozynek; Physics, Adam Mickiewicz University, Poznan, Poland.

Droplets fully covered by particles serve as models for biological containers. They are also extensively used to stabilize emulsions and enable encapsulation and controlled release of materials such as medicines and self-healing materials. For many container and delivery applications, especially involving rupture and release, an understanding and characterization of the mechanical properties of the particle shell is essential. There are various methods for probing the mechanical properties of shells, but few of them are non-contact or tested on particle-covered droplets. We utilize electric fields and droplets as a contactless method to both fabricate particle shells of tailored composition and to control their deformation. By deforming particle shells, crumpling of their particle layers is induced which can be measured and used to determine the elasticity of the shell.

We investigate droplets that are covered by nano – and micrometer sized particles, and suspended in another fluid. Subjected to electric field-induced stress, we observe that particle shells on silicone oil droplets fail in various crumpling instabilities, including wrinkling, ridge formation, buckling and folding. In this research, we demonstrated how the strength and type of electric field can be used to control the crumpling behavior of the particle shell, and found that the crumpling wavelength decreases with the size of the particles at the drop interface. Moreover, the method for forming particle shells and controlling crumpling dynamics by applying electric-fields can easily be extended to multiple particle shells. The utilization of electric fields for both fabrication of shells and probing of their mechanical properties make the approach attractive for development of advanced materials with properties tailored to specific applications.

#### PM05.03.02

**Isolating the Effects of Sample Geometry on the Resulting Properties and Onset Conditions of Flash Sintering** Edgar Mendoza Jimenez and B. Reaja Jayan; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Flash sintering allows for the rapid densification of ceramics at lower temperatures than conventional ceramic powder sintering. It involves the application of an electric field across a green ceramic compact while being heated in a furnace; when the material reaches an onset temperature, which is dependent on process parameters, the sample's conductivity and densification rate drastically increase and full densification is achieved within seconds (typically <5 seconds). Although the mechanisms that explain the drastic increase in densification are not well understood, it is clear that electric field-assisted sintering has unique outcomes that cannot be reproduced with only a conventional furnace.

Past studies document the effects of various process parameters, including particle size, pressure, and atmosphere, on the resulting material properties and onset conditions (furnace temperature and electric field) of flash sintering. However, little attention is paid to the effects produced by sample geometry. To better understand these effects, we flash sintered samples with different surface areas and volumes in a modified tube furnace with base electrodes. By isolating the effects of sample geometry from other physical parameters, we gain insight into the effects of sample surface to volume ratio on the resulting material properties and onset conditions.

#### PM05.03.03

**W-Band Dielectric Constant of Aluminium Nitride Molybdenum Matrix Composites Near the Percolation Threshold of Electrical Conductivity** Martin Hilario<sup>1</sup>, Brad Hoff<sup>1</sup>, Anthony E. Baros<sup>1</sup>, Frederick W. Dynys<sup>2</sup>, Ender Savrun<sup>3</sup> and Maxwell R. Telmer<sup>4</sup>; <sup>1</sup>Air Force Research Laboratory, Albuquerque, New Mexico, United States; <sup>2</sup>NASA Glenn Research Center, Cleveland, Ohio, United States; <sup>3</sup>Sienna Technologies Inc.,

Woodinville, Washington, United States; <sup>4</sup>Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

The complex dielectric properties of Aluminum Nitride-Molybdenum ceramic matrix composites around the percolation threshold (5-25% Mo by weight) are measured using free-space transmission methods in the W-Band frequency range (75-110 GHz) and temperatures between 20-1000 degrees C. These investigations of the high temperature electromagnetic properties of ceramic composites at millimeter-wave frequencies enable predictions of the absorption properties of these materials under millimeter-wave irradiation. The ceramics are fabricated with hot pressing to obtain a range of composite samples having compositions ranging between 5-25% Molybdenum (by weight) in an Aluminum Nitride matrix. The relationship between the DC conductivity, grain boundary, and grain bulk conductivity of a ceramic matrix with distributed metal particles is compared with the measured complex dielectric constant to describe millimeter-wave absorption properties near the percolation threshold for electrical conductivity. In addition, thermal conductivity data is presented using differential scanning calorimetry to determine the heat capacity and laser flash method to determine the thermal diffusivity of each composition up to 1000 degrees C. Chemical and microstructural analyses are performed to identify mechanisms giving rise to millimeter-wave absorption and dielectric losses, and include scanning electron microscopy, energy dispersive spectroscopy, x-ray diffraction, tomography, mass spectroscopy, temperature-dependent AC impedance (1Hz-1MHz) using a Solartron furnace, and DC conductivity measurements using a high temperature four-point probe up to 1000 degrees C. Millimeter-wave heating and interactions based on complex dielectric properties are investigated using a 100 Watt klystron source operating at 95 GHz to study the millimeter-wave interactions, including measurements of the through and reflected power, with temperature, for refractory ceramics at high temperature under free-space irradiation.

#### PM05.03.04

**Synthesis of Un-Doped, Metastable ZrO<sub>2</sub> Phases Using Microwave Radiation** Maxwell R. Telmer<sup>1</sup>, B. Reeja Jayan<sup>1</sup>, Nathan Nakamura<sup>1</sup>, Martin S. Hilario<sup>2</sup> and Brad Hoff<sup>2</sup>; <sup>1</sup>Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; <sup>2</sup>Air Force Research Laboratory, Albuquerque, New Mexico, United States.

Electromagnetic fields are used constantly in industry and research to order or disorder a material's crystal lattice on very short timescales, however the fundamental mechanisms that underly these processes are still unknown. Primarily the existence of non-thermal effects (when the field couples directly with the lattice) and how they can be distinguished from thermal effects (when the field's energy is first converted to thermal energy before inducing lattice changes). In an effort to identify these effects we have been studying the phase formation and coverage of zirconia (ZrO<sub>2</sub>) thin films grown using microwave radiation. Formation of cubic and tetragonal zirconia (*c*-ZrO<sub>2</sub>, *t*-ZrO<sub>2</sub>), metastable phases that usually use yttria (Y<sub>2</sub>O<sub>3</sub>) doping to become stable, suggest non-thermal effects. These phases were identified using glancing incidence X-Ray diffraction. This suggests existence of a non-thermal effect, as our syntheses don't exceed 250 °C and these phases are not stable below 1,170 °C. Our films are grown in the microwave by selectively heating a conductive layer via ohmic heating. Upon changing the pattern of this conductive layer (while maintaining the same area) the phase that formed as well as the coverage of this pattern by the thin film was changed. We hope to continue exploring this relationship using a design of experiments approach. We are also in the process of modeling the scattering by the conductive layer to observe how its geometry influences heating and hope to use finite element modeling in future to expand on this model. Dielectric properties of ZrO<sub>2</sub> will also help describe how the films are growing, which we are obtaining using W-band free space characterization methods.

#### PM05.03.05

**A 2D Computational Model of a Triple Layer Electromagnetic Heat Exchanger** Ajit A. Mohekar, Vadim V. Yakovlev and Burt Tilley; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

An electromagnetic heat exchanger (EMHE) is a device which converts electromagnetic (EM) energy into usable form of heat energy. The working principle of the EMHE is based on a collective effect of EM wave propagation, heat transfer and fluid flow, so the development of an efficient device requires complicated experimentation with processes of different physical nature. In this paper, we present a 2D multiphysics model mimicking operation of a layered EMHE that simulates the nonlinear interaction between EM, thermal, and fluid flow phenomena involved in the operation of the EMHE. The model is built for a triple layered (fluid-ceramic-fluid) EMHE and is capable of capturing the S- and SS-profiles of power response curve which determines steady-state temperature solution as a function of incident power. We show that a EMHE with particular thickness and dielectric properties of the layers can operate efficiently by keeping temperatures during thermal runaway under control. Overall temperatures increase rapidly as soon as the local maximum temperature reaches a critical value. This condition is held true both in absence and in presence of fluid flow. It is demonstrated that the efficiency of the EMHE dramatically increases when thermal runaway is achieved. It is also shown that, with appropriate length of the layered EMHE, thermal runaway can be achieved at a lower power level.

SESSION PM05.04: Multiscale Materials Characterization in Field-Assisted Processing I

Session Chairs: B. Reeja Jayan and Woohong (Rick) Kim

Tuesday Morning, November 27, 2018

Hynes, Level 1, Room 101

#### 8:30 AM \*PM05.04.01

**Field Induced Mass Transport Phenomena in Flash Sintered High Temperature Ceramics Explored by *In Situ* SEM and TEM** Haiyan Wang; Purdue University, West Lafayette, Indiana, United States.

Haiyan Wang, Jin Li, X.L. Phuah, Jaehun Cho, Han Wang, Suryanarayana Karra, Edwin Garcia, and Xinghang Zhang, Purdue University  
Amiya Mukherjee, UC Davis  
H. Charalambous, S.K. Jha, Thomas Tsakalakos, Rutgers University

Flash sintering has attracted significant attention lately as its remarkable rapid densification process at low sintering temperature leads to the retention of fine grains and enhanced dielectric properties. However, the underlying mechanism of flash sintering and mechanical behaviors of flash-sintered ceramics remain poorly understood. Here, we report the microstructure of flash-sintered yttria-stabilized zirconia (YSZ) and TiO<sub>2</sub> by transmission electron microscope (TEM) and their high temperature *in-situ* micropillar compression studies inside a scanning electron microscope (SEM). Our studies on flash-sintered YSZ show that YSZ exhibits high inelastic strain (~ 8%) primarily due to phase transformation toughening below 400°C. At higher temperatures, crack nucleation and propagation are significantly retarded and prominent plasticity arises mainly from dislocation activities. The holding time and current density limit after the onset of flash for flash-sintered TiO<sub>2</sub> significantly affect the microstructure and mechanical behavior. High dislocation density and stacking faults have been observed in the flash-sintered TiO<sub>2</sub> under TEM. The presence of high-density defects generated during

flash sintering plays a major role in the overall microstructure and mechanical behavior of ceramics.

#### 9:00 AM PM05.04.02

**Low-Temperature Phase Transitions in Microwave-Assisted Synthesis—The Role of Oxygen Defects and Non-Thermal Effects** Nathan Nakamura<sup>1</sup>, Elizabeth Culbertson<sup>2</sup>, Han Wang<sup>3</sup>, Haiyan Wang<sup>3</sup>, Simon J. Billinge<sup>2, 4</sup> and B. Reeja Jayan<sup>1</sup>; <sup>1</sup>Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; <sup>2</sup>Columbia University, New York, New York, United States; <sup>3</sup>Purdue University, West Lafayette, Indiana, United States; <sup>4</sup>Brookhaven National Laboratory, Islip, New York, United States.

Electromagnetic (EM) radiation can significantly affect ceramic synthesis and processing, inducing rapid, low-temperature crystallization, non-equilibrium phase formation, and altered material properties. In particular, microwave radiation (MWR)-assisted synthesis has demonstrated the ability to crystallize high-temperature ceramic phases at significantly lower temperatures than conventionally required and impact local atomic ordering relative to furnace-based techniques. However, the mechanisms underlying these effects are not well understood. To understand these mechanisms, it is necessary to characterize EM field effects not only on crystalline phase formation, but also on non-crystalline local atomic order due to defects or amorphous components. It has been theorized that defect generation and transport may play an important role in promoting the effects seen under EM field exposure. Therefore, the relationship between synthesis and processing parameters (e.g., temperature, pressure) and the type, concentration, and response of defects is critical to the efficient design of these materials. An increased understanding of the potential mechanisms underlying EM field-assisted techniques will create the opportunity to utilize these methods to stabilize non-equilibrium phases or phase mixtures with desirable material properties.

To better analyze how EM fields influence phase formation and transitions, we utilize X-ray pair distribution function (PDF) analysis complimented by transmission electron microscopy (TEM) and Raman spectroscopy to study the crystallization and local atomic order in ZrO<sub>2</sub>, TiO<sub>2</sub>, and ZnO thin films. We demonstrate that the low-temperature crystallization and phase transitions observed during MWR-assisted synthesis are not a result of purely thermal effects. In all materials studied, we find that MWR helps to crystallize phases at much lower temperatures than conventionally required, and that the local order differs in MWR and furnace-grown films. This indicates a clear effect of MWR exposure on phase formation. By analyzing the local atomic order across various synthesis conditions, we find that thermal effects (e.g., reaction temperature, heating rate) do not fully explain the phase transitions observed. From our results, we are able to gain insight into the importance of defects and potential mechanisms underlying field-assisted phase formation.

#### 9:15 AM PM05.04.03

**In Situ Pair Distribution Function Analysis of Atomic Displacement in TiO<sub>2</sub> During Flash Sintering** Bola Yoon<sup>1</sup>, Devinder Yadav<sup>1</sup>, Rishi Raj<sup>1</sup>, Emanuele Sortino<sup>1</sup>, Sanjit Ghose<sup>2</sup>, Pankaj Sarin<sup>4</sup> and Daniel Shoemaker<sup>3</sup>; <sup>1</sup>Materials Science and Engineering Program, Department of Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado, United States; <sup>2</sup>Energy Sciences Directorate/Photon Science Division, NSLS II, Brookhaven National Laboratory, Upton, New York, United States; <sup>3</sup>Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; <sup>4</sup>School of Materials Science & Engineering, Oklahoma State University, Tulsa, Oklahoma, United States.

Flash sintering is a novel field assisted sintering technique, whereby ceramics can be sintered in just a few seconds. For example, 3 mol% yttria stabilized zirconia (3YSZ) was shown to sinter in < 5 seconds at a furnace temperature of 850°C under electric field of 120 V/cm. Recently, flash sintering has been expanded to synthesize unusual materials which are far from equilibrium. However, the mechanism of flash sintering is still controversial. Several mechanisms have been proposed for flash sintering, such as joule heating and defect avalanche. Here, we study atomistic understanding of flash sintering on TiO<sub>2</sub>, to elucidate its underlying mechanism. For this purpose, *in-situ* experiments of total X-ray scattering has been conducted at the National Synchrotron Light Source II at the Brookhaven National Laboratory. We have measured atomic displacement of O and Ti atoms within a unit cell, and found the unusual displacements in O atoms which are far greater than that from thermal expansion. It might imply that these atoms movements are the precursors to the generation of Frenkel pairs.

#### 9:30 AM \*PM05.04.04

**Developing the Underlying Principles for Electric Field Assisted Sintering for Improved Ceramic Manufacturability** Clement Nicollet, Jing Yang, Minh A. Dinh, Harry L. Tuller and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Field assisted sintering (FAST) has demonstrated great potential in reducing temperature constraints imposed on ceramic materials during sintering. While there have been many phenomenological observations of FAST processes, mechanistic understanding of the effect of electric field has been understudied and remains open. In particular, quantifying cation diffusion at different temperatures and polarizations both in bulk and at grain boundary is important for resolving the densification process under electric field. To that end, we studied the effect of defect chemistry on the field assisted sintering of TiO<sub>2</sub> by both sintering experiments and first-principles based modeling. Sintering experiments under electrical field were conducted inside a dilatometer to control the shrinkage of the material in real time. To separate out the Joule heating effect, we used controlled doping concentration and oxygen partial pressure to controllably vary the electronic conductivity of TiO<sub>2</sub>, thereby controlling the extent of the Joule heating contribution. By varying the main cationic defects between Ti vacancies and interstitials, as well as their concentrations, we studied their effect on the FAST process. In parallel, the equilibrium defect concentrations under relevant conditions were predicted utilizing a first-principles based computational framework. By combining equilibrium defect concentration with defect diffusivities obtained from force field molecular dynamics, we constructed Ti diffusion profiles as a function of temperature, oxygen partial pressure and electric polarization. The predicted Ti self-diffusion coefficient agrees reasonably well with experimental measurements and in both cases Ti interstitial contributes dominantly. Moving from bulk to grain boundary, we found a very weak space-charge effect and a three-order-of-magnitude increase in the diffusion coefficient due to decreased Ti migration barrier. This result implies that Ti diffusion is greatly accelerated at the grain boundary. Identifying these factors advances our understanding of the individual effects of Joule heating, bulk cation diffusion, grain boundary mobility and electric polarization on flash behavior, and thereby, guide better control of ceramic materials manufacturing by FAST technology.

#### 10:00 AM BREAK

#### 10:30 AM \*PM05.04.05

**Implications of Point Defect Redistribution During Electric-Field Processing of Oxides** Elizabeth C. Dickey, Carolyn Grimley and Neal Lewis; North Carolina State University, Raleigh, North Carolina, United States.

Processes that utilize DC or low-frequency electric fields provide a driving force for ion migration in ionic materials. This is particularly true in electric-field-assisted sintering where both high fields and high temperatures are involved, which enhance the kinetics of ion migration. This talk will discuss the effects of sample and electrode boundary conditions on electric-field-induced ion migration and resulting stoichiometry gradients in the context of field-assisted sintering. The implications for conductivity evolution and microstructure development will be illuminated, with examples from field-assisted sintering of yttria-stabilized ZrO<sub>2</sub> (YSZ) and BaTiO<sub>3</sub>. Lateral and axial microstructural gradients will be discussed with respect to the electrochemical, thermal and mechanical boundary conditions of the ceramic body during sintering. In addition, more complex composite systems, such as layered systems of YSZ and Al<sub>2</sub>O<sub>3</sub> which exhibit interesting asymmetrical sintering behaviors, will be discussed.

**11:00 AM PM05.04.06**

**High Temperature *In Situ* Micromechanical Testing of Flash-Sintered Ytria Stabilized Zirconia** Jaehun Cho<sup>1</sup>, Qiang Li<sup>1</sup>, Han Wang<sup>1</sup>, Zhe Fan<sup>2</sup>, Jin Li<sup>1</sup>, Sichuang Xue<sup>1</sup>, K. S. N. Vikrant<sup>1</sup>, Haiyan Wang<sup>1</sup>, Troy Holland<sup>4</sup>, Amiya Mukherjee<sup>3</sup>, Edwin D. Garcia<sup>1</sup> and Xinghang Zhang<sup>1</sup>; <sup>1</sup>Purdue University, West Lafayette, Indiana, United States; <sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; <sup>3</sup>University of California, Davis, Davis, California, United States; <sup>4</sup>Colorado State University, Fort Collins, Colorado, United States.

Nanostructured ceramic materials have various structural and functional applications. Flash sintering has attracted significant attention as its remarkably rapid densification process at low sintering furnace temperature leads to the retention of nanograins. However, high-temperature mechanical behaviors of flash-sintered ceramics remain poorly understood. Here, we present the high temperature *in-situ* microcompression studies on ultrafine grained yttria-stabilized zirconia (YSZ) processed by flash sintering technique. At room temperature, the flash-sintered YSZ sustains a large strain before fracture due to phase transformation induced toughening, and dislocation activities. At higher temperatures, crack nucleation and propagation are significantly retarded. The influence of test temperature on deformation mechanisms of YSZ is discussed.

**11:15 AM PM05.04.07**

***In Situ* X-Ray Diffraction Study to Measure Local Temperature During Microwave Radiation-Assisted Synthesis** Shikhar K. Jha, Nathan Nakamura and B. Reaja Jayan; Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Microwave radiation-assisted synthesis reduces the reaction temperature and improves the yields compared to a conventional furnace synthesis. Additionally, it has been shown to alter the material properties of final product by incubating new phases, changing crystallinity, or modifying particle size distributions. For example, during an experiment involving synthesis of TiO<sub>2</sub> on an indium tin oxide (ITO) layer under microwave radiation, a mixed phase structure consisting of a long-range anatase phase and a short-range amorphous phase was obtained. The results were linked to the formation of an oxygen-deficient meta stable phase under microwave irradiation. The exact mechanism, however, remains undetermined, as there is no direct method to measure the local temperature during this process. It is disputed whether the observed phenomena are thermal or non-thermal in nature. It is possible that coupling between microwave and matter can lead to localized heating, which would also result in rapid reaction/diffusion kinetics at preferential sites. But, this temperature inhomogeneity still does not explain the nucleation of meta stable phases under microwave. In this work, microwave radiation-assisted synthesis of TiO<sub>2</sub> is performed with three different materials as substrate. *In situ* x-ray diffraction (XRD) is used to track the change in lattice parameters of both the substrate and the synthesized TiO<sub>2</sub> powder during growth and crystallization. The lattice expansion was correlated with the actual temperature at the ceramic/substrate interface and within the ceramic itself. The temperature distribution and change in crystal structure is used to differentiate the thermal from the non-thermal contribution of externally applied fields during the process.

**11:30 AM \*PM05.04.08**

**Characterization of AlN-Based Ceramic Composites for Use as Millimeter Wave Susceptor Materials at High Temperature** Brad W. Hoff<sup>1</sup>, Martin S. Hilario<sup>1</sup>, Anthony E. Baros<sup>1</sup>, Steven C. Hayden<sup>2</sup>, Rachael O. Grudt<sup>2</sup> and Frederick W. Dynys<sup>3</sup>; <sup>1</sup>Directed Energy Directorate, Air Force Research Laboratory, Albuquerque, New Mexico, United States; <sup>2</sup>Aramco Research Center, Boston, Massachusetts, United States; <sup>3</sup>NASA Glenn Research Center, Cleveland, Ohio, United States.

In some wireless power transfer systems utilizing thermo-mechanical conversion methodologies, bulk susceptor materials are required to convert microwave or millimeter wave radiation to thermal power which is, in turn, converted to electrical power. These bulk susceptor materials may take the form of composites formed from a high thermal conductivity ceramic matrix in combination with a radiation-absorbing additive, such as lossy ceramic or metal particles.

For ease of design, the effective dielectric loss of the susceptor composite should be dominated by the additive material. Additionally, the temperature-dependent dielectric loss of the composite should be as weakly exponential as achievable to limit the likelihood of thermal runaway effects and to better enable optimization over a wide range of operating temperatures.

Ceramic composites presently under investigation for use as mm-wave susceptors include aluminum nitride composited with molybdenum power (AlN:Mo) and aluminum nitride composited with titanium diboride (AlN:TiB<sub>2</sub>). Thermal properties, compositional and structural analysis, and high-temperature complex permittivity data will be presented for AlN:Mo composites ranging from 0.25% to 4% Mo (by weight). Preliminary complex permittivity measurement data will also be presented for selected AlN:TiB<sub>2</sub> formulations. Data presented on these AlN-based ceramic composites will be discussed in the context of suitability of these materials for use in future wireless power transfer experiments.

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SESSION PM05.05: Multiscale Materials Characterization in Field-Assisted Processing II

Session Chair: B. Reaja Jayan

Tuesday Afternoon, November 27, 2018

Hynes, Level 1, Room 101

**1:30 PM \*PM05.05.01**

**Dielectric Breakdown in Ceramics—Conduction Mechanisms, Conducting Filaments and Breakdown Toughness** Gerold A. Schneider and Pia-Kristina Fischer; Hamburg University of Technology, Hamburg, Germany.

Even though dielectric breakdown in ceramics is a limiting factor for the reliability of electronic devices and components and despite almost 100 years of research there is no commonly accepted understanding of this phenomenon. In this talk a Griffith-type dielectric breakdown model is presented. The difference to previous models is that it is based on space charge limited conduction (SCLC) and not on ohmic conduction. It is shown that in a lot of ceramics SCLC is most likely the dominating conduction mechanism at very high electric fields. As the origin of dielectric breakdown it is assumed that tiny electrically conducting filaments get unstable at the breakdown field and grow to the well known breakdown channels. To investigate this hypothesis artificial conducting channels were prepared in borosilicate glass using a Focused Ion Beam. It will be shown that the breakdown strength is linearly dependent on the inverse square root of the lengths of these filaments, which is in agreement with the prediction of the model. From these results a breakdown toughness for borosilicate glass can be determined. In summary it is possible to describe the size dependence and scattering of the breakdown

strength with this approach.

## 2:00 PM PM05.05.02

**Electrochemistry and Electro-Kinetics in Zirconia Ceramics** Yanhao Dong<sup>1</sup>, Liang Qi<sup>2</sup>, Ju Li<sup>1</sup> and I-Wei Chen<sup>3</sup>; <sup>1</sup>Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; <sup>2</sup>University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; <sup>3</sup>University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Field assisted sintering such as flash sintering and spark plasma sintering attracts much attention in the ceramic community. It is of particular interest to clearly identify non-thermal effects, to understand diffusion/phase-transformation kinetics and to control microstructural evolution, aided by an electric field and maybe enhanced by far-from-equilibrium defects. To echo and argue on such non-equilibrium effects, we shall present our recent work on how electric field influences zirconia's microstructure and how we can understand it within equilibrium. We emphasize applied electric field can greatly change local thermodynamics, hence influencing kinetics indirectly.

Phenomenological correlation: By grain growth experiments, we show hydrogen and electrochemical reduction enhances grain boundary mobility and cation diffusion in zirconia and ceria. [1-2]

Electrochemistry: Anions and electrons set up local equilibrium. Zirconia is a fast oxygen ion conductor with little electronic conductivity. So electrode reactions at metal/zirconia interface are necessary to convert electron flow in outer circuit to oxygen ion flow inside zirconia electrolyte. Yet it must in the end become sluggish, creating huge overpotentials and shift equilibrated defect concentrations. Through continuum-level simulations, we obtain a step-like oxygen potential profile responsible for observed grain-size transition inside electrically loaded zirconia, and a flux discontinuity at grain boundary responsible for observed cavitation.

Electro-kinetics: Cation diffusion determines global microstructure evolution. Cation diffusion in zirconia and ceria takes place via a vacancy mechanism [3-4], yet it is enhanced by reduction, which according to defect chemistry decreases the concentration of cation vacancy. This conundrum has been resolved by our recent first-principles calculations. We found reduction-created electrons can greatly lower cation's migration barrier. It suggests a critical role of minor electronic defects in determining mass transport for oxides (even as ionic as zirconia), which had been totally overlooked by classical nonstoichiometric defect chemistry.

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## 2:15 PM PM05.05.03

**In Situ Characterization of Phase-Change Materials (PCMs)** Shalini Tripathi<sup>2,3</sup>, Matthew T. Janish<sup>3</sup>, Nafisa Noor<sup>2</sup>, Katherine L. Jungjohann<sup>1</sup>, Doug Pete<sup>1</sup>, Paul G. Kotula<sup>5</sup>, Helena Silva<sup>2</sup> and C B. Carter<sup>3,1,4</sup>; <sup>1</sup>Center for Integrated Nanotechnologies (CINT), Sandia National Laboratories, Albuquerque, New Mexico, United States; <sup>2</sup>Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut, United States; <sup>3</sup>Material Science and Engineering, University of Connecticut, Storrs, Connecticut, United States; <sup>4</sup>Chemical & Biomolecular Engineering, University of Connecticut, Storrs, Connecticut, United States; <sup>5</sup>Materials Science & Engineering Center, Sandia National Laboratories, Albuquerque, New Mexico, United States.

To understand the mechanism underlying the fast, reversible, phase transformation, information about the atomic structure and defects structures in phase change materials class is key. PCMs are investigated for many applications. These devices are chalcogenide based and use self heating to quickly switch between amorphous and crystalline phases, generating orders of magnitude differences in the electrical resistivity. The main challenges with PCMs have been the large power required to heat above crystallization or melting (for melt-quench amorphization) temperatures and limited reliability due to factors such as resistance drifts of the metastable phases, void formation and elemental segregation upon cycling. Characterization of devices and their unique switching behavior result in distinct material properties affected by the atomic arrangement in the respective phase. TEM is used to study the atomic structure of the metastable crystalline phase. The aim is to correlate the microstructure with results from electrical characterization, building on R vs T measurements on various thicknesses GST thin films.

To monitor phase changes in real-time as a function of temperature, thin films are deposited directly onto Protochips carriers. The Protochips heating holders provides controlled temperature changes while imaging in the TEM. These studies can provide insights into how changes occur in the various phase transformations even though the rate of temperature change is much slower than the PCM device operation. Other critical processes such as void formation, grain evolution and the cause of resistance drift can thereby be related to changes in structure and chemistry. Materials characterization is performed using Tecnai F30 and Titan ETEM microscopes, operating at 300kV. Both the microscopes can accept the same Protochips heating holders. The K2 direct electron detector camera equipped with the ETEM allows high-speed video recording (1600 f/s) of structural changes occurring in these materials upon heating and cooling. In this presentation, we will describe the effect of heating thin films of different thickness and composition, the changes in crystallinity and grain size, and how these changes correlate with changes in the electrical properties of the films. We will emphasize that it is always important to use low-dose and/or beam blanking techniques to distinguish changes induced by the beam from those due to the heating or introduction of an electric current.

Funded by NSF under award DMR-1710468. TEM was performed at CINT, an Office of Science User Facility operated for the U.S. DOE, and in the Materials Characterization Department. Sandia National Labs is managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's NNSA contract DE-NA-0003525. The views expressed here do not necessarily represent the views of the U.S. DOE or the U.S. Government.

## 2:30 PM \*PM05.05.04

**Advanced Iron Oxide-Based Nanostructured Ceramics with Tailored Magnetic and Mechanical Properties** Diletta Giuntini<sup>1</sup>, Elisa Torresani<sup>2</sup>, Kyle Chan<sup>3</sup>, Buesra Bor<sup>1</sup>, Berta Domenech<sup>1</sup>, Javier Garay<sup>3</sup>, Eugene A. Olefsky<sup>2</sup> and Gerold A. Schneider<sup>1</sup>; <sup>1</sup>Hamburg University of Technology (TUHH), Hamburg, Germany; <sup>2</sup>San Diego State University, San Diego, California, United States; <sup>3</sup>University of California, San Diego, California, United States.

Nano-structured and nano-grained materials are among the most promising applications of field-assisted sintering techniques, thanks to their characteristic ability to enhance densification and hamper grain growth through high heating rates and the aid of electric fields and current. The introduction of multifunctionality is also often made possible by combining tailored nano-architectures with such ultra-rapid processing methods. This study addresses the

potential of spark plasma sintering for the production of advanced iron oxide-based ceramics with an enhanced combination of magnetic and mechanical properties. The green samples consist of organically-covered magnetite nanoparticles, with diameter below 18 nm and monomodal size distribution, self-organized into an extended tightly-packed supercrystalline lattice. The application of relatively low-temperature spark plasma sintering regimes leads to the controlled development of bulk nanocrystalline ceramic materials with tunable magnetic properties and a unique combination of strength, hardness, stiffness and toughness. The interrelationships between supercrystalline structure and overall magnetic and mechanical features are explored, together with the path towards the manufacturing of novel bulk iron oxide materials with superparamagnetic behavior.

### 3:00 PM BREAK

#### 3:30 PM \*PM05.05.05

**Neutron Diffraction—A Useful Tool to Study Structures of Polycrystalline Compounds** [Ashfia Huq](#); Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Sensitivity to light elements in the presence of heavier elements makes neutron diffraction an ideal tool to study oxides, hydrides and compounds containing Li. As a result, neutron crystallography has been very successfully used to elucidate structures of energy materials and correlated electron systems. In this presentation, I will introduce the technique and its usefulness in structural characterization with several examples.

#### 4:00 PM PM05.05.06

**Polymer Patterning Via Electrohydrodynamic Instabilities** [Katherine E. Copenhaver](#) and Jason H. Nadler; Georgia Institute of Technology, Atlanta, Georgia, United States.

Patterned polymer surfaces can provide high-index contrast over a periodic matrix with 3-dimensional element shapes. The dielectric contrast and array pitch and height can be tuned to control specular reflection and achieve specific scattering characteristics. Surfaces with tailored scattering characteristics in the aforementioned ranges could be useful in producing frequency-selective windows for glare reduction, anti-reflective solar cells with enhanced efficiency, surface waveguides and whispering gallery-mode resonator arrays for integrated photonics and sensors, and surfaces with controlled emissivity for directed heat dissipation. Electrohydrodynamic (EHD) instabilities can be induced in polymers by placing a polymer film above its  $T_g$  in a strong electric field between two capacitor plates or electrodes. The polymer experiences an electrostatic stress at the interface between the polymer and air due to a mismatch in their dielectric constants. This stress, along with thermal fluctuations, induces small magnitude capillary waves in the polymer film, and the minima and maxima of those waves experience slightly different electric field strengths. In a sufficiently strong electric field, the capillary wave maxima, where the distances between the polymer film and the top electrode(s) are the smallest, are eventually drawn up to the top electrode. The wavelength of the instabilities in the film and the ability of the polymer to be drawn upward is a dependent on the competition between surface tension forces and the electrostatic stress imparted on the polymer. While EHD instabilities are typically used to pattern polymer surfaces on a nanometer-scale, instabilities have been induced in polymer films with air gaps up to 500  $\mu\text{m}$ . Upper electrodes with non-planar structures have also been used to induce instabilities in polymer films, resulting in patterned polymer surfaces without contact. Size, shape, arrangement, and placement of the upper electrode relative to the polymer film and lower electrode, as well as the processing conditions such as temperature and applied voltage, can all be modified to produce a desired array of structures with tailored performance characteristics.

#### 4:15 PM PM05.05.07

**Controlling Catalytic Reaction Pathways via Magnetic Heating** Natalia da Silva Moura, Pragathi Darapaneni, Kerry Dooley and [James A. Dorman](#); Louisiana State University, Baton Rouge, Louisiana, United States.

The catalysis market is responsible for more than 35% of the world's GDP, and it is involved in the most successful industrial sectors: energy generation, chemicals, and pharmaceuticals. Despite the remarkable advances in catalytic technologies, the industry still faces thermal management issues and accumulation of heat on reactor walls. Alternatively, it is possible to overcome the activation barrier using in situ methods via iron oxide ( $\text{Fe}_3\text{O}_4$ ) exposed to an alternating magnetic field. In this work,  $\text{Fe}_3\text{O}_4$  nanoparticles will be used to convert alternating magnetic fields to heat to study the effects of localized energy on the chemical transformation in a reference alcohol condensation reaction.

20 nm iron oxide nanoparticle spheres, cubes, and truncated octahedrons of tunable sizes are exposed to RF fields to drive an alcohol dehydration reaction. The size and shape of these particles are controlled by varying surfactant to precursor ratio in thermal decomposition reactions. These facets allow for the tuning of surface activity and heat generation, key parameters for selectivity and activity engineering. The heat generated is dependent on the spin configuration on the surface, with minimum heating rates at least 34% higher than commercially available particles. Surface functionalization with hydroxyl groups is performed to increase the interaction of  $\text{Fe}_3\text{O}_4$  with alcohols in dehydrogenation reactions. This localized heat generation can be used to control surface functionalization for dispersion in aqueous solutions and conversion of alcohols. For spherical particles, the GC-MS data shows production of aldehydes and esters via thermal routes while RF induced reactions result in longer alkenes, such as decene, which is dependent on the applied magnetic field. These results indicate changes in the reaction mechanism associated with RF activation. Furthermore, to investigate the role of the surface of iron oxide without any surfactants on the mechanism of the reaction, spherical nanoparticles are also synthesized via co-precipitation routes. The catalyst is characterized before and after functionalization and reaction steps to probe the crystal structure, oxidation states of iron and morphology of the particles, using XRD, XPS, and HRTEM respectively. The reaction products are characterized via GC-MS to elucidate the reaction mechanism.

### SESSION PM05.06: Multiscale Modeling of Field-Assisted Processing

Session Chairs: B. Reaja Jayan and Eugene Olevsky

Wednesday Morning, November 28, 2018

Hynes, Level 1, Room 101

#### 8:00 AM \*PM05.06.01

**Charged Grain Boundaries and the Microstructural Evolution of Ionic Ceramics** K. S. N. Vikrant and [Edwin Garcia](#); Purdue University, West Lafayette, Indiana, United States.

The macroscopic properties of polycrystalline ionic ceramics are determined by the doping levels, point defects, and their interaction with the microstructure, as they are specified via processing and the target application. Here, the starting powders react, densify, and coarsen into microstructurally

tailored grain topologies that are aimed to enhance (but sometimes limit) the performance of the device that are part of. The extent of these interactions varies with grain size, crystallographic orientation, and misorientation distribution, as well as applied fields, such as stress or electric fields. In order to understand the grain boundary characteristics, including their electrochemical properties and the driving forces that control grain coarsening, a thermodynamically consistent diffuse interface theory is being developed. The theory naturally incorporates the effects of drag as they are imposed by the interfacially accumulated charged defects on the grain growth of polycrystalline ceramics. Applications to materials such as YSZ, GCO, and STO (and comparisons against experimental results) are presented.

#### 8:30 AM PM05.06.02

**High-Frequency Homogenization of Porous Media Electromagnetic Heat Exchangers** Joseph M. Gaone, [Burt Tilley](#) and Vadim V. Yakovlev; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Electromagnetic (EM) heat exchangers are devices which absorb EM radiation converting it into thermal energy to do work, such as run a turbine. Applications involving both solar and microwave energy have garnered increasing attention but have yet to utilize the potential benefits of short-wave interactions when the wavelength is comparable to a material's microstructure. It has been shown for a three-layer laminate the Bragg resonance that occurs at this scale can be used to control steady state temperature and thermal runaway effects. We investigate these effects in a mathematical model approximating a porous medium for use in a heat exchanger. Classical homogenization methods average over the microscale to obtain a macroscopic description of the material, however they are incapable of describing short-wave behavior. High-frequency homogenization methods have been developed but are restricted to cases incompatible with modeling heat exchangers, such as assuming a lossless medium, spatially uniform dielectric constants, and reducing Maxwell's equations to the Helmholtz equation. We develop a high-frequency homogenization technique that relax these assumptions, considering a laminate geometry composed of alternating layers of lossy dielectric material and lossless fluid channels in the homogenization limit. This model advances the designing of porous materials for efficient collection of energy in electromagnetic heat exchangers.

#### 8:45 AM PM05.06.03

**Nucleation of Metastable Vaterite CaCO<sub>3</sub> is Mediated by Electric Fields** [Wenhao Sun](#) and Gerbrand Ceder; Lawrence Berkeley National Labs, Berkeley, California, United States.

Vaterite is a transient metastable polymorph of calcium carbonate that often appears during the multistage crystallization of CaCO<sub>3</sub>. Nucleation of vaterite prior to the equilibrium phase calcite should, according to classical nucleation theory, be facilitated by a lower surface energy of vaterite than calcite. We perform a thorough density functional theory investigation of calcite and vaterite surface energies, and find, contrary to expectations, that vaterite unequivocally has the higher surface energy of the two phases. Here, we present a novel mechanism to rationalize the preferential nucleation of vaterite. Because the vaterite crystal structure is composed of alternating Ca<sup>2+</sup>/CO<sub>3</sub><sup>2-</sup> planes in the [001] direction, nanoparticles of vaterite possess a permanent electrostatic dipole moment. We show that nuclei of vaterite can be stabilized relative to calcite under electric fields that are consistent with charge inhomogeneities on mineral surfaces, in biogenic macromolecules, and in aqueous electrolyte solutions. The role of electric fields in nucleating the polar polymorph of CaCO<sub>3</sub> can be more generally leveraged to synthesize metastable polar phases of other materials, potentially opening the door to materials with novel or superior functionality.

#### 9:00 AM \*PM05.06.04

**Coupling Between Electrons and Defects in Flash Sintering** [C. Stephen Hellberg](#); Naval Research Laboratory, Washington, District of Columbia, United States.

During "flash sintering," the application of an external electric field results in rapid densification at significantly reduced temperatures in many materials. The flash event is accompanied by a dramatic increase in the conductivity of the sample and an expansion of the lattice constants. I will discuss the microscopic processes contributing to flash sintering. In particular, I will discuss the coupling between a non-equilibrium carrier distribution and defects within the grains. I will present examples of density functional calculations of defects in yttria-stabilized zirconia and titania. This work was performed in collaboration with Noam Bernstein and Steven C. Erwin at the Naval Research Laboratory.

#### 9:30 AM BREAK

#### 10:00 AM \*PM05.06.05

**Laser Flash Sintering of Ceramics** [Joseph J. Beaman](#), Desiderio Kovar and Deborah Hagen; Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States.

Additive manufacturing enables production of complex shapes and customizable designs, using a wide variety of materials. Direct layer-wise sintering of ceramics using additive manufacturing techniques, however, has been an elusive goal due in part to the rapid kinetics required to sinter ceramic powders together one layer at a time. Flash sintering research using conventional furnace heating has demonstrated that application of an electric field during furnace sintering results in very rapid densification of ceramics, in most cases decreasing over an hour of sintering time to seconds. The simultaneous application of an electric field with laser scanning of ceramic powders is investigated as a method of enabling the processing of ceramic powder using selective laser sintering.

#### 10:30 AM PM05.06.06

**Electrochemical Effects on the Microstructural Evolution of STO** [Suryanarayana V. Karra](#), Rheinheimer Wolfgang and R. Edwin Garcia; Purdue University, West Lafayette, Indiana, United States.

Grain growth experimental studies on perovskites exhibit unimodal or bimodal microstructures as a function of temperature and dopant concentrations, as a result of the underlying point defects and their interaction with the grain boundaries. The extent of these interactions varies with grain size, orientation and misorientation distribution, as well as processing temperature and amount of doping. A theoretical formulation based on a thermodynamically consistent diffuse interface model has been developed to understand the effects of dopants on the grain coarsening of polycrystalline ionic solids. The theory is applied to Fe-doped Strontium Titanate (STO). At small Fe amounts and low temperatures the microstructures exhibit unimodal and coarse microstructures. An increase in Fe concentration or temperature results in a bimodal grain size distribution that affects the overall grain growth dynamics. In agreement with experimental results, the developed theory provides a starting point to understand the effects of the structural and electrochemical state of the grain boundary properties and its impact on the microstructural evolution of STO, including the possibility of abnormal grain growth.

#### 10:45 AM \*PM05.06.07

**Electric Field-Induced Softening (EFIS) of Alkali Silicate Glasses** Charles McLaren<sup>2</sup>, William Heffner<sup>1</sup>, Surapong Panyata<sup>1</sup>, Bernhard Roling<sup>3</sup>, Rishi Raj<sup>4</sup>, Nicholas Smith<sup>2</sup> and [Himanshu Jain](#)<sup>1</sup>; <sup>1</sup>Lehigh University, Bethlehem, Pennsylvania, United States; <sup>2</sup>Corning Incorporated, Corning, New York,

United States; <sup>3</sup>University of Marburg, Marburg, Germany; <sup>4</sup>University of Colorado Boulder, Boulder, Colorado, United States.

Inspired by the observations of dramatic effects of electric field on sintering of ceramic powders, we investigated the effect of electric field on the softening of alkali silicate glasses that were heated at a constant rate under static load and fixed voltage. We observed abrupt softening and viscous flow at furnace temperatures well below the glass transition temperature, resulting in a new phenomenon, termed electric field induced softening (EFIS) of glass. The strain, the specimen temperature (obtained with a pyrometer), and the optical emission spectrum have been measured simultaneously as a function of time. Preceding the overall softening, localized hot spots are observed near the anode, which may meander before leading to an abrupt increase in electrical conductivity as well as photoemission. The effect is more pronounced (that is, it occurs at a lower temperature) with AC field of ~1 kHz than with DC electric field. Unusual events at the metal-glass interface, resembling dielectric breakdown are observed, which, however, are less localized in AC than in DC experiments. These observations suggest the following sequence of events: polarization of the sample from ion displacement under the application of electric field as in electro-thermal poling, formation of an alkali ion depletion layer, development of large internal electric fields across this layer, electrolysis and charge injection followed by dielectric breakdown, and very high localized heating near the anode, ultimately leading to thermal runaway and softening throughout the sample. The results suggest that AC electric field assisted softening may be better suited to practical applications of this phenomenon. The magnitude of EFIS is significantly larger in single alkali than in relatively lower conductivity mixed-alkali glass of same mole fraction of silica, raising the possibility that EFIS can be induced in highly conductive glasses even at ambient furnace temperature. Potential applications of EFIS will be presented.

**11:15 AM \*PM05.06.08**

**Laser Fabrication of Single Crystal within Glass—Influence of Polarization** Volkmar Dierolf<sup>1</sup>, Keith Veenhuizen<sup>2</sup>, Courtney Au-Yeung<sup>1</sup>, Sean McAnany<sup>1</sup>, Lejla Hoxha<sup>1</sup>, Khalil Tafiti<sup>1</sup>, Bruce Aitken<sup>3</sup>, Dan Nolan<sup>3</sup>, Dmytro Savytskyi<sup>1</sup> and Himanshu Jain<sup>1</sup>; <sup>1</sup>Lehigh University, Bethlehem, Pennsylvania, United States; <sup>2</sup>Lebanon Valley College, Annville, Pennsylvania, United States; <sup>3</sup>Corning Incorporated, Corning, New York, United States.

Spatially selective heating of a glass using lasers allows to precisely control the conversion of a glass into a single crystal. In particular, we have shown that it is possible to perform this conversion without ever melting the glass. In such a solid-solid conversion, the growth conditions are highly constrained, which produce unusual crystallization characteristics. In this presentation, we will give an overview of the most unique features which include preferred orientation of seed crystals and controlled rotation of the crystal lattice orientation both along and perpendicular to the growth axis. These concepts will be introduced for crystallization on the surface of a chalcogenide glass using a cw-laser as well as for 3D-crystallization inside a lithium niobosilicate glass. The dependence of these phenomena on the properties of the laser irradiation, in particular the laser polarization will be discussed. We will report on how the polarization determines the orientation of the seed crystal as well as how it determines the crystal growth. Interpretations of these phenomena will be presented.

**11:45 AM ANNOUNCEMENT PRESENTATION/POSTER AWARDS**