## EMN MEETING on CERAMICS January 26-29, 2015 Double Tree by Hilton Hotel Orlando at SeaWorld, Orlando FL USA

# **Program & Abstract Book**













### DOUBLETREE BY HILTON ORLANDO AT SEAWORLD LAKES CONFERENCE CENTER



## **General Information**

The EMN MEETING on Ceramics 2015 will take place at Double Tree by Hilton Hotel Orlando at SeaWorld, Orlando, USA. The conference will be held from January 26 to January 29, 2015.

Workshops on selected focus topics in Ceramics science will include invited and contributed oral presentations from Monday to Thursday, and the poster session will be presented on the afternoon of Tuesday, January 27.

### **Registration Desk Hours**

The EMN MEETING on Ceramics registration desk, located in the Hilton hotel lobby, will be open during the following hours:

Sunday, January 25th	14:00pm -18:00pm
Monday, January 26th	7:00am -18:00pm
Tuesday, January 27th	7:00am -18:00pm
Wednesday, January 28th	7:00am -18:00pm

### **Committees and General Chairs**

The 2015 EMN Ceramics Meeting is co-chaired by Zhiming Wang, University of Electronic Science and Technology of China, China and Anuja Datta, University of South Florida, USA.

### **International Advisory Committee**

A. DOMINGUEZ-RODRIGUEZ, University of Seville, Spain
 R. GADOW, University of Stuttgart, Germany
 Hideo HOSONO, Tokyo Institute of Technology, Japan
 P. SAJGALIK, Slovak Academy of Sciences, Slovakia
 Masahiro YOSHIMURA, National Cheng Kung University, Taiwan

### **International Organizing Committee**

Paolo COLOMBO, University of Padova, Italy Francesco Dal CORSO,University of Trento, Italy Malek MAAZA, iThemba LABS, South Africa Xiaoqing PAN, University of Michigan, USA Andrea PICCOLROAZ, University of Trento, Italy V. K. SRIVASTAVA, Indian Institute of Technology, BHU, India Yiquan WU, Alfred University, USA



Anuja Datta University of South Florida, USA



Zhiming Wang University of Electronic Science and Technology of China, China

## **Meeting Program**

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EMN MEETING on Ceramics January 26th – January 29th Double Tree by Hilton Hotel Orlando at SeaWorld, FL, USA		
Monday Jan. 26 Room A (Superior at Lakes Conference Center)		
7:00-7:45AM	Breakfast	
7:50-7:55AM	<b>Opening Ceremony</b> Chair: Zhiming Wang	
Session: Keynote Speakers Chair: Zhiming Wang		
8:00-8:30AM	A01: Oxide Materials for Emerging Memory Devices: Resistive Switching Characteristics	Ram S. Katiyar University of Puerto Rico San Juan, USA
8:30-9:00AM	A02: Feature and Future of Soft Processing (Green Processing) for Advanced Ceramic Materials	Masahiro Yoshimura National Cheng Kung University, Taiwan
9:00-9:30AM	A03: Science and Technology of Multifunctional Oxide and Ultrananocrystalline Diamond (UNCD) Films and Applications to a New Generation of Multifunctional Devices	<b>Orlando Auciello</b> University of Texas-Dallas, USA
9:30-10:00AM	A04: Regenerative Nanooxides in mediating ROS Mediated Cell Disorders	Sudipta Seal University of Central Florida, USA
10:00-10:30AM	A05: Structuring intuition with theory: the high-throughput way	Marco Fornari Central Michigan University, USA
10:30-10:45AM	Session B	reak
Session: Ceramic Nanostructures I Chair: Marco Fornari		
10:45-11:10AM	A06: Hybrid Physical/Chemical Synthesis Strategies for Noncentrosymmetric Perovskite Oxide Nanostructures with Enhanced Functionality	<b>Anuja Datta</b> University of South Florida, USA
11:10-11:35AM	A07: Designing nanostructured oxygen electrode for energy conversion	Elisabeth Djurado University of Grenoble Alpes, France

11:35-12:00PM	A08: Ceramic nanocomposites with alumina matrix	<b>Dusan Galusek</b> Alexander Dubcek University of Trencin, Slovakia	
12:00-12:25PM	A09: Photophysical andmorphological study of doped $Ag_2WO_4$ :Eu <sup>3+</sup>	<b>Ieda Lúcia Viana Rosa</b> Federal University of Sao Carlos, Brazil	
12:25-13:25PM	Lunch Br	eak	
	Session: Ceramic Nanostructures II Chair: Koichi Eguchi		
13:25-13:50PM	A10: Multifunctional materials for electronics and photonics	Federico Rosei INRS-EMT, the University of Quebec, Canada	
13:50 -14:15PM	A11: 2D Oxide Nanosheets: New Atomic Sheets from Layered Ceramics	Minoru Osada National Institute for Materials Science, Japan	
14:15 -14:40PM	A12: The Role of Nanostructure in Thermal Expansion, Including Negative Thermal Expansion Materials and their Composites	Mary Anne White Dalhousie University, Canada	
14:40 -15:05PM	A13: Nanostructured transparent Nd:YAG and Nd:RE <sub>2</sub> O <sub>3</sub> ceramics for laser applications: elaboration by non- conventional ceramic process and correlations with their optical properties	Alexandre Maitre CNRS, France	
15:05-15:20PM	Session B	reak	
	Session: Ceramics for Energy I Chair: Minoru Osada		
15:20-15:45PM	A14: Microstructure-performance relations for the ceramic electrodes of solid oxide fuel cells	Koichi Eguchi Kyoto University, Japan	
15:45-16:10PM	A15: Visible Light-Induced Overall Water-Splitting over Solid State Z-Scheme Photocatalysts	<b>Hiroshi Irie</b> University of Yamanashi, Japan	
16:10-16:35PM	A16: Model for coupled ferroelectric hysteresis using time fractional operators: Application to innovative energy harvesting	<b>Benjamin Ducharne</b> INSA-Lyon, France	
16:35-17:00PM	A17: High Temperature Piezoelectrics: Guidelines and Realities	Alp Sehirlioglu Case Western Reserve University, USA	
17:30PM	Dinner So	ocial	

Tuesday Jan. 27 Room B (Okeechobee 1 at Lakes Conference Center)		
7:00-8:00AM	Breakfast	
Session: Advanced Ceramic Thin Films and Coatings for Functional Applications I		
	Chair: Anuja Datta	
8:00-8:25AM	B01: Strain Induced Dielectrophoretic Behavior in Electronically Phase Separated Manganite Thin Films	Amlan Biswas University of Florida, USA
8:25-8:50AM	B02: Nano Materials for Light Harvesting	Amitava Patra Indian Association for the Cultivation of Science, India
8:50-9:15AM	B03: Energy Harvesting from Heart Beating based on Low-Frequency Periodic Buckling of PZT Films	<b>Chaofeng Lu</b> Zhejiang University, China
9:15-9:40AM	B04: Non-Epitaxial Semiconducting Heterostructures with Controllable Nanostructure	Matt Beekman Oregon Institute of Technology, USA
9:40-10:05AM	B05: Surface Functionalization of Polystyrene with Biomimetic Apatite and Culture of Bone-Related Cells Thereon	<b>Kazutoshi Iijima</b> Tokyo University of Science, Japan
10:05-10:20AM	Session B	reak
Session: A	Advanced Ceramic Thin Films and Coatings fo Chair: Amitava Patra	or Functional Applications II
10:20 -10:45AM	B06: Growth and Structural Characterization of Anatase/Rutile–Tio <sub>2</sub> Thin Films; Optical, Surface and Catalytic Properties	<b>Anna-Karin Axelsson</b> London South Bank University, UK
10:45-11:10AM	B07: Design and Fabrication of Functional Nanocomposite Coatings by the Sol-Gel Process	Goutam De Council for Scientific and Industrial Research - Central Glass and Ceramic Research Institute, India
11:10-11:35AM	B08: Luminescent Properties of Perovskite-Type Phosphor Thin Films	Kazushige Ueda Kyushu Institute of Technology, Japan
11:35-12:00PM	B09: Pulsed Laser Deposition of Multiferroic and Ferroelectric Perovskite-Oxide Thin-Film Heterostructures	<b>Devajyoti Mukherjee</b> University of South Florida, USA
12:25-13:20PM	Lunch Br	eak
Session: Advanced Ceramic Thin Films and Coatings for Functional Applications III Chair: Annia Datta		

13:45 -14:10PM	B10: Ink Jet Printing of Transparent Conductive Oxide Thin Films and Patterns	<b>Klaartje De Buysser</b> Ghent University, Belgium
14:10 -14:35PM	B11: Interfacial Structure and Functional Properties of Complex Oxide Heterojunctions	<b>Liang Qiao</b> The University of Manchester, UK
14:35 -15:00PM	B12: Structure, Composition, Electrical and Optical Properties of Sputtered PbSe Thin Films on Si	<b>Alex Volinsky</b> University of South Florida, USA
15:00-16:00PM	Poster Ses	sion
Session: General I Chair: Klaartje De Buysser		
16:00-16:25PM	B13: Magnetoelectric thin film composites as magnetic field sensors or energy harvesters	<b>Eckhard Quandt</b> University of Kiel, Germany
16:25-16:50PM	B14: In Situ Deformation of Metallic Interlayers	<b>Finn Giuliani</b> Imperial College London, UK
16:25-16:50PM 16:50-17:15PM	<ul> <li>B14: In Situ Deformation of Metallic Interlayers</li> <li>B15: Temperature Dependent Ionic Transport Properties in layered perovskite (Sr,La)<sub>3</sub>Fe<sub>2</sub>O<sub>7-δ</sub></li> </ul>	Finn Giuliani Imperial College London, UK Isao Kagomiya Nagoya Institute of Technology, Japan

Tuesday Jan. 27 Room C (Okeechobee 2 at Lakes Conference Center)		
7:00-8:00AM	7:00-8:00AM Breakfast	
	Session: Ceramic Nanostructures III Chair	: Vladimir Sobolev
8:00-8:25AM	C01: Electrical and thermal transport in nanostructured ceramics: grain boundary and size effects	Marco Antonio Lopez de la Torre University of Castilla-La Mancha, Spain
8:25-8:50AM	C02: Doping as a simple way to control the microstructure of zirconia-toughened alumina composites	Laurent Gremillard INSA-Lyon, France
8:50-9:15AM	C03: High-Efficiency SERS Substrate Based on Mullite Nanowhisker Arry Decorated with Siliver Nanoparticles	Xinmei Hou University of Science and Technology Beijing, China
9:15-9:40AM	C04: Thin layer glass and vanadium-boride coatings with self-healing property	<b>Lionel Montagne</b> CNRS, University of Science and Technology in Lille, France
9:40-10:05 AM	C05: Fabrication of Glass-Ceramic Materials by SPS	<b>Lianjun Wang</b> Donghua University, China
10:05-10:20AM	Session B	reak
Session	n: Electronics in Ceramics I Chair: Marco A	antonio Lopez de la Torre
10:20 -10:45AM	C06: Ferroelectrics with coexisting ferroelectric and antiferroelectric phases: Peculiarities of properties and possible applications	Vladimir Sobolev South Dakota School of Mines and Technology, USA
10:45-11:10AM	C07: Low temperature Preparation of Barium Titanate-based Nano-complex Ceramics by Solvothermal Solidification Method and Their Dielectric Enhancement	Satoshi Wada University of Yamanashi, Japan
11:10-11:35AM	C08: MgZnO/ZnO based electronic devices fabricated using large-area compatible processes	<b>Jian Zhang Chen</b> National Taiwan University, Taiwan
11:35-12:00PM	C09: Surface Chemistries of Amorphous Oxide Semiconductors	<b>Gregory S. Herman</b> Oregon State University, USA
12:00-12:25PM	C10: Synthesis of spinon thermal conductive SrCuO <sub>2</sub> by glass-crystallization methods: Thermal and structural properties	<b>Nobuaki Terakado</b> Tohoku University, Japan
12:25-13:25PM	Lunch Br	eak
Session: Ceramic-matrix Composites I Chair: Samuel Georges		

13:45 -14:10PM	C11: Dielectric behavior of ceramic-nano carbon composites around the percolation threshold	<b>Lucia Fernandez-Garcia</b> CINN-CSIC, Spain
14:10 -14:35PM	C12: Tuning the dielectric constant in ferrite-carbon nanofibres composites	Jose Luis Menendez CINN-CSIC, Spain
14:35 -15:00PM	C13: High-temperature mechanical properties of ultrarrefractory boron carbide ceramics	<b>Diego Gomez-Garcia</b> University of Seville, Spain
15:00-16:00PM	Poster Ses	sion
Session: Ceramics for Energy II Chair: Lucia Fernandez-Garcia		
16:00-16:25PM	C14: Design of anodic architectures for direct methane SOFC	Samuel Georges University of Grenoble Alpes, France
16:00-16:25PM 16:25-16:50PM	C14: Design of anodic architectures for direct methane SOFC C15: Hydrogen evolution reaction at titanium carbide-supported, platinum-doped tetrahedral amorphous carbon array electrodes	Samuel Georges University of Grenoble Alpes, France Nicolas Glandut University of Limoges, France
16:00-16:25PM 16:25-16:50PM 16:50-17:15PM	C14: Design of anodic architectures for direct methane SOFC C15: Hydrogen evolution reaction at titanium carbide-supported, platinum-doped tetrahedral amorphous carbon array electrodes C16: New Aspects of Oxide Ceramic Materials for Thermoelectric Energy Conversion	Samuel Georges University of Grenoble Alpes, France Nicolas Glandut University of Limoges, France Michitaka Ohtaki Kyushu University, Japan

Tuesday Jan. 27 Room D (Superior at Lakes Conference Center)		
7:00-8:00AM	Breakfa	st
Session: Hierachical Materials Chair: Byung-Nam Kim		
8:00-8:25AM	D01: Zinc Oxide Ordered Nanostructures obtained through Soft Processing Strategies	Marco Peiteado Polytechnic University of Madrid, Spain
8:25-8:50AM	D02: Elastic and thermal properties of some organized clay-based materials	<b>Nicolas Tessier-Doyen</b> European Ceramic Center, France
8:50-9:15AM	D03: Bio-sourced sustainable Materials: organic-mineral reactions and shaping process?	<b>Gisele Lecomte</b> ENSCI, France
9:15-9:40AM	D04: Hydrothermal synthesis route for processing functional ceramics based on mineral pseudomorphic reactions	Juan Carlos Rendon-Angeles Research Institute for Advanced Studies of the NPI, Mexico
9:40-10:05AM	D05: Approaches to improving the visible light absorption and uprising the conduction band minimum of photocatalysts from first-principles calculation	<b>Junying Zhang</b> Beihang University, China
10:05-10:20AM	Session B	reak
Session:	Advanced Problems in the Mechanical Model Chair: Andrea Piccolroaz	lling of Ceramic Materials I
10:20 -10:45AM	D06: Modeling of densification by grain-boundary sliding and diffusion	<b>Byung-Nam Kim</b> National Institute for Materials Science, Japan
10:45-11:10AM	D07: Oxygen Separating Membranes Fabricated from Perovskite-like Materials	Magdalena Gromada Institute of Power Engineering, Poland
11:10-11:35AM	D08: Micromechanical modeling of porous ceramic composites using direct microstructural reconstructions	<b>Kawai Kwok</b> Technical University of Denmark, Denmark
11:35-12:00PM	D09: A Thermomechanical Contact Problem For Microstructured Solids	<b>Francesco Dal Corso</b> University of Trento, Italy
12:00-12:25PM	D10: Model reduction methods in inverse analysis: improvement of accuracy by uniform space filling techniques	<b>Vladimir Buljak</b> University of Belgrade, Serbia
12:25-13:20PM	Lunch Break	
Session: Advanced Problems in the Mechanical Modelling of Ceramic Materials II Chair: Francesco Dal Corso		

13:20-13:45PM	D11: Modelling, characterization and simulation of refractory materials for liquid steel technology	<b>Davide Bigoni</b> University of Trento, Italy
13:45 -14:10PM	D12: New biomimetic ceramics for the regeneration of load-bearing bones	Simone Sprio ISTEC-CNR, Italy
14:10 -14:35PM	D13: Smart bio-inspired hybrid nano-composites for multifunctional applications	<b>Anna Tampieri</b> ISTEC-CNR, Italy
14:35 -15:00PM	D14: Fracture in ceramics with microstructure	Andrea Piccolroaz University of Trento, Italy
15:00-16:00PM	Poster Ses	sion
Session: General II Chair: Davide Bigoni		
16:00-16:25PM	D15: Novel strategies for sintering oxides using microwave energy	Sylvain Marinel University of Caen Basse-Normandie, France
16:25-16:50PM	D16: Valence Electron Density Study on Phase Transitions in Perovskite-type Ceramics by Synchrotron Radiation X-ray Diffraction	<b>Yoshihiro Kuroiwa</b> Hiroshima University, Japan
16:50-17:15PM	D17: Strain Rate Dependent Failure of Glass/Epoxy Interfaces at nano-microscale via Nanoimpact Experiments	<b>Vikas Tomar</b> Purdue University, USA
17:30PM	Dinner So	cial

Wednesday Jan. 28 Room B (Okeechobee 1 at Lakes Conference Center)		
7:00-8:00AM Breakfast		
Session: Electronics in Ceramics II Chair: Scott P. Beckman		
8:00-8:25AM	B16: Microstructural evidences of extrinsic magnetization in Fe-doped 6H-BaTiO <sub>3</sub>	<b>Matjaz Valant</b> University of Nova Gorica, Slovenia
8:25-8:50AM	B17: Sr-a-Doped La <sub>2</sub> CuO <sub>4</sub> Heterostructures: Cation Redistribution and High-Tc Superconductivity	Peter van Aken Max Planck Institute for Intelligent Systems, Germany
8:50-9:15AM	B18: Electrical and magnetic properties of transition and rare-earth metal molybdates and tungstates – potential materials for laser matrices and light–emitting diodes	<b>Tadeusz Gron</b> University of Silesia, Poland
9:15-9:40AM	B19: Sol-Gel-Derived Amorphous Semiconductor TFT Fabrication and its Performance	<b>Tohru Sugahara</b> Osaka University, Japan
9:40-10:05AM	B20: Improving the properties of BiFeO <sub>3</sub> ceramics	<b>Donna Arnold</b> University of Kent, UK
10:05-10:20AM	Session Br	eak
	Session: General III Chair: Matja	z Valant
10:20 -10:45AM	B21: Modeling the chemical complexity of the metal borides using the hybrid SQS/VCA alloy method and data informatics	Scott P. Beckman Iowa State University, USA
10:45-11:10AM	B22: Novel highly transparent polycrystalline ceramics synthesised by full crystallization from glass	Mathieu Allix CNRS, France
11:10-11:35AM	B23: Electrospinning of Ceramics	Johan E. ten Elshof University of Twente, The Netherlands
11:35-12:00PM	B24: Medium Range structure, ionic conductivity and fragility of superionic glasses	Masaru Aniya Kumamoto University, Japan
12:25-13:25PM	Lunch Bra	eak
Session: Ceramics for Energy III Chair: Masanori Kikuchi		
14:15 -14:40PM	B25: ABO <sub>3</sub> perovskite thin films for fuel cell and sensor applications	<b>Mohammad Arab Pour Yazdi</b> IRTES-LERMPS, UTBM, France

14:40 -15:05PM	B26: 3C-SiC on Si: A Biocompatible Material for Advanced Bioelectronic Devices	<b>Stephen E. Saddow</b> University of South Florida, USA
15:05-15:20PM	Session Br	reak
Session: Ceramic-matrix Composites II Chair: Mohammad Arab Pour Yazdi		
15:20-15:45PM	B27: Preparation of directionally solidified eutectic ceramic with induction Zone Melting	<b>Juncheng Liu</b> Tianjin Polytech University, China
15:45-16:10PM	B28: Hydroxyapatite/collagen bone-like nanocomposite: Its biological reactions and usefulness in surgery	Masanori Kikuchi National Institute for Materials Science, Hokkaido University, Japan
16:10-16:35PM	B29: A Mechanical Model to Predict Phase Stress for Ceramic Laminates during Sintering	Kouichi Yasuda Tokyo Institute of Technology, Japan
17:30PM	Dinner So	cial

Wednesday Jan. 28 Room C (Okeechobee 2 at Lakes Conference Center)		
7:00-8:00AM	7:00-8:00AM Breakfast	
Session: Ceramic Nanostructures IV Chair: Hiroshi Maiwa		
8:00-8:25AM	C17: Strongly correlated transition metal ceramic nanostructures investigated by soft x-ray spectroscopies and multiplet calculations	Guillermo Manuel Herrera Perez National Autonomous University of Mexico, Mexico
8:25-8:50AM	C18: Nitrogen and Carbon Mobility in SiCO and SiCN Polymer-Derived Ceramics	Hans-Joachim Kleebe Darmstadt University of Technology, Germany
8:50-9:15AM	C19: Nanostructured pure and doped ferrites: synthesis by electrospinning and study of their magnetic properties	Sagrario M. Montemayor Research Center of Applied Chemistry, Mexico
9:15-9:40AM	C20: Doping Effect on Sinterability and Grain Boundary Nanostructure in Polycrystalline Yttria	Hidehiro Yoshida National Institute for Materials Science, Japan
9:40-10:05AM	C21: Band gap narrowing and widening of ZnO nanostructures and doped materials	<b>Norlida Kamarulzaman</b> MARA University of Technology, Malaysia
10:05-10:20AM	Session B	reak
	Session: General IV Chair: Guillermo Man	uel Herrera Perez
10:20 -10:45AM	C22: Electrocaloric Properties of PZT-based Ceramics, PVDF Films and PMN-PT Crystals	Hiroshi Maiwa Shonan Institute of Technology, Japan
10:45-11:10AM	C23: Functional metastable phase formation from undercooled melt by containerless processing	Atsunobu Masuno University of Tokyo, Japan
11:10-11:35PM	C24: Lead-Free Functional Oxides for Applications	<b>Didier Fasquelle</b> ULCO, France
11:35-12:00PM	C25: Epitaxial growth of flower and pillar indium nitride by APHCVD method	Naonori Sakamoto Shizuoka University, Japan
12:25-13:25PM	Lunch Br	eak
Session: Electronics in Ceramics III Chair: Romain Gaume		
13:25 -13:50PM	C26: Electrocaloric Refrigeration in Perovskite-structure Ferroelectric Materials	Yang Bai University of Science and Technology Beijing, China

13:50 -14:15PM	C27: Doped-sepiolite for humidity and gas detection	<b>Jean-Marc Tulliani</b> Polytechnic University of Turin, Italy
14:15 -14:40PM	C28: Use of nanoparticles for improved ceramics: A case study of thermoelectric Bi <sub>2</sub> Ca <sub>2</sub> Co <sub>1.7</sub> O <sub>x</sub>	Andres Sotelo University of Zaragoza, Spain
14:40 -15:05PM	C29: Relaxor ceramics for new electrocaloric cooling technology	Zdravko Kutnjak Jozef Stefan Institute, Slovenia
15:05-15:20PM	Session Br	eak
Session: Ceramics for Energy IV Chair: Jean-Marc Tulliani		
15:20-15:45PM	C30: Fabrication and performance of titanium oxide Magn di phase nanoceramics for thermoelectric applications	<b>Romain Gaume</b> University of Central Florida, USA
15:45-16:10PM	C31: Structural Analysis of Carbon Spheres Synthesized by Hydrothermal Carbonization Process and its Capacitive Property	<b>Miki Inada</b> Kyushu University, Japan
15:45-16:10PM 16:10-16:35PM	C31: Structural Analysis of Carbon Spheres Synthesized by Hydrothermal Carbonization Process and its Capacitive Property C32: The potential applications of luminescence nanomaterials for energy harvesting from sunshine and radiation sources	Miki Inada Kyushu University, Japan Wei Chen The University of Texas at Arlington, USA

Wednesday Jan. 28 Room D (Superior at Lakes Conference Center)		
7:00-8:00AM	Breakfast	
Session: General V Chair: Toshinori Okura		
8:00-8:25AM	D18: Strategies for enhancing the thermoelectric performance of oxides	Udo Schwingenschloegl King Abdullah University of Science and Technology, Saudi Arabia
8:25-8:50AM	D19: Diffraction, ab-inito calculations and elastic constants of the MAX phases $Ti_3XC_2$ , X=Si,Al	Oliver Kirstein University of Newcastle, Australia
8:50-9:15AM	D20: Ferroelectric nanodomain dynamics in morphotropic phase boundary piezoelectrics studied via in-situ transmission electron microscopy	<b>Yukio Sato</b> Kyushu University, Japan
9:15-9:40AM	D21: Ferroelectricity in Bismuth Silicate	<b>Hiroki Taniguchi</b> Nagoya University, Japan
9:40-10:05AM	D22: Doping structures and luminescence properties of SiAlON:Ce and SiAlON:Eu ceramics	Fangfang Xu Shanghai Institute of Ceramics, CAS, China
10:05-10:20AM	Session Br	reak
	Session: General VI Chair: Udo Schwi	ingenschloegl
10:20 -10:45AM	D23: Effects of Microstructure on Conductivity of Narpsio Glass-Ceramics	<b>Toshinori Okura</b> Kogakuin University, Japan
10:45-11:10AM	D24: Transparent Ceramic Scintillators: Compositional Stability, Fabrication, and Scale-Up	Zachary Seeley Lawrence Livermore National Laboratory, USA
11:10-11:35AM	D25: Brazing of SiC/SiC composite by dicilides	<b>Laurence Maill é</b> University of Bordeaux, France
11:35-12:00PM	D26: Thin Film Dielectrics BaTiO3-Ceramics Improved Capacitors Fractal Nature	<b>Vojislav Mitic</b> University of Nis, Institute of Technical Sciences of Serbian Academy of Sciences, Serbia
12:25-13:25PM	Lunch Br	eak
Session: Defects in Ceramics Chair: Narendra Kumar Pandey		
13:25 -13:50PM	D27: Evaluation of Point Defects in Novel BaTiO <sub>3</sub> -based Ceramics with High Permittivity and Dielectric-Temperature Stability	<b>Da-Yong Lu</b> Jilin Institute of Chemical Technology, China

13:50 -14:15PM	D28: Sub-stoichiometric functionally graded titania fibres for water-splitting applications	<b>Vaia Adamaki</b> University of Bath, UK
14:15 -14:40PM	D29: Critical Issues of Ceramic Injection Molding Feedstocks	<b>Berenika Hausnerova</b> Tomas Bata University in Zlin, The Czech Republic
14:40 -15:05PM	D30: Diffusion and reactions of interstitial excess oxygen species in amorphous SiO <sub>2</sub>	<b>Koichi Kajihara</b> Tokyo Metropolitan University, Japan
15:05-15:20PM	Session Break	
Session: Ceramic Nanostructures V Chair: Berenika Hausnerova		
15:20-15:45PM	D31: Colloidosomes and Diamondosomes: Multifunctional Inorganic Microcapsules	Michael Maas University of Bremen, Germany
15:20-15:45PM 15:45-16:10PM	D31: Colloidosomes and Diamondosomes: Multifunctional Inorganic Microcapsules D32: Noble metal loaded ceramic nanocomposites for solid state moisture sensing studies	Michael Maas University of Bremen, Germany Narendra Kumar Pandey University of Lucknow, India
15:20-15:45PM 15:45-16:10PM 16:10-16:35PM	<ul> <li>D31: Colloidosomes and Diamondosomes: Multifunctional Inorganic Microcapsules</li> <li>D32: Noble metal loaded ceramic nanocomposites for solid state moisture sensing studies</li> <li>D33: Fully Dense Single Phase Nanocrystalline Ceramics by Enhanced High Pressure Sintering</li> </ul>	Michael Maas University of Bremen, Germany Narendra Kumar Pandey University of Lucknow, India Boris Feigelson Naval Research Laboratory, USA

Thursday Jan. 29 Room B (Okeechobee 1 at Lakes Conference Center)		
7:00-8:00AM	Breakfast	
Session: Ceramic-matrix Composites III Chair: Hirokazu Masai		
8:00-8:25AM	B30: Ag nanoparticle deposition on TiO <sub>2</sub> nanostructures for efficient photoelectric conversion	<b>Go Kawamura</b> Toyohashi University of Technology, Japan
8:25-8:50AM	B31: Compressive behaviour of hollow and porous ceramic spheres in metal matrix syntactic foams	Yuyuan Zhao University of Liverpool, UK
8:50-9:15AM	B32: Strategies for preparing CNT-ceramic composites with high toughness and good resistance to friction and wear	<b>Christophe Laurent</b> University of Toulouse, France
9:15-9:40AM	B33: Platinum-doped Tin Oxide Nanoparticles as efficient Catalyst for Methane Oxidation	<b>Umapada Pal</b> Autonomous University of Puebla, Mexico
9:40-10:05AM	B34: High Peak Power Composite Material Passively Q-switched Microchip Lasers	<b>Jun Dong</b> Xiamen University, China
10:05-10:20AM	Session Break	
Session: General VII Chair: Christophe Laurent		
10:20 -10:45AM	B35: Luminescence of ns <sup>2</sup> -type Emission Center in Oxide Glasses	Hirokazu Masai Kyoto University, Japan
10:45-11:10AM	B36: Surface Modification on Li-rich Layered Cathode Material for Li-Ion Batteries	Liu Li National University of Singapore, Singapore
11:10-11:35AM	B37: Atomic-scale characterization of SiAlON ceramics through aberration-corrected microscopy and spectroscopy	Hilmi Yurdakul Dumlupinar University, Turkey
12:25PM	Lunch Break	

Thursday Jan. 29 Room C (Okeechobee 2 at Lakes Conference Center)		
7:00-8:00AM	Breakfast	
Session: Electronics in Ceramics IV Chair: Vaia Adamaki		
8:50-9:15AM	C33: Development for novel Bi based high Curie-temperature ferroelectrics	<b>Jingzhong Xiao</b> University of Coimbra, Portugal
9:15-9:40AM	C34: Distinctive Contributions to High-Temperature Dielectric Response of Relaxor Ferroelectric Lead Scandium Niobate Ceramic System	<b>Vid Bobnar</b> Jozef Stefan Institute, Slovenia
9:40-10:05AM	C35: Relaxor and ferroelectric behavior in tetragonal tungsten bronze ceramics	<b>Xiaoli Zhu</b> Zhejiang University, China
10:05-10:20AM	Session B	reak
Session: General VIII Chair: Xiaoli Zhu		
10:20 -10:45AM	C36: Electrochemical Performance of Micron and Nano Overlithiated Li <sub>1+X</sub> Ni <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub> : Structural and Oxidation State Studies	<b>Roshidah Binti Rusdi</b> MARA University of Technology, Malaysia
10:45-11:10AM	C37: Spinel-Based Cathode with Extended Capacity for High Energy/Power Lithium-Ion Batteries	<b>Jia Lu</b> National University of Singapore, Singapore
12:25PM	Lunch Break	

<b>Tuesday Jan. 27</b> 15:00-16:00PM		
Poster Session		
P1	Band Gap Tuning in ZnSnO <sub>3</sub> Nanorods by Site Specific Doping and Core-Shell Approach for Solar Cell Applications	<b>Corisa Kons</b> University of South Florida, USA
P2	Rapid Microwave Synthesis of Perovskite Oxide Nanostructures with Enhanced Functionality	<b>Gregory Salazar</b> University of South Florida, USA
Р3	Cost-effective synthesis and characterization of $Yb^{2+}$ doped $\beta$ -SiAlON phosphors for light emitting diodes (LEDs)	<b>Arife Yurdakul</b> Dumlupinar University, Turkey
P4	Hierarchical TiO <sub>2</sub> Anatase Microspheres Crystallized Under Microwave Radiation	<b>Teresa Jardiel</b> Institute of Ceramics and Glass-CSIC, Spain
Р5	The Grüneisen Parameter of Ionic Conductors	<b>Eita Hirano</b> Kumamoto University, Japan
P6	Co-substitution of carbonate and fluoride in Hydroxyapatite: Effect of the addition way and order of carbonate and fluoride sources	<b>Qingxia Zhu</b> Jingdezhen Ceramic Institute, China
P7	A study on improving photoelectric conversion efficiency of dye-sensitized solar cell by using light scattering layer of hollow TiO <sub>2</sub> and SnO <sub>2</sub> nanoparticles	<b>Seung-Ho Jeon</b> Chonbuk National University, Korea
P8	Solid Oxide Fuel Cells with (La,Sr)(Ga,Mg)O <sub>3-δ</sub> Electrolyte Film Deposited by RF Magnetron Sputtering	<b>Sea-Fue Wang</b> National Taipei University of Technology, Taiwan
Р9	Nanotribological characterization of polystyrene microspheres using atomic force microscopy	<b>Himanshu Verma</b> University of South Florida, USA
P10	Preparation of Hollow TiO <sub>2</sub> Nanoparticle Film on FTO Glass by Electrophoreticy Deposition for DSSC Applications	<b>Yeon-Tae Yu</b> Chonbuk National University, South Korea

## **Keynote Session**

### A01: Oxide Materials for Emerging Memory Devices: Resistive Switching Characteristics

<u>Ram S. Katiyar</u>, S.P. Pavunny, Y. Sharma, R.K. Katiyar, G. Khurana, and P. Misra Department of Physics and Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, PR 00931

Among all nonvolatile memory device concepts currently being explored to overcome the problems associated with existing charge storage based nonvolatile memories, resistive memory devices based on switching of the resistance between the two or more states (high and low) of resistances through external electrical stimulus has gained tremendous attention for the development of next generation low power, high speed, rugged, high density, and nonvolatile resistive random access memory (RRAM) devices. Compared to FRAM, MRAM and PMC cells, the RRAM offers better potential for practical applications mainly due to its scalability which is <10 nm<sup>1,2</sup>, low energy consumption ~  $0.1 \text{pJ/operation}^3$ , faster switching rates ~100 ps<sup>4</sup>, capability of having multiple nonvolatile resistance states in simple device architecture<sup>5</sup> and hence holds promise to meet the ITRS requirements for the next-generation memory technology.

The memory effect in RRAM devices is realized through switching of the resistance of device between the two states (high and low) of resistances. Based on whether the switching characteristic depends on the voltage polarity, resistive switching is generally classified as unipolar and bipolar switching. Switching is termed as unipolar when it is independent of the polarity of the applied voltages. We have studied resistive switching phenomenon in mixed oxides, such as amorphous thin films of rare earth ternary oxides LaGdO<sub>3</sub> and LaLuO<sub>3</sub>, SmGdO<sub>3</sub>, BiFeO<sub>3</sub>, and Graphene Oxide thin films. In case of amorphous lanthanum based ternary oxides we observed unipolar resistive switching with well defined and non overlapping switching voltages although an initial forming process was essential to start repeatable switching. On the other hand, forming free bipolar switching was observed in case of Graphene Oxide thin films. Reliable and repeatable nonvolatile switching of the resistance of these materials was obtained with sufficiently large resistance ratio and non-overlapping and low switching voltages. In the case of SmGdO<sub>3</sub>, a multilevel resistive switching with 4 resistance states was observed by controlling the compliance current which opens the possibility of multi bit storage. The switching mechanism in ternary oxides and BiFeO3 was found to follow formation of metallic filaments between the electrodes through the agglomeration of oxygen vacancies and metal atoms in films and their subsequent rupture on application of suitable bias bringing the low and high resistance states while multilevel switching was attributed to the variation in diameter of conducting filaments with changing compliance current. On the other hand, forming free bipolar resistive switching behavior was found in graphene oxide (GO) thin films on ITO substrate with platinum as the top electrode. The switching between the low resistance state and high resistance state showed a reliable and repeating behavior with an on/off ratio of 10<sup>4</sup> at room temperature. The device showed good endurance and retention characteristics. The switching mechanism was found to be governed by migration of oxygen between GO layer and bottom ITO electrode. Detailed results of these studies will be presented.

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### A02: Feature and Future of Soft Processing (Green Processing) for Advanced Ceramic Materials

### Masahiro YOSHIMURA<sup>1,2</sup>

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Advanced inorganic (ceramic) materials have been used in wide area of applications like structural, mechanical, chemical, electrical, electronic, optical, photonic, biological, medical, etc. They have generally been fabricated by so-called high-technology, where high temperature, high pressure, vacuum, molecule, atom, ion, plasma, etc. have been used for their fabrications, because inorganic materials are difficult in shape forming and fixing due to their intrinsic rigidity and brittleness. Even though nano-sized particles of inorganic materials could be synthesized by low-energetic route, i.e. "soft chemistry" or "green chemistry", their shape forming and fixing cost energetically and environmentally in even using nano-particles.

We have challenged to fabricate those advanced ceramics with desired shape/size/location, etc. directly in low energetic routes using aqueous solutions since 1989 when we found a method to fabricate BaTiO3 film on Ti substrate in a Ba(OH)2 solution by Hydrothermal Electrochemical[HEC] method at low temperatures of 60-200 C. We proposed in 1995-2000 an innovative concept and technology, "Soft Processing" or "Soft Solution Processing." which aims low energetic (=environmentally benign) fabrication of shaped, sized, located, and oriented inorganic materials in/from solutions. It can be regarded as one of bio-inspired processing, green processing, or eco-processing.<sup>1,2)</sup> Please note, [1] Most of ceramics except for bio-ceramics are not water soluble, thus "firing" be seems to essential, and [2] Ecology(Bio-based) systems have not included most of ceramics as well as semiconductors and metallic materials(alloys).

When we have activated/stimulated interfacial reactions locally and/or moved the reaction point dynamically, we can get patterned ceramic films directly in solution without any firing, masking nor etching. They can be called Direct Patterning methods which differ from previous patterning methods consisting of multi-step processes. The notable feature of Direct Patterning is that each reactant reacts directly on site, at the interface with the substrate. Therefore, the chemical driving force of the reaction, A+B=AB, can be utilized not only for synthesis but also for crystallization and/or consolidation of the compound AB. It is rather contrasting to general patterning methods where thermal driving force of firing is mostly used for the consolidation of the particles.<sup>3)</sup>

We have developed the Direct Patterning of CdS, PbS and CaWO4 on papers by Ink-Jet Reaction method<sup>3).</sup> Furthermore, we have succeeded to fabricate BaTiO3 patterns on Ti by a laser beam scanning and carbon patterns on Si by a needle electrode scanning directly in solutions.<sup>4)</sup> TiO2 and CeO2 patterns by Ink-Jet Deposition, where nano-particles are nucleated and grown successively on the surface of substrate thus become dense even below 300 C<sup>3)</sup> will be presented. Nano-structured films will be also talked<sup>4,5</sup>. In the formation of films, additional activation(s) with thermal one are very useful. Particularly electrochemistry is very attractive to prepare oxide films and patterns. Our proposal: Growing Integration Layer [GIL] method<sup>6)</sup> is also using electrochemistry to make oxide layer(s) on metallic material(s) to improve adhesion. anti-oxidation, bioactivity and/or other functionalities. A recent novel subject, Soft Processing for various nano-carbons including Graphene and functionalized Graphene,<sup>7-8)</sup> will be introduced.

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A03: Science and Technology of Multifunctional **Oxide and Ultrananocrystalline Diamond (UNCD)** Films and Applications to a New Generation of **Multifunctional Devices** 

### Orlando Auciello<sup>1</sup>

<sup>1</sup>Endowed Chair Professor, Materials Science and Engineering and Bioengineering, University of Texas-Dallas, USA

**R&D:** Science and technology of multi-component oxide thin films and application to devices (ferroelectric and resistive change memories, nanoscale CMOS devices, photovoltaic energy generation / storage devices, high-frequency devices, piezoelectric thin films for MEMS/NEMS.

Science and technology of а novel ultrananocrystalline (UNCD) diamond coating developed and patented by Auciello and colleagues, which exhibit multifunctionalities and is already marketed in sevreral industrial products (mechanical pump seals and bearing, and electrodes for water purification systems) and is being developed for a new generation of implantable medical devices (hips. knees, dental implants, UNCD-coated implantable microchips to restore vision to blind people, neural stimulation electrodes, and more).

R&D of novel multifunctional oxide and nanocarbon thin films are providing the bases for new physics, new materials science and chemistry, and their impact in a new generation of multifunctional devices. This talk will focus on discussing a new paradigm in multifunctional oxide and novel ultrananocrystalline diamond (UNCD) thin films and integration into devices as described below:

1. Science and technology of complex oxide thin films and application to key nanoelectronics, energy storage and energy saving devices: Novel TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> superlattices, exhibiting giant dielectric constant (up to k=1000), low leakage current  $(10^{-7}-10^{-9} \text{ A/cm}^2)$  and low losses ( $\leq \tan d = 0.04$ ), based on new physics, enable a new generation of energy storage microchip embedded capacitors for new electronics, including electronics implantable in the human body, the next generation of gates for nanoscale low energy consumption CMOS devices, and super-capacitors for energy storage systems;

2. Science and technology of novel UNCD films and integration with oxide films for fabrication of a new generation of multifiunctional devices/systems: UNCD films co-developed and patented by Prof. Auciello and colleagues are synthesized by novel microwave plasma chemical vapor deposition and hot filament chemical vapor techniques deposition using an Ar-rich/CH<sub>4</sub> chemistry that produces films with 2-5 nm grains, thus the name UNCD to distinguish them from nanocrystalline diamond films with 30-100 nm grains. The UNCD films exhibit a unique combination of outstanding mechanical, trtibological, electrical, thermal, and biological properties, which already resulted in industrial components and devices currently commercialized by Advanced Diamond Technologies (a company co-founded by O. Auciello and colleagues in 2003). Devices and systems reviewed include: a) UNCD-coated mechanical pump seals, providing up to 20% energy cost saving via friction reduction, for the petrochemical, pharmaceutical and car industries (shipping to market); b) UNCD-coated bearings for mixers for the pharmaceutical industry (shipping to Merck-Millipore market); c) new electrically conductive UNCD-coated metal electrodes for water purification system, which outperform all other electrodes in the market today (shipping to market); d) UNCD-based MEMS energy harvesting devices and biosensors; g) potential NEMS switch-based logic with lower energy consumption; e) New generation of Li-ion batteries and Thermal Li-Sulfur batteries with  $\geq 10x$  longer life and reduced size, using UNCD-based coatings technology for new anodes, membranes and inner wall battery case chemically resistant coating; f) new generation of medical devices (e.g., artificial retina to restore partial sight to blind people, dental implants, hips,

knees, and more) based on biocompatible UNCD coatings.

### A04: Regenerative Nanooxides in mediating ROS Mediated Cell Disorders

### Sudipta Seal\*

Advanced Materials Processing and Analysis Center, Nanoscience Technology Center, Materials Science and Engineering, College of Medicine, University of Central Florida, USA \*Email: Sudipta.Seal@ucf.edu

Nanomaterials, especially cerium oxide nanoparticles (from rare earth oxide family), have been shown to effectively protect stainless steels from high temperature degradation. However, recently we discovered the unique antioxidant properties of Nanoceria, where it protects mammalian cells against damage caused by increased reactive oxygen or nitrogen species, and has been shown to act as effective superoxide dismutase mimetic in vitro. The redox ability of rare earth oxides (ceria, lanthanides, etc) has been used in a wide range of applications such as three way catalysis, oxygen buffer systems, sensors and corrosion prevention. While these nanostructures have been widely used in many inorganic applications, their role in biology as catalyst is not explored fully. This presentation will provide a brief overview of the applications of nanoceria in treatment of disorders caused by ROS. The role of size, surface chemistry and stability has also been explored. For various practical applications, synthesis of biocompatible and stable suspensions of nanoceria is essential. It was found that the redox kinetics of regenerative ceria nanoparticles can be controlled with the type of medium and their implications in nanobiomedicine is presented.

# A05: Structuring Intuition with Theory: the High-throughput way

### Marco Fornari

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First principles methodologies have grown in accuracy and applicability to the point where large databases can be built, shared, and analyzed to predict novel compositions, optimize functional properties, and discover unexpected relationships between the data. In order to be useful to a large community of users, data should be standardized, validated, and distributed. In addition, tools to easily manage large datasets should be made available to effectively lead to materials development.

Within the AFLOW<sup>1</sup> consortium we have developed a simple frame to expand, validate, and mine data repositories: the MTFrame. Our approach aims to integrate data generation with data analysis.

We present examples from our work on materials for energy conversion with the specific intent to pinpoint the usefulness of high-throughput methodologies to guide the discovery process and manufacturing.

1: http://www.aflowlib.org.

## **Invited Talk Sessions**

A06:HybridPhysical/ChemicalSynthesisStrategiesforNoncentrosymmetricPerovskiteOxideNanostructureswithEnhancedFunctionality

### <u>Anuja Datta</u>

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Perovskite oxides are important class of materials possessing high dielectric and piezoelectric coefficients, switchable ferroelectric (FE) polarization, large nonlinear optical coefficients and interesting electrical properties. These properties may be exploited in applications such as nonvolatile memory devices, thermistors, multilayer capacitors, dynamic random access memories and as cathode electron sources. Noncentrosymmetric (NCS) derivatives of perovskite oxides are interesting for their symmetry-dependent polarization properties [1]. In particular, Pb-free LiNbO<sub>3</sub> (LN)-type ZnSnO<sub>3</sub> with R3c space group has attracted special attention due to theoretically predicted high its spontaneous polarization ( $\approx 59 \,\mu\text{C/cm}^2$ ) [2], and the demonstration of large remanent polarization in epitaxial LN-type ZnSnO<sub>3</sub> thin films (Pr  $\approx$  47  $\mu$ C/cm<sup>2</sup>) [3] and recently, in welded-nanowire arrays (Pr  $\approx$  30  $\mu$ C/cm<sup>2</sup>), reported by our group [4]. However large-scale synthesis and integration of NCS-type materials with ordered low-dimensional structures and controlled crystal orientations is a challenge, due to their complicated methodologies, high-cost and difficulties with phase stability. Particularly for Pb-free complex NCS oxides, it is difficult to synthesize these metastable phases by traditional solid state synthesis processes under ambient conditions. Here, we adopted a combined pulsed-laser deposition (PLD) technique and a solvothermal synthesis scheme to synthesize phase pure LN-type ZnSnO<sub>3</sub> nanostructure arrays ( $\approx 20 \ \mu m$  thick) on Si substrates assisted by template-layers. The similar ZnO:Al crystal symmetry and comparable lattice parameters between the template-layer and LN-type ZnSnO<sub>3</sub> facilitated the dense growth of high-quality ZnSnO<sub>3</sub> nanostructure arrays in the form of one-dimensional vertical nanowires, nanorods and two-dimensional nanoflakes. These approaches discussed here allow improved tunability of the size, shape, and orientation of the structures as investigated by X-ray diffraction, scanning electron microscopy, atomic force microscopy, microscopy, transmission electron Raman spectroscopy and UV-vis spectroscopy. [3-5] The as-grown nano- and micro-structured phases showed unique electrical and FE (hysteresis) properties which are hitherto unknown in these materials systems. We discuss the results in context of understanding the potential of these low-dimensional structures for advanced electronic and FE device applications.

### Acknowledgements

The presenter acknowledges Dr. D. Mukherjee, Ms. Corisa Kons, Prof. S. Witanachchi and Prof. P. Mukherjee for their collaboration and contributions to this work. This work was partially supported by the Florida Cluster for Advanced Smart Sensor Technologies (FCASST) and the United States Army (Grant No. W81XWH1020101/3349).

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## A07: Designing nanostructured oxygen electrode for energy conversion

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Since the operation of solid oxide fuel cells at intermediate temperature (IT-SOFCs) causes an increase of the interfacial polarization losses as well as ohmic loss in the electrolyte, the cell performance has to be improved. To compensate for the efficiency reduction, alternative electrolyte and cathode materials are being evaluated as potential candidates for IT-SOFCs. However, the performance of the cell is not only dependent on the properties of the materials that comprise it, but also on their microstructures, mainly that of the cathode. It is known that porosity allows permeation of gaseous species to and from reactive sites, while its geometry controls the surface area available for such reactions to occur. A comprehensive analysis of this correlation is therefore desirable in that it isolates the contribution of the architecture of the cathode film from that of its intrinsic properties.

This work describes a wide variety of original microstructures of  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  (LSCF6428) ceramics prepared by electrostatic spray deposition (ESD) on dense  $Ce_{0.9}Gd_{0.1}O_{2-}$  substrate. The ESD process, unique in France, operates at relative low temperature while allowing excellent degree of control over the stoichiometry and microstructure of the films, which makes it most adequate in this study. Dense, columnar and coral

single phased LSCF6428 films have been systematically mapped by SEM (Fig. 1) and XRD observations varying ESD parameters such as nozzle-to-substrate distance, solution flow rate and substrate temperature for a given solution of precursors [1] with thickness ranging from 1 to 30  $\mu$ m.

The influence of the LSCF6428 microstructure has been investigated on the electrochemical performance of LSCF cathodes using AC impedance spectroscopy at OCP using a Solartron (SI 1280B) potentiostat/galvanostat frequency response analyzer with frequencies between 0.01Hz and 20kHz. The best electrical data of nanostructured LSCF6428 films, 3µm thick, using AC impedance spectroscopy, were obtained for columnar on CGO leading to ASR values as low as 0.13  $\Omega$ .cm<sup>2</sup> at 600 °C [2].

To conclude, the dependence of electrochemical performances on the LSCF6428 cathode microstructure has been clearly highlighted showing the best cathodic performances at 600 °C for only 20 mol.% Co.



Fig. 1. Dense, columnar and coral, single phased, LSCF6428 films fabricated by ESD.

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## A08: Ceramic nanocomposites with alumina matrix

### Dušan Galusek

Joint Glass Centre of the Institute of Inorganic Chemistry SAS, Alexander Dubček University of Trenčín, and Faculty of Chemical and Food Technology STU, Trenčín, Slovakia

The addition of SiC or TiC nanoparticles to polycrystalline alumina matrix has been long known as an efficient way of improving mechanical properties of alumina-based ceramics, especially strength, creep and wear resistance. Recently, new types of (nano)additives, such as carbon nanotubes, carbon nanofibers, and graphene sheets are studied in order to improve not only the mechanical properties, but also to prepare materials with added functionalities, such as thermal and electrical conductivity. The paper provides a concise review of several types of alumina based nanocomposites, evaluating the efficiency of various preparation methods and additives in terms of their influence on the properties of composites.

### Acknowledgements

The financial support of this work by the grant APVV 0108-12 is gratefully acknowledged. This work was created in the frame of the project "Centre of excellence for ceramics, glass and silicate materials," ITMS code 26220120056, based on the Operation Program Research and Development funded from the European Regional Development Fund.

# A09: Photophysical and Morphological study of doped Ag<sub>2</sub>WO<sub>4</sub>:Eu<sup>3+</sup>

<u>Ieda L. V. Rosa<sup>1</sup></u>, I. M. Pinatti<sup>1</sup>, P. F. S. Pereira<sup>2</sup>, J. A. Varela<sup>2</sup>, E. Longo<sup>2</sup>

### <sup>1</sup>Chemistry Department, UFSCar, São Carlos, São Paulo, Brazil. Email:ilvrosa@ufscar.br web site: http://www.ufscar.br <sup>2</sup>Department of Chemistry, UNESP, Araraquara, São Paulo, Brazil.

Silver Tungstate (Ag<sub>2</sub>WO<sub>4</sub>) and Europium doped Silver Tungstate (Ag<sub>2</sub>WO<sub>4</sub>:Eu<sup>3+</sup>) powders were synthesized by co-precipitation method at 80  $\,^{\circ}$ C for 15 minutes using Sodium tungstate dehydrate (Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O), Silver nitrate (AgNO<sub>3</sub>) and Europium Oxide ( $Eu_2O_3$ ) as precursors. Trivalent rare earth ions presenting in different molar ratio concentrations were introduced into the Ag<sub>2</sub>WO<sub>4</sub> lattice aiming to study their structural and photoluminescence properties. This methodology was used because it is simple, cheap, does not need high production temperatures, is industrially favorable, as well as yields materials with homogeneous shape and size without deleterious phases. X-ray diffraction presented a single phase indexed as orthorhombic structure with space group Pn2n (PDF#34-0061), showing crystallinity at long-range. The optical properties of these microcrystals were investigated by ultraviolet-visible (UV-vis) spectroscopy and (PL) photoluminescence measurements. The emission spectra excited at 350 nm (kr laser) showed the characteristic  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$  (J=0, 1, 2, 3 and 4) transitions of Eu<sup>3+</sup> resulting in a red luminescence emission corresponding to the stronger  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  at around 615 nm, and a broad band in the blue region (~450 nm) related to the structural defects and electronic structure of the  $Ag_2WO_4$  (Figure 1) Micro-Raman were used to analyze the degree of structural order-disorder at short-range and revealed the presence of at least 5 high intensity Raman-active vibrational modes. The FE-SEM micrograph showed hexagonal rod-like elongated  $\alpha$ -Ag<sub>2</sub>WO<sub>4</sub> microcrystals with agglomerate nature and average height of 1 µm. These results show novel and interesting properties for these new materials.





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### Acknowledgments

This work was supported by CNPq, CAPES and FAPESP.

## A10: Multifunctional materials for electronics and photonics

#### Federico Rosei

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The bottom-up approach is considered a potential alternative for low cost manufacturing of nanostructured materials [1]. It is based on the concept of self-assembly of nanostructures on a substrate, and is emerging as an alternative paradigm for traditional top down fabrication used in the semiconductor industry. We demonstrate various strategies to control nanostructure assembly (both organic and inorganic) at the nanoscale. Depending on the specific material system under investigation, we developed various approaches, which include, in particular: (i) control of size and luminescence

semiconductor properties of nanostructures, synthesized by reactive laser ablation [2]; (ii) we developed new experimental tools and comparison with simulations are presented to gain atomic scale insight into the surface processes that govern nucleation, growth and assembly [3-7]; (iii) we devised strategies new for synthesizing multifunctional nanoscale materials to be used for electronics and photovoltaics [8-24].

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## A11 : 2D Oxide Nanosheets: New Atomic Sheets from Layered Ceramics

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Two-dimensional (2D) nanosheets with atomic molecular thickness and infinite or planar lengths have been emerging as important new materials due to their unique properties. Inspired by the intriguing properties of graphene, many efforts have been devoted to synthesising 2D inorganic nanosheets of various materials with atomic thickness including metal oxides. hvdroxides. and transition-metal chalcogenides as well as primarily investigating their unique electronic structures and physical properties. Among the types of inorganic nanosheets, oxide nanosheets are important, fascinating research targets because of the virtually infinite varieties of layered oxide materials with interesting functional properties. We are working on the creation of new oxide nanosheets and exploration of their novel functionalities the in electronic applications [1,2].

A variety of oxide nanosheets (such as  $Ti_{1-x}O_2$ ,  $Ti_{1-x}Co_xO_2$ , MnO<sub>2</sub>, and perovskites) were synthesized by delaminating appropriate layered precursors into their molecular single sheets *via* soft-chemical process. These oxide nanosheets have distinct differences and advantages compared with graphene because of their potential to be used as insulators, semiconductors, and even conductors, depending on their composition and structures. Recently, we found that titania- or perovskite-based nanosheets exhibit superior high-performance ( $\varepsilon_r$  = 100–320) even at a few-nm thicknesses, essential for next-generation electronics. Additionally, nanosheet-based high-capacitors exceeded textbook limits, opening a route to new capacitors and energy storage devices.

Another attractive aspect of oxide nanosheets is that nanosheets can be organized into various nanoarchitectures applying solution-based by synthetic techniques involving electrostatic layer-by-layer assembly and Langmuir-Blodgett deposition. It is even possible to tailor superlattice assemblies, incorporating into the nanosheet galleries with a wide range of materials such as organic molecules, polymers, and inorganic/metal nanoparticles. Sophisticated functionalities or nanodevices can be designed through the selection of nanosheets and combining materials, and precise control over their arrangement at the molecular scale. We utilized oxide nanosheets as building blocks in the LEGO-like assembly, and successfully developed various functional nanodevices such as all nanosheet FETs, artificial Pb-free ferroelectrics, spinelectronic magneto-plasmonic materials, devices, Li-ion batteries, metamaterials, etc. Our work is a proof-of-concept, showing that new functionalities nanodevices and can be made from nanosheet-architectures.



Fig1. Oxide nanosheets and their applications.

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A12: The Role of Nanostructure in Thermal Expansion, Including Negative Thermal Expansion Materials and Their Composites

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Most materials expand when heated and, after a large temperature change, the resultant thermal stress can exceed the material strength, leading to catastrophic failure. A few materials exhibit negative thermal expansion (NTE), also known as thermomiotic behaviour. An example is ZrW2O8 which shows significant negative thermal expansion (CTE ~  $-9 \times 10^{-6}$  K<sup>-1</sup>) from 0.3 to 1050 K [1]. For a recent review of thermomiotic materials, see [2]. It is generally thought that thermomiotic materials could be used to make composites with reduced thermal stress. However, nanostructuring plays an important role.

Here we present results of experimental studies of thermal expansion of thermomiotic materials in pure form, and also composites of thermomiotic materials in other matrices. The focus of the presentation is on the role of nanostructure in thermal expansion.

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[2]Negative Thermal Expansion (Thermomiotic) Materials. C.P. Romao, K.J. Miller, C.A. Whitman, M.A. White and B.A. Marinkovic, in *Comprehensive Inorganic Chemistry II*, J. Reedijk and K. Poeppelmeier, Eds. Vol. 4. Oxford: Elsevier; 2013, p. 128-151. A13: Nanostructured transparent Nd:YAG and Nd:RE<sub>2</sub>O<sub>3</sub> ceramics for laser applications: elaboration by non conventional ceramic process and correlations with their optical properties

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Since twenty years, transparent ceramics are developed for laser applications but it is still difficult to reach high laser power/energy with high efficiency. The main challenge to overcome is that ceramic material must be highly transparent in a large wavelength range comprising the emission and pumping wavelengths, generally from the visible to the near infrared range.

It is now well admitted that  $Nd^{3+}$  or  $Yb^{3+}$ -doped ceramic materials of garnet ( $Y_3Al_5O_{12} - YAG$ ) and rare-earth sesquioxide ( $Y_2O_3$ ,  $Lu_2O_3$ ,  $Sc_2O_3$ ) families are of primary interest as amplifier media for high power lasers [1,2]. Several research works were carried out in the order to better control and understand each elaboration step of these ceramics (powder synthesis, powder shaping to obtain the "green" body of compacted powder, thermal treatment -sintering to densify the powder compact).

At SPCTS laboratory in Limoges, an integrated approach of ceramic processes (*i.e.* from powder synthesis to the final piece with desired properties) allows understanding and mastering each step of the process. In order to obtain highly efficient laser ceramics, it is first of primary interest to limit optical losses, thus to control transparent ceramics microstructure, especially grain size and residual porosity content. This presentation will show how the final (nano-, micro-)structure and optical properties of the obtained transparent material can be controlled thanks to suitable thermal treatment. Whatever the sintering treatment, the aim is to promote porosity elimination and to remove all the microstructural defects without exaggerated grain growth. The latter point is deleterious because grain growth leads to pore entrapment inside grains. In this context, this presentation will show that non-conventional sintering treatments like post-HIP (*Hot-Isostatic Pressing* under 150-200 MPa of argon gas) or SPS (*Spark Plasma Sintering* under 100-150 MPa of uniaxial pressure) allow to limit drastically the grain growth and to promote densification. This presentation will finally show that such transparent ceramics are suitable for laser operation.



**Figure 1.** Nd:YAG (a) and Nd:Lu<sub>2</sub>O<sub>3</sub> (b) transparent ceramics; with large grains after natural sintering under vacuum at 1750  $^{\circ}$ C (Nd:YAG) (c), small grains after post-HIP at 1650  $^{\circ}$ C under 150 MPa of argon gas (Nd:YAG) (c) or nanograins after SPS at 1400  $^{\circ}$ C under 130 MPa of uniaxial pressure (Nd:Lu<sub>2</sub>O<sub>3</sub>) (e).

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## A14: Microstructure-performance relations for the ceramic electrodes of solid oxide fuel cells

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During operation of solid oxide fuel cells (SOFCs), microstructure and chemical composition of Ni-oxide anode were changed accompanying various degradation factors of the cell performance. Focused ion beam-scanning electron microscope (FIB-SEM) observation revealed that Ni sintering and, therefore, decrease in length of triple phase boundary significantly proceeded with long term operation, thermal cycles, and redox treatment of the Ni-oxide anode (Fig. 1). With supply of hydrocarbon and CO, two types of deposited carbon species, i.e., graphite-like and amorphous carbon, were observed by a Raman microscope. The carbon species were formed by disproportionation of CO at relatively low temperatures and cracking of hydrocarbon. Especially, deposition of amorphous carbon led to degradation of the cells by blocking gas supply to the triple phase boundary. The reduction-oxidation cycles of cerium in Ni-ceria anode is expected to promote removal of deposited carbon with a change in atmosphere. The deposited carbon was oxidized by steam in the fuel mixture with the catalytic action of The oxidation state of cerium in Ni-ceria ceria. anode systematically changed with the oxygen potential of supplied fuel. In severe reducing atmosphere, the fluorite type phase of ceria was transformed into rare earth C-type phase accompanied by the formation of oxygen vacancy in the lattice, which was observed by X-ray diffraction and Raman spectroscopy. Ni-Ceria anode is also effective for direct ammonia SOFC.



Green: Ni, Yellow: ceria, Open space: pore **Fig.1** (a) Reproduced three dimensional microstructure and (b) extracted triple phase boundary of Ni-ceria cermet anode for SOFC.

### A15: Visible Light-Induced Overall Water-Splitting over Solid State Z-Scheme Photocatalysts

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Various photocatalytic materials aiming at water splitting have been reported because produced hydrogen (H<sub>2</sub>) is attractive as a clean and renewable fuel. [1-4] To date, one of the candidate methods to split water to  $H_2$  and oxygen ( $O_2$ ) at a stoichiometric ratio under visible light is a combined system of half reaction photocatalysts, that is, H<sub>2</sub>-evolution and O<sub>2</sub> evolution photocatalysts. [5] However, because such the combination system, which is termed "Z-scheme", requires the presence of a suitable redox couple, the system is not in fact capable of splitting pure water. Recently, solid-state Z-scheme systems that function in the absence of a redox couple were reported. These combined systems, which consisted of ruthenium (Ru)-loaded SrTiO<sub>3</sub>:Rh (Ru/SrTiO<sub>3</sub>:Rh) and BiVO<sub>4</sub> with and without photoreduced graphene oxide

(PRGO), acted overall water-splitting as photocatalysts under irradiation with visible light. [6,7] However, Ru/SrTiO<sub>3</sub>:Rh and BiVO<sub>4</sub> or PRGO/BiVO<sub>4</sub> were assembled to form aggregates in acidified water (H<sub>2</sub>SO<sub>4</sub> aqueous solution, pH 3.5) through the electrostatic attractive interaction between the surface charges of Ru/SrTiO3:Rh and BiVO4 or PRGO/BiVO4, and these are not therefore considered as pure water-splitting catalysts. In the present study, we therefore tried to combine H<sub>2</sub>- and O<sub>2</sub>-evolution photocatalysts via a conducting layer to construct an all solid-state Z-scheme system and demonstrated that this system can split "pure" water (i.e., distilled water without adding any chemicals) under visible light irradiation.

One example is that Zinc rhodium oxide  $(ZnRh_2O_4, band-gap (Eg) = 1.2 eV and defective$ silver antimonate (Ag<sub>1-x</sub>SbO<sub>3-v</sub>, Eg = 2.7 eV) as H<sub>2</sub>and O<sub>2</sub>-evolution photocatalysts, respectively, were connected with silver (Ag) as the conducting layer to prepare the solid-state Z-scheme photocatalysis system. In short, commercially available powder of Ag<sub>2</sub>O and prepared powders of ZnRh<sub>2</sub>O<sub>4</sub> and AgSbO<sub>3</sub> were thoroughly mixed and heat-treated at 900°C, which is slightly lower than the melting temperature of Ag. Then, the obtained powder was washed with HNO<sub>3</sub> aqueous solution to remove excess Ag, forming the solid-state photocatalyst, ZnRh<sub>2</sub>O<sub>4</sub>/Ag/Ag<sub>1-x</sub>SbO<sub>3-y</sub>. In this system, Ag acted as the solid-state electron mediator for the transfer of electrons from the conduction band of Ag<sub>1-x</sub>SbO<sub>3-y</sub> to the valence band of ZnRh<sub>2</sub>O<sub>4</sub>. Utilizing thus constructed photocatalyst, the simultaneous liberation of H<sub>2</sub> and O<sub>2</sub> from pure water at a molar ratio of  $\sim 2:1$ was achieved under irradiation with visible light with wavelength at > 460 nm (Fig. 1). In addition, we confirmed this photocatalyst could utilize visible light up to 545 nm. [8] Utilizing the same strategy by changing the O<sub>2</sub>-evolution photocatalyst, we recently succeeded in pure water-splitting under visible light up to 600 nm. Detailed investigations will be discussed at the conference.



Fig. 1 Photocatalytic evolution of  $H_2$  and  $O_2$  from pure water under irradiation with visible light (>460 nm).

### Acknowledgements

The author is grateful to Prof. Bunsho Ohtani at the Catalysis Research Center, Hokkaido University for collaboration with this work. This study was partially supported by the Cooperative Research Program of the Catalysis Research Center, Hokkaido University (Grant #13B1011).

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### A16: Model for coupled ferroelectric hysteresis using time fractional operators: Application to innovative energy harvesting

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The interest in ferroelectric properties, materials and devices has been increased considerably over the last 30 years. One of the most outstanding challenges for the researchers working around ferro-electricity is to developed efficient energy harvester systems based on natural surrounding mechanical vibrations. Last developments of the material properties associated to the recent diminution of the small electronic consumptions have considerably increased the potential of such systems. Unfortunately, one of this development major limitation remains the experimental validations which are always numerous and longs. To overcome this limit, in our laboratory, we have developed a high performance model for the dielectric polarization in ferroelectric ceramics under varying external conditions (electric field, mechanical stress). This model is constituted of two contributions. The first contribution is related to the quasi-static behavior (low frequencies) and a second contribution linked to the frequency dependence of the material. Fractional mathematical operators are employed in this second contribution. This model has demonstrated valuable performances under extreme external conditions. In particular, it is well adapted to model the polarization variations under Ericsson loop energy harvesting system conditions. Here, varying frequencies and amplitude of natural mechanical vibrations are artificially synchronized to an imposed external electric field. This synchronism leads to a maximization of the amount of energy harvested.

# A17: High Temperature Piezoelectrics: Guidelines and Realities

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A variety of piezoelectric applications have been driving the research in development of new high temperature ferroelectrics; ranging from broader markets such as fuel and gas modulation and deep well oil drilling to very specific applications such as thermoacoustic engines and ultrasonic drilling on the surface of Venus. The focus has been mostly on increasing the Curie temperature. However, greater challenges for high temperature ferroelectrics limit the operating temperature to levels much below the Curie temperature. These include enhanced loss tangent and dc conductivity at high fields as well as depoling due to thermally activated domain rotation. The initial work by Eitel et al. increased interest in investigation of Bismuth containing perovskites in solid solution with lead titanate. Issues that arise vary from solubility limits to increased tetragonality; the former one prohibits processing of morphotropic phase boundary, while the latter one impedes thorough poling of the polycrystalline ceramics. This talk will summarize recent advances in development of high temperature piezoelectrics and provide information about challenges encountered as well as the approaches taken to improve the high temperature behavior of ferroelectrics with a focus on applications that employ the converse piezoelectric effect.

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### **B01: Strain Induced Dielectrophoretic Behavior in Electronically Phase Separated Manganite Thin Films**

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The crystal structures of certain perovskite-type transition metal oxides are such that small changes in the interatomic distances can lead to drastic changes in the electronic and magnetic properties. Due to this sensitivity transition metal oxides can have competing phases with different electronic, magnetic, and structural properties under the same external conditions. This competition sometimes results in the material existing in a micrometer scale phase separated state. In high quality thin films of the transition metal oxide  $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ , the competing phases have shown evidence that they behave in a fluid-like manner and can move spatially within the solid sample under the influence of strain and electric field which is reminiscent of dielectrophoresis [1,2,3]. In this presentation, I will discuss the fluid-like behavior of the competing phases starting with the growth of high-quality thin films of (La<sub>1-v</sub>Pr<sub>v</sub>)<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> using pulsed laser deposition [2]. I will describe the local and bulk properties of the thin films and fabricated micro/nanostructures which were studied using techniques such as low temperature conducting atomic force microscopy, spin-polarized neutron reflectometry, resistivity. and magnetization measurements. Our results point to a unique type of magnetoelectric coupling in which an electric field affects the magnetic anisotropy of the material.

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#### **B02:** Nano Materials for Light Harvesting

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There has been a growing interest on utilizing semiconductor quantum dot (QD) for technological applications for their attractive properties. The detailed understanding of the carrier relaxation dynamics is essential because it dictates the overall efficiency in various optoelectronics, photovoltaic, light harvesting and sensing applications. Recent studies reveal that the energy transfer between QD and dye is a Förster resonance energy transfer (FRET) process as established from 1/d<sup>6</sup> distance graphene-semiconductor dependence. Again, composite nanostructures have been recently emerged as a new class of functional materials because of their potential applications i.e. solar energy conversion, optoelectronic devices, catalysis and sensing. We have analyzed the decays of the fluorescence of OD in GO-CdTe OD composite by using a proposed stochastic model to estimate the number of sites available and the fractional surface coverage of QD by GO sheet. The photoconductivity properties of GO-QD composites with visible illumination have been studied to understand transport properties of GO-QD composite.

**Keywords**: Energy transfer, QD, GO, photoluminescence

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#### B03: Energy Harvesting from Heart Beating Based on Low-Frequency Periodic Buckling of PZT Films

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The soft and flexible features of bio-organs and bio-tissues hastened а new generation of bio-integrated or bio-implantable devices based on the flexible and stretchable electronics. Potential applications of theses bio-devices include EEG/ECG monitors, heart pacemakers, nerve stimulators, epidermal electronics, and so on. All these devices must be powered by integrated batteries or external electric source so as to operation properly. However, these batteries need to be charged frequently or the external power supply always involves complex electric cables, and, hence, these power supply cannot ensure full-time operation or portable applications of these devices. This talk aims to report a new energy supply module that exploits a flexible piezoelectric device to translate the natural motion of bio-organs (e.g. heart beating) to electric power. The piezoelectric film is integrated on a soft sheet and driven to buckle periodically by the heat beating. The energy harvesting effects of the piezoelectric device in low-frequency motion is modeled theoretically, and the output powers are given analytically dependent on the amplitude and period of the buckling behavior. The effects of closed or open chest on the efficiency of energy harvesting are investigated. The solution is validated by comparing numerical results to experimental measurements. The present simple analytical model

will provide a simple guideline for the design and operation this kind of energy harvesters for flexible bio-devices.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China at grants Nos. 11322216 and 11321202. It was also partly supported by the Zhejiang Provincial Natural Science Foundation of China at grant No. LR13A020001.

## **B04:** Non-epitaxial semiconducting heterostructures with controllable nanostructure

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Utilizing dimensional and two quasi-dimensional "crystals" as building blocks for multi-component heterostructures is an attractive approach for formation of new materials with potential for unprecedented tunable functionality. [1] By locally nucleating individual component structures from designed thin film precursors with locally modulated compositions, we have demonstrated a synthetic approach to kinetically trap a variety of intergrowths of semiconducting compounds. As an example, by targeting interleaved SnSe and MoSe<sub>2</sub> heterostructures, which correspond to bulk and 2-D semiconductors of interest for electronic and energy conversion applications, we have demonstrated the ability to access more than 500 new compounds in the Sn-Mo-Se system by

controlling the number and sequence of the stacked SnSe and MoSe<sub>2</sub> layers. [2] X-ray reflectivity, laboratory and synchrotron XRD, STEM and HRTEM imaging, and electron microprobe analysis provide conclusive evidence of the formation of layered intergrowths with well-defined structure and composition. Synchrotron X-ray diffraction, Raman spectroscopy, and first-principles calculations reveal a size-induced structural transition occurring in the SnSe component as the layer thickness is increased, suggesting a novel method for controlling the crystal structure and therefor properties in nanoscale materials. [3] The synthetic method has also been extended to prepare other compositions, e.g. tellurium-based  $[(PbTe)_{1,17}]_m(TiTe_2)_n$ , which are not accessible by other preparation methods. [4]



**Figure 1.** High angle annular dark field scanning transmission electron microscope images for (a) [(SnSe)<sub>1.04</sub>]<sub>1</sub>[MoSe<sub>2</sub>]<sub>1</sub>, (b) [(SnSe)<sub>1.04</sub>]<sub>4</sub>[MoSe<sub>2</sub>]<sub>4</sub>, and (c) [(SnSe)<sub>1.04</sub>]<sub>16</sub>[MoSe<sub>2</sub>]<sub>16</sub>. High resolution transmission electron microscope images for (d) [(SnSe)<sub>1.04</sub>]<sub>16</sub>[MoSe<sub>2</sub>]<sub>16</sub> and [(SnSe)<sub>1.04</sub>]<sub>21</sub>[MoSe<sub>2</sub>]<sub>4</sub>. Reproduced from M. Beekman, S. Disch, N. Gunning, and D. C. Johnson, *Inorg. Chem.* in press (2014).

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### **B05:** Surface Functionalization of Polystyrene with Biomimetic Apatite and Culture of Bone-Related Cells Thereon

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Hydroxyapatite (HAp,  $Ca_{10}(PO_4)_6(OH)_2$ ) is the major inorganic component of human bones and teeth enamel, and widely used as coating of orthopedics and dental implants. For coating materials with HAp, methods like plasma spray, sol-gel process, sputtering technique, and biomimetic process have been developed. Simulated body fluid (SBF), a solution having similar inorganic ion concentrations to those of human plasma, and 1.5SBF, a solution having 1.5 times higher ion concentrations than those of SBF, has been used to biomimetic deposition of bone-like HAp on material surfaces having acidic groups such as carboxylic acid group under mild conditions [1]. Although HAp coating on commonly used polymers such as polystyrene (PS) using SBFs can expand the availability of these materials in biomedical

applications, these polymers do not display effective functional groups for biomimetic HAp mineralization, therefore pre-treatments such as plasma treatment, UV-irradiation, and alkaline treatment are needed. We have demonstrated that introduction of adsorption layers of serum proteins such as human serum albumin (HSA) and human immunoglobulin G (hIgG) on PS substrate using casting techniques or dipping in protein solution resulted in deposition of HAp on these surfaces when immersed in 1.5SBF [2, 3]. This method enables to form bone-like HAp without high-cost physical or chemical pre-treatments: however, complete surface coverage with HAp has not been achieved. In this study, the PS plates completely covered with HAp were prepared using aqueous calcium chloride treatments and their interaction with bone related cells were investigated.

At first, HSA solutions were added into each well of a commercial 24 well PS plate and incubated. After treatment with 2.5 M calcium chloride solution, the plate was immersed in 1.5SBF [4]. Scanning electron microscopy (SEM) observation showed complete coating of each well of the PS plate with deposits having plate-like structure of HAp (Fig. 1(a)). From energy dispersive X-ray spectrometry (EDX) analysis, it was found that the deposits contained Ca, P, O, and small amounts of Na and Mg. The Ca/P elemental ratio of the deposits appeared smaller than that of stoichiometric HAp (1.67). Such tendencies obtained from the EDX spectra are also sometimes seen for HAp deposited from SBFs and indicated deposition of bone-like HAp.

Then, we cultured bone-related cells on the substrates to evaluate effect of biomimetic HAp coating on spreading, proliferation and differentiation of cells using mouse preosteoblast MC-3T3-E1 cell line. PS plates coated with HAp were transparent under optical microscopic observations. MC3T3-E1 cells attached and spread on HAp-coated PS plate than those on non-treated PS plate (Fig. 1(c)) and numbers of attached cells were almost equal to those on PS cell culture treated plates.



**Fig. 1** (a) Schematic illustration of coating of polystyrene (PS) substrate with biomimetic HAp via HSA-adsorption layers. (b) SEM image of the surface of HSA-adsorbed PS plate after incubation in 1.5SBF for 48 h. (c) Morphology of MC3T3-E1 cells cultured on PS plate coated with biomimetic HA.

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# **B06:** Growth and structural characterization of anatase/rutile–TiO<sub>2</sub> thin films; optical, surface and catalytic properties

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Titanium dioxide  $(TiO_2)$  is one of the most investigated oxide materials due to its high refractive index, high dielectric constant, and optical transmittance in the visible and near-IR region and found in a wide range of optoelectronic application such as dye-sensitized solar cells, photocatalysts, optical coatings and self-cleaning windows. Synthesizing methods and engineering the applications of TiO<sub>2</sub> whereas it is single or poly crystal form or as film, nanoparticle or bulk ceramics or with the most common morphologies anatase or rutile is still expanding.

Here we present a thorough investigation of preferential crystal growth crystal TiO<sub>2</sub> thin films grown by pulsed laser deposition on amorphous fused silica glass substrate and compare the result with epitaxial growth on SrTiO<sub>3</sub> (001) and MgO (001) substrates. It is shown the possibility to grow uniaxial films on amorphous substrates. Further by varying the kinetics of the ablation and the surface diffusion, it is possible to produce films that departure from their thermodynamic equilibrium. On the amorphous substrates different morphologies and directions of either anatase (101) or rutile (110) films were formed depending on deposition parameters. With oxygen background pressure between 10-30 mTorr a high crystallinity anatase film with 101 out of plane grown direction with no substrate heating and an ex-situ post annealing of 300°C was formed on the amorphous glass. In spite of post annealing up to 1000°C this anatase 101 phase was stable, whereas in-situ annealing substrate heating up to 800°C formed mixed phases of anatase 101 and 001 and gradually rutile 110 towards 800°C.

Structural evaluation and characterization were analyzed by XRD, Raman, TEM and AFM and related to the film growth kinetics.

Optical properties of the films were investigated by spectroscopic methods.



**Figure1**: Surface analysis of anatase 101 film showing the typical anatase bipyramidial crystal growth with Rms = 0.18 nm on top of the 101 anatase film structure and Rms=0.89nm on a 3x3  $\mu$ m acan.

# **B07:** Design and Fabrication of Functional Nanocomposite Coatings by the Sol–Gel Process

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The ability of controlling surface functionality by depositing transparent coatings at the nanoscale is the key issue for large-scale industrial development of nanotechnology. Considering the global scenario, work related to the functional nanocomposite coatings on glass, plastic and related substrates has enormous potential both from scientific and technological point of view. I will highlight some of our recent activities on the fabrication of the following functional coatings:

• Different types of inorganic–organic hybrid nanocomposite based scratch-resistant coatings on optical quality plastics [1],

• Wavelength selective antireflective coatings on plastics with hydrophobic surfaces [2],

• Superhydrophobic coatings on glass surfaces for self-cleaning applications [3],

• Metal nanoparticles (NPs) doped coatings highlighting the plasmon tunibility and applications [4],

• Ordered mesoporous alumina films with metal NPs doping for high performance reusable film catalysts [5],

• Electrically conducting black RGOorganically modified silica (RGO-ORMOSIL) composite coatings on glass [6] and

• Fluorescent ( $Cd_{0.5}Zn_{0.5}S$ :Cu and carbon) nanodots incorporated films with high quantum yields [7].

In this lecture key issues regarding the synthesis of inorganic-organic hybrid nanocomposite sols, formation of covalent bonding leading to the generation of uniform hybrid network, in-situ generation with shape control of NPs in sols, use of different surfactants to obtain ordered mesoporous coatings and controlled encapsulation of quantum dots in hybrid films will be discussed.

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# **B08:** Luminescent properties of perovskite type phosphor thin films

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It is known that several perovskite type oxides show photoluminescence (PL) by doping lanthanide ions. For instance, Pr<sup>3+</sup> doped titanates or Eu<sup>3+</sup> doped zirconates show red luminescence. Tb<sup>3+</sup> doped stannates show green luminescence and Tm<sup>3+</sup> doped hafnates show blue luminescence. To apply these phosphors to optoelectronic devices, the preparation of their thin films were carried out using various deposition methods such as sputtering and pulsed laser deposition. The high quality films showing bright PL were reported in Pr<sup>3+</sup> doped titanates, Tm<sup>3+</sup> hafnates and Ln<sup>3+</sup> doped stannates. [1-4] Using these films, electroluminescence devices were demonstrated and red electroluminescence in (Ca,Sr)TiO<sub>3</sub>:Pr<sup>3+</sup>, and green electroluminescence in  $CaSnO_3:Tb^{3+}$  have been observed. [5-7]

These perovskite type phosphors showing visible light have potential for optoelectronic applications such as solid state lighting and recently they have been investigated extensively. On the contrary, perovskite type oxides showing uv light have been hardly examined except for YAlO<sub>3</sub>: $Ce^{3+}$  and YAlO<sub>3</sub>: $Pr^{3+}$  for scintillator applications. In a material survey of uv phosphors in perovskite type

oxides, we recently found  $Gd^{3+}$ – $Pr^{3+}$  codoped or  $Gd^{3+}$ doped YAlO<sub>3</sub> showed intense UV emission at 314 nm from  $Gd^{3+}$  ions. [8-10] In the present study, the preparation of thin films of YAlO<sub>3</sub>:Gd<sup>3+</sup>, Gd<sup>3+</sup>– $Pr^{3+}$  is reported with its PL and cathodoluminesecnce properties.

The epitaxial thin films were obtained on LaAlO<sub>3</sub> single crystal substrates by RF sputtering or PLD. The films were transparent in the visible region and their surfaces were smooth enough to develop future optoelectronic devices. The films showed intense  $Gd^{3+}$  emission at 314 nm; YAlO<sub>3</sub>: $Gd^{3+}$ – $Pr^{3+}$  film showed  $Gd^{3+}$  emission under excitation at 217 nm as shown in Fig.1.



**Fig1**. PL and PLE spectra of YAlO<sub>3</sub>:Gd<sup>3+</sup>–Pr<sup>3+</sup> film.

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# B09: Pulsed laser deposition of multiferroic and ferroelectric perovskite-oxide thin-film heterostructures

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Multiferroic heterostuctures of ferroelectric (FE) and ferromagnetic (FM) perovskite-oxides are attractive for their multifunctional properties and potential applications in magneto-electric (ME) memories. Pulsed laser deposition (PLD) technique has been quite successful in the growth of complex-oxide thin films, however, it is complicated in the fabrication of multilayered FE/FM heterostructures. This is mainly due to the dissimilar ablation conditions of the insulating FE and the conducting FM phases in these structures. Here, we address some of the challenges in the laser ablation of epitaxial multilayered thin films of the FE perovskite  $PbZr_{0.52}Ti_{0.48}O_3$  (PZT) with the FM half-metallic oxide La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSMO) [1,2]. Incorporation of hard-magnetic oxide  $CoFe_2O_4$ (CFO) in а PZT/LSMO heterostructures can potentially enhance their intrinsically soft FM properties. and consequently the ME device performance. However, it introduces dielectric losses which degrade the FE polarization of the PZT layer, thus, limiting the long-sought mutual control of ferroelectricity and magnetism in these multiferroic composites. In this direction, we report the simultaneous enhancements of polarization and magnetization in PZT/LSMO hetrostructures enabled by ultrathin CFO sandwich-layers. High quality, epitaxial PZT/CFO/LSMO heterostructures with the thickness of the CFO layer varying from 0 nm to 50 nm were grown on SrTiO<sub>3</sub> (100) substrates using an optimized PLD technique. An ultrathin (10 – 20 nm) CFO layer was found to simultaneously improve the FM and FE characteristics of the system through distinct mechanisms. The increase in magnetization and magnetic coercivity in the PZT/CFO/LSMO was associated with a tetragonal distortion of the CFO lattice under epitaxial strain, while perpendicular anisotropy generated by the distortion stabilized an out-of-plane orientation of the easy axis of magnetization in the thinnest CFO layers. Trapped charge at the CFO/PZT interface in PZT/CFO/LSMO induced an internal built-in field in the heterostructures, resulting in the accumulation of higher switched charges during voltage cycling and enhanced polarization in the samples over PZT/LSMO. An increase in electric coercivity was also observed in the CFO-containing heterostructures, and is discussed in terms of a dielectric/FE layered capacitor model. In a different direction, we report on a novel combined physical/chemical methodogy using PLD and solvothermal process that has been successful in the growth of nanostructured films of both Pb-based PZT [4] and the emergent Pb-free non-centrosymmetric FE oxide LiNbO<sub>3</sub>-type (LN-type)  $ZnSnO_3$  [5,6]. In this combined technique, initially, a seed-layer of a lattice-matched material is deposited on a suitable substrate using PLD; followed by the chemical syntheses of the FE nanostructures on the pre-orientating seed-layers. The similar crystal symmetry between the seed-layers and FE phase facilitates the growth of highly crystalline FE nanostructured films. The structural integrity and high density of the nanostructures facilitate a direct

measurement of the intrinsic FE polarization from the resulting nanostructured device without the using of any dielectric fillers to prevent shorting of the device. Detailed study on the structural and FE properties of nanostructured films of PZT and LN-type ZnSnO<sub>3</sub> will be presented. The results presented here summarize the recent advances in laser ablation techniques for the fabrication of multiferroic and FE heterostructures which is crucial for the coherent design of future memory devices based on these composite systems.

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### **B10:** Ink jet printing of transparent conductive oxide thin films and patterns

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Ceramic materials are of utmost importance in daily use for a large variety of application. Unfortunately their brittle nature forces researchers to search for ways to overcome this problem for instance by the deposition of a thin film of ceramic material onto a flexible substrate. Often there is no need for a bulk ceramic but for a functional ceramic coating. Besides vacuum based deposition techniques such as chemical vapor deposition, sputtering, ALD the choice to apply a chemical solution deposition (CSD) technique can be made. In the presentation the use of CSD for the deposition of Al-doped ZnO is explored. Al-ZnO is a typical example of an transparent conductive materials.

The development of transparent conductive oxides (TCO) with low resistivity and high transmittance in the visible region is of utmost importance. [1] Tin doped Indium oxide (ITO) is one most widely applied TCO material for optoelectrical devices. However, the high cost price and the resource availability problem of indium promote the search for alternative materials. By doping ZnO with group-III elements such as B, Al, Ga and In a good transmittance in the visible region of the electromagnetic spectrum and high electrical conductivity is obtained which makes those materials attractive as transparent conductive materials and replacement for ITO. Al-doped ZnO is very promising candidate due to its good transparency, high conductivity, low cost of Al and Zn and non-toxicity. [2,3] A CSD process is presented here as it is simple, cost effective and allows a high controllability of the dopant concentration. By selecting the CSD method several deposition methods can be applied such as dip-coating, spin-coating, spray-coating and ink jet printing. Ink jet printing is favored for its multiple benefits: (1) Via Ink jet printing there is no direct contact between the solution and the substrates, meaning a closed ink container prevents ink losses and solvent evaporation will be avoided which increases the ink lifetime. (2) High precision of the deposited ink droplets allows printing of thin films but also high-resolution patterns. (3) By using a multi-nozzle print head an easy scalable industrial process is obtained.

In this research, the deposition of AZO thin films via ink jet printing is explored combined with the possibility of using this ink for direct patterning without etching is being tested. The transparency and the electrical properties of the films and patterns such as resistivity, mobility and carrier concentration will be presented. We have studied intensively the influence of the composition of the precursor, thermal processing, used atmosphere and post-annealing processing on the resistivity, morphology of the films, crystallinity and porosity. Figure 1 shows a fully processed 80 nm thick, Al-ZnO film with a resistivity of 2.8  $10^{-2} \Omega$  cm.



Fig1. Al-ZnO film prepared by ink-jet printing (80 nm thick)

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### **B11:** Interfacial Structure and Functional Properties of Complex Oxide Heterojunctions

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Due to delicate balance among crystal structure, chemical composition and electronic configurations, bulk perovskite complex oxides have demonstrated a broad range of electronic, magnetic and optical functional properties. Recent advance in thin-film fabrication and characterization techniques have further made it possible for precise control of material synthesis and perfecting their properties for important information technology and energy-related applications. The most exciting part of oxide thin-film research lies in the fact that it offers extra degrees of freedoms to tune the functionalities, e.g. epitaxial strain, interface formation, and crystal symmetry mismatch, which are not available in their bulk form.

In this talk, I will be focusing on the inter-correlations among epitaxial film growth, interface structure, and induced (electronic and magnetic) properties of perovskite oxide heterojuncitons. Driven by chemical solubility and inherent polar discontinuity, these material systems are prevented from forming structurally coherent and chemically abrupt interfaces, as demonstrated by state-of-art spectroscopy and microscopy techniques. Intermixing of the cations at interfaces is demonstrated to result in dramatic change of electronic structure and electrical behaviors for LaAlO<sub>3</sub>/SrTiO<sub>3</sub> and LaCrO<sub>3</sub>/SrTiO<sub>3</sub>. In addition to intermixing, the interfacial symmetry-mismatch is shown to surpass the traditional lattice mismatch to stabilize novel interfacial states with unique octahedral structure and spin configuration. The symmetry breaking at LaCoO<sub>3</sub>/SrTiO<sub>3</sub> interface dramatically modifies the structure of fundamental CoO<sub>6</sub> building-blocks. The combination of epitaxial strain and octahedral tilting results in pronounced  $t_{2g}^*$  $\rightarrow e_{\rm g}$  spin-transition and a microscopic long-range magnetic ordering in LaCoO<sub>3</sub>, which doesn't have this property in bulk phase.

# **B12:** Structure, Composition, Electrical and Optical Properties of Sputtered PbSe Thin Films on Si

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Lead selenide (PbSe) thin films were prepared by magnetron sputtering, and the deposition conditions were optimized based on the orthogonal array method. The films were characterized by FE-SEM, EDX, XRD, XPS and FTIR. The surface of as-prepared films is quite smooth and crack-free; the highest resistance change rate is 38.4%. If only the relative sensitivity is considered as the quality standard, the optimal parameters for depositing high quality PbSe thin films are: 100 W sputtering power, 150 °C substrate temperature, 1 sccm oxygen flux and 30 min deposition time. The band gap  $(E_g)$  of all nine deposited PbSe thin films is about 0.39 eV, much larger than the bulk material (0.28 eV at 300 K). The selenium concentration is lower than the lead concentration, according to the EDX results. The prominent diffraction peak is (200) PbSe, and the average crystal size is less than the Bohr radius, which leads to the quantum confinement and increases the band gap. The surface composition of the PbSe thin films is mainly affected by the oxygen flux during the deposition process. The Pb element has PbSe and PbO two chemical states, the Se element has PbSe, Se and SeO<sub>2</sub> three chemical states, while the O element has lattice and absorbed oxygen two chemical states. The lattice oxygen content is the main factor affecting the resistance of the sputtered PbSe thin films.

# **B13:** Magnetoelectric thin film composites as magnetic field sensors or energy harvesters

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Magnetoelectric (ME) composite materials show ME coefficients that are larger than that of natural multiferroics by several orders of magnitude. These ME composites have high potential for applications, e.g. as very sensitive ac magnetic field sensors or as energy harvesters. Special features of magnetic field sensors are their passive nature, their high sensitivity, and their large dynamic range with linear response. By magnetic field annealing it is possible to obtain a sensor element that has a pronounced sensitivity in only one dimension being a component of a 3-dimensional vector field sensor, which is highly desirable for applications like magnetoencephalography or -cardiography as a replacement for today's sensors based on liquid He cooled SQUIDs. In energy harvesting it is promising to combine magnetic and acoustic harvesting into a single device.

The thin film ME 2-2 composites of this work consist of AlN or ferroelectric piezoelectrics and different magnetostrictive layers. Upon magnetic field annealing of amorphous magnetostrictive FeCoSiB layers these ME composites with AlN as the piezoelectric layer show an uniaxial magnetic anisotropy [1] and an extremely high ME coefficient of up to 20 kV/cmOe at mechanical resonance in vacuum [2].

However, these composites require in general the presence of an external d.c. magnetic bias field, which is detrimental to their use as sensitive magnetic-field sensors or energy harvesters. Composites consisting of piezoelectric AlN and multilayers with e.g. the sequence Ta/Cu/Mn70Ir30/FeCoSiB serving as the magnetostrictive component rely on intrinsic magnetic fields arising from the induced exchange bias [3]. The thickness of the different ferromagnetic layers and angle dependency of the exchange bias field are used to adjust the shift of the magnetostriction curve in such a way that the maximum magnetoelectric coefficient occurs at zero magnetic bias field.

In this presentation different thin film composites will be discussed in view of their piezoelectric material, different concepts of the magnetostrictive component and different electrode concepts [4] in view of their use as very sensitive magnetic field sensors in the pT range [5] or as energy harvesters.

Funding by the German Science Foundation (DFG) is gratefully acknowledged.

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### B14: In Situ Deformation of Metallic Interlayers

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There are many interesting mechanical properties that can be achieved with metal/ceramic multilayers especially if they are defined more broadly to include structures such as MAX phases. However, the deformation mechanisms, such as hysteresis, can be complex. To simplify the problem, in this work we have concentrated on the effect of a single metal interlayer within a ceramic bi-crystal. The samples were produced by sputtering niobium on to sapphire substrates and then diffusion bonding the two coated crystals together. This allowed the production of sapphire micropillars with containing a ~50-200 nm niobium layer. These were then loaded in situ within a microbeam laue set up. By varying the layer thickness the measured strength of the pillar could be varied along with the magnitude of the hysteresis. This hysteresis was tracked by the load-displacement trace along with the movement and elongation of diffraction spots associated with the interlayer.

### **B15:** Temperature Dependent Ionic Transport Properties in Layered Perovskite (Sr,La)<sub>3</sub>Fe<sub>2</sub>O<sub>7-δ</sub>

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Typical examples of electronic- and ionic-mixed conductors are simple cubic or rhombohedral perovskite oxides (Sr, La)FeO<sub>3</sub>.[1] The perovskite oxides reveal higher mixed conductivity, resulting in higher oxygen permeability at elevated temperatures. The permeability is applicable to oxygen separators for partial oxidation reforming. However, there are still some obstacles for the application. One of them is that the oxygen permeability abruptly decreases with decrease of temperatures. A strategy to improve the oxygen permeability at lower temperatures is to reduce activation energies for oxide ionic transportations. With the point of view, we focused on a layered perovskite (Sr,La)<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub>, which is composed of the same element as the simple perovskite of (Sr, La)FeO<sub>3</sub>. We tried to investigate the difference in crystal structure on the ionic transportation as well as oxygen permeability between them. It was found that activation energy of the oxygen permeability of a layered perovskite  $Sr_{2.46}La_{0.54}Fe_2O_{7-\delta}$  (SLF327) was relatively lower than those of the (Sr, La)FeO<sub>3</sub>. The lower activation energies are owing to the characteristic oxygen deficiencies and ionic transportation properties in the layered perovskite structure.

To make clear the oxide deficiencies and the transportation mechanism in the SLF327, we made combination studies of experimental techniques: X-ray powder diffraction (XRPD) and investigations of the oxygen vacancy formation reaction and computational techniques: the bond valence sum (BVS) approach and ab initio density functional theory (DFT). The XRPD and the DFT showed that the defects are located at the O1 site among the three different O sites in the crystal structure of SLF327.(Fig. 1) The temperature dependence of XRPD indicates that the host structural possesses no phase transition, while the defect arrangement did change around 830 °C. The BVS and DFT studies suggested a change in the ion transportation mechanism at higher temperatures than 830 °C. Based on the obtained results, we will discuss the

detailed temperature dependent ion transportation mechanism in the SLF327.



Fig1. Crystal structure of the SLF327.

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C01: Electrical and thermal transport in nanostructured ceramics: grain boundary and size effects

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Nanostructured ceramics are an interest research subject due to the prospect of technological applications in different fields, for example as materials for fuel cell technology, thermal barrier coatings, thermoelectric devices and others. The reason is that nanostructured materials can display physical properties very different to those of their conventional bulk microcrystalline counterparts. Regarding electrical and thermal transport in nanostructured ceramics, grain boundaries and size effects play a decisive role.

In this work we will show how grain boundary and size effects produce substantial changes in the electrical and thermal conductivity of nanostructured ytria stabilized zirconia (YSZ) and CuAlO<sub>2</sub>. The very low values of ionic conductivity observed for nanocrystalline YSZ are interpreted in terms of a space charge layer that develops at the grain boundaries [1]. On the other hand, both in YSZ [2] and  $CuAlO_2$  [3] the thermal conductivity drops to very low values when reducing the grain size down to the nanometer range (see figure 1), very likely due to enhanced phonon scattering at the grain boundaries. The results presented in this work will be discussed considering the feasibility of using this type of effects in order to improve the thermal and electrical properties of ceramic materials for different technological applications bv tailoring their nanostructure.



**Figure 1**. Thermal conductivity of nanocrystalline YSZ (from reference [2]). Lines are fits of the results in terms of a model based on phonon hopping through the grain boundaries (PHM).

#### Acknowledgements

This work was supported by JCCM (Projects PAI-05-013 and PCI08-0091) and Spanish MICINN (Project MAT2012-34655).

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# C02: Doping as a simple way to control the microstructure of zirconia-toughened alumina composites

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Although current orthopedic ceramic biomaterials provide an effective immediate solution for many patients, concerns have arisen over their short- and long-term clinical success revealing the need for improved materials. Existing ceramics have already showed their own limits. For example, the brittleness of alumina increases the risk of acetabular cups fracture; Yttria Stabilized Zirconia is prone to hydrothermal degradation, decreasing lifetime of implants. Zirconia-toughened alumina (ZTA) composites provide both good stability and great mechanical properties, and a proven biocompatibility. Such composites are already commercialized all around the world and are commonly called "micro-composites".

The aim of our research is to show how, using simply natural sintering, doping ZTA with different dopant oxide can alter the microstructure and the reinforcement mechanisms of the composite. In controlling the microstructures, the pinning effect of zirconia was preponderant as compared to the dopant effect on grain boundaries mobility in most cases. Only high addition of both calcium and silica resulted in increased alumina grain boundaries mobility (thus intragranular composites, figure 1), for higher sintering temperature and low amount of zirconia. Depending on the zirconia content, dopants and temperature, different toughening sintering mechanisms observed: toughening are by phase-transformation, microcracking or internal stresses.



Fig1. Example of intragranular zirconia-toughened alumina composite

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### C03: High-Efficiency SERS Substrate Based on Mullite Nanowhisker Arry Decorated with Siliver Nanoparticles

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Preparation of surface enhanced Raman scattering (SERS) nanostructures with both high sensitivity as well as simplification has always been difficult for routine SERS detection. Mullite as an engineering material has been widely used in the last decades because of its good mechanical strength, excellent thermal shock and high creep resistance, low thermal conductivity and good stability under corrosion condition. [1] Recently mullite nanowires have been reported using various methods such as sol-gel [2, 3], high-energy ball milling process [4, 5], thermal decomposition of minerals and molten salt synthesis (MSS) [6, 7] etc.. This will absolutely extend its application field. Considering mullite is very stable even at acid and alkali atmosphere [1], it offers us a hint that mullite nanowires can be adopted as the SERS substrate used under corrosion condition. Aiming at enhancing the detection sensitivity, it requires the morphology of the substrate should be highly ordered along one direction to get good repeatability and at the same time has "hot spots" as many as possible. Therefore mullite nanowires with highly ordered structure are primarily requirement as SERS substrate.

Here mullite nanowhisker array was first prepared by a facile technique using mica and AlF<sub>3</sub> as raw material. Mica acts as reactant as well as substrate. By controlling the reaction temperature and holding time, the mullite nanowhisker array with uniform morphology can be tuned at 900  $^{\circ}$ C for 3 h in static air (as shown in Fig.1). The nanowhisker array possesses Al-rich single crystalline with an average of 80 nm in diameter and 20 µm in length. After decorated with Au nanoparticles, the array exhibits high surface enhanced Raman scattering (SERS) activity with an *EF* of  $1.35 \times 10^9$ . It is very sensitive in the detection of a target analyte, Rhodamine B (RhB) using SERS with a detection limit of 10<sup>-14</sup>M. It also remains good SERS signal detection with a relative standard deviation of 7.33% under corrosion

(2005).

condition (as shown in Fig.2). Therefore the mullite nanowhisker array is a promising candidate in the trace detection of chemical and biological molecules under corrosion condition.



**Fig.1** A facile method to produce mullite nanowhisker array from mica. (a) mica substrate. inset mica ore. (b) mullite nanowhisker arrays on the surface of mica. (c)(d) SEM image of mullite nanowhisker arrays.

**Fig.2** Mullite nanowhisker array decorated with Ag nanoparticles shows extremely sensitive in the detection of RhB using SERS with a detection limit of  $10^{-14}$ M.

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## C04: Thin layer glass and vanadium-boride coatings with self-healing property

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Glass-ceramics are a technological solution to achieve efficient materials able to operate at high temperatures, such as for enamel protective coatings applications. To overcome cracking of the glass when subjected to thermal cycles, self-healing is shown to be a promising solution. The self-healing property is defined as the capacity of a material to recover its mechanical integrity and initial properties after destructive actions of external environment or under internal stresses. Coillot *et al.* [Coillot *et al.*, Adv. Funct. Mater., 2010] have shown that the self-healing processing can be obtained in two different ways: *autonomous* or *non-autonomous*.

Based on the non-autonomous processing, we propose an innovative approach based on self-healing glassy thin films. They can be used for protective coating applications in the aerospace field. The present study is based on a heterostructure made of alternating layers of glass-ceramics and active particles, deposited by pulsed laser ablation. The properties of the deposited films are function of many parameters such as: number of pulse and laser power, atmosphere, temperature of the substrate, target-substrate distance, etc... We have shown that the best deposition is obtained under high vacuum, at room temperature using a pulse energy of 225 mJ. Varying the target-substrate distance from 3.5 to 5.5 cm, we obtain homogenous layers of about 100 to 200 nm.

The characterization of the multi-layers films has been carried out with different techniques: ellipsometry, ToF-SIMS, AFM, Castaing microprobe; the homogeneity has been evaluated by Castaing microprobe and XPS; and structural characterization has been done by ATR-FTIR spectroscopy. The efficiency of the self-healing effect is demonstrated by an *in-situ* experiment performed into an environmental scanning electron microscope (HT-ESEM).



Fig 1 : SEM image of a 5 layers glass-VB coating



Fig 2: In-situ observation of the self-healing effect

## C05: Fabrication of Glass-Ceramic Materials by SPS

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Zeolites crystalline aluminosilicates are characterized by open structures made by three dimensional frameworks composed of linked TO4 tetrahedral units, where T = Si or Al atoms.[1] These structures contains microscopic channels and holes, often named pores, that let the zeolites act as microporous molecular sieves.[2] Several well known cases exist where zeolites have been used in industry, for instance, for applications such as shape-selective catalysts, ion exchangers or adsorbents.2 However, the long-range order found in the zeolite crystal structure is sensitive and will easily collapse and transform to an amorphous solid upon heating and/or under stress. [3]

With ZSM-5 powders as starting materials, novel bulk silica glasses that possess unusual ultraviolet photoluminescence properties were synthesized by order-disorder transition (ODT) method by SPS. Photoluminescence measurements showed that as-sintered glass samples have a strong UV peak and weak peak at about 370 nm and 440nm in wavelength in the emission spectrum, respectively. The transparent zeolite-derived glass has the potential for practical applications in the field of lighting products and related optoelectronic and display technologies.

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### C06: Ferroelectrics with coexisting ferroelectric and antiferroelectric phases: Peculiarities of properties and possible applications

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The talk presents a review of results of studies of inhomogeneous states caused by the coexistence of FE and AFE phases in solid solutions with perovskite crystal structure. Detailed analysis of "composition-temperature" and "electric field-temperature" phase diagrams and influence of ion substitutions on these phase diagrams and properties of the substances will be discussed. PbZr<sub>1-y</sub>Ti<sub>y</sub>O<sub>3</sub>-based solid solutions are considered as an example.

Distinguishing feature of these materials is a small difference in the free energies of the FE and AFE states and as a result, the inhomogeneous state of domains of coexisting FE and AFE phases takes place in a wide interval of compositions. Local decomposition of solid solutions in the vicinity of AFE/FE interdomain boundaries leads to formation of mesoscopic structure of the segregates. Mechanisms controlling the kinetics of formation of system of segregates were investigated. the Manifestation of this mesoscopic segregate structure in piezoelectric, dielectric, and other properties of the above-mentioned compounds will be discussed from the point of view of possible applications.

C07: Low temperature Preparation of Barium Titanate-based Nano-complex Ceramics by Solvothermal Solidification Method and Their Dielectric Enhancement

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Barium titanate (BaTiO<sub>3</sub>, BT)-based nano-complex with ceramics various perovskite-structured materials, i.e., such as potassium niobate (KNbO3, KN), bismuth ferrite (BiFeO<sub>3</sub>, BF) and so on, were prepared at temperature below 230 °C by solvothermal method. In this study, KN had larger cell volume by 0.5 % than that of BT, while BF had smaller cell volume by 1 % than that of BT. Therefore, we expected that the dielectric properties for the BT-KN nano-complex ceramics were quiet different from those for the BT-BF nano-complex ceramics. Their interfaces were assigned to epitaxial interfaces by transmittance electron microscope (TEM). Moreover, X-ray diffraction (XRD) measurement with Rietveld refinements revealed that in the interfaces for BT-KN and BT-BF, there were structure-gradient region (SGR). Moreover, these nano-complex ceramics prepared in this study were porous with a porosity of around 25 ~ 35 %. The dielectric measurements showed that for the BT-KN nano-complex ceramics with KN/BT ratio of 1, the dielectric constant was 300 at 20 °C and 1 MHz, while for the BT-BF nano-complex ceramics with BF/BT ratio of 1, the dielectric constant was 70 at 20 °C and 1 MHz. To

explain the results, we proposed SGR model dependent of lattice mismatch and material hardness. **Reference** 

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# C08: MgZnO/ZnO based electronic devices fabricated using large-area compatible processes

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Oxide heterostructures and interfaces exhibit many interesting properties. Highly conductive interfaces or two-dimension electron gases (2DEGs) have been identified in many oxide heterostructures such as LaTiO<sub>3</sub>/SrTiO<sub>3</sub>, LaAlO<sub>3</sub>/SrTiO<sub>3</sub>, and MgZnO/ZnO. Usually, high quality crystals are essential for the existence of 2DEGs. However, highly conductive interfaces also have been noted in amorphous SrTiO<sub>3</sub>-based oxide interfaces [1] and defective rf-sputtered MgZnO/ZnO heterostructures fabricated on foreign substrates (glass, polyimide, and stainless steel substrates) [2-4]. In defective rf-sputtered MgZnO/ZnO heterostructures grown at room temperature, thermal annealing or atmospheric pressure plasma jet (APPJ) treatment on ZnO prior to the deposition of MgZnO is a critical step to obtain a highly conductive interface. Both the mobility and carrier concentration increase after the deposition of MgZnO capping layer. The possible reasons are the interfacial polarization induced charges that screen the grain boundary potentials to facilitate the electron transport [2-5]. Passivation of surface states by the MgZnO capping layer may also increase the carrier mobility [7]. Top-gated rf-sputtered Mg<sub>0.2</sub>Zn<sub>0.8</sub>O/ZnO thin film transistor with a field-effect mobility of ~84  $cm^2V^{-1}s^{-1}$  has been successfully implemented [6]. Experimental results on rf-sputtered MgZnO/ZnO metal-semiconductor-metal UV detectors with ZnO annealed by APPJs will also be presented in this talk [7].

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## C09: Surface Chemistries of Amorphous Oxide Semiconductors

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Transparent amorphous oxide semiconductors (TAOS) are of much interest, in part, due to the ability to fabricate thin film transistors (TFT) at relatively low processing temperatures while still maintaining large electron mobilities. The primary applications for these materials include TFTs for flexible active matrix displays. Recent potential

applications include non-volatile memory, sensing, and memristive neurological networks. We have studied a variety of TAOS materials, and have recently focused on amorphous zinc tin oxide (ZTO)<sup>1,2,3</sup> and indium gallium zinc oxide (IGZO).<sup>4</sup> We have evaluated the electrical characteristics of the films using both TFT and metal-insulator-metal We have found that the memristive devices. chemistry of absorbed species on the back-channel strongly influences the bias stress stabilities of ZTO and IGZO TFTs, reactions at the Al/ZTO interface influences the resistive switching characteristics of memristors, and low temperature annealing drives interfacial reactions and modifies the Schottky barrier heights for Pt/IGZO diode structures. To control surface chemistries we have used n-hexylphosphonic acid (n-HPA) and (3,3,4,4,5,5,6,6,6-nonaflurohexyl)phosphonic acid (FPA) self assembled monolayers (SAM) as molecular passivation layers for TFTs. Figure 1 shows a schematic of an IGZO TFT with SAMs adsorbed to the back channel surface. To better understand the role of interfacial reactions on TFT and memristive devices we have developed methods to prepare clean well defined TAOS surfaces, and characterized their surface and interface properties with X-ray photoelectron spectroscopy and secondary ion mass spectrometry. Finally, we will demonstrate the use of TAOS based field effect devices for sensing applications.



**Fig1**. Schematic illustration of SAM functionalized IGZO TFT structure showing the mono-, bi-, and tri-dentate binding of SAM to IGZO.

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### C10: Synthesis of spinon thermal conductive SrCuO<sub>2</sub> by glass-crystallization methods: Thermal and structural properties

<u>Nobuaki Terakado</u>, K. Watanabe, T. Kawamata, Y. Yokochi, Y. Takahashi, Y. Koike, T. Fujiwara Department of Applied Physics, Tohoku University, Sendai, Japan Email:terakado@laser.apph.tohoku.ac.jp Oxide glasses have thermal conductivity of ~1 W K<sup>-1</sup> m<sup>-1</sup>, which is lower than those of oxide crystals, semiconductors and metals by 1-3 orders of magnitude, and accordingly tend to be utilized as heat resistors or insulators. The reasons for this lowness are that, firstly, *phonon* is the only heat-transport carrier, and secondly, its mean free path is shortened because of scattering by other phonons and the disordered and inhomogeneous structure peculiar to non-crystalline solids.

However, if high thermal-conductive lines or areas can be patterned onto the glasses, where such patterning can be carried out by spatially-selected crystallization methods by using laser irradiation [1] or heat treatment, novel heat-transport devices are produced. Such heat-transport devices will collect and exhaust heat effectively and contribute to an increase in efficiency of electric devices and thermoelectric transduction. For application to the high thermal-conductive devices, we have tried to synthesize SrCuO<sub>2</sub> crystal (orthorhombic) [2], which is known to exhibit high, anisotropic thermal conductivity (~50 W K<sup>-1</sup> m<sup>-1</sup> toward *c*-axis) due to *spinon* [3,4], by heat treatment and laser irradiation onto melt-quenched oxides.

A sample employed was melt-quenched oxide with batch a composition of 38(SrO-CuO)-8(Li<sub>2</sub>O-Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>). The melt-quenched sample was heat-treated over the crystallization temperature determined by differential thermal analysis. The following measurements were carried out for the melt-quenched and the heat-treated samples: Thermal conductivity was measured by use of the steady-state method at temperature of 5-100 K and the laser flush method at room temperature. Microscopic structures were investigated through scanning and transmission electron microscopy (SEM and TEM), X-ray and electron diffraction (XRD and ED), and Raman scattering. Specific heat at low temperature was measured by a physical property measurement system.

Fig. 1 shows temperature dependence of the thermal conductivity for the melt-quenched and the

heat-treated (750 °C for 3 hours) samples. The thermal conductivity in the melt-quenched sample increases with an increase in temperature and becomes to be ~ 2 W  $K^{-1}$  m<sup>-1</sup> at room temperature. After the heat treatment, the value at room temperature is  $\sim 5$  W K<sup>-1</sup> m<sup>-1</sup>, which is 2.5 times larger than that before the heat treatment. TEM images are inset in Fig. 1. In the melt-quenched, spherical aggregations composed of nanocrystals are dispersed in a non-crystalline medium. On the other hand, in the heat-treated, several kinds of crystallites with a size of ~200 nm are packed fully, in which SrCuO<sub>2</sub> (orthorhombic) is detected by XRD and ED. Moreover, anomaly specific heat, which is attributable to spins on Cu2+ in SrCuO2 and can contribute to the increase in the thermal conductivity, is detected at low temperature. These result suggest that the precipitation of the SrCuO<sub>2</sub> by heat treatment gives rise to the increase in the thermal conductivity. In the present talk, the author will also speak about laser-induced crystallization of the samples.



**Fig. 1**. Temperature dependence of thermal conductivity in the melt-quenched and the heat-treated samples. TEM images are inset.

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# C11: Dielectric behavior of ceramic-nano carbon composites around the percolation threshold

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The development of ceramic matrix-carbon nanofibre composites arises as a solution for applications in which materials with an electrical conductivity similar to those of metals and mechanical properties, particularly hardness, are simultaneously required [1].

In this work, we report on how the dielectric properties are determined by the changes in the microstructure due to the introduction of a second phase. Two systems are studied: Al<sub>2</sub>O<sub>3</sub>/carbon nanofibers (CNFs) and BaTiO<sub>3</sub>/graphene. It is shown that the addition of CNFs to the alumina matrix changes the dielectric behavior of the composites in such a way that increasing the amount of the conductive second phase even decreases the conductivity of the composite under certain circumstances (Fig. 1a), leading to the presence of two percolation thresholds in the same system. The existence of a double percolation threshold has been used to obtain a giant increase of the dielectric constant in barium titanate-graphene composites with concentrations between 0 and 0.6% in weight of graphene. As in the previous case, two percolation thresholds are found in which an increase over a factor of ten of the dielectric constant vs. pure barium titanate is obtained. In particular,  $\mathcal{E} \approx 45000$  for the composite of 0.4% and  $\mathcal{E} \approx 15000$  for the composite of 0.6% at a frequency of 1 kHz are obtained (Fig. 1b).



**Figure 1**. Evolution of the conductivity as a function of the CNF content (Fig. 1a) and the real part of the dielectric constant of BaTiO<sub>3</sub>-graphene composites vs. graphene weight concentration (Fig 1b) at a frequency of 1 kHz.

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## C12: Tuning the dielectric constant in ferrite-carbon nanofibres composites

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Ferrites are materials of a great scientific interest and widely used in the electronic and telecommunication industry in different applications such as microwaves devices, isolators, circulators or phase shifters [1,2].

In this work, we report on the dielectric behavior in a broad frequency range of percolative (Ni,Zn) ferrite-CNF composites. For this, powders having concentrations between 0 and 5 % in volume of CNF were prepared by the traditional ceramic processing route. The raw materials, (Ni,Zn)Fe<sub>2</sub>O<sub>4</sub> with an average particle size of around 3  $\mu$ m and carbon nanofibers with the fiber diameter around 50 nm and fiber length up to 30  $\mu$ m, were mixed in propanol and ball milled for 1 h. The powder mixtures were spark plasma sintered at a heating rate of 50 °C min<sup>-1</sup> under an applied pressure of 80 MPa at a final sintering temperature of 860 °C and a holding time of 1 min.

The conductivity in these samples only depends on the amount of the conductive phase present in the composites and increases with the amount of CNF since all the composites present similar microstructures. When a critical value of the conductivity is reached, it is possible to tune the dielectric constant and find both negative or positive values along a large frequency range (<1 MHz-1GHz) with an external DC magnetic field as shown in Figure 1. In order to understand the behavior of the composite, a model based on a LCR circuit is proposed. From this model, the combination of values of dielectric constant and magnetic permeability that allow this tuning is shown.



**Fig1**. Dependence of the real part of the dielectric constant in ferrite-carbon nanofibre composites with an external DC magnetic field.

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# C13: High-temperature mechanical properties of ultrarrefractory boron carbide ceramics

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### C14: Design of anodic architectures for direct methane SOFC

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Among energy conversion systems, high temperature Fuel Cells are considered of great interest for delocalized, renewable and clean electricity and heat power production. The high operating temperature  $(500 \, \text{C} - 800 \, \text{C})$  is likely to allow the use of various types of hydrocarbons instead of hydrogen as the fuel with high efficiency and flexibility. Theoretically, the fuel can be catalytically converted into hydrogen directly at the anodic side. However, one of the main current challenges remains the increase of the life-time of these systems (especially avoiding carbon deposition and anode pollution), and long term reliable operation with fuel flexibility. Such performances have not been demonstrated yet.

Current developments and technological simplifications based on new principles of operation and original architectures designed in this finality will be presented. In particular the presentation will emphasize on the Gradual Internal Reforming and Electro-catalytic separation principles applied to the design of original anodic systems, and on the demonstration of the reliability of the systems in different pure hydrocarbons or carbon-based fuels (no  $H_2O$ ,  $CO_2$ ,  $O_2$  or carrier gas addition) [1-4].

The perspectives of direct operation of SOFC on waste fuels in order to decrease the amount of  $CO_2$  rejects in delocalized energy production systems will be discussed.



**Fig1**. Sketch of the Gradual Internal Reforming and Electro-catalytic separation principles.

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C15: Hydrogen evolution reaction at titanium carbide-supported, platinum-doped tetrahedral amorphous carbon array electrodes

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Thin films of tetrahedral amorphous carbon doped at ca. 10 at. % with platinum, ta-C:Pt, have been deposited by pulsed laser deposition on several substrates (silicium, titanium carbide, etc.). They have been tested as potential electrodes for dihydrogen evolution reaction, HER. When these films had a cracked-mud morphology on TiC, we observed that the kinetics of HER was much higher than when the same films were not cracked, i.e., covering completely the substrates, whatever the substrates were. Hence, we have decided to design array electrodes made of ca. 100 nm thick,  $100 \times 100$  $\mu$ m<sup>2</sup> squares of ta-C:Pt on TiC electrodes. The space between the squares has been set at 75 µm. The result is shown on Fig. 1, left. We confirmed that the electrochemical response of these array electrodes is higher of several order of magnitude compared to the two components, taken separately (synergetic effect). Indeed, the exchange current density,  $j_0$ , has been estimated at ca. 10  $\mu$ A/cm<sup>2</sup>, compared to ca. 0.1 and 0.01  $\mu$ A/cm<sup>2</sup> for pure TiC and ta-C:Pt, respectively (Fig. 1, right). For the moment, we do not have clear explanation for this very recent, original result. Probably, the substrate made of titanium carbide forms first a carbide-hydride at its surface thanks to the carbon vacancies. And then, this surface hydride is easily reduced at platinum sites of the ta-C:Pt squares. In other words, the first step (Volmer) of Equation (1) may occur on the carbide with a high rate, and the second one (Heyrovsky) of Equation (2) may occur on ta-C:Pt with a high rate:

$$H^+ + s + e^- \rightarrow H$$
-s (Volmer step) (1)  
 $H^+ + H$ -s + e<sup>-</sup> → H<sub>2</sub> + s (Hevrovsky step) (2)

To finish, one can notice that 10  $\mu$ A/cm<sup>2</sup> is the value of state-of-the-art, nickel-based electrolyzers in basic electrolyte medium, but with loadings around 5 mg/cm<sup>2</sup>. Here, in the present work, the loading is only ca. 50  $\mu$ g/cm<sup>2</sup>, that is, 100 times lower. Better performances could be reach in the future, by slightly increase this loading, or change the size and shape of the array.



**Fig. 1**: (a): Optical micrograph of a titanium carbide-supported, platinum-doped amorphous carbon array electrode. (b): Tafel representation of steady-state polarization curves for HER occuring on pure platinum-doped tetrahedral amorphous carbon, pure

titanium carbide, and on the array electrode of the left figure.

### **C16:** New Aspects of Oxide Ceramic Materials for Thermoelectric Energy Conversion

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Recuperation of decentralized waste heat energy, which amounts to two-third of the total primary energy supply in our modern society, is attracting more and keener interests particularly in the manufacturing, energy, and transportation sectors in industry. Diversification of energy resources is becoming more and more of vital importance for better energy security options. Oxide materials, which are highly durable at high temperature in air, non-toxic, low cost with minimal environmental impact, are apparently promising for recuperation of decentralized waste heat energy at the temperature range of > 400 °C, where all the non-oxide candidate materials will eventually be oxidized under aerobic conditions. Although strongly ionic characters of oxide materials has been regarded as an inherent disadvantage leading to low carrier mobility and high lattice thermal conductivity, it has been revealed that such disadvantages are not always the case with all oxides.

Recent findings strongly suggest that the simple picture of ionic compound no longer holds for some oxide materials. This paper showcases promising thermoelectric properties of some oxide materials such as ZnO-based oxides with nanosized inhomogeneity in the bulk [1], and  $\beta$ -pyrochlore oxides with cage-like crystal structure [2], discussing quantitatively about potential performances of oxide materials for high-temperature applications.



**Fig. 1**. Observed thermal conductivity of cage-structured oxides ATaWO<sub>6</sub> and those of state-of-the-art non-oxide TE materials; a)  $Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$ , b)  $Ba_8Ga_{16}Ge_{30}$ , c)  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub>, d) Yb<sub>14</sub>MnSb<sub>11</sub>, e) Bi<sub>2</sub>Te<sub>3</sub>, f) PbTe.

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# **D01:** Zinc Oxide Ordered Nanostructures obtained through Soft Processing Strategies

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Nanostructured oxides are at the forefront of recent advances in materials science and technology since, due to their exceptional intrinsic characteristics, they hold the key to discover novel electronic, optical, mechanical or transport properties (and phenomena) which may be required to overcome many of today's technological challenges. With recent advances in film deposition techniques (laser molecular beam epitaxy, on and off-axis high pressure sputtering, pulsed laser deposition, etc.), artificial multifunctional devices involving oxide-based arrays and nanostructures are now fabricated worldwide to continuously improve the quality of our daily lives. However, all these manufacturing processes entail sophisticated high-energy consuming technologies that unavoidably exert a harmful contribution to the global climates on earth. Obviously, to fit the balance between environment, resources and energy concerns, the development of innovative sustainable processing technologies is also an absolute requirement which should not be overlooked when transferring new knowledge on functional properties into materials and devices. Within this frame, the concept of bio-inspired soft solution processing freshly emerged as the sustainable way of processing advanced materials [1]; inspired by the natural processes and the energy by them required, it basically covers all kind of processes to prepare materials which can be operated under ambient, near ambient or just above the ambient conditions. This concept has superlative benefits like energy saving, simplicity, cost effectiveness and nor or little waste so, in essence, with an eye on the environmentally benign conditions and without contributing to the global warming. Following this approach the work here presented describes the preparation of controlled arrays of semiconductor ZnO at the nanoscale level. The key point to successfully attain this goal is that by precisely controlling the internal structures of the targeted materials, the thermodynamic and/or kinetic features involved in the synthesis and growth stages can be modulated under soft conditions, with no need for intricate or energy-consuming techniques.

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### **D02:** Elastic and thermal properties of some organized clay-based materials

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Ceramic shaping processes such as uni axial pressing, tape casting or extrusion favor the orientation of clay platelets in silicate materials. For example, kaolinite and muscovite phyllosilicates exhibit an anisotropic structure which has attracted considerable interest in optimizing materials characteristics in service conditions. As а consequence, mechanical and thermal properties can be significantly different in function of considered directions. However, controlling post thermal treatment is also essential in such mixtures to keep the anisotropic microstructure of green specimens after sintering and to optimize amount, organization and size of the occurred mullite phase. Moreover, adding a slight proportion of a second phase such as low cost alumino-silicate long fibers can also enhance mechanical properties such as Young's modulus, fracture toughness and/or stress to rupture.

In this work, two types of silicate ceramic materials are presented:

(i) a commercial extruded clay material [1]: mainly composed of kaolinite, quartz and muscovite, thermo-physical properties have been investigated in the parallel and perpendicular to the extrusion axis directions (see Figures 1.a and 1.b) . Local texturation has been highlighted by Scanning Electron Microscopy observations and X-ray diffraction. Anisotropy at macroscopic scale has been evidenced by thermal conductivity (laser flash method) and Young's modulus (pulse echography technique) measurements denoting a decrease of anisotropic degree when the temperature of sintering increases. These results are in agreement with significant transformations occurring in kaolinite phase;

(ii) mullite ceramic composites based on kaolinite and added alumino-silicate fibers [2,3]: starting from aqueous suspensions, thick substrates (about 700 µm in thickness) have been individually shaped by tape casting process and then thermo-compressed in order to obtain multilayered materials with a promoted orientation of kaolinite sheets and fibers in the plane of tapes. It has been shown that mechanical properties of final obtained substrate specimens are closely related to the organization degree of mullite crystals, due to the formation of a specific mullite network at different scales of the microstructure (see Figure 1.c). The anisotropy of elastic properties has also been evidenced by a difference between Young's modulus values in directions parallel and perpendicular to the casting direction. Despite the very low proportion of added fibers (less than 5wt.%), Young's modulus and bia-axial stress to rupture are improved of about 20 and 50% respectively. Moreover, fracture toughness values are multiplied at least by 2 compared to the single substrate layer because of crack defection and crack bridging mechanisms occurring at the fiber/matrix interface. These results emphasize that low cost silicate ceramics with significantly improved mechanical properties (both strength and toughness) can be obtained thanks to a very small addition of fibers.



**Fig1**. Microstructures of green extruded clay material a: perpendicular and b: parallel cut and c: fiber/mullite composite

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# **D03 : Bio-sourced sustainable Materials:** organic-mineral reactions and shaping process?

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Sustainability is of great interest worldwide regarding the preservation of Earth. Among the various aspects pointed out by the scientific community, the Energy and resources preservation targets can be achieved by using natural raw materials. In fact most phyllosilicates are widely available and environmentally friendly minerals. Besides, organics residues such as household food garbage and other green wastes generally generate humic substances during their end-disposal within composts. Advantage can be taken from these substances by separating the fulvic and humic acids and used them for different applications.

In a cradle-to-cradle thinking, a new class of bio-sourced product has been developed by combing such fulvic and/or humic acids, and raw clays (phyllosilicates). The formulation and curing conditions are determinant to control the final properties of use of these so-called "geomimetic" products. The present conference will emphasize on the major consolidating mechanisms, in particular on the effective reactions between the organic and mineral phases. The final characteristics will be described and compared to that of similar commercial products, taking into account the shaping process influence.

**Keywords:** fulvic/humic acids, phyllosilicates, phase interactions, processing, properties of use

### D04: Hydrothermal synthesis route for processing functional ceramics based on mineral pseudomorphic reactions

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Functional ceramics are materials that perform specific functions other than possessing a load bearing capacity. Typical examples of functional ceramics include semiconductors, magnetic materials, piezoelectric, ionic conductors, optical and catalytic, etc. Functionality of the smart ceramic materials is based on a structure-property relationship whose determination begins at an atomic level associated to their crystalline structure. Hitherto, a wide number of ceramic materials with exceptional functional properties have been synthesized via the solid state processing method, but the high energy cost involved with the high temperatures at which process is carried out, is one of the main economical disadvantages associated to this process. The chemical processing routes have emerged to overcome the economical and environmental problems caused during the high temperature processing the functional ceramics. Over the last three decades, one of the chemical processing technique that has receive particular attention in the green chemistry field is the hydrothermal synthesis. This technique has exhaustibly been used for synthesizing a great number of ceramic compounds with different functional properties abovementioned. hydrothermal processing is The а typical solution-based approach, which has been proven to be effective and convenient for preparing various inorganic materials with diverse controllable morphologies and architectures in terms of cost and potential for large-scale production [1-3]. Additionally, a different approach derived from the experimental work carried out on the pseudomorphic transformation of strontium inorganic species, namely SrCO<sub>3</sub>; Sr(OH)<sub>2</sub> or SrF<sub>2</sub> from SrSO<sub>4</sub> mineral ore under alkaline hydrothermal conditions. This was taken into account to propose a simple reaction system for exploring the feasibility for preparing strontium and barium inorganic compounds, such as SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrMoO<sub>4</sub>, SrWO<sub>4</sub> oxides (Fig. 1) and SrSn(OH)<sub>6</sub>, these perovskite and scheeelite like compounds are of interest because of their potential electronics. for industrial applications in photoluminescence and catalysis. The hydrothermal conversion of strontium and barium bearing mineral sulphates can be achieved on either pure or impure species; the chemical reactions associated with the mineral dissolution process are affected by several hydrothermal parameters, namely the temperature and the hydrothermal media pH value. The control of these parameters achieves optimum conditions that reduce the mineral chemical stability in the alkaline solvent employed resulting in a rapid dissolution of the mineral ore under hydrothermal conditions. Hence, the aspects related to the synthesis of strontium compounds via a single step reaction will be discussed, based on the chemical stability and reactivity of sulphate ores in alkaline hydrothermal solvents for preparing single phase ceramic compounds using low cost raw minerals as reagent precursors.



**Figure 1.** Micrographs of the transformed powders a) BaTiO<sub>3</sub>, b) SrTiO<sub>3</sub>, c) SrMoO<sub>4</sub> and d) SrWO<sub>4</sub> via hydrothermal treatments conducted in the temperature range of 150-250  $^{\circ}$ C in alkaline solvents, the earth alkaline metal ion raw precursor were the mineral phases of barite (BaSrO<sub>4</sub>) and celestite (SrSO<sub>4</sub>).

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D05: Approaches to improving the visible light absorption and uprising the conduction band minimum of photocatalysts from first-principles calculation

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In order to enhance the visible light absorption and achieve hydrogen production via water-splitting, wide band gap photocatlysts were usually doped with metals and/or non-metals. We have studied the effects of different doping strategies on the energy band configuration, the local crystal structure and the photocatalytic activities of semiconductors such as TiO<sub>2</sub>, AgTaO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> using the first-principles calculation.

Isovalent  $In^{3+}$  mono-doping in  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> upraises the conduction band minimum and deduces photocatalytically hydrogen release from water. Furthermore,  $In^{3+}$  doping causes the morphology change, improves the electron mobility and hence enhances the photocatalytic activity of decoloring dye solution. Aliovalent mono-doping usually induces the localized energy bands in the forbidden gap of photocatalysts, such as TiO<sub>2</sub> and AgTaO<sub>3</sub>, while compensated co-doping is an effective approach to improving the photocatalytic activity via narrowing the band gap without generating the localized energy band. N-doping as an efficient method to achieve visible-light absorption, produces different effects on the electronic structures of various photocatalysts.

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## **D06:** Modeling of densification by grain-boundary sliding and diffusion

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The densification behavior in the final and intermediate stage of sintering is analyzed for spherical isolated pores embedded in dense polycrystalline matrix. In the final stage, the shrinkage driven by grain-boundary diffusion is analyzed for small pores comparable to the grain size, and in the intermediate stage, the shrinkage driven by both grain-boundary sliding and diffusional accommodation is analyzed for large pores. From the analysis, the bulk viscosity, the densification rate and the pore-shrinkage rate are predicted as a function of the porosity, pore size, grain size and grain-boundary viscosity. The dependence of the pore-shrinkage rate on the relative density is opposite for the two sintering stages. In the intermediate stage, the shrinkage rate decreases with densification, whereas it increases in the final stage. With decreasing pore size, the contribution of grain-boundary sliding to the pore shrinkage decreases gradually due to restricted pore space, and further shrinkage occurs by grain-boundary diffusion only in the final stage. The present study suggests that the transition of the densification mechanism would occur during sintering. The occurrence of the mechanism transition confirmed from the inflection is observed experimentally in the pore-size distribution during sintering. We propose a new criterion to distinguish the sintering stage by a densification mechanism, not by a pore shape conventionally. The theoretical prediction of the present discrete model is also with the continuum model compared and experimental results. The dependence of the predicted densification rate on the porosity and on the grain size is well consistent to the experimental results for ceramics.

### **D07: Oxygen Separating Membranes Fabricated** from Perovskite-like Materials

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The mixed oxides revealing perovskite-like structure and both ion and electron conductivities are successfully used for manufacturing the dense membranes separating clean oxygen from air. Perovskite materials are characterised by the oxygen deficiency in the structure caused by presence of oxygen vacancies, through which the oxygen ions are displaced. The effectiveness of membrane described by the oxygen flow permeating through it depends, among others, on the chemical composition of perovskite material, the membrane thickness (range controlled by diffusion or surface processes), its microstructure and the operating temperature as well as the gradient of oxygen partial pressures at both side of membrane. [1]

Figure 1 presents the dense planar, tubular and monolithic oxygen membranes manufactured by CEREL. The high values of the oxygen permeation flux have been obtained for the dense planar BSCF membranes as well as the long-lasting test (two thousand hours) confirmed their durability. [2] Tubular membranes that are more useful in industrial practice due to their greater effective surface, mechanical stability and easiness of application, were manufactured as the dense thin-walled tubes made by isostatic pressing and extrusion. The measurements of the oxygen permeation flux confirmed that the extruded membrane exhibits almost two times higher oxygen permeation flux than the membrane made by isostatic pressing.



Fig1. The oxygen membranes in the shape of disk, tube and monolith.

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#### Acknowledgments

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n °PITN-GA-2013- 606878.

D08: Micromechanical modeling of porous ceramic composites using direct microstructural reconstructions

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Porous ceramic composites have important applications in energy technologies. Devices of considerable recent interest include solid oxide fuel cells (SOFCs) and gas separation membranes in which the functional layers are supported on a thick porous ceramic or composite substrate. During manufacturing and operation at elevated temperatures, appreciable stresses arise and often lead to failure of the substrates. An understanding of the mechanical behavior of the porous substrates is important for improving the reliability of the technologies.

Porous ceramic composites have a complex microstructure and distinct behaviors in the constituent phases. Both the stress distribution in the phases and the effective mechanical properties are strongly influenced by the microstructure. While micromechanical models have been established for composites in the literature, they are based on simplified microstructures. In this work, mechanical behaviors of porous ceramic composites are investigated using microstructure representation directly reconstructed from three-dimensional images. Figure 1 shows a finite element model of a porous composite made of nickel and yttria-stabilized zirconia (Ni-YSZ) created from the microstructural reconstruction obtained by focused ion beam serial sectioning and scanning electron microscopy techniques. The Ni-YSZ composite is a substrate

material used in state-of-the-art SOFCs. Time-dependent stress distributions in the individual phases and the effective creep response at elevated temperature are studied based on homogenization theory.



**Fig1.** Finite element model created from direct microstructural reconstruction of porous Ni-YSZ composites.

### **D09:** A thermomechanical contact problem for microstructured solids

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The analytical solution for a rigid flat punch indenting a homogeneous classical (Cauchy) elastic half-plane, where heat conduction is permitted [1], shows that three different types of contact can occur. In particular, depending on the ratio of the total heat flux Q (positive in the direction pointing to the interior of the half-plane) to the applied (compressive) load P (Fig. 1), perfect contact is attained for small values of Q/P, while when Q/Pexceeds a finite negative (positive) value an imperfect (a separation) contact occurs [3].



**Fig1.** Possible contact types during the indentation of a rigid flat punch into the surface under the action of the compressive force P. A temperature difference between the two bodies under contact induces a heat flux Q and the state of thermal stress is expected to alter the macroscopic contact characteristics, modifying the contact area.

The classical contact solution is extended to the analogous case of an indented microstructured solid with reference to the couple–stress theory of thermo-elasticity [2]. The obtained solution shows that the thermo–mechanical response is strongly affected by the internal microstructural length  $\ell$  and, in particular, the macroscopic conditions (essentially Q/P) for which the type of contact passes from perfect to separation or to imperfect contact change with varying characteristic length-scale (Fig. 2).



**Fig2**. Influence of the internal characteristic length-scale  $\ell$  on the limit values of  $\tau^* = \mu \alpha b Q / k P$  for which transition from perfect to imperfect or to separation contact occurs.

#### Acknowledgements

The authors gratefully acknowledge support from the European Union FP7 project "HOTBRICKS - Mechanics of refractory materials at high–temperature for advanced industrial technologies" under contract number PIAPP–GA–2013–609758.

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### D10: Model reduction methods in inverse analysis: improvement of accuracy by uniform space filling techniques

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Inverse analyses represent a fast growing area of mechanics which, when applied to material characterization problems, can replace with advantages traditional procedures based on empirical ways of transition from experimental data to mechanical properties of materials [1]. Such techniques require recurrent test simulations since numerical optimization algorithms are used to solve resulting minimization problem. Due to the non linearity present in the model the application of FEM makes the whole task rather time consuming, and therefore in recent applications recourse is made to

model reduction techniques [2]. These techniques generate low-order models in order to allow for efficient evaluation of complicated and highly non-linear system responses in many-query and real-time context. Most of the methods applied to this purpose are dividing the computation work in two phases: a time consuming "off-line" phase needed to "train" a low-order model which is further used in an "on-line" phase providing accurate results in much faster way.

The accuracy of these models rests on the adopted total number of points (called "nodes") in parameter space in which the system response is evaluated within "off-line" phase on one side, and on their distribution on the other side. The most obvious way of increasing the accuracy of a reduced basis model is to extend the number of nodes used in the training phase. For a given fixed number of nodes the accuracy can be further improved by picking up particular distribution of them in a parameter space. The choice of locations of the evaluation points becomes even more important when the evaluations are expensive, and the number of parameters is elevated. A method presented in this communication is based on dynamic simulation of interactive nodes of evaluation points which leads to designs that are filling the space with controlled uniformity. It starts from a random distribution of nodes, attributing a unitary mass to them and introduces a system of repulsive forces proportional to the distances, followed by explicit dynamic simulation until the stable solution is found. The proposed method is easily extended to the case with different priorities of diverse parameters on which the system depends, which is a frequent case in parametric studies and material characterization problems.

Numerical exercises considered in this study concern the design of reduced basis model of indentation test and biaxial cruciform test of orthotropic material. Developed models are using a method based on Proper Orthogonal Decomposition as described in [3], trained with the set of nodes with controlled uniformity. In these two different applications it is evidenced that the accuracy of reduced basis techniques can be improved for a given number of evaluation points if the method of interactive nodes is used for the determination of nodes distribution prior to the training phase. By using this tool it is possible with the same numerical effort (i.e. "cost" for the training) to achieve further improvement of accuracy of low-order models.

#### Acknowledgments

The results referred research to in this communication have been achieved within European Union's Seventh Framework Programme FP7/2007-2013/ under REA grand agreement number PITN-GA-2013-606878-CERMAT2, and the authors are gratefully acknowledging the financial support from it.

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# **D11:** Modelling, characterization and simulation of refractory materials for liquid steel technology

Davide Bigoni<sup>1</sup>, Francesco Dal Corso<sup>1</sup>, S & astien Gregoire<sup>2</sup>, Massimo Penasa<sup>1,2</sup>, Severine Romero-Baivier<sup>2</sup> <sup>1</sup> University of Trento, Trento, Italy Email: bigoni @ing.unitn.it <sup>2</sup>Material Modeling and Characterization Division, Vesuvius Group S.A., Rue de Douvrain 17, 7011 Ghlin, Belgium The use of refractory materials in the liquid steel technology has to meet strict safety and functionality requirements.

The rational approach to this problem is through characterization, constitutive description, computer implementation, and simulation of the thermo-mechanical behaviour of these materials. A damage surface for ceramic materials [1] is proposed, equipped with temperature dependent yield and thermoinelastic hardening laws capable of describing the behaviour of ceramics at high temperature. Implementation of the constitutive model in a UMAT routine for ABAQUS is developed following the approach proposed in [2].

The role of material viscosity is finally discussed in view of possible extension of the constitutive framework.

#### Acknowledgements

The authors gratefully acknowledge support from the European Union FP7 project "HOTBRICKS - Mechanics of refractory materials at high–temperature for advanced industrial technologies" under contract number PIAPP–GA–2013–609758.

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### D12: New biomimetic ceramics for the regeneration of load-bearing bones

<u>Simone Sprio</u>, Andrea Ruffini, Massimiliano Dapporto, Anna Tampieri *Institute of Science and Technology for Ceramics, National Research Council, Faenza, Italy Email: simone.sprio@istec.cnr.it web site: http://www.istec.cnr.it*  The regeneration of load-bearing bone parts, e.g. limbs (femur, metatarsus, tibia, humerus) and vertebral bodies, is particularly relevant since such bones are destined to sustain critical body functions such as deambulation and manipulation. In this respect, the current approaches for bone repair are prevalently based on substitution of missing or diseased bone parts with inert devices that do not enable bone regeneration and recovery of the original functionality.

Calcium phosphates, particularly hydroxyapatite (HA), are elective biomaterials for bone regeneration; however they are characterized by intrinsic weakness that limits potential applications in regeneration of load-bearing bone parts. Moreover the sintering process required for consolidation of ceramic materials reduces the surface activity and limit cell adhesion and proliferation, as well as progressive bio-resorption in vivo. In this respect new strategies can be adopted to develop new regenerative devices with improved biologic and mechanical competence, so to be adequate for withstanding biomechanical loading in vivo.

Bioactive ceramic composites can synergistically associate osteogenic character and mechanical strength. In this respect titanium dioxide promising material, is а very with good biocompatibility, mechanical strength and relative density close to that of inorganic bone that can be associated to apatite phases to form new composites exhibiting higher osteogenic character than HA as well as enhanced compressive and flexural strength, and potential bio-resorbability in vivo<sup>1,2</sup>.

Different approaches enable the achievement of solid implants without recurring to any thermal treatment of sintering. For the regeneration of vertebral bodies, injectable ceramic pastes based on metastable calcium phosphates can be developed, to take advantage of their ability to self-harden in vivo by physical entanglement of nanosized apatite elongated particles. These new cements can provide early sustain to bone tissue weakened by trauma or metabolic diseases such as osteoporosis. The bone-like composition and porosity can drive bone cells to fast tissue regeneration, and progressively increase the bio-competence of damaged bone until complete regeneration.

Regeneration of long segmental bones is probably the most challenging clinical issue to be addressed: the hierarchically organized structure of bones and mechano-transduction ability of bone cells enable complex response to ever changing biomechanical loads thus driving self-repair and remodeling. Therefore, to induce formation of well-organized bone it is required the implantation of scaffolds with bone-like composition, complex 3-D structure, open porosity conducive to extensive angiogenesis and sufficient mechanical strength to withstand early physical stimulation. The convergence of all these requirements is hard to achieve, due to intrinsic limitation in the conventional manufacturing techniques. In this respect a promising approach is to take inspiration from Nature and biologic structures endowed with insuperable mechanical and functional properties, such as exoskeletons, plants and shells. Therefore, the application of thermal-chemical processes for biomorphic transformation of native wood structures into biomimetic bone scaffolds with hierarchically organized structure<sup>3</sup> is a new approach to achieve new devices with bone-like features that can pave the way to a new generation of devices for regeneration of long segmental bones.



(a)



**(b)** 

**Fig1**. (a) Hierarchical Organization of bone; (b) similarity between structure of bone and Rattan wood.

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### D13: Smart bio-inspired hybrid nano-composites for multifunctional applications

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The formation of human bones is governed by self-assembling and organization of collagen molecules in a complex 3-D structure, acting as a template for simultaneous mineralization with nanocrystalline, ion-substituted apatite. Since a decade, the reproduction of the conditions of bone formation allowed to settle a biomimetic synthesis process generating hybrid constructs where the mineral phase, i.e. a biomimetic, nanosized hydroxyapatite, is heterogeneous nucleated on Type I collagen. This process is directed and controlled by the chemical features and physical confinement imposed by the self-organizing polymeric matrix, so that the mineral phase has physical, chemical and ultra-structural resemblance with mineral bone<sup>1,2</sup>. the possibility of tailoring Moreover, the mineralization extent also enabled the synthesis of graded constructs mimicking different areas of multifunctional joint regions<sup>3</sup>. It was demonstrated that these unique features can trigger, in vivo, the cascade of events leading to regeneration of bone and multifunctional anatomical areas. such as osteochondral and periodontal regions.

The same biomineralization process can be applied on blends of polymeric matrices by imposing synthesis conditions yielding chemical or physical interaction between the different components and simultaneous mineralization, thus opening the way to achieve new device with enhanced mechanical strength and wider potential applications.

The characterization of such hybrid composites requires a deep knowledge of the interaction of apatite nanoparticles with the various organic templates. In fact, in such devices the organic and inorganic components are intimately connected into nanosized hybrid building blocks that are assembled in a hierarchic manner. Such constructs possess unique properties since their assembling and 3D organization are governed by interactions occurring at a molecular level that influence the crystal features, specific orientation and morphology of the inorganic phase. In consequence, the functional and mechanical properties of the final device result greatly influenced by the type and level of interaction and assembling among the different polymeric components and between the organic and inorganic phases.

So far, overall mechanical properties of compressed hybrid bone-like composites were obtained by uniaxial loading so that evaluation of the compressive strength of the actual porous scaffolds can be extrapolated. However, to elucidate the ultra-structural properties of these complex devices, careful investigation has to be performed, including
spectroscopic and microscopic investigation, in association with techniques based on nano-indentation that shall be specifically designed to evaluate space-dependent mechanical properties at various size scales, up to the level of the nanosized inorganic phase, i.e. a biomorphic apatite phase the properties of which are strongly influenced by its strong chemical and topotactic interaction with the polymeric matrix.





**(b)** 

**Figure 1**. (a): TEM image of a collagen fibre presenting heterogeneously nucleated apatite nanophase; (b): SEM image of a 3D graded device for osteochondral regeneration.

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#### D14: Fracture in ceramics with microstructure

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Influence of the microstructure on the mechanical behavior of brittle materials such as ceramics, composites, cellular materials, foams, masonry, bones tissues, glassy and semicrystalline polymers, has been observed in many experimental analyses. In particular, relevant size effects have been found when the representative scale of the deformation field becomes comparable to the length scale of the microstructure. These size effects influence strongly the macroscopic fracture toughness of the materials (Rice et al., 1980 and Rice et al., 1981), and cannot be predicted by classical elasticity theory. In order to describe accurately these phenomena, generalized theories of continuum mechanics involving characteristic lengths, such as micropolar elasticity, indeterminate couple stress elasticity and strain gradient theories have been developed and used in many experimental and theoretical studies (Radi and Gei, 2004, Itou, 2013a and Itou, 2013b).

In this paper, we present recent analytical results of fracture mechanics in materials with microstructure. Both fracture toughness and energy release rate will be analysed and the microstructural parameters will be incorporated into the model.

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#### Acknowledgments

A.P. and G.M. gratefully acknowledge the support from European Union FP7 projects under contract numbers PCIG13-GA-2013-618375-MeMic and PITN-GA-2013- 606878-CERMAT2, respectively.

# D15: Novel strategies for sintering oxides using microwave energy

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Microwave energy is a very efficient way for high temperature processing of materials, including synthesis and sintering of ceramics [1]. In the last years, many improvements have been realized, including the design of original susceptors, the finding of the most suitable thermal insulators and the development of specific instrumentation for temperature control and shrinkage measurement [2]. All these improvements were carried out to optimize the conversion of the electromagnetic energy into heat and to improve the control of the overall microwave process. However, until now, most of the performed developments result by trial and error methods. This strategy can be time consuming and is not the most suitable way to optimize any processes. Figure 1 shows the electrical field distribution within a 2.45 GHz single mode applicator, equipped with an originally designed susceptor, having different values of permittivity. This simulation data shows how the dielectric constant of the susceptor impacts on the microwave electrical field within the sample. In this work, we have experimentally designed and used original assemblies (susceptor thermal and insulation), based on simulation data performed at 915 MHz and 2.45 GHz in single-mode applicator. The relation between the experimental results like the temperature distribution, homogeneity of the microstructure, and the modelling results has been discussed. It is shown how this strategy was successful to improve the overall control of the microwave process for sintering alumina. For instance, 52 mm diameter alumina disks (figure 2), dense at ~99%, were successfully microwave sintered using a 915 MHz single mode applicator.



**Fig1.** Modelling data showing the electrical field distribution within a 2.45 GHz single mode cavity, as a function of the dielectric constant of the 'crucible'.



**Fig2**. 52 mm diameter ~ 99 % dense alumina disk sintered in 915 MHz single mode applicator.

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### D16: Valence Electron Density Study on Phase Transitions in Perovskite-type Ceramics by Synchrotron Radiation X-ray Diffraction

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The polar lattice distortion and the lattice stability of perovskite-type oxides with the chemical formula  $ABO_3$  are strongly influenced by substituting

other ions for the A- and/or B-site ions. For example, primal 2nd-order (pseudo) Jahn-Teller distortion is caused in BaTiO<sub>3</sub> at 403 K by the octahedrally coordinated high-valent  $d^0$ -ness Ti ion at the B-site, whereas a structure with a large tetragonal distortion is stabilized up to higher temperature 763 K in PbTiO<sub>3</sub> by cooperation of the Ti ion at the *B*-site and the Pb ion with lone pair electrons at the A-site. Most of valence electrons in perovskite-type oxides are distributed in shells of oxygen ions in general, while a small part of valence electrons of such ferroactive ions remains at the A- and/or B-sites to form covalent bonding with oxygen ions. The chemical bonding between the ferroactive ions and the oxygen ions is a clue for understanding phase transitions in perovskite-type oxides.

Our group has been devoted to visualizing the electron density distribution of perovskite-type oxides by analyzing the synchrotron-radiation x-ray powder diffraction (SXRD) data measured at SPring-8 using the maximum entropy method (MEM)/Rietveld method. MEM is a powerful tool, which enables us to reproduce total electronic density distribution accurately from a limited number of diffraction data. [1, 2] We have applied the method to PbTiO<sub>3</sub>, and showed the first experimental evidence for covalency between the Pb and O ions. [3] The valence electron density distribution is, however, more informative in many cases from the viewpoint of materials science. Then Tanaka and coworkers have proposed a smart method evaluating valence electron density distribution, and shown an example for crystalline Si. [4] It is now improved, and applicable to any crystal structures consisting of most kind of atoms in the periodic table. Our group has also developed a method evaluating the electrostatic potential and electric field distributions on the basis of MEM, and applied it to PbTiO<sub>3</sub>. Visualized electrostatic potential and electric field distributions on the isosurface of electron density distribution give an evidence for the dipolar polarization of the Pb ion. They show close agreement with results by ab initio calculations [5]. Nowadays the method has been successfully applied to a large variety of structural studies, for example, to reveal electronic polarization of ions [6] and to visualize a conduction path of ions in the crystal. [7]

In this study, valence electron density distributions in the outer shells of atoms are derived accurately from the SXRD data for various perovskite-type oxides to prove the characteristic chemical bonds which govern the ferroelectric phase transition. Ferroelectricity originates from the balance between the long-rage Coulomb force and the short-range repulsion force. The obtained results provide direct experimental evidence that the hybridization of electron orbitals forming the B-O bonds weakens the short-range repulsion force, and causes the polar lattice distortion on the  $BO_6$ octahedron. The electronic polarization caused by the lone-pair cation at the A-site is more clearly visualized in the valence electron density distribution.

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D17: Strain Rate Dependent Failure of Glass/Epoxy Interfaces at nano-microscale via Nanoimpact Experiments Devendra Verma, Vikas Tomar\* School of Aeronautics and Astronautics, Purdue University, West Lafayette, IN 47907, USA \*Corresponding Author, Email: tomar@purdue.edu.

The overall strength of the material depends on the properties of constitutive materials and on the interfaces where constitutive materials interact with each other. Defects in laminated materials mostly occurs/starts at the interfaces that leads to its overall failure. Individual properties of constitutive materials are well investigated in the literature but there are not enough studies to quantify the interface strength between two different materials. In the present work we have performed experiments on the glass-epoxy interfaces at different strain rates using nano-impact experiments. The strain rate in the experiments are up to 300 s<sup>-1</sup>. The experiments are conducted on samples with different interface thickness from 10 to 200 µm. The effect of interface layer thickness and strain rate on fracture and toughness resistance is presented along with failure mechanisms.

# **B16:** Microstructural evidences of extrinsic magnetization in Fe-doped 6H-BaTiO<sub>3</sub>

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Simultaneous presence of semiconducting and ferromagnetic properties makes dilute magnetic oxide (DMO) materials attractive for applications in spintronic and magnetoelectronic devices. However, the room temperature magnetism in these compounds would be of technological importance only if the magnetic coupling is of intrinsic character and not a consequence of paramagnetic dopant segregation, formation of secondary phases or any other extrinsic reason.

The room temperature ferromagnetism is broadly accepted as an intrinsic property of Fe-doped 6H-BaTiO<sub>3</sub> material, despite its unusual dependence on doping concentration and processing conditions. However, despite intensive research and a number of reports, the origin of the ferromagnetic coupling still remains unknown. The presentation will initially focus on cation ordering in Fe-doped 6H-BaTiO<sub>3</sub> perovskite, which has been assumed to induce the room temperature ferromagnetism. The disordered system is paramagnetic and only after additional heat treatment, which is associated with relocation of Fe<sup>3+</sup> ions to a specific crystallographic site, the ferromagnetism appears. The relocation is a continuous order-disorder transition driven by reduction in electrostatic repulsion of the cations. The observed cation ordering is the first documented case of such process in 6H hexagonal perovskites. have crystalographically Although we fully characterized the cation ordering processes, it was not possible to confirm the intrinsic origin of the magnetization of Fe-doped 6H-BaTiO<sub>3</sub>.

An extremely small average value of the ordered magnetic moment that was measured for this material casted further doubts on intrinsic origin of the magnetization. Moreover, several additional magnetic instabilities were detected at lower temperatures. These coincide with electronic instabilities of the Fe-doped  $3C-BaTiO_3$ , i.e. tetragonal perovskites polymorph. It has previously been shown that this polymorph can be stabilized as a thin film at strained interfaces. The magnetic measurements confirmed that the strain-induced tetragonal phase can also be locally stabilized by internal strain fields in bulk. We will also report on our efforts to visualize these tetragonal domains by TEM and MFM studies.

#### Acknowledgment

This work has been supported by the Slovenian Research Agency Programmes P1-0112, P1-0125, P2-0377, and PR-04988, project N2-0005, DESY and

EC FP7 Programme under grant agreement CALIPSO n 312284 (EU Support of Access to Synchrotrons/FELs in Europe). Access to synchrotron radiation facilities of HASYLAB (project I-20110082 and ELETTRA (project 20110127) EC) is acknowledged. We would like to thank Roman Chernikov and Edmund Welter of HASYLAB and Giuliana Aquilanti of ELETTRA for expert advice on beamline operation.

### B17: Sr- $\delta$ -Doped La<sub>2</sub>CuO<sub>4</sub> Heterostructures: Cation Redistribution and High-T<sub>c</sub> Superconductivity

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The role of the local charge carrier concentration profiles is paramount for the occurrence of superconductivity in low dimensional systems. Superconductivity in copper oxides arises when a parent insulator compound is doped beyond some critical concentration. [1] In the case of La<sub>2</sub>CuO<sub>4</sub> (LCO), high-T<sub>c</sub> superconductivity is obtained by substituting La<sup>3+</sup> with Sr<sup>2+</sup> or by inserting interstitial O<sup>2-</sup>. [2] Atomic layer-by-layer oxide molecular beam epitaxv (ALL-MBE) growth together with state-of-the-art characterization techniques discloses new ways for the synthesis of novel superconducting epitaxial hetero-structures. In this contribution, we present the exciting findings of the study of Sr-\delta-doped LCO. [3] δ-doping, which represents a novel approach in the field of layered complex oxides, here relies on the substitution of a full La-O atomic layer by a Sr-O layer. Artificial super-lattices having different spacing between two subsequent Sr-O layers

were grown on LaSrAlO<sub>4</sub> (001) (LSAO) substrates, and by appropriately tuning the super-lattice structure, high-T<sub>c</sub> superconductivity up to about 40 K has been obtained. Here we lay emphasis on the TEM analysis.

The structure and cations redistribution in the Sr-δ-doped LCO multilayers on LSAO substrate was investigated using a JEOL ARM 200CF scanning transmission electron microscope (STEM) equipped with a cold field-emission electron source, a DCOR probe corrector, a large solid angle SDD-type JEOL Centurio EDX detector, and a Gatan GIF Quantum ERS spectrometer. Cross-sectional STEM images of the interface between LCO and LSAO do not show structural defects, where atomically resolved high-angle annular dark-field (HAADF) and annular bright-field (ABF) images show the orientation relationship between LCO and LSAO. Furthermore, HAADF and ABF images of the Sr-δ-doped region, which were simultaneously acquired, illustrate a perfectly defect-free atomic arrangement. The local lattice and oxygen octahedral distortion were evaluated by image analysis. Sr redistribution at the interface was studied by atomic resolution HAADF in combination with EDX and EELS (Figure 1). Due to the difference in atomic number ( $Z_{Sr} = 38$ ,  $Z_{La} = 57$ ), the atomic columns dominated either by La or Sr give rise to different contrast in the HAADF image. In Sr-δ-doped regions the atomic column intensity is significantly lower than in pure LCO. Integrated image intensity profiles perpendicular to the growth direction yield for the Sr- $\delta$ -doped region a relatively sharp image intensity drop followed by a slowly increasing intensity pointing at an asymmetric distribution of Sr in the growth direction. In addition, Sr-L EDX and Sr-L<sub>2,3</sub> EELS line-scan profiles provide a robust proof that the Sr concentration in LCO is (i) distributed across a few layers and (ii) has an asymmetric profile. These findings, suggesting a rather complex mechanism of charge rearrangement, are discussed. [4]



**Fig1**. HAADF image of Sr- $\delta$ -doped LCO. The inset shows the integrated Sr-L EDX and Sr-L<sub>2,3</sub> EELS line profiles.

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#### Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme [FP/2007-2013] under grant agreement no312483 (ESTEEM2). U. Salzberger is particularly acknowledged for TEM specimen preparation.

B18: Electrical and magnetic properties of transition and rare-earth metal molybdates and tungstates-potential materials for laser matrices and light-emitting diodes

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Numerous rare-earth (RE) metal molybdates and tungstates exhibit various crystal structures (e.g. wolframite, scheelite, perovskite), good mechanical strength, and excellent thermal as well as chemical stability. For these reasons, single-crystals, ceramic and nanocrystalline materials based on RE molybdates or tungstates are very good candidates for luminescent and laser applications. They are used for a fabrication of white light-emitting diodes (WLEDs) showing high stability, energy-saving and safety. [1,2] For example, a substitution of yttrium ions by trivalent europium ones in zinc and yttrium tungstate, ZnY<sub>4</sub>W<sub>3</sub>O<sub>16</sub>, leads to a novel promising phosphor for WLEDs. [3] It has been also demonstrated that at the  $Eu^{3+}$  concentration of 1 mol. % in ZnY<sub>4</sub>W<sub>3</sub>O<sub>16</sub> matrix the obtained ZnY<sub>4</sub>W<sub>3</sub>O<sub>16</sub>:Eu<sup>3+</sup> phosphor can emit light in the visible region. [3] Previous electrical and magnetic studies of RE compounds, *i.e.* RE<sub>2</sub>WO<sub>6</sub> (RE = Nd, Sm, Eu, Gd, Dy, Ho, and Er), [4]  $(Co,Zn)RE_4W_3O_{16}$  (RE = Nd, Sm-Gd, Dy, and Ho), [5]  $CdRE_2W_2O_{10}$  (RE = Y, Nd, Sm-Er) [6] and CdMoO<sub>4</sub>:Gd<sup>3+</sup> single crystal [7] showed insulating paramagnetic state well and as as the superparamagnetic-like behavior depending on strength of the spin-orbit coupling.

The present contribution reports the electric and magnetic properties for RE<sub>2</sub>W<sub>2</sub>O<sub>9</sub> (RE = Pr, Sm-Gd), AgY<sub>1-x</sub>(Gd,Nd)<sub>x</sub>(WO<sub>4</sub>)<sub>2</sub> (x = 0.005, 0.01, 0.025, 0.05, 0.1, 0.2, and 1), MRE<sub>2</sub>W<sub>2</sub>O<sub>10</sub> (M = Co, Cd, Mn; RE = Y, Pr, Nd, Sm-Ho) tungstates and Cd<sub>1-3x</sub>Gd<sub>2x</sub> $\square_x$ MoO<sub>4</sub> (x = 0.0005, 0.0098, 0.0238, 0.0455, 0.0839, 0.1667, 0.2000, and 0.2222) molybdates. For these purposes, a KEITHLEY 6517B Electrometer/High Resistance Meter, a Seebeck Effect Measurement System (MMR Technologies, Inc., USA) and a Quantum Design System (MPMS XL) were used.

The results of magnetic measurements showed paramagnetic behavior for all analyzed samples. In case of the phases containing the Gd<sup>3+</sup> ions, which

carry only a spin magnetic moment, magnetic isotherms are characteristic for the Brillouin function in the paramagnetic region. Next, in case of the compounds containing the Sm<sup>3+</sup> and Eu<sup>3+</sup> ions, with the narrower multiplet widths, comparable to the thermal energy, kT, the Curie-Weiss region is not observed because their levels above the ground state do not contribute to the magnetic susceptibility. All molybdates and tungstates under study are insulators with an electrical resistivity of  $10^8 \Omega m$  except for  $(Co,Mn)Pr_2W_2O_{10}$  and  $Cd_{1-3x}Gd_{2x}\Box_xMoO_4$  around the critical content parameter x = 0.0839, for which a thermally activated conduction of the Arrhenius-type is observed. Generally, the sign of thermopower is negative, indicating the residual electrical *n*-type conduction usually associated with an excess of the oxygen vacancies. The I-V characteristics, measured at 300 and 400 K, showed a symmetric and linear behavior as well as an almost constant value of the conductance G vs. the applied voltage V. characteristic for the Ohm law. The most spectacular observation is that the emission of electrons is 3 orders of magnitude larger for MPr<sub>2</sub>W<sub>2</sub>O<sub>10</sub> with M =Co and Mn and 2 orders of magnitude larger for  $Cd_{1-3x}Gd_{2x}\square_xMoO_4$  with x= 0.0839, as a result of lowering the potential barrier. Unexpectedly in case of AgY<sub>1-x</sub>(Nd,Gd)<sub>x</sub>(WO<sub>4</sub>)<sub>2</sub> emission of electrons is greater at 300 K than at 400 K for all x-content due to the existence of deep trapping centers associated with high energy form of silver vacancies.

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# **B19:** Sol-Gel-Derived Amorphous Semiconductor TFT Fabrication and its Performance

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In recent years, metal oxide semiconductors (MOS) such as IZO, ZnO, and IGZO are applied for thin-film transistors (TFTs) semiconductor layer in terms of low temperature fabrication approaches. These candidates are expected for next generation TFTs realizing superior flexibility, stretchability, and transparency. In this research, deposition of IGZO/SiO<sub>2</sub> layers on Si substrate using a sol-gel methodfor TFT are investigated [1], particularly in the stabilizers effect of sol-gel derived IGZO layer. The electrical conductivity, surface morphologies, and TFT performance are studied for the fabricated layer structures.

In the sol-gel deposition process, the stoichiometric ratio of initial inorganic salts were remain constant as In:Ga:Zn = 2:1:1, and these were dissolved in 5 ml 2-methoxyethanol (2ME) solvent at room temperature. Acetylacetone (AcAc) and diethanolamine (DEA)/monoethanolamin (MEA) are

added as sol-stabilizers. A few different molar ratio concentrations of the sol-stabilizers are prepared corresponding to IGZO211 of 1 mol. The prepared solutions were then stirred at room temperature for 1 – 12 h, to be homogeneous sol-gel solution for clear transparent IGZO films. The precursor solution was deposited on SiO<sub>2</sub>/Si substrate by spin coating at 1000 rpm for 10 s. The coated thin films were then dried and sintered at 773 K for 3 min in an electric furnace. The targeted IGZO/SiO<sub>2</sub>/Si structure are achieved by repeating the coating and sintering process several times.

Fig.1 shows cross-sectional SEM observations of IGZO deposited on the SiO<sub>2</sub>/Si with different AcAc:DEA ratio of the sol-stabilizer: (a) AcAc:DEA = 16:16, (b) 8:8, and (c) 4:4. As seen in the SEM images, the deposited IGZO layer forms uniform thickness are about 150 - 200 nm on the substrate. The surface flatness is increased with decreasing AcAc:DEA sol-stabilizers ratio. This is because the evaporation rate of the precursors depends on the molar ratio of the including organic portion or carbon chain in the solution. In the cross-section images, no nano- or micro-particles are found in the deposited structure, indicating successful formation of amorphous oxide film layers. The results clarify the importance of sol-stabilizer for uniform amorphous oxide formation at low temperature thin films fabrications.



**Fig1.** Cross-sectional FE-SEM image of IGZO/SiO<sub>2</sub>/Si structure depend on precursors including stabilizer ratio. The ratio of AcAc : DEA in each precursors are (a) 16 : 16, (b) 8 : 8 and (c) 4 : 4, corresponding to IGZO 1 mol.

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#### **B20:** Improving the properties of BiFeO<sub>3</sub> ceramics

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The drive to find novel materials for applications such as data storage, spintronics, and microelectronic devices has led to a resurgence in research into multiferroic materials. Bismuth ferrite is the most widely studied multiferroic material primarily due to its room temperature (anti)ferromagnetic ( $T_N \sim 630$  K) and ferroelectric  $(T_C \sim 1100 \text{ K})$  ordering.<sup>1</sup> At room temperature BiFeO<sub>3</sub> exhibits a distorted perovskite structure with rhombohedral polar R3c symmetry with the magnetic ordering characterized as a G-type antiferromagnet with an incommensurately modulated spin cycloid structure which propagates along the [110] direction and has a repeat distance of approximately 62 - 64nm.<sup>1</sup> However, bismuth ferrite suffers from high leakage currents and the presence of a complex incommensurate spin cycloidal magnetic ordering, which has limited its commercial viability. This has led researchers to investigate the functionality of doped BiFeO<sub>3</sub> ceramics. In particular interest is aimed at materials with compositions close to structural morphotropic phase boundaries (MPBs), since these may lead to materials with enhanced electronic and magnetic properties analogous to the highly relevant PbZrO<sub>3</sub> - PbTiO<sub>3</sub> solid solution. Doping of either the Bi3+ and/or Fe3+ sites has recently been demonstrated as a viable methodology to improve both the ferroelectric response as well as realize commensurate antiferromagnetic or ferromagnetic ordering. Replacing Bi<sup>3+</sup> with rare earths such as La<sup>3+</sup> or Nd<sup>3+</sup> has been shown to lead to a rich phase diagram<sup>2</sup> for example Bi<sub>1-x</sub>Nd<sub>x</sub>FeO<sub>3</sub> exhibits PbZrO<sub>3</sub>-type antiferroelectric behavior between  $0.15 \le x \le 0.20$ .<sup>3</sup> The addition of Dy<sup>3+</sup> onto the Bi<sup>3+</sup> A-site of the perovskite structure.

In this paper we report a detailed powder neutron and synchrotron diffraction study coupled with a complementary Raman spectroscopy study of the addition of Dy<sup>3+</sup> onto the Bi<sup>3+</sup> A-site in BiFeO<sub>3</sub> ceramics. The composition driven structural phase transitions can be seen to be far more complex than previously reported. The large size mismatch between the two A-site cations (Dv<sup>3+</sup> and Bi<sup>3+</sup>) results to destabilize the R3c symmetry resulting in a lowering of the symmetry to a probable polar Cc model. In contrast materials with  $x \ge 0.30$  exhibit non-polar Pnma symmetry with phase co-existence observed between  $0.05 \le x \le 0.30$ . Magnetic measurements suggest weak ferromagnetic character which increases in magnitude with increasing Dy<sup>3+</sup> content. Powder neutron diffraction experiments suggest that whilst the G-type antiferromagnetic spin cvcloid is maintained in Bi0.95Dy0.05FeO3, Bi<sub>0.70</sub>Dy<sub>0.30</sub>FeO<sub>3</sub> most likely adopts a G-type antiferromagnetic collinear structure. Electrical measurements suggest that whilst Bi0.95Dy0.05FeO3 is most likely polar (with T<sub>c</sub> approximately 700 K); Bi<sub>0.70</sub>Dy<sub>0.30</sub>FeO<sub>3</sub> shows low temperature relaxor-type behavior.<sup>4</sup> We demonstrate the power of using complimentary techniques to unravel complex behaviors in multiferroic materials.

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# **B21:** Modeling the chemical complexity of the metal borides using the hybrid SQS/VCA alloy method and data informatics

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Metal borides are known to adopt a wide variety of electronic configurations that result in crystals with mixed bonding: covalent, ionic, and metallic bonds can all be present. In addition these compounds have outstanding thermal stability and mechanical strength. They also are known to possess unique and sometimes highly functional electronic properties. For example the boron-rich metal borides with compositions XYB<sub>14</sub> have been shown to have very good thermoelectric behavior at relatively high temperatures, T>1000 K.

Metal borides, because of their ability to form a highly diverse range of compounds and their unique properties, are an ideal platform for materials by design engineering activities. Here we demonstrate our laboratory's capabilities to deploy a variety of theoretical methods to predict the structure and properties of metal boride alloys. Data informatics methods are used to determine structure property relationships, which allows for the prediction of compounds with optimal engineering properties.

B22: Novel highly transparent polycrystalline ceramics synthesized by full crystallization from glass

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Transparent polycrystalline ceramics are an emerging class of photonic quality materials competing with single crystal technology for a diverse range of applications including high-energy lasers, scintillating devices, optical lenses, and transparent Polycrystalline ceramics offer several armor. advantages, particularly in the fabrication of complex shapes and large-scale industrial production, and enable greater and more homogenous doping of optically active ions than is possible in single crystals. However, up to date, only a limited number of transparent polycrystalline ceramics has been reported. These are either cubic or nanocrystalline transparent polycrystalline ceramics which require complex, time-consuming and so expensive synthetic approaches.

Our recent work shows the possibility to obtain transparent polycrystalline ceramics by full and congruent crystallization from glass. Transparency is observed despite micrometer scale crystals and a non cubic symmetry (no structural isotropy) of the crystalline phase. Interestingly, crystallization from glass gives access to new crystalline phases given the relatively low crystallization temperature compared to classic solid state synthesis. This is demonstrated in the case of a new composition, BaAl<sub>4</sub>O<sub>7</sub>, showing the existence of two orthorhombic polymorphs both showing high transparency in the visible and infra-red ranges [1,2]. The crystallographic structures of these polymorphs have been determined ab initio from powder diffraction data. From these structural models, the optical birefringence has been obtained by DFT calculations of the dielectric function. These results enable to discuss the transparency property of these materials as a function of the determined crystalline structures and the observed microstructures. Remarkably, these materials show promising scintillation properties when doped by europium [3]. The same elaboration process has been applied to cubic compositions, Sr<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and Sr<sub>3</sub>Ga<sub>2</sub>O<sub>6</sub>, allowing very high transparencies to be attained [4]. Lastly, we have focused our work on strontium aluminosilicate compositions, the addition of silica enabling large scale glass samples to be obtained. The full and crystallization  $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_{8}$ congruent of compositions leads to new transparent polycrystalline ceramics forming a crystalline solid solution exhibiting hexagonal symmetry. These materials show an impressive transmittance higher than 90%. A crystallographic study coupled to NMR experiments and DFT calculations of the birefringence allowed us to evidence the role of structural disorder (Al/Si substitution and presence of vacancies on strontium sites) in the origin of the optical isotropy observed in these structurally anisotropic materials. These results propose an innovative concept, the addition of a controlled structural disorder within crystalline structures, in order to lower the birefringence and to elaborate new transparent ceramics [5].



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#### **B23: Electrospinning of Ceramics**

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Electrospinning is a well-known process for the fabrication of polymeric nanofibers, and is nowadays widely used for making scaffolds for biological cell growth, high specific surface area architectures for battery electrodes and water treatment systems, and various other applications. Electrospinning can also be used to make ceramic nanofibers. In this presentation we provide an overview of the possibilities that the electrospinning method offers to form advanced ceramic nanofibers, nanotubes and ceramic films with well-defined functionalized nanopore architectures, and we show some examples of applications. The focus is on yttria-stabilized zirconia (YSZ) nanofibers and nanotubes, but also bioglass and hydroxyapatite nanofiber scaffolds for bone cell regeneration are discussed.

We employed sol-gel processing to make precursor solutions and optimized these with respect to rheology and rate of evaporation for the electrospinning process. YSZ nanofibers were made in this way. The mechanical properties of individual YSZ nanofibers were determined. The YSZ fibers were subsequently used to fabricate highly flexible non-woven ceramic mats.

Hollow YSZ nanofibers were made by coaxial electrospinning. In this case the spinneret can handle two solutions and generate a core-shell nanofiber architecture. For YSZ nanotubes the central core fiber consisted of a viscous polymer that is immiscible with the YSZ precursor/polymer electrospinning solution of the shell layer. After thermal removal of the polymer and sintering, the resulting hollow fibers, shown in Figure 1, had an average inner diameter of 230 nm and an average outer diameter of 530 nm. The process was reproducible and yielded very homogeneous fiber dimensions. The porosity and morphology of the fibers could also be modified further by selected heat treatments.

A third way of applying electrospinning is to utilize electrospun polymeric nanofibers as pore forming templates in sol-gel derived YSZ films, to make highly porous YSZ films with straight channel pores with a constant diameter of 220 nm. Moreover, by incorporating a nickel precursor in the polymer solution, the inner YSZ pore walls could be functionalized by nickel nanoparticles with a high degree of dispersion. The dispersion of Ni in a highly porous YSZ film large surface area and placement of the catalyst on its most active site is of interest for applications in which oxygen exchange between the gas phase and YSZ is targeted, e.g. as in Solid Oxide Fuel Cell (SOFC) anodes. The processing and influence of processing variables is discussed.



Fig. 1. Electrospun YSZ nanotube.

# **B24:** Medium Range Structure, Ionic Conductivity and Fragility of Superionic Glasses

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Superionic conducting glasses have attracted considerable interest in the research fields of energy related materials. However, despite the large number of studies, no theory of ion conduction in glasses has yet received general acceptance. Most existing models relate the ion transport to some specific structural features. However, there is a lack of investigation concerning the role of the medium range structure in the ionic conduction mechanism. Some years ago, the relationship between the FSDP (First Sharp Diffraction Peak) that reflects the intermediate range ordering within the glass and the ionic conductivity has been studied [1]. The result revealed that the activation energy for ion conduction decreases with the decrease of FSDP wave number. The result is surprising, because naively, we expect that the activation energy is determined mainly by short range interatomic interactions, and we do not expect that it depends on intermediate range order so drastically.

On the other hand, related with the glass formation processes, the concept of fragility has been used widely to characterize the temperature dependence of the viscosity of different glass forming materials. The author has developed an analytical expression for the fragility based on a simple model of the melt [2]. According to the model, the fragility is determined by the relaxation of structural units that form the melt, and is described in terms of the bond strength, coordination number and their fluctuations. It has been shown that the model reproduces the experimental data of many types of materials that extends from covalent to ionic, molecular and metallic systems. In a recent study, such a model has been applied to understand how the medium range structure in glasses is formed and developed [3].

In the present contribution, after reviewing the above findings, new results regarding the role of the medium range structure in the ionic transport and other physical properties of superionic glasses will be shown. Topics such as extension of the relation between FSDP and ionic conductivity to other glassy systems, correlations between medium range structure, optical properties and relaxation behavior will be discussed.

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# **B25:** ABO<sub>3</sub> perovskite thin films for fuel cell and sensor applications

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Perovskite oxides of general formula ABO<sub>3</sub>, where A is an alkali, alkaline earth or lanthanide metal and B is a transition metal, have attracted the interest for their potential applications in electrochemical systems, in particular in Protonic Ceramic Fuel Cells (PCFCs) and gas sensors.

The recent concept of PCFCs has seen increasing developments due to its potential operation at lower temperature than Solid Oxide Fuel Cells (SOFCs), i.e. in the range of 673-873 K. Numerous ABO<sub>3</sub> perovskite oxides substituted on the B site by lower valence cations ( $Y^{3+}$ ,  $Sc^{3+}$ ,  $Yb^{3+}$ , etc), display protonic conductivity and good stability at high temperature and can be potentially applied as electrolyte in PCFCs. Therefore, the challenge is to develop a thin and dense electrolyte with high chemical stability and proton conductivity.

On the other hand in sensor application, the performance of gas sensor active layers is strongly related to their specific surface and composition, so that deposition of these oxides in the form of nanowires and control of their composition would increase evidently the sensor performance.

In this presentation, we investigate the feasibility of ABO<sub>3</sub> coatings with dense and nanowires morphologies by reactive magnetron sputtering for application as PCFC electrolyte and sensor active layer, respectively.

In the first part,  $SrZr_{0.84}Y_{0.16}O_{3-\alpha}$  (SZY16), BaZr<sub>0.84</sub>Y<sub>0.16</sub>O<sub>3- $\alpha}$ </sub> (BZY16), BaCe<sub>0.8</sub>Zr<sub>0.1</sub>Y<sub>0.1</sub>O<sub>3- $\alpha$ </sub> (BCZY10) and BaCe<sub>0.90</sub>Y<sub>0.10</sub>O<sub>3- $\alpha$ </sub> (BCY10) dense coatings are suitably deposited and the characterisation results are compared.

In the second part, double substituted lanthanum cobalt ( $La_{1-x-y}Sr_xAg_yCoO_{3-\alpha}$ ) dense and nanowires are deposited (Fig1) and their performance as heavy hydrocarbon sensor are discussed depending on hydrocarbon concentration and sensitive surface's temperature.



**Fig.1** La<sub>1-x-y</sub>Sr<sub>x</sub>Ag<sub>y</sub>CoO<sub>3-α</sub> dense and nanowires coatings deposited by reactive magnetron sputtering

**Keyword:** Perovskite, thin films, nanowires, reactive magnetron sputtering, fuel cell, sensor

### **B26: 3C-SiC on Si: A Biocompatible Material for** Advanced Bioelectronic Devices

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Crystalline silicon carbide (SiC) has long been known as a physically and chemically robust semiconductor with superior properties to silicon for power electronic applications. The cubic SiC polytype (3C-SiC) has not been normally considered for power applications due to its lower band gap (2.3 eV) when compared with 4H- and 6H-SiC (3.2 and 3.0 eV, respectively); however, 3C-SiC has demonstrated application in the fabrication of micro-electromechanical machine (MEMS) devices as it can be grown as a thin film heteroepitaxially on silicon substrates [1]. Unlike the crystalline polytypes, the amorphous form of SiC (a-SiC) is highly insulating and can be deposited using several different techniques, such as sputtering, pulsed laser deposition, and evaporation, among others [2, 3]. Another advantage of a-SiC is that it can be deposited at low temperatures, which allows for the coating of polymers and other temperature sensitive materials [4].

These two forms of SiC are ideal for use in the fabrication of long term implantable biomedical devices as they encompass a cost-effective processing approach which allows for the synthesis of chemically and physically resistant thin films with less expensive materials, like silicon and polymers. Additionally, the combination of *a*-SiC and crystalline SiC also opens the possibility for the fabrication of single material devices, eliminating issues like delamination which have plagued many long-term implantable biomedical devices. In this paper, we will review nearly a decade of activity in the development of 3C-SiC and a-SiC for biomedical device applications [5]. We have demonstrated that 3C-SiC is one of the few semiconductor materials that had demonstrated multiple indicators of superior bio- and hemacompatibility. We will detail our findings in three specific device applications: in vivo continuous glucose monitoring [6], organic molecule surface functionalization of SiC [7], and biomedical

implants for connecting the human nervous system to advanced prosthetics [8]. With this ever growing wealth of evidence, SiC has the potential to possibly be a game changing material which can finally live up to the promises made by many previous biomedical devices constructed from less robust materials.

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# **B27:** Preparation of directionally solidified eutectic ceramic with Induction Zone Melting

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The oxide eutectic ceramics has been attracting a lot of attention because of its unique mechanical properties at high temperature and potential application to the structural components of aero engine. However, most of the eutectic ceramics with promising experimental results, which have been reported, are almost based on the rare earth oxides, such as Al<sub>2</sub>O<sub>3</sub> / GdAlO<sub>3</sub> (GAP), Al<sub>2</sub>O<sub>3</sub> / Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG), Al<sub>2</sub>O<sub>3</sub> / EAG, Al<sub>2</sub>O<sub>3</sub> / YAG / YSZ, and so on. However, they are all based on rare earth oxides. High price will be one of the obstacles to their wide application.

Another question is how to get large oxide eutectic ceramic sample. Although the Bridgman method is preferable to prepare a large size eutectic crystal, its temperature gradient is relatively low, leading to large interphase spacing. The LHFZ,  $\mu$ -PD, and EBFZM methods are preferable to prepare the eutectics with fine interphase spacing near the micron range. However, it is hard to get large sample with regular shape with them, please see the following pictures.



Al<sub>2</sub>O<sub>3</sub>/Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/ZrO rod with LHFZ J Cryst Growth, 2007, 307: 448–456 Al<sub>2</sub>O<sub>3</sub>/YAG/YSZ rod with EBFZM Materials letters, 2013, 91: 92-95

In order to develop low-cost large eutectic ceramic, Al<sub>2</sub>O<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>/ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> eutectic ceramic crystal was prepared with induction zone melting. Dense rod samples were prepared, shown as in Fig. (a) and (b). Their composition and

microstructure were investigated with XRD and SEM respectively, and mechanical properties were tested with micro-indentation (MI) and three-point bending method.

The microstructure of  $Al_2O_3/MgAl_2O_4/ZrO_2$  rod reveals that the  $Al_2O_3-MgAl_2O_4$  phase is the matrix, the ZrO<sub>2</sub> stick sets in the matrix, shown in Fig. (c). Its hardness reaches 12 GPa, is about two times of the sintered sample. Its fracture toughness reaches 6.1 MPa m<sup>1/2</sup>, is about 1.7 times of the sintered sample.

The microstructure  $Al_2O_3/MgAl_2O_4$  rod reveals that  $Al_2O_3$  phase is the matrix, and the discrete  $MgAl_2O_4$  slices set in the matrix uniformly. Its density reaches 99% of the theoretical value. Its hardness and fracture toughness reach 18.7 GPa and 3.74 MPa m<sup>1/2</sup> respectively, which are about 2 times of the sintered sample.

The improvement of the hardness and the fracture toughness may results from the disappearance of the pores and the amorphous phase on the grain boundary, and the existence of the single crystal matrix.





B28: Hydroxyapatite/collagen bone-like nanocomposite: Its biological reactions and usefulness in surgery

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Bone has two roles: One is as structural material that protects important organs such as brain and heart from outer forces and another is as biochemical material that stores mainly calcium for its homeostasis. The first generation bone filler mainly tried to mimic structural properties of bone. Thus, the first generation is dense or porous body with low porosity composed of mainly hydroxyapatite (HAp). Unfortunately, even the strongest dense bioactive ceramics does not have enough mechanical properties. Thus, the second generation artificial bone aimed to improve mainly biological properties, higher cell migration by higher porosity and interconnectivity, biodegradability or injectable self-setting property. The second generation spread artificial bone market in Japan approximately 10 %. In addition, many researchers tried to improve biochemical and biological properties by important minor element substitution for calcium phosphate to improve cells' osteogenic functions, preparing composite of polymer and bioactive ceramics to allow close fit to bone defect edge for improvement regeneration, etc.; however, no enough improvements as the third generation artificial bone were achieved except in case of our HAp/collagen bone-like nanocomposite (HAp/Col). [1] Of course, many of composite materials composed of HAp and collagen were reported and clinically available, even though, they have several lacks in biological functions. Mixtures of HAp (or bioactive calcium phosphate) and collagen, such as Collagraft®, and HAp formation on collagen thick fibers, such as Healos®, showed no enough viscoelastic properties and bone-like biological reactions, *i.e.*, incorporation into bone remodeling process completely. The HAp/Col (now sold in Japan as ReFit®) showed bone-like oriented structure of HAp and collagen as shown in Fig. 1 and fully incorporation into bone remodeling metabolism as shown in Fig. 2.

The HAp/Col showed improvement of alkaline phosphatase activity of osteoblastic MG63 cells and also acceleration of bone-like nodule in its pore by 3D culture of MG63 cells in pressure/perfusion culture. Osteoclastic differentiation of bone marrow cells co-cultured with osteoblasts was also improved by presence of the HAp/Col. Sponge-like visoelastic property is very confortable for surgeon to fit its shape completely to the "irregular" bone defect shape with very small effort including cutting of materials. Bone regeneration properties in human bone defects were 20.6 % higher in average in comparison to Osferion®, the best bioresorbable materials in Japan before the ReFit<sup>®</sup>. [2] Thus, the HAp/Col is the real third generation artificial bone which acquires all three functions, a good fitting to bone defect, improve biological functions to regenerate bone almost the same as the autologous bone transplantation and resorbed by osteoclasts in 3-6 months.



**Fig. 1**. TEM photo of the HAp/Col. The HAp nanocrystals aligned along collagen molecules.



**Fig. 2.** Hematoxylin-eosin stained section of the HAp/Col with surrounding tissues. The HAp/Col was incorporated into bone remodelling process.

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### **B29:** A Mechanical Model to Predict Phase Stress for Ceramic Laminates during Sintering

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Email: kyasuda@ceram.titech.ac.jp, web site: http://www.cmc.ceram.titech.ac.jp/index\_e.html Ceramic laminates are basis to support energy and environmental applications including electrodes in SOFC systems, thin film / substrate systems, sensors, multilayer capacitor, piezoelectric actuator, and coating etc. However, combination of different materials causes internal phase stress in each layer, and sometimes leads to cracking in the laminates during sintering.

Recently, the author has developed а one-dimensional elastic model to estimate phase stress of symmetrical 3-layered laminates during sintering [1]. And its experimental verification was shown by making dense alumina / porous alumina / dense alumina laminates [2]. By this model, we discussed the internal stress caused by both mismatches in thermal expansion and sintering shrinkage between the layers. However, most of composed laminates are of multi-layers (multi-phases) and also their constitutive equations are not limited to elastic one, sometimes, elasto-plastic or viscous behavior can be observed.

In this presentation, this model is extended into multilayered (multi-phase) laminates as shown in

Fig.1, and also elasto-plastic and viscous behaviors are incorporated in the model.



Derivation is based on "balance of force" equations and "compatibility in total strain" equations. By solving these equations (viz. they form a simultaneous linear equation system), we obtain the phase stress equations as below,

 Elastic laminates: Each lamina *i* is elastic with Young's modulus *E*<sub>i</sub> and volume fraction *f*<sub>i</sub>. The phase stress is,

$$\sigma_{i}(T) = E_{i}(T) \left\{ \frac{\sum_{k=1}^{n} f_{k} E_{k}(T) \left( \epsilon_{i}^{SI}(T) + \epsilon_{i}^{TH}(T) + \epsilon_{i}^{PT}(T) \right)}{\sum_{k=1}^{n} f_{k} E_{k}(T)} - \left( \epsilon_{i}^{SI}(T) + \epsilon_{i}^{TH}(T) + \epsilon_{i}^{PT}(T) \right) \right\}.$$
 (i = 1, n)

(2) Elasto-plastic laminates: Lamina *i* is only elasto-plastic material with yield stress σ<sub>yield</sub> and other laminas are elastic material. After yielding of lamina *i*, The phase stress of lamina *i* is,

$$\sigma_i(T) = \sigma_{yield}(T)$$

(3) Viscous Laminates: Lamina *i* is only viscous material with viscosity η<sub>i</sub> and other laminas are elastic material. For quasi-static condition, the phase stress is,

$$\sigma_1(T) = \eta_1(T) \frac{d}{dt} \left[ \frac{f_1 \eta_1(T) \varepsilon_1^{sigen}(T) + \sum_{k=2}^n f_k E_k(T) \varepsilon_k^{sigen}(T)}{\sum_{k=2}^n f_k E_k(T)} - \varepsilon_1^{sigen}(T) \right]$$

where,  $\varepsilon_i^{eigen}$  the non-elastic strain such as sintering strain  $\varepsilon_i^{SI}$ , thermal expansion strain  $\varepsilon_i^{TH}$ , phase transformation strain  $\varepsilon_i^{PT}$ , and their summation.

#### Acknowledgement

This research was in-part supported by Grant-in-Aid for Scientific Researches (A) (24246108) and (C) (25420706) from Japan Society for the Promotion of Science, and also Joint Research Project of Joining and Welding Research Institute, Osaka University, and also Collaborative Research Project (No.78) of Materials and Structures Laboratory, Tokyo Institute of Technology.

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C17: Strongly Correlated Transition Metal Ceramic Nanostructures Investigated by Soft X-ray Spectroscopies and Multiplet Calculations

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X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), both as core-level spectroscopies are important tools for the study of the electronic structure of transition metal (TM) compounds [1]. XAS provides information about electronic states in the conduction band and XES gives complementary information about occupied states at the valence band [1]. In the soft X-ray region the electronic transitions follow electric-dipole selection rules and therefore one probes electronic states with inherent atomic and orbital selectivity. The absorption spectra are quite sensitive to the intra-atomic effects, including the TM oxidation state. The TM L<sub>23</sub> absorption spectra can help to identify the TM oxidation state and ligand to metal charge transfer effects [1]. A comparison of emission at the metal L $\alpha$  and the ligand K $\alpha$  lines gives a very good indication of the site- and symmetry-projected states of the valence band [1].

In this presentation we show recent work in which we observed the transition from charge transfer insulator for  $MVO_4$  (monazite and zircon) compounds to Mott–Hubbard insulator for  $MVO_3$ -perovskites (M=La, Y).  $MVO_4$  compounds

the sol-gel acrylamide were synthesized by polymerization route. This route was used in order to control particle size and shape distribution in the nanometer range [2,3]. For a comparative evaluation,  $MVO_4$  were prepared by solid-state reaction. The structures of MVO4 and MVO3 have been refined from powder X-ray diffraction data using Rietveld method with Fullprof software [4]. All X-ray absorption and emission measurements took place at beamline 8.0.1 of The Advanced Light Source in Berkeley [5]. Experimental X-ray absorption spectra were recorded in the total electron yield (TEY) mode. XAS and XES spectra presented in this work were collected at room temperature.

Atomic multiplet crystal-field calculations for X-ray absorption (using CTM4XAS codes [6]) were performed for  $MVO_4$  [7,8] and  $MVO_3$ . These calculations included intra-atomic multiplet, crystal field effects and charge transfer effects for the perovskites. For the  $MVO_4$  compounds the nominal vanadium oxidation state is  $V^{5+}$  with a strong ionic character. The evidence for the L<sub>2</sub>L<sub>3</sub>v Coster-Kronig decay was observed in these compounds [7,8]. For  $MVO_3$ -perovskites, evidence of the presence of  $V^{3+}$  and  $V^{4+}$  were found with strong presence of  $V^{4+}$  in the bulk.

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# C18: Nitrogen and Carbon Mobility in SiCO and SiCN Polymer-Derived Ceramics

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Silicon carbonitride and silicon oxycarbide ceramics were intensely studied by transmission electron microscopy (TEM) upon isothermal annealing at  $1300 \,^{\circ}$  for 1 to 200 hours. TEM investigations in conjunction with energy-dispersive X-ray spectroscopy (EDS) analysis revealed a pronounced reduction of the local nitrogen and/or carbon content in close proximity of internal surfaces. Such small microcracks are a consequence of the polymer-to-ceramic transition and, hence, are commonly formed upon thermal annealing. [1]

Figure 1 shows a typical feature of such materials:  $SiO_2$  enrichment near internal surfaces. A systematic study of the degradation of SiCN [2] and SiCO was performed, in particular, with focus on the nitrogen and carbon depletion in the vicinity of internal surfaces. The profiles of the carbon content between surface and bulk were analyzed employing error functions to yield carbon diffusivities. Apart from the lowering of the carbon content, surface crystallization of cristobalite was also observed after an incubation period of approximately 5 hours. The presented results clearly imply that the often reported high thermal stability of such polymer-derived ceramics can be rather limited, especially when thin

film applications are anticipated. Moreover, electron diffraction studies were performed to highlight differences in the initially amorphous structure of both systems. A possible mechanism for different behaviour of SiCN versus SiCO will be presented.



**Fig1.** TEM bright field image of SiCO revealing a  $SiO_2$  enriched region near an internal surface with cristobalite formation.

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### C19: Nanostructured pure and doped ferrites: synthesis by electrospinning and study of their magnetic properties

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The synthesis of pure and copper, gadolinium, zinc doped cobalt iron nickel, and oxide nanostructures is carried out by the electrospinning technique. Nanostructured CoFe<sub>2</sub>O<sub>4</sub>, (Cu, Ni and  $Zn)_xCo_{1-x}Fe_2O_4$  and  $Gd_xCo_{1-x}Fe_2O_4$  are successfully obtained using polyvinylpyrrolidone (PVP) as polymeric media during the electrospinning process and metal nitrates as source of metallic ions (M), in the precursor solutions, to form the ferrites. FTIR spectra show that PVP and M are present, in the electrospun precursor solutions, bounded through amide-M coordination bonds. Thermogravimetric analyses show that 400  $^{\circ}$ C is the temperature at which samples lose the maximum amount of weight. After thermal treatments at 300, 600, 800, and 900 °C/2 hours black powders were obtained. Their XRD patterns show the presence of a pure crystalline spinel-type phase. SEM micrographs of selected samples show the fibers with diameters sizes around 100 nm. Vibrating sample magnetometry (VSM) measurements show the characteristic ferrimagnetic behavior and saturation magnetization and coercivity values around 78 emu/g and 1000 Oe, respectively. Figure 1 shows some selected results obtained for CoFe<sub>2</sub>O<sub>4</sub> system, FTIR of precursor solution, TG-DTA of nanofibers treated at 300 °C by 2 hours, XRD of sample treated at 600 °C, SEM of sample treated at 800 °C and hysteresis loop of sample treated at 900 °C.



Fig 1. Selected results of the synthesis of nanostructured CoFe<sub>2</sub>O<sub>4</sub> by the electrospinning method.

### **C20:** Doping Effect on Sinterability and Grain Boundary Nanostructure in Polycrystalline Yttria

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Yttria ( $Y_2O_3$ ) is receiving much attention not only as a refractory material, but also as a new component of dry-etching equipment because of its excellent corrosion resistance to halogen-family plasma. In general, high pressures (>40MPa) and/or high temperatures (>1600 °C) under a reduced or hydrogen atmosphere have been used to obtain fully densified  $Y_2O_3$  polycrystals. On the other hand, it has been reported that the sintering temperature of  $Y_2O_3$ can be reduced by the doping of divalent alkaline metal cations, such as  $Mg^{2+}$  and  $Ca^{2+}$  [1]. More recently, our group has found that the sinterability of  $Er^{3+}$ -doped  $Y_2O_3$  is highly improved by doping of 1mol% Ni<sup>2+</sup> or Mn<sup>2+</sup> [2]. In the present study, sintering behavior of polycrystalline  $Y_2O_3$  doped with 1mol% of a divalent, trivalent or tetravalent cation was investigated by pressureless sintering in air [3,4].

Mixtures of commercially-available  $Y_2O_3$ powder and dopant source were prepared by ball-milling process. Green compacts of the mixed powder were formed by cold-isostatic pressing at 120MPa following uniaxial compression at approximately 20MPa. The green compacts were sintered at temperatures between 1200  $^{\circ}$ C and 1800  $^{\circ}$ C for 3 h in air at the heating rate of 300 °C/h. An interdiffusion experiment was performed on the diffusion couples of polycrystalline Er<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> doped with Ni<sup>2+</sup> or Zr<sup>4+</sup>, which are some of the most effective and least effective dopants for the improvement of the sinterability, respectively. Microstructure of the sintered bodies were observed by SEM, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), attached with nano-probe X-ray energy dispersive spectroscopy (EDS).

The sintering temperature required for full densification in Y<sub>2</sub>O<sub>3</sub> was reduced by 100 °C-400 °C by doping of the divalent cation, while undoped  $Y_2O_3$ was densified above 1600 °C. The doping effect depended on the type of doped cations; among the investigated cations,  $Zn^{2+}$  and  $Ni^{2+}$  was the most effective dopant for improving the sinterability of  $Y_{2}O_{3}$ .  $Ga^{3+}$ or Ge<sup>4+</sup>-doping also enhanced densification of  $Y_2O_3$ , while  $La^{3+}$  or  $Zr^{4+}$ -doping suppressed that. In addition, the average grain size of the cation-doped samples depends on the dopant species as well as the sinterability. The interdiffusion the diffusion experiment on couples of polycrystalline  $Er_2O_3$  and  $Y_2O_3$  revealed that grain boundary diffusion coefficients of the Er<sup>3+</sup> cation in  $Y_2O_3$  were increased by the Ni<sup>2+</sup>-doping, but were decreased by the  $Zr^{4+}$ -doping. HRTEM observations and nano-probe EDS analyses confirmed that the doped cations segregate in the vicinity of grain boundaries without forming amorphous layer [3,4]. The doping effect on the sinterability of  $Y_2O_3$  must result from the change in the mass transport in  $Y_2O_3$ owing to the grain boundary segregation of the doped cations.

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### C21: Band gap narrowing and widening of ZnO nanostructures and doped materials

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Band gap is one of the most important properties of materials due to the direct relationship with their electrical properties. It is found that band gap narrowing and broadening (obtained via UV-visible spectroscopy, Fig. 1) can occur depending on the dimensions of the nanostructures and the doping element used. In this work, band gap changes of ZnO nanorods with the dimensions of the rods were investigated. Band gap changes with elemental doping of Cu and Mn were also investigated. In terms of low dimensionality, results showed that band gap values becomes larger as the aspect ratio of the nanorods increases. The shape of the nanorods is also believed to influence the value of the band gap. The band gaps for nanosized crystallites and larger micron sized crystallites were studied and results showed that they vary according to different length and diameter sizes. The crystal structure, in terms of cell parameters, was studied over a range of annealing temperatures and it was found that some materials show band gap variations with slight changes in cell parameters at different annealing temperatures. Band gap narrowing or widening is dependent on the doping element as well as crystallite dimensions. In this work, two dopant elements, Cu and Mn were substitutionally doped into the lattices of ZnO. X-Ray diffraction results showed that the substitutional doping was successfully done, showing pure, single phase materials. X-Ray Photoelectron Spectroscopy reveals that the oxidation states of the dopant is not unique. Several oxidation states exists for Cu and Mn. There are changes observed of the valence band spectra of the materials. This was also found to be dependent on the nano structure dimensions. Quantitative XRD analysis also shows that there are changes with the lattice parameters of the doped compounds relative to the undoped ZnO. Comparisons of the band gaps of the doped materials with pure ZnO showed that there is band gap narrowing and widening of the nanostructured materials and doped compounds depending on dimensions, crystallite size and dopant element. This can be explained by the shifts of the valence band maximum as was observed from XPS valence band spectra of the materials.



**Fig. 1** The UV-Visible spectra of of Zn<sub>0.99</sub>Mn<sub>0.01</sub>O annealed at different temperatures.

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### C22: Electrocaloric Properties of PZT-based Ceramics, PVDF Films and PMN-PT Crystals

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The electrocaloric effect (ECE) is a phenomenon in which a material shows a reversible temperature change under an applied electric field. In order to create ECE cooling devices, materials with large ECEs are required. In this study, the sample temperature changes derived from ECE under bipolar electric field were directly measured.  $Pb(Zr,Ti)O_3$  (PZT)-based ceramics with various Tcs. (Ba,Ca)(Zr,Ti)O<sub>3</sub> (BCZT) ceramics, PolyVinylidene DiFluoride (PVDF) films. Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>(PMN-PT) crystals were used as samples. The temperatures of these samples were periodically changed by application of alternating electric field applications. The temperature change exhibited butterfly-shaped hystsresis loops with the field. Figure 1 shows the strain-electric field (S-E)loops and the temperature-electric field (T-E) loops of the PZT-based ceramics (a) hard PZT with Tc of 330 °C. (b) soft PZT with Tc of 190 °C, and (c) soft PZT with Tc of 140 °C are shown The similar shapes are observed in these samples. The temperature changes in PZT ceramics induced by bipolar switching field of 40kV/cm were 0.3-0.4K, those in BCZT ceramics induced by bipolar switching field of 40kV/cm were 0.1K, and those in PVDF films induced by bipolar switching field of 2500kV/cm were 0.6K, respectively. The comparison with the estimations from indirect approach based on Maxwell's equation will be discussed. [1]

#### Acknowledgements

This study is partly supported by grant from KAKENHI, GRENE (Green Network of Excellence) project from The Ministry of Education, Culture, Sports, Science and Technology, Japan and Kato Science Foundation.



**Fig1.** Strain-electric field (S-E) loop (above) and temperature-electric field (T-E) loop (below) of the PZT-based ceramics.

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### C23: Functional metastable phase formation from undercooled melt by containerless processing

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Containerless processing is well suited to promote deeper undercooling in molten materials because it suppresses inhomogeneous nucleation at the boundary between the melt and the container wall. A levitated melt is easy to solidified without crystallization even though the glass forming ability is low [1,2]. New oxides glass systems without any network former oxides have been prepared in bulk form by using containerless processing with an aerodynamic levitation furnace. Among them, colorless and transparent TiO<sub>2</sub>-based, Nb<sub>2</sub>O<sub>5</sub>-based, WO<sub>3</sub>-based, and La<sub>2</sub>O<sub>3</sub>-based glasses have attracted much attention since the refractive index n is quite high  $(n\approx 2.3)$ , and the wavelength dispersion of the refractive index is rather low in visible range [3-5]. These excellent optical glasses will be used as thinner lens for digital camera of smart phones, and solid immersion lens for next-generation optical disk system. The structural analyses by using X-ray and diffraction and reverse Monte-Calro neutron simulation, and molecular dynamics simulation revealed that the glass structures of the high refractive index glasses were quite different from those of the conventional oxide glasses consisting of network former oxides. It was suggested that the unusual local and intermediate structures of the high

refractive index glasses caused the high oxygen packing density leading to the high refractive index.

Containerless processing is also a technique to prepare metastable crystalline phases [6]. A metastable phase has inevitably a lower melting point than a competing stable phase. Hence, if the temperature of the melt is lowered than the melting point of the metastable phase, the metastable phase will be solidified directly from the undercooled melt. We have succeeded in making metastable hexagonal LuFeO<sub>3</sub> by containerless processing [7,8]. It was revealed that the hexagonal LuFeO<sub>3</sub> showed a weak ferromagnetic transition at 150 K with a dielectric anomaly, indicating it is an alternative multiferroic materials instead of hexagonal manganese oxides system.



Figure 1. Schematic illustration of an aerodynamic levitation system.

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## C24: Lead-Free Functional Oxides for Applications

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During the last decades, functional oxides have been intensively studied by the scientific community. They present a wide range of interesting functionalities, such as high dielectric permittivity, piezoelectricity, pyroelectricity and ferroelectricity which have been largely developed in applications such as ceramic capacitors, tunable devices, actuators and sonars, I-R sensors and ferroelectric memories, respectively. More recently, the community attention has been attracted by other properties and materials such as high temperature superconductivity, colossal magneto-resistance, multiferroics, gas sensing, half-metallic behaviour, thermoelectrics and oxides for fuel cells. These materials are characterized by strong interactions between the fundamental degrees of electron freedom (electron spin), charge, orbital and their interplay with the lattice [1]. On the other hand, the nano-scale complexity, driven by chemical/ionic/electronic inhomogeneities is a key feature that underpins large physical responses such as piezoelectric/dielectric responses in relaxors, colossal in magneto-resistance doped manganites. high-temperature superconductivity in cuprates and high-temperature conductivity in cobaltites. All oxides exhibit various crystalline structure. One of the best-known family is lead-free oxides with a perovskite-type crystal structure (ABO<sub>3</sub>). In these crystalline structures, the grain boundaries, impurities and structural defects strongly influence the dynamics of ferroelectric or ferroic domains. Among numerous oxides, ferroelectrics display a hysteresis of the electrical polarization, characterized by a remnant polarization at zero electrical field and the possibility to continuously pole the material between positive and negative extrema. Ferroelectrics offer not only possibilities for data storage, their applications cover a wide range, such as microwave devices, or nowadays with structures integrated onto Si chips such as piezoelectric microfluidic systems, electrocaloric coolers or phased-array radars [2]. In microwave devices, some components have to be tuned to adjust oscillators or filter bandwidths. In this case, ferroelectric thin films are of great interest due to their wide frequency range which can be extended up to 60 GHz [3].



**Figure 1**: Capacitance evolutions of the BTS950 film versus frequency under different bias points with and without de-embedding.

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# C25: Epitaxial growth of flower and pillar indium nitride by APHCVD method

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The III-group nitride materials attract attentions due to their electroluminescence properties. The GaN based nitride materials, e.g. AlGaInN, AlGaN etc. are under intense investigation[1-4] and widely applied for the blue and UV Light Emitting Diode since it has a band gap energy of the UV regions, which can be designed merely by controlling the composition of the solid solution between them. On the other hand, InN, which has a band gap energy of the IR region ~0.65eV, is far from practical application even though it has a unique properties of the high mobility of electrons and a promising material for the IR emitting/receiving optical devices.

One of a key issue for application of the InN is its instability against high temperature. Unlike the other nitride materials, the InN is known to be unstable at high temperature and therefore it is quite difficult to control crystal growth mechanisms of the InNs. On this regard, many efforts have been made for investigating crystal growth mechanisms and for producing structure designed InN nano structures. L-Weber et al., reported InN layers and InN nanorods grown on the c- and r-planes of sapphire, where InNs were epitaxially grown on those substrates by the MOVPE method[5]. Hu et al., reported fabrication technique for InN nanobelts using a guided-stream thermal CVD [6]. They also reported the nanobelt structures with 40 to 250 nm width and 10 to 35 nm thickness showed infrared lasing. As an example of a two dimensional growth of InN nanostructure, a heteroepitaxial growth of the InN was reported by Harui et al[7]. They reported position controlled InN nanocolumns grown by MOVPE method on a patterned GaN epitaxial layers grown on sapphire substrate, on which reticular patterns of holes were intentionally fabricated by a focused ion beam (FIB) before the InN growth. These reports involves interesting results, however, they still have grown the InN in one or two dimensional growth direction, i.e. the nanocolumns or films.

On the other hand in our previous reports, InN flower structures were successfully fabricated by Atmospheric Pressure Halide CVD (APHCVD) method [8-10]. Interestingly enough, it has three dimensionally uniform microstructures. In the present reports, we have fabricated the flower/pillar structured InN on Si(100) and/or a-plane sapphire substrate, respectively, in order to investigate the effect of the substrate on crystallization behavior of the InN crystals. Fabrication of pillar structure by controlling growth condition is not shown in this proceeding but will be presented at the conference site.

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### C26: Electrocaloric Refrigeration in Perovskite-structure Ferroelectric Materials

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Recently, increased attention has been paid on the electrocaloric effect (ECE) in ferroelectrics to explore a compact and environmental friendly solid-state cooling technology owing to its advantages of easy miniaturization, high efficiency, and low cost. The ECE refers to a reversible temperature and/or entropy change of a ferroelectric material during the application or removal of applied electric fields, which is a basic characteristic of ferroelectric materials. This presentation focused on the effect of phase transition character on the ECE, and demonstrated the ECE in various perovskite-structure ferroelectric materials, including BaTiO<sub>3</sub> (BT), (BaSr)TiO<sub>3</sub> (BST), (BaCa)(TiZr)O<sub>3</sub> (BCZT), Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> (NBT) and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PMNT).

For ferroelectrics with first ordered phase transition (FOPT), such as BT, the ECE always exhibits a giant value around the phase transition point. For example, a giant ECE strength of 0.48K·cm/kV was observed in a new BT single crystal just above the phase transition point. In a vicinity of a FOPT, the ECE is dominated by the phase transition entropy, which is several orders of magnitude higher than the polarization order entropy. If the FOPT is diffused gradually, the ECE peak turns wider and lower, but the ECE maximum also occurs around the phase transition temperature. In ferroelectric relaxors, the ECE may exhibit an optimized value around the morphortropic phase boundary (MPB). For ferroelectrics with FOPT, the different orientation does not change the phase transition characters and the ECE, but the case is different for the ferroelectric relaxors with MPB. If there are complex transitions between several ferroelectric and/or antiferroelectric phases with different dipole orientations, the ECE may exhibit negative values.

# C27: Doped-sepiolite for humidity and gas detection

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Sepiolite is a clay having the chemical formula Mg<sub>8</sub>Si<sub>12</sub>O<sub>30</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>.8H<sub>2</sub>O and it consists of octahedrally coordinated magnesium layers and tetragonally coordinated silicon layers with nano-sized channels containing water [1]. Acid treatment removes Mg2+ but leaves Si4+ in its tetrahedral layer [1]. This novel structure of sepiolite is of particular interest, since it can permit the insertion of other molecules into the channels. In our case, different oxides/hydroxides were precipitated under basic conditions (based on W<sup>4+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>,  $Gd^{3+}$ ,  $La^{3+}$ ,  $Mn^{2+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Sr^{2+}$ ,  $Y^{3+}$  and  $Zn^{2+}$ ions). This process allows to synthesize metal oxide nanoparticles fully dispersed onto the inert matrix.

First, the prepared powders were uniaxially pressed and heat treated at  $550 \,^{\circ}$ C for 1 h, before gold electrodes screen-printing. The humidity sensing properties of these sensors were then investigated at room temperature (Figure 1a &b). The sensor response (SR), expressed in %, was defined as the relative variation of the starting resistance, compared with the resistance measured under gas exposure (eq. 1):

$$SR(\%) = 100 \frac{|R_0 - Rg|}{R_0}$$
(1)

Where  $R_0$  and  $R_g$  are the starting (in the absence of the test gas) and the gas exposed measured resistances of the sensors, respectively. Among the studied compositions, tungsten-doped sepiolite showed a significant response towards humidity from 40% relative humidity (Figure 1). Response times were quite high, while recovery times were very short. The influence of leaching time onto the sensing properties of the final material has been investigated too.



**Fig1**. Sensors response to relative humidity after: a) Co<sup>2+</sup>, Cu<sup>2+</sup>, Gd<sup>3+</sup>, La<sup>3+</sup>, Mn<sup>2+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Sr<sup>2+</sup>, Y<sup>3+</sup> or Zn<sup>2+</sup> ions precipitation; b) W<sup>4+</sup> ions precipitation.

In a second moment, pure and zinc-doped sepiolites were screen-printed onto alumina

substrates and their sensitivity to NO<sub>2</sub> and H<sub>2</sub> was studied. As received sepiolite gave no response neither under NO<sub>2</sub> nor under H<sub>2</sub>, while zinc-doped one was sensitive towards both gases at 300°C. However, the presence of water vapor led to strong interferences as the sensor response was lower both under NO<sub>2</sub> and H<sub>2</sub>.

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### C28: Use of nanoparticles for improved ceramics: A case study of thermoelectric Bi<sub>2</sub>Ca<sub>2</sub>Co<sub>1.7</sub>O<sub>x</sub>

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Since the discovery of high thermoelectric (TE) properties in p-type Na<sub>x</sub>CoO<sub>2</sub> ceramic material [1], many works have been performed in CoO-based materials. Following these efforts, other members of this CoO family, as Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> or Bi<sub>2</sub>Ca<sub>2</sub>Co<sub>2</sub>O<sub>x</sub>, where discovered [2,3]. These materials possess attractive TE properties even if they are still low for their practical applications. As a consequence, many attempts are being made to raise their TE performances, evaluated through the dimensionless Figure-of-Merit, ZT (=S<sup>2</sup>T/ $\rho\kappa$ , where S, T,  $\rho$ , and  $\kappa$  are Seebeck coefficient, absolute temperature, electrical resistivity and thermal conductivity, respectively). In this expression, the electrical part, S<sup>2</sup>/ $\rho$  is called power factor (PF).

The improvement of these TE materials is usually performed in two main directions. The first

one exploits their anisotropic properties, by aligning the grains in the current flow direction to reach electrical TE properties comparable to those obtained in single crystals [4]. On the other hand, the second approach uses doping to modify the electrical properties but also to decrease the thermal conductivity and raise the ZT values [5].

In this work, a third approach, and much less exploited, will be performed by using synthesis methods which produce nanoparticles as starting materials, and compared with the results obtained by the classical solid state process, used as reference. Three different synthesis methods will be applied to the synthesis of Bi<sub>2</sub>Ca<sub>2</sub>Co<sub>1.7</sub>O<sub>x</sub> thermoelectric ceramics: coprecipitation with ammonium carbonate, coprecipitation with oxalic acid, and attrition milling. As can be clearly observed in Fig. 1, the use of nanoparticles as starting materials promote improvements in PF until about six times higher than the values obtained by the classical solid state route. All these TE results will be related with the miocrostructural evolution of the different samples.



**Fig1.** Power factor *vs.* temperature as a function of the synthesis method.

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# C29: Relaxor ceramics for new electrocaloric cooling technology

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The electrocaloric effect (ECE) has attracted great interest for developing new cooling devices that have the potential to reach better efficiency than the existing cooling technologies [1,2]. The direct confirmation of large ECEs in ferroelectric polymers and relaxor ceramic thin films have attracted great interest for developing new cooling devices that have the potential for miniaturization and application in microelectronic components cooling.

Recently, it was also shown that it can be exploited in studies of the electric field-temperature phase diagram of relaxor ferroelectrics [3,4] since the sharp discontinuous anomaly can be observed at the ferroelectric phase transition [5]. It was shown by direct measurements that the large ECE is common in polymer and ceramic relaxor ferroelectrics [6,7] and that the electrocaloric responsivity in relaxor materials is significantly enhanced in the proximity of the critical point similarly to the enhancement of the giant electromechanical response [8]. The high resolution electrocaloric measurements in the lead free BaTiO3 show that the highest electrocaloric response in classic ferroelectrics is achieved always at the temperature corresponding to the  $T_C(E=0)$ . A review of recent ECE findings obtained in polymeric and perovskite ceramic relaxor materials including thick ceramic multilayers, substrate-free thick films, thin films and liquid crystals will be given. Besides the recent advances in development of practical cooling devices utilizing different approaches and materials will be presented.

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### C30: Fabrication and performance of titanium oxide Magn di phase nanoceramics for thermoelectric applications

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This talk will focus on the thermoelectric properties of Magn di phase Ti<sub>5</sub>O<sub>9</sub> nano-ceramics investigated form room temperature to 973K. ZT values of 0.9 were measured at 973K and we will

discuss our modeling of the Seebeck coefficient and electrical conductivity in terms of small polaron hopping.

### C31: Structural Analysis of Carbon Spheres Synthesized by Hydrothermal Carbonization Process and its Capacitive Property

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Carbon materials have been widely used for energy and environmental field, such as electrode materials, catalyst supports and adsorbents. Many researchers focus on the control of carbon nanostructure in order to improve the specific surface area, porous structure and surface modification.

Carbon spheres are easily synthesized by hydrothermal carbonization of glucose in aqueous solution [1]. In this study, we carried out the structural analysis of carbon spheres synthesized by hydrothermal carbonization process. In addition, the capacitive properties of synthesized carbon spheres before and after heat treatment were measured.

The 1 M glucose aqueous solution was heated at 200  $\,^\circ$ C by using autoclave. After heating, the products were washed with distilled water and ethanol, and dried at 50  $\,^\circ$ C. The as-synthesized carbon spheres were heat-treated under N<sub>2</sub> flow at 200-1000  $\,^\circ$ C for 1 h. The morphology of products was observed by SEM. XRD, Raman, FT-IR and N<sub>2</sub> adsorption were measured in order to clarify the change in the internal structure of carbon spheres before and after heat treatment.

Figure 1 shows the SEM images of products synthesized by hydrothermal carbonization before and after heat treatment at 800  $^{\circ}$ C. When the glucose solution was heated at 200  $^{\circ}$ C for 5 h, carbon spheres of 50-100 nm in diameter formed. There was no

change in the morphology even after heat treatment of as-synthesized carbon spheres at 1000 %. According to XRD, FT-IR and N<sub>2</sub> adsorption, it was clarified that carbon spheres were more carbonized and the specific surface area was increased by heat treatment.

When heat treatment of synthesized carbon spheres was carried out at 800 °C, the capacitance was remarkably enhanced. This is due to the improvement of carbon structure by heat treatment. The change in carbon structure and the enhancement of capacitive property after heat treatment will be discussed in presentation.



**Fig.1** SEM images of products synthesized by hydrothermal carbonization (a) before and (b) after heat treatment at 800  $^{\circ}$ C.

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### C32: The potential applications of luminescence nanomaterials for energy harvesting from sunshine and radiation sources

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Persistent luminescence or afterglow materials can give out luminescence or light after activation. It has been reported that the longevity of some afterglow can last for a few hundred hours and sunlight or high energy radiation beams can be absorbed by these materials for activation. In this presentation. the mechanisms of persistent luminescence are introduced and the strategies for the design and synthesis of afterglow nanoparticles are described. Then the potential applications of afterglow nanomaterials for solid state lighting, emergency indicators, security are described. New development for using afterglow nanoparticles to improve photosynthesis and crop productivity, the applications of afterglow nanoparticles for photodynamic activation for cancer treatment and light-sensitive drug delivery are introduced. A new hot topic is the application of afterglow for solar cell enhancement which is also illustrated, and in the last part, the combination of light harvesting and heat harvesting for electricity is introduced. These new concepts of energy harvesting may provide some good solutions for the foreseen energy crisis in the future and are new applications of nanomaterials.

# **D18:** Strategies for enhancing the thermoelectric performance of oxides

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We use first-principles calculations to develop strategies for improving the thermoelectric response of selected oxides. The talk first focusses on substitutional doping in prototypical  $SrTiO_3$ , in particular on the consequences of induced spin polarization. In addition, we take into account uni-axial and bi-axial strain. The second part of the talk deals with the thermoelectric properties of the layered rhodates  $K_xRhO_2$  and  $Na_xRhO_2$ , for which the roles of the cation concentration and the lattice parameters are being investigated. Comparison of 2H and 3R phases (modified stacking of the atomic layers) provides insight into the effect of the interlayer coupling.

# D19: Diffraction, *ab-inito* calculations and elastic constants of the MAX phases Ti<sub>3</sub>XC<sub>2</sub>, X=Si,Al

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 $M_{n+1}AX_n$  Phase Ceramics are referred to more commonly as MAX phases where M is an early transition metal, A is a group IIIA or IVA element, and X is C and/or N. These materials possess the desirable properties of metals (good thermal and electrical conduction, machinability, and thermal shock resistance) and ceramics (good resistance to chemical attack, oxidation and creep) [1], leading to potential applications in industries such as energy generation, chemical processing, and medicine [2].

The first comparison of an experimentally measured phonon Density of States (DOS) for Ti<sub>3</sub>SiC<sub>2</sub> to DFT lattice dynamics and DFT-MD simulation was presented by Kearley et al. [3]. The inelastic neutron scattering (INS) was measured on TOSCA at the ISIS facility using a sample prepared by self-propagating high-temperature synthesis. Above an energy transfer of 25meV the experimentally observed spectrum more closely resembles the MD augmented simulation. From the DFT-MD simulation it can be concluded that the mismatch between spectra is likely due to anharmonic motion or anharmonic atomic potentials between Si and Ti.

To further understand the observed mismatch between calculations and experiments the phonon DOS of both  $Ti_3SiC_2$  and  $Ti_3AlC_2$  were taken covering 0-70meV using the PHAROS spectrometers at LANSCE focusing on the low energy regime of the inelastic spectrum, which is closely related to the acoustic phonons. For  $Ti_3SiC_2$ , measurements were taken at temperatures of 10, 30, 50 and 70K to allow comparison with DFT lattice dynamics (0K) and DFT-MD (30K, 50K and 70K) simulations.

By comparing experimental measurements to simulations and DFT-MD simulations, in particular in case of  $Ti_3SiC_2$ , the anharmonic motion of Si in case of  $Ti_3SiC_2$ , and apparent harmonic motion of Al in case of  $Ti_3AlC_2$ , has been identified.

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D20: Ferroelectric nanodomain dynamics in morphotropic phase boundary piezoelectrics studied via in-situ transmission electron microscopy

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Morphotropic phase boundary ferroelectrics are known to exhibit superior piezoelectricity and is used for practical applications. One of the structural feature of these systems is that the ferroelectric domain structure scales down to nano-meter level. Here, two questions arose to us. One is crystal structure of single nanodomain is really of monoclinic phase as was reported by diffraction study that measured averaged structure over micron scale [1]. The other is how the nanodomains respond to external electric field. In order to address these issues, we have carried out transmission electron microscopy (TEM) studies to a typical morphotropic phase boundary ferroelectric, PMN-PT (Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> - PbTiO<sub>3</sub>)) [2-4].

Figure 1 shows the electron diffraction pattern measured from the area including two nanodomain component [2]. Two distinct spots are observed clearly. And, careful analysis of the position of individual spots suggests that the crystal structure of nanodomain would be of monoclinic phase [2]. On the other hand, *in-situ* TEM studies have clearly visualized domain response in PMN-PT [3,4]. Detail about these results will be given in my talk.



**Fig1**. Electron diffraction pattern taken from morphotropic phase boundary PMN-PT [2].



Fig1. Electron diffraction pattern taken from morphotropic phase boundary PMN-PT

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#### **D21: Ferroelectricity in Bismuth Silicate**

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To date, ferroelectric materials have been widely applied in various electronic devices, including actuators, non-volatile memory, and sensors. Ferroelectric materials traditionally comprise oxygen octahedral units, such as those found in perovskite-type oxides. The strong covalency of the cations in the perovskite structures plays an important role for achieving robust ferroelectricity with a high- $T_c$  and a large spontaneous polarization. With this in mind, recent ferroelectric devices typically rely on the use of lead-based compounds such as  $Pb(Zr,Ti)O_3$ (PZT) to achieve such robust ferroelectricity. Mindful of the toxicity of Pb, there is increasing demand for sustainable and an environmentally friendly electronic devices, free from toxic elements. As such, a new guiding principle for designing ferroelectric materials is necessary.

Here we demonstrate the occurrence of ferroelectricity in a silicate-based compound, Bi<sub>2</sub>SiO<sub>5</sub>, by direct observation of polarization switching. The novel mechanism of ferroelectricity in Bi<sub>2</sub>SiO<sub>5</sub> has been elucidated from comprehensive studies employing Raman scattering, transmission electron microscopy, X-ray powder diffraction, and principles calculations. The obtained first experimental results and calculations clarified that the observed ferroelectricity in Bi2SiO5 stems from twisting of the one-dimensional SiO<sub>4</sub> tetrahedral chain.[1,2] This recent discovery opens up a new frontier for designing functional oxides based on "tetrahedra-engineering", as opposed to conventional "octahedra-engineering". Furthermore, it also provides a guiding principle for the development of sustainable and environmentally friendly electronic and electro-mechanical devices, as compounds comprising tetrahedral chains are widely found in rock-forming oxides, which are abundant in the earth's crust.

#### Acknowledgements

A. Kuwabara and H. Moriwake (Japan Fine Ceramics Center), J. Kim, Y. Kim, and M. Takata (Spring-8, RIKEN), S. Kim (Sungkyunkwan Univ.), S. Mori (Osaka Pref. Univ.), Y. Inaguma (Gakushuin Univ.), and H. Hosono and M. Itoh (Tokyo Inst. Tech.).

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# D22: Doping structures and luminescence properties of SiAlON:Ce and SiAlON:Eu ceramics

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Effects of doping structures on the luminescence properties in Ce and Eu doped  $\alpha$ -SiAlON ceramics have been examined via atom-resolved Cs-corrected scanning transmission electron microscopy (STEM), cathodoluminescence (CL) spectroscopy in SEM and image simulations. Ce<sup>3+</sup> ions are found to locate inside the  $\alpha$ -SiAlON crystal lattice at a site close to the center of structural interstices. The stability and solubility of Ce<sup>3+</sup> ions could be remarkably enhanced via congregation into the planar defects formed by a 1/3<210>-type lattice displacement along with an inversion operation. The formation of cylindrical chambers near the faults is believed to provide effective structural relaxation upon doping of large rare-earth ions into the interstices in their neighborhoods. SEM-CL microanalyses revealed enhancement of emission at fault sites with a wide dimension (Fig. 1) while quenching occurs at zigzag shaped faults where more partial dislocations are present. Compared to Ce doped  $\alpha$ -SiAlON, the Eu doped ceramics contain more faults of wavy and zigzag shapes hence exhibit lower critical doping concentration for quenching.



Fig1. Enhanced emission at broad faults.

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# D23: Effects of Microstructure on Conductivity of Narpsio Glass-Ceramics

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Glass-ceramics of the phosphorus containing Na<sub>5</sub>RSi<sub>4</sub>O<sub>12</sub>(N5)-type (R=rare earth) Na<sup>+</sup>-superionic conductors have been developed by crystallization of glasses with the composition  $Na_{3+3x-y}R_{1-x}P_ySi_{3-y}O_9$ (Narpsio). These materials are comparable to the conventional ceramic Na<sup>+</sup>-conductors such as NASICON,  $\beta$ - and  $\beta$ "-aluminas (e.g., NaAl<sub>11</sub>O<sub>17</sub> and NaAl<sub>5</sub>O<sub>8</sub>). Our phosphorus containing compositions have been confirmed superior to the mother composition of N5-type, especially in the production of the single-phase glass-ceramics. Considering the inference, our main work has recently been focused on the synthesis of various glass-ceramics with N5-type single-phase. In the present study, the glass-ceramics of the phosphorus containing N5-type Na<sup>+</sup>-superionic conductors were prepared by

crystallization of glasses, and the influence of the crystallization conditions on the conduction properties of the glass-ceramics were discussed.

The precursor glasses were made by melting stoichiometric mixtures of reagent-grade powders of anhydrous Na<sub>2</sub>CO<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and SiO<sub>2</sub> at 1300~1400 °C for 1 h. The temperatures employed for nucleation and crystallization of glass specimens were also determined by DTA analysis. Crystalline phases were identified by the X-ray diffraction (XRD) method. Ionic conductivities of sintered disks were measured by the ac two-probe method with Au-sputtered blocking electrodes with LF impedance analyzer. The temperature dependence of the conductivity was measured in a similar way at several temperatures ranging from room temperature to 350 °C.

Glass-ceramic N5-type Narpsio conductors were successfully produced while changing the crystal growth time. Figure 1 shows the measured conductivities ( $\sigma_{300}$ ) for total, grains and grain boundaries of the glass-ceramics. The microstructural effects on the conduction properties, which were dependent upon the heating conditions of crystallization, were understood in relation to the grain and grain boundary conduction properties.



Fig. 1 Ionic conductivities of Narpsio glass-ceramics (300 ℃).

### **D24:** Transparent Ceramic Scintillators: Compositional Stability, Fabrication, and Scale-Up

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As a relatively new class of optical materials, fabrication of transparent polycrystalline ceramics with high optical transparency and production of large, commercial-size ceramic optics is an evolving field of research. Compared to single crystals, transparent ceramics offer improved mechanical properties, and fabrication cost is significantly reduced. At Lawrence Livermore National Laboratory, we are developing scalable fabrication techniques for two transparent ceramic scintillators, with applications in gamma spectroscopy and X-ray computed tomography imaging.

Gadolinium based garnets, GYGAG(Ce) were  $Gd_{3-x}Y_{x}(Ga,Al)_{5}O_{12}(Ce),$ or down-selected from a broad list of cubic oxide candidates as a high-performing scintillator for gamma spectroscopy, offering high light yield, high effective Z, and fast decay time [1,2]. While performance degradation of large scintillator optics is often problematic in single crystal scintillators, due to gradients in dopants and composition, transparent ceramics offer a route to highly uniform doping throughout the volume of even very large size samples. As a result, we obtain energy resolution of R(662 keV) = 4.6% for >1 in<sup>3</sup> size GYGAG(Ce) ceramic scintillators. Further scale-up is in progress.

For MeV X-ray computed tomography imaging, lutetium-based bixbyites doped with europium,  $Gd_{2-x}Lu_xO_3(Eu)$  or GLO(Eu), were selected for their high light yield, density and effective Z [3,4]. In comparison to CsI(Tl) and CdWO<sub>4</sub>, much larger, optically contiguous plates can be obtained by ceramics processing. With a melting point of 2,490 °C, melt growth of Lu<sub>2</sub>O<sub>3</sub> and related crystals is
not feasible. Transparent ceramic GLO provides a combined improvement in stopping power and light yield, compared to scintillator glasses, the other option for large optically transparent windows.

Ceramics with low optical scatter may be formed by vacuum sintering and hot isostatic pressing to full density for ~1 cm<sup>3</sup>-scale samples. However, upon scaling up to larger sizes (>10 cm<sup>3</sup>), the volumetric shrinkage during sintering becomes increasingly difficult to accommodate without accumulated stress and eventual cracking. To overcome this dimensional obstacle, we implemented an intermediate hot pressing step as the compact is formed, allowing the first stages of sintering to occur while under pressure, resulting in a higher green strength and a density closer to 60% (Fig. 1). Using this technique we have successfully produced a 10 inch transparent bixbyite ceramic window and a highly transparent 5 cubic inch garnet.



Figure 1. Fabrication methodology for large ceramics.

#### Acknowledgments

This work was performed under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344, and was supported by the U.S. Department of Homeland Security, Domestic Nuclear Detection Office, under competitively awarded IAA HSHQDC-12-X-00149, and the US DOE, Office of

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#### D25: Brazing of SiC/SiC composite by dicilides

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The present work is part of the Fourth Generation reactors program where is described the methodology and the results for joining SiC substrates by metallic silicides with SiC powder reinforcements. The more severe temperature in service are in the range of  $1000 \,^{\circ}$ C but short time incursions at 1600 or 2000  $^{\circ}$ C have to be anticipated. One of the key issues is the joining of the SiCf/SiCm composites to seal the combustible cladding.

We describe the results for joining SiC and SiCf/SiCm plates at liquid state using disilicides. Joint integrity and joint strength can be improved by adding small SiC particles to the silicides powders. The assemblies have been performed in an inductive furnace. Wettability tests and thermo-mechanical properties analysis have been carried out on the joints and will be introduced. Cross sections of the assembly were prepared to study the joint/substrate chemical bonding, the cracking and the crack deflection in the vicinity of the interface. Post thermal treatments in the solid state performed under a controlled atmosphere have been carried out in order to study the thermal stability of the assembly. Finally, results on 4-bending point mechanical tests will be presented to validate the compositions.

#### **D26:** Thin Film Dielectrics BaTiO3-Ceramics Improved Capacitors Fractal Nature

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The impact of fractal nature geometry on electronic components and deep level electronic circuit integration records a notable increment in recent literature. This contribution is an intention to suggest a methodic way for versatile class of new capacitors' shapes based on fractal curves and intergranular thin film ceramics dielectrics. Our experimental work is done mostly on BaTiO<sub>3</sub> and silicates ceramics with additives (CeO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, MnCO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, CaZrO<sub>3</sub>, Dy, La, Er<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>,  $Ho_2O_3$  etc.). The advantage of this suggestion is its fair simplicity and flexibility in choice among practically unlimited set of forms and considerable increasing of capacity because of fractal surfaces growth impact on super microcapacitors energy and especially an energy storage. The fractal correction coefficient that encounters BaTiO3-ceramics fractal morphology coming separately from grains and pores plus dynamics complexity caused by the flux of different micro particles. This is a new frontier door for developing new, fractal electronics.



Fig1. Fractal model of an intergranular microcapacitor.

## D27: Evaluation of Point Defects in Novel BaTiO<sub>3</sub>-based Ceramics with High Permittivity and Dielectric-Temperature Stability

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For novel rare-earth-doped BaTiO<sub>3</sub> ceramics with high [1-3]permittivity and dielectric-temperature stability [4–6] that were developed using the solid state reaction method, the point defects were identified with the aid of electron paramagnetic resonance (EPR), X-ray diffraction (XRD), and Raman spectroscopy [1–12]. These point defects includes Ba vacancies [4,7,8], Ti vacancies [1,6,7,9,11,12], and doping ions [1-12]. The visible [2,9,11,12] or thermally accessible [6] EPR signals of some rare earth Kramers ions along with the type of vacancy defects [1–12] provide the evidence for their valence states and site occupation of doping ions.

Figure 1 shows the EPR signals of intrinsic Ba vacancies [4] and Ti vacancies [7], Er/Dy-induced Ba vacancies [4,8], Eu<sup>2+</sup> (4f<sup>7</sup>) [2] and Tb<sup>4+</sup> (4f<sup>7</sup>) Kramers ions [12], and thermally accessible  $Pr^{4+}$  (4f<sup>1</sup>) [6] in undoped and doped BaTiO<sub>3</sub> ceramics.



**Fig1.** EPR signals of (1) Ba and Ti vacancies, (2) Er/Dy donors induced Ba vacancies, (3)  $Eu^{2+}$  and (4)  $Tb^{4+}$  Kramers ions, (5) thermally accessible  $Pr^{4+}$ .

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## **D28:** Sub-stoichiometric functionally graded titania fibres for water-splitting applications

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The photo-electro-chemical (PEC) splitting of water requires semiconductors with a minimum energy gap of 1.23eV and with conduction and valence bands overlapping the oxidation of H<sub>2</sub>O and the reduction of H<sup>+</sup> respectively. Titania (TiO<sub>2</sub>) has been extensively investigated as photo-anode for PEC water splitting due to its suitable band-edge positions, chemical resistance, environmental suitability and low cost. The main limitations of stoichiometric TiO<sub>2</sub> are its large band gap (3.2 eV) and electron-hole recombination. However, previous work on Ti-suboxides has shown that it is possible to control the extent of oxygen vacancies and the electrical conductivity can be altered from  $10^{-9}$  S/m (TiO<sub>2</sub>) to  $10^4$  S/m (Magn di phases) [1].

The approach of this work is to overcome the limitations of stoichiometric titania by manufacturing fine scale fibres (500 µm) that exhibit a compositional gradient of oxygen vacancies across the fibre length (Fig. 1a). In such a fibre configuration the end of the fibre reduced to a relatively low extent (left hand side of Fig 1a) performs as the photoanode and the oxygen vacancies enhance the absorption of light. The heavily reduced fibre end (right hand side of Fig.1a) consists of Magn di phases and exhibits metallic like electrical conductivity that enhances the electron-hole separation. This conductive end is bonded with Ag wires using Al paste; which is known to exhibit

ohmic behaviour [1]. The structure of the functionally graded fibres, which have been manufactured through carbo-thermal reduction, is studied using XRD and electron microscopy. The PEC measurements were performed in a three-electrode electrochemical system, using Ag/AgCl as reference electrode and a Pt wire as counter electrode. Linear sweeps were collected from a single fibre electrode in 1M KOH electrolyte under five different wavelengths (368, 455, 525, 590 and 618 nm) at various intensities using an array of LEDs (ENGIN LED). The efficiency of the system was evaluated at different wavelengths together with the effect of the increasing intensity on the photocurrent. Fig.1b presents the current density under UV light (368nm) at 160mW.

#### Acknowledgements

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement no. 320963 on Novel Energy Materials, Engineering Science and Integrated Systems (NEMESIS).





**Fig. 1**: (a) Ti-suboxides fibres with a compositional gradient of oxygen defects across its length. Dark regions of fibre on the right correspond to greater degree of reduction and high oxygen vacancy content. (b) Photocurrent density under UV light (368nm) at 160mW.

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## **D29:** Critical Issues of Ceramic Injection Molding Feedstocks

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Efficiency of ceramic injection moulding is to a great extent limited by material components' separation during processing. It originates from the high shear rates gradients located close to the walls of injection molding cavities. Resulting inhomogeneous redistribution of ceramic powder (ZrO<sub>2</sub>) within a polymer binder based on polyolefins, polyethylene glycol and waxes is evaluated with the help of specially developed testing mold allowing observing the progress of separation during injection molding. [1]

In this contribution we focus on testing the method, recently developed [2] for quantification of the separation for commercially available metallic feedstocks, on fine ( $D_{10} - 1.69 \ \mu m$ ,  $D_{50} - 3.24 \ \mu m$ ) ZrO<sub>2</sub> based feedstocks. The approach results in a single characteristic parameter, which help to predict the structure defects as unacceptable porosity and/or cracks arising from injection molding affected by separation.

The scanning electron microscopy (SEM, VEGA II LMU, TESCAN) of the particular areas derived from the testing mold is combined with energy dispersive X-ray (EDX) analysis of the distribution of elements typical for powder (zirconium). SEM images of molded parts were taken at the magnifications 78, 94 and 115 times according to the size of the particular square element of the testing mold, and accelerating voltage of 30 kV with BSE detector. Data collection for EDX was 20 times. The size of EDX maps were (2.8x2.8) mm on the first element and then gradually decreased to (2.4x2.4)mm and (1.9x1.9) mm on the second and third elements, respectively. EDX quantification maps were derived with a resolution (128x128) pixels, representation of elements is expressed as weight % (wt%). SEM images (Fig.1 - left) and EDX maps (Fig. 1 - middle) of separated samples are shown below. Bright points represent powder and dark points represent binder. Also quantitative X-ray mapping was created, Fig. 1 - right.



Figure 1. SEM and EDX maps of ZrO<sub>2</sub> feedstock (first element of testing mold cavity).

Then, an analytical approach was employed to derive a quantitative parameter describing the tendency of highly filled feedstocks to the separation -a variability number. The rate of the phase separation represents non-uniformity of powder and binder distribution, i.e. non-uniformity of bright and dark points on EDX maps. The low and uniform variability anticipates an efficient PIM process without defects arising from the separation. The variation in zirconium is stable through the testing positions in the mold and reach the value  $16\pm 5$ 

corresponding to fluctuations in the zirconium concentration about 70-75 %. The result is confronted with the surface appearance of the final parts (after polymer extraction and sintering) evaluated with the help of a contactless CLA scanner.

#### Acknowledgements

Operational Program Research and Development for Innovations co-funded by the ERDF and national budget of Czech Republic, within the framework of project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111)is acknowledged for the financial support. This study was also supported by the internal grant of TBU in Zl ń IGA/FT/2015 funded from the resources of specific university research.

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## D30: Diffusion and reactions of interstitial excess oxygen species in amorphous SiO<sub>2</sub>

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Oxygen atoms  $(O^0)$  are among the most important reactive oxygen species in excess oxygen

species in amorphous SiO<sub>2</sub> (*a*-SiO<sub>2</sub>) and are considered to play a crucial role in various reactions in *a*-SiO<sub>2</sub>. For example, oxidation of silicon with O<sup>0</sup> is faster than that with oxygen molecules (O<sub>2</sub>) and enables low-temperature synthesis of dielectric *a*-SiO<sub>2</sub> films. Theoretical studies have predicted that interstitial O<sup>0</sup> is readily incorporated into the framework of *a*-SiO<sub>2</sub> and forms peroxy linkages (POL,  $\equiv$ Si-O-O-Si $\equiv$ ). However, interstitial O<sup>0</sup> in *a*-SiO<sub>2</sub> is difficult to study experimentally because of the lack of distinct spectroscopic signatures. Isotope labeling, which is a powerful tool for investigating diffusion and reactions of chemical species, has also not been used to study interstitial O<sup>0</sup> in *a*-SiO<sub>2</sub>.

To gain insight into the properties and reactivities of interstitial  $O^0$  in *a*-SiO<sub>2</sub>, we combined three techniques, which we developed to study excess interstitial oxygen species in  $a-SiO_2$ : the efficient formation of interstitial  $O^0$  via  $F_2$  laser (hv = 7.9 eV) photolysis of interstitial  $O_2, [1,2]$ a photoluminescence (PL) technique to measure the <sup>18</sup>O fraction of interstitial  $O_{2}$ ,[3,4] and the synthesis of oxygen excess a-SiO<sub>2</sub> containing <sup>18</sup>O-labeled interstitial O<sub>2</sub>.[5] Figure 1 shows schematic illustration of diffusion and reactions of interstitial O<sup>0</sup> in a-SiO<sub>2</sub> photogenerated by F<sub>2</sub> laser photolysis of interstitial <sup>18</sup>O<sub>2</sub> at 77K.[6] At the initial stage of the low-temperature F<sub>2</sub> laser photolysis, an efficient formation of interstitial ozone (O<sub>3</sub>) molecules vield ≥0.06) of (quantum via permeation  $\mathbf{O}^0$ photogenerated interstitial without network-interstitial oxygen exchange is observed. Subsequent extended F<sub>2</sub> laser irradiation at 77 K and heat treatment at  $\gtrsim 200$  °C give rise to oxygen exchange between residual interstitial O<sub>2</sub> and oxygen atoms in the a-SiO<sub>2</sub> network, and these temperatures are far lower than the temperature at which conventional thermal network-interstitial oxygen exchange in unirradiated a-SiO<sub>2</sub> occurs ( $\gtrsim$ 700 °C [5]). These observations indicate the presence of two different diffusion modes of interstitial O<sup>0</sup>, i.e., migration of photoexcited O<sup>0</sup> without exchange with

the Si–O–Si network at 77K and thermal diffusion of interstitial  $O^0$  as POL at  $\gtrsim 200$  °C.



**Figure 1**. Schematic illustration of formation of interstitial <sup>18</sup>O<sub>3</sub> via exchange-free diffusion of interstitial <sup>18</sup>O<sup>0</sup> created by F<sub>2</sub> laser photolysis of interstitial <sup>18</sup>O<sub>2</sub> at 77K, thermal decomposition of interstitial O<sub>3</sub> at 100–200 °C, and recovery of interstitial O<sub>2</sub> via diffusion of interstitial O<sup>0</sup> as POL at  $\gtrsim$ 200 °C, which is accompanied by the oxygen exchange between POL and preexisting interstitial O<sub>2</sub>.

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## D31: Colloidosomes and Diamondosomes: Multifunctional Inorganic Microcapsules

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The preparation of multifunctional microcapsules in the submicrometer range is one of the main challenges for producing carrier systems for theranostic nanomedicine. A variety of strategies and materials exist for the generation of capsules for diverse applications. Ideally, a microcapsule could be produced with properties that would be chosen from a construction kit of components which can be assembled to from a multifunctional, tailored carrier system. A specific type of microcapsule, the colloidosome, consists of a shell assembled from microcarriers nanoparticles. These can be self-assembled from a wide range of colloidal particles with selective chemical, physical, and morphological properties and show promise for application in the field of theranostic nanomedicine. Previous studies have mainly focused on fairly large colloidosomes (> 1 mm) based on a single kind of particle; however, the intrinsic building-block nature of this microcarrier has not been exploited so far for the introduction of tailored functionality at the nanoscale. We report a synthetic route based on interfacial shear rheology studies that allow the simultaneous incorporation of different nanoparticles with distinct physical properties. We present the synthesis of colloidosomes that include both superparamagnetic iron oxide and fluorescent silica nanoparticles in a single submicron colloidosome. Additionally, we used nanodiamonds to prepare colloidosomes with enhanced shell stability. These tailor-made microcapsules can potentially be used in various biomedical applications, including magnetic

hyperthermia, magnetic particle imaging, drug targeting, and bioimaging.



**Fig1**. (A) Concept sketch of a multifunctional colloidosome; (B-E) submicron colloidosomes prepared from (B) silica and (C) nanodiamond.

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## D32: Noble metal loaded ceramic nanocomposites for solid state moisture sensing studies

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Ceramic humidity sensors based on porous and sintered metal oxides have attracted attention due to their chemical and physical stability and mechanical strength [1]. These materials possess a unique structure consisting of grains, grain boundary surfaces and pores, which make them suitable for this kind of sensors. Sensing mechanism of metal oxide based humidity sensors lies in changes in oxide resistance resulting from physisorption, chemisorptions and catalytic reactions of gas phase species at the surface of the semiconductor devices. With the aim of achieving improvements in their sensing properties, small amounts of noble metals are added to metal oxide active layers. Metal additives dispersed in the oxide matrix act as activators or sensitizers. Addition of a noble metal results in changes in the electronic states of the active layer and can also modify the microstructure of the base material. All of these strongly influence sensor performance [2-3]. Samples with 0-4% Ag doped in WO<sub>3</sub> (AW-0, AW-1, AW-2, AW-3, AW-4) were tested. Figures 1 depicts humidification graphs for sintering temperature  $700 \, \text{C}$  for relative humidity range 20-90%. Reduced aging and hysteresis were observed with noble metal additive. XRD pattern showed formation of Ag:WO<sub>3</sub> bronze, viz. hexagonal tungstite and orthorhombic silver tungsten oxide  $(Ag_8W_4O_{16}, Ag_2W_2O_7)$ , anorthic silver ditungstate (Ag<sub>2</sub>WO<sub>4</sub>) due to intercalation of silver atoms into the WO<sub>3</sub> tunnel. Figures 2 shows SEM micrograph of sensing element of 4% Ag doped WO<sub>3</sub> sintered at temperature 700°C. WO<sub>3</sub> mixed with Ag powder has a grain like morphology. Upon treatment of heat, clusters of Ag are formed at the surface of the WO<sub>3</sub> grains. Ag:WO<sub>3</sub> bronze forms at the interface between the grains and the clusters due to diffusion of Ag in WO<sub>3</sub>. As the doping percent of Ag in WO<sub>3</sub> is increased there is an evolution in the distribution of the grain size, and that the crystallinity increases with increase in the % of Ag in WO<sub>3</sub>.



**Fig 1**. Variation of resistance of sensing elements with relative humidity for increasing cycle of relative humidity. **Insert:** Variation of grain size of Sensing elements with % loading of Ag in WO<sub>3</sub>.



Fig 2. SEM micrograph of sensing element AW-4.

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### D33: Fully Dense Single Phase Nanocrystalline Ceramics by Enhanced High Pressure Sintering

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nanopowder consolidation techniques Few permit the possibility of producing large ceramic components  $(\geq 1 \text{ cm}^3)$  while simultaneously retaining truly nano length scales (<50nm). Many oxide nanopowder consolidation techniques often produce ceramics that have coarsened dramatically or contain significant porosity. Previous success has been achieved by novel means, including the formation of composite or dual-phase structures where small secondary phases pin grain boundaries to retain nanoscale structures. However, such produced materials limit the exploration of fundamental nanoscale phenomena. We present an integrated approach to high-pressure consolidation that permits processing of oxide nanopowders into bulk fully dense three dimensional nanostructured ceramics. results producing Recent fully transparent nanocrystalline magnesium aluminate spinel ceramics suggest that Hall-Petch type (strengthening via grain size reduction) relations exist at least down to 30nm [1]. The nanocrystalline ceramics are colorless, transmit in the visible and infrared wavelengths, and boast hardness for the spinel in excess of 20 GPa (Fig. 1).



**Fig. 1**. Hall–Petch plot comparing Vickers hardness and grain size for magnesium aluminate spinel ceramics.

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# **B30:** Ag nanoparticle deposition on TiO<sub>2</sub> nanostructures for efficient photoelectric conversion

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Photovoltaics is now taking part in the global movement from fossil fuels to renewable sources. Dye-sensitized solar cell (DSSC) has been recognized as a probable competitor to the widely used but relatively expensive solar cells including silicon, and copper indium gallium diselenide (CIGS) due to its lower cost and easy fabrication on flexible substrates [1]. The power conversion efficiency of DSSC has now reached 12.3% [2], which is still less than half of the high-efficiency solar cells mentioned above.

DSSCs are generally composed of a photoanode consisting of anatase nano-particulate film with thicknesses of > 10  $\mu$ m on a transparent conducting oxide (TCO) glass substrate supporting a monolayer of a dye, a platinum foil or a platinum coated-TCO glass counter-electrode, and an iodide electrolyte between them. The electrons generated in the dye by light irradiation are injected into the anatase nano-particulate film, and then diffuse through the nanoparticle network in the film before reaching to the TCO substrate. Therefore an increase in the TiO<sub>2</sub> film thickness significantly increases electrical resistivity of DSSCs, though thick TiO<sub>2</sub> films are generally employed to enhance light harvesting ability.

In order to achieve high energy conversion efficiency of DSSC with thinner TiO<sub>2</sub> films thickness, vertically aligned TiO<sub>2</sub> architectures such as nanorod and nanotube arrays that offer longer electron diffusion lengths and shorter electron transport time have been investigated. Among various architectures, the most promising one for solar energy conversion appears to be TiO<sub>2</sub> nanotube arrays prepared through anodization of titanium [3]. The 3 times longer electron diffusion length in TiO<sub>2</sub> nanotube arrays than nano-particulate films was recently revealed [4]. However, the highest power conversion efficiency of DSSCs with TiO<sub>2</sub> nanotube arrays reported so far is only 6.9%, which is about half of DSSCs with conventional  $TiO_2$  nano-particulate films [5]. The authors of the paper concluded that the major issue that limited the conversion efficiency was the low fill factor, which was obtained from the degradation of the fluorine-doped tin oxide (FTO) substrates. This degradation of FTO occurred during long-term heat treatment at high temperature which was necessary to improve crystallinity of TiO<sub>2</sub> nanotube arrays with the length of 17.6 µm, which is about 5 times longer than TiO<sub>2</sub> nanotube arrays commonly fabricated by anodization.

In this work, Ag nanoparticles were deposited on the wall of the  $TiO_2$  nanotube arrays on FTO substrates. Ag nanoparticles exhibit localized surface plasmon resonance (LSPR) that strongly absorbs and scatters photons compared to dyes and TiO<sub>2</sub>. The enhanced electric field by LSPR of Ag nanoparticles efficiently excites electrons in neighboring dyes. The photon scattering phenomenon by LSPR works as mirror-like scattering layers, which also enhances light harvesting ability of DSSCs. DSSCs with the TiO<sub>2</sub> nanotube arrays on FTO as photoanode were fabricated and the effects of Ag nanoparticle deposition onto the arrays on the performance of DSSCs were investigated.

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## **B31:** Compressive Behaviour of Hollow and Porous Ceramic Spheres in Metal Matrix Syntactic Foams

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Metal matrix syntactic foams are composite materials consisting of a continuous metal matrix embedded with hollow or porous ceramic particles. They have higher strengths than polymeric syntactic foams and can be used as lightweight structures at higher temperatures and in more harsh environments. They are also capable of absorbing impact energies, because the porosity contained in the ceramic particles can provide extensive strain accumulation. Compared with metal foams with the same alloy matrix, they are usually cheaper to produce and have higher yield strengths. They have great potential for applications as energy absorbers where a high plateau stress is desirable.

Different compressive deformation behaviours and failure mechanisms have been observed in metal matrix syntactic foams [1]. Both ductile failure and brittle fracture are common, as shown in Figure 1. The ductile deformation of the syntactic foam is due to the crushing of the embedded ceramic particles and the subsequent collapse of the metal network. The brittle fracture can be attributed to shear failure or Griffith rupture. The are key The nature of the failure is critically dependent upon the porous structure of the ceramic particles and their strength.

This presentation reviews the roles played by the ceramic particles in the behviour of metal matrix syntactic foams under compression. Hollow ceramic particles generally have a higher strength than porous particles. However, they tend to be shattered when the pressure on them exceeds their strength. As a consequence, the resultant metal matrix syntactic foam is more apt to brittle fracture. The dominant failure mechanism is often brittle Griffith rupture with the cracks inclined at an angle close to 30° to the loading direction. In contrast, porous ceramic particles have a lower strength than hollow particles and collapse gradually under pressure. The resultant metal matrix syntactic foam generally undergoes plastic deformation without disintegration under compression.



**Fig. 1**. Macrographs of longitudinal cross sections of two syntactic foams compressed to a strain of 0.2, showing different failure mechanisms: (left) progressive collapse; (right) brittle rupture [1].

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## **B32:** Strategies for Preparing CNT-Ceramic Composites with High Toughness and Good Resistance to Friction and Wear

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Carbon nanotubes (CNTs) show some characteristics such as lightness and a very high length/diameter ratio as well as physical and mechanical properties that make them interesting for ceramic-matrix composites applications [1, 21. notably when high toughness and self-lubrication are required. Moreover, the presence of CNTs induces changes in the sintering kinetics and mechanisms, which can greatly modify the matrix microstructure, which may in turn have a greater effect on the properties than the actual presence of CNTs.

Key parameters related to the CNTs include the number of walls, length and covalent or non-covalent functionalization. The influence of some parameters on the SENB toughness and on the resistance to friction and wear of CNT-oxide composites will be discussed. Results on CNT-MgO [3], CNT-Al<sub>2</sub>O<sub>3</sub> [4], CNT-ZrO<sub>2</sub> [5] and CNT-mullite [6] composites will be presented. The composite powders are prepared either by the *in situ* formation of the CNTs within the oxide grains or by mixing routes. Densification is achieved by spark plasma sintering.

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## **B33:** Platinum-doped Tin Oxide Nanoparticles as efficient Catalyst for Methane Oxidation

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Tin oxide (SnO<sub>2</sub>) is an important metal oxide semiconductor with high band gap energy (3.6 eV at 300K) and interesting chemical and physical properties [1], suitable for applications as gas sensor, fabrication of solar cells and transistors, catalyst and photocatalyst [2], electrode for Li-ion battery [3] etc. Both undoped and metal incorporated/supported SnO<sub>2</sub> nanostructures have been vastly utilized for catalytic, photocatalytic and electocatalytic applications [4]. It has been demonstrated that  $SnO_2$ nanoparticles can be utilized as efficient, cheap and eco-friendly catalyst for the synthesis of 2-aryl or alkylbenzoxazole derivatives [5]. While Au nanoparticle supported SnO2 nanostructures have been utilized for several catalytic applications such as oxidation of CO, Pt-supported SnO<sub>2</sub> nanostructures have been shown to be highly active for electrocatalytic oxidation of methanol [6] and hydrogenation of methyl ester.

In the present work we demonstrate the fabrication of well dispersed Pt-doped  $SnO_2$  nanoparticles though hydrothermal method and their application as efficient catalyst for methane oxidation. Apart from structure and morphology evaluation, the nanoparticles with different Pt contents have been tested for the combustion of natural gas (containing >99% methane) and their reusability for the process. It has been seen that the  $SnO_2$  nanoparticles with an optimum percentage of incorporated Pt can act as excellent catalyst of methane oxidation, which can be utilized as durable exhaust converter for abating methane emissions from the natural gas driven motor vehicles. The mechanism of the catalytic process has been discussed.



Figure 1. Typical a) TEM and b) HRTEM images of the  $SnO_2$ :Pt (0.5%) nanoparticles showing their homogeneity and crystallinity.

#### Acknowledgements

The work was financially supported by CONACyT (Grant# CB-2010/151676) and VIEP-BUAP (Grant # VIEP/EXC/2015), Mexico.

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### **B34: High Peak Power Composite Material Passively Q-switched Microchip Lasers**

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High peak power passively Q-switched microchip lasers have wide applications on laser processing, laser ignition, efficient nonlinear conversions, and so on. Composite materials fabricated with thermal bonding technology have been widely used for thermal management, fabrication of compact multifunctional lasers. Yb:YAG as crystals and polycrystalline ceramics are one of the dominant laser gain media used for solid-state lasers owing to the excellent optical, thermal, chemical and mechanical properties. With development of transparent ceramic sintering technology, transparent laser ceramics become one very important solid-state laser materials because they have several remarkable advantages compared with single-crystal laser materials, such as high concentration and easy fabrication of large-size ceramics samples, multilayer and multifunctional ceramics laser materials. Yb:YAG laser materials are more suitable for generation of high pulse energy and high peak power in passively Q-switched Yb:YAG lasers with Cr<sup>4+</sup>:YAG as saturable absorber.

Progress of passively Q-switched lasers based on composite materials has been summarized. Optical properties of Yb:YAG/Cr<sup>4+</sup>:YAG composite crystals and ceramics were measured and compared with Nd:YAG/Cr<sup>4+</sup>:YAG composite materials. Effects of Yb<sup>3+</sup> ions doping concentrations and thickness in Yb:YAG materials, and Cr<sup>4+</sup> ions concentration and thicknesses of Cr4+:YAG materials on the laser performance were investigated in experiments and theoretical simulations. The design and fabrication of Yb:YAG/Cr<sup>4+</sup>:YAG composite materials for high power generation based on passively peak Q-switched microchip lasers were discussed. The polarization states of passively O-switched Yb:YAG/Cr4+:YAG microchip lasers with Yb:YAG crystal or ceramic as gain medium and Cr4+:YAG crystal or ceramic as saturable absorber were also presented. Efficient laser performance of Yb:YAG/Cr<sup>4+</sup>:YAG passively Q-switched lasers was obtained with different combinations of Yb:YAG, Cr<sup>4+</sup>:YAG ceramics and crystals. Linearly polarized were observed in Yb:YAG/Cr<sup>4+</sup>:YAG states combinations with at least one crystal. For Yb:YAG/Cr<sup>4+</sup>:YAG all-ceramics combination, the laser oscillates at random polarization state. The effect of polarized states of passively Q-switched Yb:YAG/Cr<sup>4+</sup>:YAG lasers on the laser performance was investigated.

Laser performance of Yb:YAG/Cr<sup>4+</sup>:YAG composite materials was studied. Highly efficient passively Q-switched lasers of Yb:YAG/Cr<sup>4+</sup>:YAG composite crystals have been demonstrated with an optical-to-optical efficiency of 36%. An average output power of over 1.75 W was obtained at an absorbed pump power of 4.8 W. Laser pulses with a pulse energy of over 180  $\mu$ J, a pulse width of 3 ns and a peak power of 60 kW were achieved. Laser pulse with pulse energy of over 172 µJ, pulse width of 237 ps and peak power of over 0.72 MW have been obtained in continuous-wave laser-diode pumped Yb:YAG/Cr<sup>4+</sup>:YAG composite ceramic passively O-switched laser. The pulse stability were investigated based on etalon effect of combined Yb:YAG and Cr<sup>4+</sup>:YAG plates. The effect of pump power intensity and heat generated by the pump power on Yb:YAG materials was investigated systematically and found the stable laser pulse can be generated by adopting suitable pump power intensity for multi-longitudinal-mode oscillation of passively lasers Q-switched microchip based on Yb:YAG/Cr<sup>4+</sup>:YAG composite materials. This provides a novel method for stabilizing laser pulses in multi-longitudinal-mode passively O-switched microchip lasers based on Yb:YAG/Cr4+:YAG composite materials. High peak power and high pulse energy passively Q-switched microchip lasers based on Yb:YAG/Cr<sup>4+</sup>:YAG composite materials were investigated with quasi continuous-wave laser-diode as pump source. Maximum output energy of 19 mJ was obtained when the available input pump energy was 86 mJ, the corresponding optical-to-optical efficiency was over 22%. A single passively Q-switched laser pulse with pulse energy of 1.6 mJ and a pulse width of 1.46 ns was achieved. The peak power was 1.08 MW. Near diffraction limited beam quality with M<sup>2</sup> of less than 1.75 was achieved in the OCW laser-diode pumped Yb:YAG/Cr<sup>4+</sup>:YAG composite crystal passively Q-switched laser. The applications of high potential peak power Yb:YAG/Cr<sup>4+</sup>:YAG composite material passively Q-switched were discussed in laser ignition, laser processing and efficient nonlinear conversion for versatile laser sources.

### **B35: Luminescence of ns<sup>2</sup>-type Emission Center in** Oxide Glasses

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Rare-earth (RE)-free phosphors have attracted considerable attention not only from an elemental viewpoint but also because of their unique emission properties. For practical application using amorphous material, it is necessary to select an emission center exhibiting the parity allowed excitation, *i.e.* the high transition probability, to attain high performance. The ns<sup>2</sup>-type emission center is one of the most favorable centers exhibiting high probability of allowed transitions, which allows the use of practical phosphors such as Sb<sup>3+</sup> and Mn<sup>2+</sup>-doped calcium halophosphate. Since the ns<sup>2</sup>-type emission centers (n  $\geq$  4) possess electrons in the outermost shell in both the ground state (ns<sup>2</sup>) and the excited state (ns<sup>1</sup>np<sup>1</sup>), the emission is strongly affected by the coordination field [1]. Therefore, the broad emission of ns<sup>2</sup>-type emission center, which is quite different from sharp emission of conventional rare earth (RE)-containing phosphors, is suitable for broad-band white light emission.

Our gourp has been focused on the ns<sup>2</sup>-type emission center, in particular  $Sn^{2+}$  emission center, as an activator. The  $Sn^{2+}$  center is the most ubiquitous and environmentally friendly ns<sup>2</sup>-type center. In addition,  $Sn^{2+}$  is one of the special non-RE centers capable of blue light emission. Using this emission center, the highest quantum efficiency (QE) for amorphous SnO-ZnO-P<sub>2</sub>O<sub>5</sub> low-melting glass has been reported [2]. It is notable that transparent glass with no RE cations has a high UV-excited emission comparable to a crystal phosphor such as MgWO<sub>4</sub>; further, this was the highest QE value ever reported for glass without an RE<sup>3+</sup> cation. In addition, this glass also showed scintillation with excitation by ionizing radiation [3]. On the other hand, the UV-excited white light emission property of MnO-doped SnO-ZnO-P<sub>2</sub>O<sub>5</sub> glasses has also been demonstrated [4]. The broad emissions of the Sn<sup>2+</sup> emission center, whose emission is strongly affected by the coordination field, could be continuously tuned by both the amount of activator and the composition of the glasses, without reduction of the QE values. Composition dependent emission property will be reported on the day.

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### **B36:** Surface Modification on Li-rich Layered Cathode Material for Li-Ion Batteries

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To conquer this critical issue, the present study is focused on surface modification of Li-rich layered cathode materials to improve their rate capability as well as maintain the high capacity retention of the pristine material. Surface modification is conducted on Li1.2Mn0.54Ni0.13Co0.13O2 using different amount of NH<sub>4</sub>F by thermal annealing at low temperature. Material characterizations (Power X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy) reveal that the modification process triggers fluorine doping and phase transition from a layered phase to a spinel phase at the particle surface. X-ray photoelectron spectroscopy is adopted to study the mechanism for this phase transformation induced by surface modification.

The enhancement in the electrochemical property of modified materials as a function of the NH<sub>4</sub>F amount is investigated by galvanostatic charge-discharge test. Fig.1 compares the electrochemical performance of pristine the Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> and the modified materials in half batterv. The NH₄F modified Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> materials exhibit greatly improved rate performance and better cycling stability compared to the pristine material, which can be attributed to the locally transformed three-dimensional spinel-like structure and F- ion doping at the particle surface, which favor fast lithium ion diffusion and structural stability.



**Fig1**. Rate capability (left) and long-term-high-rate cyclic performance (right) of the pristine and modified  $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$  materials.

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### B37: Atomic-scale characterization of SiAlON ceramics through aberration-corrected microscopy and spectroscopy

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SiAlONs are new generation solid-solution ceramics derived from the same crystal structures of  $\alpha$ - $\beta$ /Si3N4 [1]. Depending on the sintering dopants, the desired engineering properties of SiAlONs for many kind of applications from cutting tools to white light emitting diodes (LEDs) can be tailored by microstructure, primarily consisting of two distinct polymorphs ( $\alpha$  and  $\beta$ ), triple junction phases and grain boundaries [2-4]. Therefore, the atomic-scale characterization is a key step in further developing and designing the SiAlONs. However, over the past three decades, although many researches have been shed light on the micro- to atomic-scale observations of SiAlONs, the atomic-resolved STEM knowledge from  $\alpha$ - and  $\beta$ -SiAlON unit-cells as well as grain boundaries has been lacking.

Here, we report the atomic-scale imaging and spectroscopy of gas pressure sintered Yb, Ce and Yb-Ce containing single and double rare-earth cation doped  $\alpha/\beta$ -SiAlONs as well as TiN reinforced β-SiAlON ceramics using Z-contrast and EELS techniques in different type of state of the art aberration-corrected STEMs [5-6]. The results demonstrate that: (i) Yb and Ce dopants were preferentially incorporated into the β-SiAlON crystal structure at the atom-specific lattice locations, with higher solubility for Yb than Ce; (ii) this observation was also confirmed in the Yb-Ce co-doped system; (iii) Ce atoms without any co-doped cation were present in the triangular-like host sites of  $\alpha$ -SiAlON unit-cell, accommodating much more atoms than Ce-doped β-SiAlON; (iv) Yb and Ce atoms were periodically and differently arranged in the grain boundaries, explaining that they are in semi-crystalline nature, not completely amorphous; and (v) Ti atoms were incorporated into the β-SiAlON unit-cell.

In conclusion, our atomic-resolved microscopy results and spectroscopy demonstrate direct visualization of the sites and solubility of rare-earth and transition metal atoms in  $\alpha$ - $\beta$  SiAlON unit-cells and grain boundaries. This capability offers new engineering insights atomic-level into how appropriate rare-earth types and SiAlON host polymorphs should be chosen for nanoscopic tailoring of both next-generation SiAlON-based structural materials and optical ceramics. We expect our observations of impurity sites and solubilities in SiAlON polymorphs and grain boundaries represents the first step towards a new paradigm for atomic-scale guidance in the production of rare-earth and transition metal atoms doped materials for a wide variety of applications.



Figure 1. Z-contrast HAADF images of interstitial Yb and Ce rare-earth atoms in  $\alpha$ - and  $\beta$ -SiAlON unit-cells as well as substitutional Ti atoms within  $\beta$ -SiAlON crystal structure through Cs-corrected STEM. Please note that unit-cells are shown by dashed parallelograms.

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#### Acknowledgement

This research was supported by The Scientific and Technological Research Council of Turkey under the contract number: 113M254. The author also would like to thank Professor Stephen J. Pennycook and Dr. Juan Carlos Idrobo from The University of Tennessee UT Knoxville and Oak Ridge National Laboratory (ORNL), TN, USA.

#### C33: Development for novel Bi based high Curie-temperature ferroelectrics

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Recently,  $Bi(Me)O_3$ -PbTiO<sub>3</sub> (Me=Sc<sup>3+</sup>, In<sup>3+</sup>,  $Yb^{3+}$ ) based system has demonstrated the potential for producing piezoelectrics with high Curie temperature of above 450 °C, [1] high piezoelectric activity, and low temperature-property dependence, which will overcome the shortage of the relaxor-based single crystal piezoelectrics with a low Curie temperature ( $T_{\rm C}$ : 140 - 180 °C), such as  $Pb(Zn_{1/3}Nb_{2/3})O_3$ --PbTiO<sub>3</sub> (PZNT) and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>--PbTiO<sub>3</sub> (PMNT) crystals. But for those special applications such as space exploration under an environment higher than 500 °C, the ferroelectrics with high piezoelectric activity and high Curie temperature(>500 °C) are desired.

Based on the relationship between the perovskite tolerance factor and Tc, Bi(Me)O<sub>3</sub>-PbTiO<sub>3</sub> solid state solutions were predicted to exhibit a higher Tc (>550 °C), and meet the requirement for working under high temperature. In this presentation, we report the current research works and possible future development direction of Bi(Me)O<sub>3</sub>-PbTiO<sub>3</sub> based advanced high Tc ferroelectric materials; especially, our report will focus on the development of Bi(Me)O<sub>3</sub>-PbTiO<sub>3</sub> based crystals (as shown in Fig.1) grown by the flux method. We had optimized the parameters for the crystal growth, and good Bi (Me)O<sub>3</sub>-PbTiO<sub>3</sub> crystals with a size of several mm scale were obtained. The structures, morphologies, electric properties and performance comparison of these materials are presented.



**Fig1**. The mm size Bi (Me)O<sub>3</sub>-PbTiO<sub>3</sub> crystal grown from flux.

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## C34: Distinctive Contributions to High-Temperature Dielectric Response of Relaxor Ferroelectric Lead Scandium Niobate Ceramic System

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Relaxor systems are believed to provide a conceptual link between ferroelectrics and dipolar glasses - relaxor state is commonly described as a network of randomly interacting polar nanoregions, embedded in a highly polarizable medium [1,2]. Such a behavior is correlated with the cationic disorder in the same crystallographic site and has predominantly been detected in lead-containing ternary compounds (with  $Pb(B',B'')O_3$  perovskite structure) and solid solutions. however, the development of compositionally disordered lead-free systems has also become a very challenging issue [3,4].

Relaxors exhibit a high dielectric constant and a high strain across a broad temperature range and are therefore very attractive for a variety of applications such as capacitors, sensors, actuators, and integrated electromechanical systems, however, their functional properties are critically dependent on the chemical homogeneity [5]. In this work we thus present dielectric properties of lead scandium niobate, Pb(Sc<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> (PSN) ceramic system, prepared by using a powerful technique for development of a variety of advanced materials with excellent functional properties, a mechanochemical synthesis [6,7].

Developed PSN ceramics shows a high degree of chemical homogeneity and almost a theoretical density has been achieved, thus we performed dielectric characterization in a broad temperature interval of 150-775 K. Various contributions were recognized in the detected dielectric response. A typical relaxor dispersive maximum, accompanied by a sharp hysteretic dielectric anomaly reveals that developed disordered PSN system even in zero electric field undergoes а spontaneous relaxor-to-ferroelectric phase transition. A special emphasis has been given to the high-temperature response. It has namely been considered that polar nanoregions in relaxors form at a so-called Burns temperature ( $T_d \approx 600$  K), where some physical quantities (including dielectric susceptibility [8]) have been reported to deviate from the usual displacive mean-field ferroelectric behavior due to the local disorder. Here, in PSN ceramics, a strong dielectric dispersion due to the Maxwell-Wagner-type surface-layer contributions governs the detected response at high temperatures. The intrinsic high-temperature response follows, however, the universal scaling rather than the classical mean-field behavior, similar to some archetypal relaxor systems like lead magnesium niobate (PMN) single crystal or lanthanum-doped lead zirconium titanate (PLZT) ceramics [9]. Moreover, the mean-field behavior can be rejected on a confidence level better than 99 %, and the analysis revealed a critical exponent indicating a behavior typically found in spin glasses. Finally, a perfect agreement between the fitting parameter of  $T_C = 372$  K (obtained by analysis in the temperature interval of 600–775 K) and the experimentally detected value of this relaxor-to-ferroelectric transition temperature manifests that the low-temperature fingerprint behavior of PSN ceramic system can be observed at much higher temperatures, well above the dispersive dielectric relaxor maximum.

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## C35: Relaxor and ferroelectric behavior in tetragonal tungsten bronze ceramics

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In the filled tungsten bronze ceramics  $M_{6-p}R_pTi_{2+p}Nb_{8-p}O_{30}$  (p=1,2; M=Ba or Sr; R=rare

earth or Bi), a ferroelectric transition is generally indicated together with up to three low-temperature dielectric relaxations. The ferroelectric transition is determined as  $4/\text{mm}\rightarrow 4\text{mm}$ and the low-temperature dielectric relaxations are deeply concerned with the structure modulations due to the order/disorder of ions in A1 and A2-sites, their random cross occupancy, and the order/disorder of B-site ions. Both the ferroelectric transition and low-temperature dielectric relaxations are dominated by the composition and radius difference between A1- and A2-site ions,  $\Delta r$ . The normal ferroelectric transition might be expected if the ratio of the biggest ion and second big ion is 2:1, otherwise the diffuse or relaxor ferroelectric is expected. Meanwhile, the larger  $\Delta r$  generally results in the normal ferroelectric, and the smaller  $\Delta r$  will lead to the diffuse or relaxor ferroelectric. Moreover, the effects of A-sites order/disorder and the random cross occupancy of A-site ions are primary, and the effects of B-site ordering/disordering are secondary.

## C36: Electrochemical Performance of Micron and Nano Overlithiated Li<sub>1+x</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>: Structural and Oxidation State Studies

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Pure layered compound of overlithiated  $Li_{1+x}Ni_{0.8}Co_{0.2}O_2$  (x=1,1.05,1.1) samples were successfully prepared by a modified combustion

method. Structural studies of the XRD results showed that when lithium was doped into the LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode materials, the structural parameters of the materials changed slightly when more lithium is doped, that is, the cell parameter decreased. Scanning electron microscopy (SEM) revealed that the morphology of the particles changed a little from rounded polyhedral-like particle to sharp edged polyhedral crystals when more lithium is doped. Energy dispersive X-Ray spectroscopy (EDX) showed that the stoichiometries of Ni and Co agrees with calculated synthesized values. X-Ray photoelectron spectroscopy (XPS) studies showed that the binding energy of Li 1s is decreased for the Li doped samples. This implies that the Li<sup>+</sup> ions can be easily extracted more easily from  $Li_{1.05}Ni_{0.8}Co_{0.2}O_2$ materials than the other stoichiometries. The decrease in the binding energy implies that it was easier to deintercalate Li from the doped compounds and agreed with the electrochemical performance of the samples. Li<sub>1.05</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> showed the best results with a specific capacity of 113.29 mAh/g compared to  $Li_{1,1}Ni_{0,8}Co_{0,2}O_2$  with a of specific capacity 112.32 mAh/g and LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> with a specific capacity of 94.71 mAh/g. Li<sub>1.05</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> also showed the best capacity retention of 92.2% over 10 cycles. Li<sub>1.05</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> material is subsequently ball-milled to reduce the crystallite size. It is found that the performance of the material show improvement in terms of specific capacity especially in the first few cycles.

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Cathode for Lithium Batteries" Int.J,Electrochem.Sci.,4 (2009) pp. 1770-1778

## C37: Spinel-Based Cathode with Extended Capacity for High Energy/Power Lithium-Ion Batteries

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Nowadays, there are urgent needs to develop lithium-ion batteries with high energy/power density for applications in hybrid-electric vehicle (HEV) and electric vehicle (EV). However, most current cathode materials show capacity of about 150 mAh g<sup>-1</sup>. Since the energy density is dependent on both capacity and voltage, the limited energy density of current cathode materials becomes one of the main obstacles of its widespread adoption as well as the cost and safety concerns. [1]

Recently, many efforts have been focused on new cathodes with high operating voltages and/or higher capacities. In this regard, the LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> spinel becomes one of the very promising materials because of its high operating voltage of  $\sim 4.7$  V compared with other cathode materials. In addition, this kind of Mn-rich material is stable, inexpensive and environmentally friendly. Although LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> suffers from its limited capacity above 3 V, doubled capacity can be obtained by insertion of lithium ion into the structure below 3V. [2] But in this case, Jahn-Teller distortion cannot be ignored and results in a fast capacity fade. On the other hand, Mn-based layered oxides also become attractive recently as a result of their ability to deliver capacities of more than 250 mAh g<sup>-1</sup> with good cycle capability. Among them, Li<sub>2</sub>MnO<sub>3</sub> has already been successfully adopted to stabilize other layered materials. [3] Since the Li<sub>2</sub>MnO<sub>3</sub> component is inactive below 3V, it is possible to stabilize the

structure of the spinel oxides and access good cycling stability.

Therefore, the present study attempts to embed the layered oxide Li<sub>2</sub>MnO<sub>3</sub> with good cycle stability into the spinel structures to extend its capacity by engineering the domain structure of the spinel and avoid the Jahn-Teller distortion. The resultant composite crystallized in both a layered and spinel structure. When it is used as a cathode material for lithium-ion batteries, it exhibits superior cycle stability after some conditioning cycles compared to pure spinel oxides and demonstrates a high energy density of about 700 Wh kg<sup>-1</sup>, showing great promise for advance high energy density lithium-ion batteries. Various characterizations have been carried out to understand the mechanisms as shown in Figure 1.



**Fig1.** A Schematic Diagram showing the Mechanisms behind the Improved Electrochemical Performance.

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## **Poster Session**

P1: Band Gap Tuning in ZnSnO<sub>3</sub> Nanorods by Site Specific Doping and Core-Shell Approach for Solar Cell Applications

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Ferroelectric perovskite materials are of much interest as potential absorbers in next generation solar cells since they exhibit spontaneous polarization properties that facilitate electron-hole separation and drive charge carriers at their opposite ends. With a large remnant and high spontaneous polarization, LiNbO<sub>3</sub> (LN) type ZnSnO<sub>3</sub>, a direct band gap material composed of earth abundant elements, is emerging as an attractive solar absorber. However, the large band gap of ZnSnO<sub>3</sub> makes it inefficient to absorb the solar range but is possible by band gap engineering. In this work, we report the effects of site specific cation doping (Sb, Cu, Ca, Ba) on band gap tuning in LN type ZnSnO<sub>3</sub> nanorods. Both doped and undoped ZnSnO<sub>3</sub> nanorods were synthesized by a low temperature solvothermal process. Band gap in ZnSnO<sub>3</sub> being an extremely strong function of the lattice constant, it allows the possibility of band gap tuning by introduction of a slight strain by lattice mismatching. This was investigated by a core shell approach with ZnSnO<sub>3</sub> as the core and ZnO, SnO<sub>2</sub> and TiO<sub>2</sub> as the shell materials. A detailed structural, optical, electrical and photoconductivity analyses are provided to understand the effects of substitution and lattice constant on modifying the band structure and the results are discussed in terms of the efficacy of using  $\text{Zn}\text{Sn}\text{O}_3$  as a future solar cell material.

### P2: Rapid Microwave Synthesis of Perovskite Oxide Nanostructures with Enhanced Functionality

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Perovskite oxides are an important class of materials having high dielectric and piezoelectric switchable ferroelectric coefficients, (FE) polarization and interesting optical and electrical properties. Realization of functional devices based on classic perovskite oxides such as Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> (PZT), and emerging Pb-free non-centrosymmetric (NCS) oxides, such as, ZnSnO<sub>3</sub>, ZnTiO<sub>3</sub> and CaTiO<sub>3</sub> have reinforced the investigation of these materials in multiple dimensions and length scales. However, large-scale synthesis and integration of ordered low-dimensional structures is a challenge, due to their complicated methodologies, high-cost and difficulties with phase stability. We discuss a generalized, cost-effective, rapid microwave synthesis route for size and shape selective nanostructure growth of these functional perovskite oxides on industrially viable flexible and hard substrates, stabilized by an enhanced ionic covalence. The rational synthesis approach allowed improved tunability of the size, shape, and orientation of the structures with improved electrical and FE properties. The facile fabrication route of these nanostructures may expand the of probes understanding outreach for the

structure-property relationships in these hitherto unexplored and technologically important materials.

P3: Cost-effective synthesis and characterization of  $Yb^{2+}$  doped  $\beta$ -SiAlON phosphors for light emitting diodes (LEDs)

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Yb<sup>2+</sup> doped  $\beta$ -Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub> (z=1) phosphor powders were produced by carbothermal reduction and nitridation (CRN) route from kaolin raw-material and carbon black as reducing agent at 1050  $\,^{\circ}$ C for 1 hour and then following 1500  $\,^{\circ}$ C for 6 hours in high purity nitrogen atmosphere. Different amount of Yb<sub>2</sub>O<sub>3</sub> additives were used to provide photoluminescence property. Phase composition and quantitative analysis of Yb<sup>2+</sup> doped β-Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub> (z=1, 0.01<x<0.07 mol %) powders were determined by XRD Rietveld method. and The photoluminescence properties of synthesized  $\beta$ -Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub> (z=1) powders were performed by florescence spectrometer. Microstructure analyses of the samples were investigated by using ultra high resolution scanning electron microscope (UHR-SEM). Based on these characterization techniques, single phase  $\beta$ -Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub> (z=1) formation from kaolin using CRN method leads to a wide emission spectrum corresponding to green and greenish yellow between 520-570 nm.

#### Acknowledgements

This research was supported by The Scientific and Technological Research Council of Turkey under the contract number: 113M254.

**Keywords:** Carbothermal reduction and nitridation, kaolin, luminescence, SiAlON.

#### P4: Hierarchical TiO<sub>2</sub> Anatase Microspheres Crystallized Under Microwave Radiation

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The unique physicochemical properties of  $TiO_2$ nanoparticles have lately attracted a tremendous interest in a wide range of scientific and technological fields. [1] Of particular interest for its potential photocatalytic applications to environmental purification, hydrogen generation and/or solar energy conversion, is the fabrication of hierarchical anatase structures with controlled size and morphology. [2.3] On one hand hierarchical structures may attain low density, high crystallinity and a large specific surface area, structural parameters all required to improve the photocatalytic performance. On the other hand the micrometric size of the organized assemblies will allow an easy recovery of the photocatalyst from the working suspension after use. In particular, nanostructures assembled on a spherical morphology have evidenced a high stability and a monodisperse nature which satisfies the above mentioned characteristics. The problem is that the synthesis of such hierarchical microspheres eventually comprises a consolidation step at high temperature which typically produces a substantial reduction in the specific surface area and the porosity of the powders, with the consequent deterioration in their photoactivity. Hereby we have tested the employ of microwave heating as an alternative energy-saving sintering method to promote fast crystallization. The

results suggest that under the microwave radiation the  $TiO_2$  hierarchical structures can effectively crystallize in a drastically reduced heating time, allowing the specific surface area and the porosity to be kept in the high values required for an improved photocatalytic response.



Fig. 1: Representative FESEM image of the TiO<sub>2</sub> hierarchical microspheres.

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#### P5: The Grüneisen Parameter of Ionic Conductors

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In recent years, much attention have been devoted to ionic conductors due to their potential applicability in energy related devices such as lithium ion batteries. Among the ionic conductors, glassy ionic conductors are of particular interest, because they exhibit high ionic conductivity at room temperature. However, concerning fundamental properties of ionic conductors, our understanding is far to be complete. For instance, it is well known that the Grüneisen parameter, or the similar quantity, the Anderson-Grüneisen parameter, reflect the anharmonicity of the lattice vibration of the materials. Therefore, it is expected that these parameters are related intimately with the ionic conduction. However, surprisingly, only few studies on these quantities are available for the case of superionic conductors. In a recent study, a comparative study of the temperature dependence of the Anderson-Grüneisen parameter in different materials was reported [1]. There, it was shown that the Anderson-Grüneisen parameter of ionic conductors exhibit anomalously large temperature dependencies. This observation is very suggestive to understand the properties of ionic conductors, because it is known that in most materials, the temperature dependence of the Anderson- Grüneisen parameter is weak. In order to reinforce the above finding and gain further understanding on ionic conductors, we need to increase the number of case studies. In the present study, the values of the Grüneisen parameter has been evaluated from the elastic constants, following the method suggested in [2].

Fig.1 shows the results obtained. We can note that the Grüneisen parameter of superionic glasses increase with the increase of temperature. On the other hand, in chalcogenide glasses which do not exhibit ionic conduction, the temperature dependence of the Grüneisen parameter is negligible.



**Figure.1** Temperature dependence of the Grüneisen parameter  $\gamma$  for some glasses. (1) AgPO<sub>3</sub>, (2)

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P6: Co-substitution of carbonate and fluoride in Hydroxyapatite: Effect of the addition way and order of carbonate and fluoride sources

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The nanosized hydroxyapatite substituted by fluoride and carbonate ions (CFHA) had been synthesized by aqueous precipitation method. The effects of synthesis parameters on the fluoride and carbonate substitution of CFHA were investigated. The morphologies of CFHAs were observed by transmission electron microscope (TEM). The carbonate substitution type and content were Fourier transform characterized by infrared spectroscope (FTIR). The fluoride contents were determined by F-selective electrode. The results show that the addition way and order of F<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> sources have significant effects on the the substitution degree of fluoride and carbonate incorporated into the apatite structure. The fluoride and carbonate contents of CFHA increase with initial substitution ions concentration nonlinearly. The existance of carbonate substitution has little influence on the substitution degree of fluoride, however, the carbonate incorporation into the apatite structure seems to be hindered by the contemporary presence of fluoride. Due to the low stability of  $NH_4HCO_3$ , the samples with  $NaHCO_3$  as  $CO_3^{2-}$  source have higher carbonate substitution amount.



Figure caption: TEM images of CFHAs prepared in different doping ion Concentrations.

**P7:** A study on improving photoelectric conversion efficiency of dye-sensitized solar cell by using light scattering layer of hollow TiO<sub>2</sub> and SnO<sub>2</sub> nanoparticles

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Dye-sensitized solar cell (DSSC) has attracted more and more attention because of their advantages such as low cost, simple preparation process, green material and relatively high conversion efficiencies. Many researches has been done to enhance the light harvesting efficiency by a light-scattering layer applied in DSSCs. SnO<sub>2</sub> has much higher reflectance ability than TiO<sub>2</sub> in wavelength 300-400nm. In this work, light scattering layer was prepared with the hollow  $SnO_2$ ,  $TiO_2$  or a mixture of hollow  $SnO_2$  and  $TiO_2$  nanoparticles (NPs) on FTO glass substrate by droping method. Hollow  $SnO_2$  and  $TiO_2$  nanoparticles are produced by selective etching of  $Au@SnO_2$  and  $Au@TiO_2$  core shell nanoparticles which were prepared by microwave assisted hydrothermal method. Figure 1 shows TEM images of hollow  $SnO_2$  and  $TiO_2$  NPs. Figure 2 shows I-V curves of DSSCs prepared with light scattering layer of hollow  $SnO_2$ , hollow  $TiO_2$  and a mixture of hollow  $SnO_2$  and  $TiO_2$  NPs.



(a)

(b)

Figure 1. TEM images for (a) hollow  $SnO_2$  and (b) hollow  $TiO_2$  NPs.



Figure 2. I-V curves of DSSCs prepared with light scattering layer of hollow  $SnO_2$ ,  $TiO_2$  and a mixture of hollow  $SnO_2$  and  $TiO_2$ .

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# P8: Solid Oxide Fuel Cells with (La,Sr)(Ga,Mg)O<sub>3-8</sub> Electrolyte Film Deposited by RF Magnetron Sputtering

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In this study, solid oxide fuel cells (SOFCs) containing a high quality La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (LSGM) film deposited on anode supported substrate using RF magnetron sputtering are successfully prepared. The anode substrate is composed of two functional NiO/Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub>(SDC) composite layers with ratios of 60/40 wt% and 50/50 wt% and a current collector layer of pure NiO. The as-deposited LSGM film appears to be amorphous in nature. After post-annealing at 1000°C, a uniform and dense film with a composition polycrystalline of  $La_{0.87}S_{r0.13}Ga_{0.85}Mg_{0.15}O_{3-\delta}$  and a thickness of 3.8 µm is obtained, which was well adhered to the anode substrate. A composite LSGM/La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF) layer, with a ratio of 30/70 wt%, is used as the cathode. The SOFC prepared reveals a good mechanical integrity with no sign of cracking, delamination, or discontinuity among the interfaces. The total cell resistance of a single cell with LSGM electrolyte film declines from 0.60 to 0.10  $\Omega$  cm<sup>2</sup> as the temperature escalates from 600 to 800°C and the open circuit voltage (OCV) ranges from 0.85 to 0.95 V. The maximum power density (MPD) of the single

cell is reported as 0.65, 1.02, 1.30, 1.42, and 1.38 W cm<sup>-2</sup> at 600, 650, 700, 750, and 800°C, respectively. The good cell performance leads to the conclusion that RF magnetron sputtering is a feasible deposition method for preparing good quality LSGM films in SOFCs.

**Keywords**: Solid oxide fuel cells; electrolyte; sputtering

P9: Nanotribological characterization of polystyrene microspheres using atomic force microscopy

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Friction between nanoscale objects has been a subject of great interest and intense research effort for the last two decades. However, the vast majority of the work done in this area has focused upon the sliding friction between two rigid, atomically smooth surfaces. Thus the parameter most explored has been the corrugation in the atomic potentials and how this affects the force required to slide one object across another. In truth, many nanoscale objects whose translation force is of practical interest are more spherical in nature. We hypothesize that the factors that determine the translation force will be related to the not only to interfacial adhesion but also to the mechanical properties of the translating object and its underlying surface. The dependence on these quantities of the friction is not known. In this work we have utilized Atomic Force Microscopy and Force Spectroscopy to study the tribological properties of submicron level particles at the micro/nano-scale to explore how the friction between submicron spherical objects translating over planar substrates is related to interfacial energy and the mechanical properties for these particles. Lateral force microscopy will be used to measure the force required to translate asymmetric,

nanoscale particles of controlled size, surface chemistry and moduli. Polystyrene microspheres of different sizes under different solvent conditions will serve as our primary investigating material. Silicon wafers have been used as substrate. The effect of work of adhesion, elastic modulus of polystyrene microspheres, and contact radius between particle and substrate have been studied in detail for the different modes of particle translation under an external force.

## P10: Preparation of Hollow TiO<sub>2</sub> Nanoparticle Film on FTO Glass by Electrophoreticy Deposition for DSSC Applications

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Dye-sensitized solar cells (DSSCs) have promoted intense research during the past two decades due to their low cost, simple fabrication process and relative high conversion efficiency. For improving photovoltaic conversion efficiency of DSSCs, a light-scattering layer has been applied in DSSCs. In this work, light scattering layer was prepared by depositing the hollow TiO<sub>2</sub> nanoparticles (NPs) on FTO glass substrate by electrophoretic deposition (EPD) method under galvanostatic conditions. EPD method can prepare efficiently better thin nanoparticle films with advantages of high smoothness and uniform thickness for the application of DSSC photoelectrodes.

Hollow  $TiO_2$  nanoparticles are produced by selective etching of  $Au@TiO_2$  core shell nanoparticles which were prepared by microwave assisted hydrothermal method. Figure 1 shows TEM images of  $Au@TiO_2$  core-shell NPs and hollow  $TiO_2$ NPs. The prepared films are structurally and morphologically characterized. A dye-sensitized solar cell based on hollow  $TiO_2$  thin film was made and its performance was measured with illumination from the counter electrode. The current–voltage (I–V) characteristics of as prepared  $TiO_2$  films were recorded and then its efficiency was calculated.



(a)

**(b)** 



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