



Nagoya Institute of Technology



Institute of Ceramics Research and Education

International Symposium on Ceramics Nanotune Technology for Young Researchers

— 7 March (Wed.) ~ 9 March (Fri.), 2012—

Place :

Auditorium of Nagoya Institute of Technology (7 March*)

Gokiso-cho, Showa-ku, Nagoya 466-8555

*Co-organized by Center for Fostering Young and Innovative Researchers.

Nagoya Trade & Industry Center (8 - 9 March)

2-6-3 Fukiage, Chikusa-ku, Nagoya 464-0856



Welcome

Chukyo area is located in the region where manufacturing industries based on ceramics are concentrated. Nagoya Institute of Technology (NITech) has been developing education/research activities on ceramics-based materials and their devices.

NITech has many groups which focus on ceramics-related researches. Institute of Ceramics Research and Education (ICRE) is organized in a cross-spectral manner by NITech educational staffs (foundation of ICRE, January 2007).

Our significant areas of research are: environmentally-benign materials, materials for energy applications, biomaterials and next-generation materials based on ceramics science and technology. Projects in cooperation with international and domestic partner institutes and companies are significant driving forces for our education/research. Through the collaboration, we foster young researchers who acquire in-depth specialty and wide-ranging globalism. We will promote International Training Program (ITP), Institutional Program for Young Researcher Overseas Visits (IPYROV) and Young Researcher Overseas Visits Program for Vitalizing Brain Circulation (YROVP), which are adopted by JSPS, and Special Program for Education and Research by MEXT to create new ceramics-based materials science and formulate an international network for ceramics education/research. ICRE supports research projects proposed by young researchers, such as assistant professors, post-doctoral researchers and graduate students in PhD/Master courses.

In this international symposium, young researchers will play the leading role. We have invited world-class young researchers, and discuss on the present and the future of ceramics for next-generation materials, especially focusing on “Ceramics Nanotune Technology”. ITP international exchange students will also communicate their collaborations.

This symposium will provide an excellent opportunity for interactions and friendships with young participants, who are involved in science, engineering and application of various materials. We would like to express our thanks to all of the participants and supporting staffs.

春日敏宏

Toshihiro Kasuga



International Symposium on Ceramics Nanotune Technology for Young Researchers

8 - 9 March 2012

Nagoya Trade & Industry Center

2-6-3 Fukiage, Chikusa-ku, Nagoya 464-0856

8 March

Opening

09:45-09:55 Toshihiro Kasuga
Director of ICRE, NITech

Materials Design for Biomedical Applications

Chair: Julian R Jones (Imperial College London) and Akiko Obata (NITech)

09:55-10:35 “O₂ regulating bioactive glasses: breathing new life into tissue engineering”

Gavin Jell

Division of Surgery and Interventional Science, UCL Medical School

10:35-11:15 “Mechanical aspects in dental restorative treatment with highly filled methacrylic polymer filling materials”

Ulrich Lohbauer

Policlinic of Operative Dentistry and Periodontology, Universität Erlangen-Nürnberg

11:15-11:55 “The role of TRIS buffer at *in vitro* testing of glass-ceramics”

Dana Rohanová¹, Diana Horkavcová¹, Aleš Helebrant¹, Aldo R. Boccaccini^{2,3}

¹Department of Glass and Ceramics, Institute of Chemical Technology, ²Department of Materials, Imperial College London, ³Institute of Biomaterials, University of Erlangen-Nürnberg

Lunch Time

Short Communications on ITP Projects

Chair: Ken-ichi Kakimoto (NITech)

13:10-13:22 “Electrophoretic deposition of bioactive glass or Biosilicate®/biopolymer coating”

Chikako Kawamura¹, Alejandra Chavez², Kenji Nagata¹, Aldo R Boccaccini²

¹NITech, ² Universität Erlangen-Nürnberg

13:22-13:34 “Preparation of PHA/SiV fibermats for bone regeneration”

Takuma Iwata¹, Akiko Obata¹, Toshihiro Kasuga¹, Ulrich Lohbauer²

¹NITech, ² Universität Erlangen-Nürnberg

13:34-13:46 “Novel anhydrous proton-conducting materials for intermediate-temperature PEM fuel cells”

Hiroki Kato¹, Robert V Law², Toshihiro Kasuga¹

¹NITech, ²Imperial College London

13:46-13:58 “Effect of the doping on thermoelectric properties of BiFeO₃ bulk ceramics”

Rempei Imura¹, Takeshi Yokota¹, Andres Osvet², Miloslaw Batentschuk²,

Manabu Gomi¹, Christoph J. Brabec²

¹NITech, ² Universität Erlangen-Nürnberg

- 13:58-14:10 “Syntheses and oxide-ion conductivity of highly *c*-axis-oriented apatite-type lanthanum silicate polycrystals”
Ryuta Hamaguchi¹, Toru Asaka¹, Takahiro Suzuki¹, Hideki Oka¹, Abid Berghout², Emilie Béchade², Olivier Masson², Isabelle Julien², Eric Champion², Philippe Thomas², Koichiro Fukuda¹
¹NITech, ² SPCTS, Centre Européen de la Céramique
- 14:10-14:22 “Fabrication of porous zirconia with high volume fraction of closed pores formed by additives”
T. Umeda^{1,2}, S. Hashimoto¹, K. Hirao², N. Kondo², Y. Zhou², H. Hyuga², S. Honda¹, Y. Iwamoto¹
¹NITech, ² National Institute of Advanced Industrial Science and Technology (AIST)
- 14:22-14:34 “The Effect of A site Disorder on Oxygen Diffusion in Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_{2.5} Perovskite”
Hiromasa Shiiba¹, Clare L Bishop², Michael J D Rushton², Masanobu Nakayama¹, Masayuki Nogami¹, John A Kiler², Robin W Grimes²
¹NITech, ²Imperial College London

Break 14:34-14:45

Smart Chemical Processing

Chair: Yukari Ishikawa (Japan Fine Ceramics Center) and Sawao Honda (NITech)

- 14:45-15:25 “Polymer-derived ceramic nanocomposites (PDC-NCs): Synthesis approaches and high-temperature behavior”
Emanuel Ionescu, Benjamin Papendorf, Christoph Linck, Hans-Joachim Kleebe, Ralf Riedel
 Fachbereich Material- und Geowissenschaften, Technische Universität Darmstadt
- 15:25-16:05 “Nanostructure, properties and applications of Si(B)CN polymer-derived Ceramics: recent developments”
Gabriela Mera, Koji Morita, Hans-Joachim Kleebe, Ralf Riedel
 Fachbereich Material- und Geowissenschaften, Technische Universität Darmstadt

Break 16:05-16:15

Chair: Tobias Fey (Universität Erlangen-Nürnberg) and Hirotaka Maeda (NITech)

- 16:15-16:55 “Advanced functional Eco-glasses prepared via spinodal-type phase separation”
Yusuke Daiko, Atsushi Mineshige, Tetsuo Yazawa
 University of Hyogo
- 16:55-17:35 “Fabrication and microstructural control of macroporous ceramics”
Manabu Fukushima¹, Paolo Colombo² and Yu-ichi Yoshizawa¹
¹National Institute of Advanced Industrial Science and Technology (AIST),
 Advanced Manufacturing Research Institute
²Università di Padova, Dipartimento di Ingegneria Meccanica

Banquet (@Kouyouen)

9 March

Materials Design for Energy Applications

Chair: Masanobu Nakayama (NITech) and Takeshi Yokota (NITech)

- 09:30-10:10 “The role of metal oxides in plastic electronics”
Martyn A. McLachlan
Department of Materials, Imperial College London
- 10:10-10:50 “Photovoltaic and diode effect in BiFeO₃ thin films deposited on glass substrates with sol-gel method”
Yiping Guo, Bing Guo, Hua Li, Hezhou Liu
School of Materials Science and Engineering, Shanghai Jiaotong University
- 10:50-11:30 “Effect of conductive additives on the structural and electrochemical properties of Li₄Ti₅O₁₂ spinel”
Sung-Soo Kim
Graduate School of Green Energy Technology, Chungnam National University
- 11:30-12:10 “Design of electrode materials for lithium rechargeable batteries by integrating *ab initio* calculations with experiment”
Kisuk Kang
Department of Material Science and Engineering, Seoul National University

Lunch Time

Short Communications on ITP Projects

Chair: Ken-ichi Kakimoto (NITech)

- 13:20-13:32 “Investigation of the lamination behavior of spinel green tapes for the manufacture of transparent sintered structures”
K. Hattori¹, M. Beck², K. Kakimoto¹, A. Roosen²
¹NITech, ² Universität Erlangen-Nürnberg
- 13:32-13:44 “Preparation and characterization of piezoelectric porous PZT Ceramics”
Akinobu Kawai¹, Ken-ichi Kakimoto¹, Tobias Fey², Peter Greil²
¹NITech, ² Universität Erlangen-Nürnberg
- 13:44-13:56 “Sol-gel preparation of nitrogen doped zinc oxide films”
Kohei Higashiguchi¹, Robert Hewlett², Yuji Iwamoto¹, Martyn A. McLachlan²
¹NITech, ²Imperial College London
- 13:56-14:08 “Evaluation of thermal conductivity in porous alumina”
N. Nishihara¹, S. Honda¹, S. Hashimoto¹, B. Nait-Ali², David S. Smith², Y. Iwamoto¹
¹NITech, ²Ecole Nationale Supérieure de Céramique Industrielle
- 14:08-14:20 “Lattice dynamics and Raman spectroscopy study of M₂TeO₃ (M=Li, Na, K, Rb, Cs, Tl)”
Y. Kasuya¹, T. Hayakawa¹, M. Nogami¹, A.P. Mirgorodsky², T. Merle-Méjean², P. Thomas²
¹NITech, ²SPCTS, Université de Limoges
- 14:20-14:32 “Small angle X-ray scattering (SAXS) analysis of mesoporous sol-gel thin films”
Y. Ishikawa¹, T. Hayakawa¹, M. Nogami¹, F. Remondiere², M. Colas², P. Thomas²
¹NITech, ²SPCTS, Université de Limoges

Break 14:32-14:45

Control of Defects and Microstructure

Chair: Tomokatsu Hayakawa (NITech) and Yusuke Daiko (University of Hyogo)

14:45-15:25 “Photoluminescence properties of Eu³⁺ doped ZrO₂ nanomaterials: determination of the various sites for the localization of Eu³⁺ ions and estimation of the corresponding proportions”

J.-R. Duclère¹, A. Lecomte¹, T. Hayakawa², L. Portal¹, F. Rémondière¹, O. Masson¹

¹SPCYS – Université de Limoges, Centre Européen de la Céramique

²Ceramics Division, Department of Materials Science and Engineering, Nagoya Institute of Technology

15:25-16:05 “Defects induced by mechanical treatment in 4H-SiC substrate”

Yukari Ishikawa

Japan Fine Ceramics Center (JFCC)

Break 16:05-16:15

Chair: Manabu Fukushima (National Institute of Advanced Industrial Science and Technology) and Gabriela Mera (Technische Universität Darmstadt)

16:15-16:55 “Microstructure controlled advanced materials using templates of elastic silicone elastomer molds and colloidal crystals”

Hiroshi Fudouzi

National Institute for Materials Science

16:55-17:35 “Cellular ceramics”

Tobias Fey

Department of Materials Science, Universität Erlangen-Nürnberg

Closing **Yuji Iwamoto**

Deputy Director of ICRE, NITech

Program at a glance

8 March

	Code	Speaker	Affiliation	Paper title
9:45				Opening
9:55				Chair: Julian R Jones (Imperial College London) & Akiko Obata (Nagoya Institute of Technology)
9:55	1	G. Jell	UCL Medical School	O ₂ regulating bioactive glasses: breathing new life into tissue engineering
10:35				
10:35	2	U. Lohbauer	Friedrich-Alexander-Universität Erlangen-Nürnberg	Mechanical aspects in dental restorative treatment with highly filled methacrylic polymer filling materials
11:15				
11:15	3	D. Rohanová	Department of Glass and Ceramics, Institute of Chemical Technolog	The role of TRIS buffer at <i>in vitro</i> testing of glass-ceramics
11:55				
Lunch				
Chair: Ken-ichi Kakimoto (Nagoya Institute of Technology)				
13:10	S1	C. Kawamura	Nagoya Institute of Technology	Electrophoretic deposition of bioactive glass or Biosilicate® /biopolymer coating
13:22				
13:22	S2	T. Iwata	Nagoya Institute of Technology	Preparation of PHA/SiV fibermats for bone regeneration
13:34				
13:34	S3	H. Kato	Nagoya Institute of Technology	Novel anhydrous proton-conducting materials for intermediate-temperature PEM fuel cells
13:46				
13:46	S4	R. Imura	Nagoya Institute of Technology	Effect of the Doping on Thermoelectric Properties of BiFeO ₃ Bulk Ceramics
13:58				
13:58	S5	R. Hamaguchi	Nagoya Institute of Technology	Syntheses and oxide-ion conductivity of highly c-axis-oriented apatite-type lanthanum silicate polycrystals
14:10				
14:10	S6	T. Umeda	Nagoya Institute of Technology	Fabrication of porous zirconia with high volume fraction of closed pores formed by additives
14:22				
14:22	S7	H. Shiiba	Nagoya Institute of Technology	The effect of A site disorder on oxygen diffusion in Ba _{0.5} Sr _{0.5} Co _{1-x} FexO _{2.5} perovskite
14:34				
Break				
Chair: Yukari Ishikawa (Japan Fine Ceramics Center) & Sawao Honda (Nagoya Institute of Technology)				
14:45	4	E. Ionescu	Technische Universität Darmstadt	Polymer-derived ceramic nanocomposites (PDC-NCs): Synthesis approaches and high-temperature behavior
15:25				
15:25	5	G. Mera	Technische Universität Darmstadt	Nanostructure, properties and applications of Si(B)CN polymer-derived ceramics: Recent developments
16:05				
Break				
Chair: Tobias Fey (University of Erlangen-Nuremberg) & Hirotaka Maeda (Nagoya Institute of Technology)				
16:15	6	Y. Daiko	University of Hyogo	Advanced functional Eco-glasses prepared via spinodal-type phase separation
16:55				
16:55	7	M. Fukushima	National Institute of Advanced Industrial Science and Technology (AIST)	Fabrication and microstructural control of macroporous ceramics
17:35				
Banquet				
18:00				
20:00				

Program at a glance

9 March

	Code	Speaker	Affiliation	Paper title
Chair: Masanobu Nakayama (Nagoya Institute of Technology) & Takeshi Yokota (Nagoya Institute of Technology)				
9:30 10:10	8	M. A. McLachlan	Imperial College London	The role of metal oxides in plastic electronics
10:10 10:50	9	Y. Guo	Shanghai Jiaotong University	Photovoltaic and diode effect in BiFeO ₃ thin films deposited on glass substrates with sol-gel method
10:50 11:30	10	S. Kim	Chungnam National University	Effect of conductive additives on the structural and electrochemical properties of Li ₄ Ti ₅ O ₁₂ spinel
11:30 12:10	11	K. Kang	Seoul National University	Design of electrode materials for lithium rechargeable batteries by integrating <i>ab initio</i> calculations with experiments
Lunch				
Chair: Ken-ichi Kakimoto (Nagoya Institute of Technology)				
13:20 13:32	S8	K. Hattori	Nagoya Institute of Technology	Investigation of the lamination behavior of spinel green tapes for the manufacture of transparent sintered structures
13:32 13:44	S9	A. Kawai	Nagoya Institute of Technology	Preparation and characterization of piezoelectric porous PZT ceramics
13:44 13:56	S10	K. Higashiguchi	Nagoya Institute of Technology	Sol-gel preparation of nitrogen doped zinc oxide films
13:56 14:08	S11	N. Nishihara	Nagoya Institute of Technology	Evaluation of thermal conductivity in porous alumina
14:08 14:20	S12	Y. Kasuya	Nagoya Institute of Technology	Lattice dynamics and Raman spectroscopy study of M ₂ TeO ₃ (M=Li, Na, K, Rb, Cs, Tl)
14:20 14:32	S13	Y. Ishikawa	Nagoya Institute of Technology	Small angle X-ray scattering (SAXS) analysis of mesoporous sol-gel thin films
Break				
Chair: Tomokatsu Hayakawa (Nagoya Institute of Technology) & Yusuke Daiko (University of Hyogo)				
14:45 15:25	12	J.-R. Duclère	SPCT, Centre Européen de la Céramique	Photoluminescence properties of Eu ³⁺ doped ZrO ₂ nanomaterials: determination of the various sites for the localization of Eu ³⁺ ions and estimation of the corresponding proportions
15:25 16:05	13	Y. Ishikawa	Japan Fine Ceramics Center (JFCC)	Defects induced by mechanical treatment in 4H-SiC substrate
Break				
Chair: Manabu Fukushima (National Institute of Advanced Industrial Science and Technology) & Gabriela Mera (Technische Universität Darmstadt)				
16:15 16:55	14	H. Fudouzi	National Institute for Materials Science	Microstructure controlled advanced materials using templates of elastic silicone elastomer molds and colloidal crystals
16:55 17:35	15	T. Fey	Friedrich-Alexander-Universität Erlangen-Nürnberg	Cellular ceramics
Closing				



2nd Symposium on Life Science in conjunction with International Symposium on Ceramics Nanotune Technology for Young Researchers

7 March 2012
Auditorium of NITECH

Opening Professor Hiroyuki Ukai
Vice President of NITech

Invited Lecture

13:05-13:45 "Structural basis of rhodopsin activation"
Oliver P. Ernst
University of Toronto

13:45-14:25 "Research trends in neurohydrodynamics"
Bryn A. Martin
Swiss Federal Institute of Technology

Break 14:25-14:45

Research Staff's Report Session

14:45-15:05 "Property of flavin-binding photoreceptors"
Tatsuya Iwata
Center for Fostering Young and Innovative Researchers, NITech

15:05-15:25 "Relationship between microscopic structure and intramural strain distribution in aortic tissues"
Shukei Sugita
Center for Fostering Young and Innovative Researchers, NITech

15:25-15:45 "Potential of calcium silicate ceramics in biomaterial applications"
Hirotaka Maeda
Center for Fostering Young and Innovative Researchers, NITech

Break 15:45-16:05

Invited Lecture

16:05-16:45 "Tough bioactive hybrids for bone regeneration and the role of calcium"
Julian R. Jones
Imperial College London

16:45-17:25 "Glyco-polymers: The biomaterials with molecular recognition ability"
Yoshiko Miura
Kyusyu University

Closing Takeo Matsumoto
Coordinator of Life Science Division, CFYIR

17:45 Banquet at Café sala, NITech

*Materials Design
for Biomedical
Applications*

O₂ regulating bioactive glasses: breathing new life into tissue engineering.

Gavin Jell

Division of Surgery and Interventional Science, UCL Medical School

The cellular response to low O₂ pressure (hypoxia) plays an important role in tissue development and regeneration. Hypoxia, via the HIF (hypoxia inducing factor) pathway, activates numerous genes required for tissue regeneration; including genes necessary for the restoration of O₂ pressure through new blood vessel formation (Fig. 1). Materials that regulate the cellular O₂ sensing pathway could therefore be an attractive target for tissue engineering. Here I describe the development of bioactive glasses (BGs) that can regulate the hypoxia pathway.

Melt derived bioactive glasses (BGs), which release the known hypoxia mimetic cobalt (at physiological concentrations), were developed. Dissolution products from the hypoxia BGs stabilised HIF-1 α expression and activated hypoxia-related regenerative responses in a variety of cell lines (endothelial, osteoblast, fibroblast and monocyte). The hypoxia BGs upregulated the expression of pro-angiogenic factors (VEGF, FGF and VEGF-C), increased cell migration, enhanced cell survival and promoted anti-microbial activity (monocyte recruitment and increasing macrophage phagocytic activity).

These hypoxia BGs were thereby shown to regulate the HIF pathway and promote a number of cellular responses favourable for tissue regeneration, including new blood vessel formation.

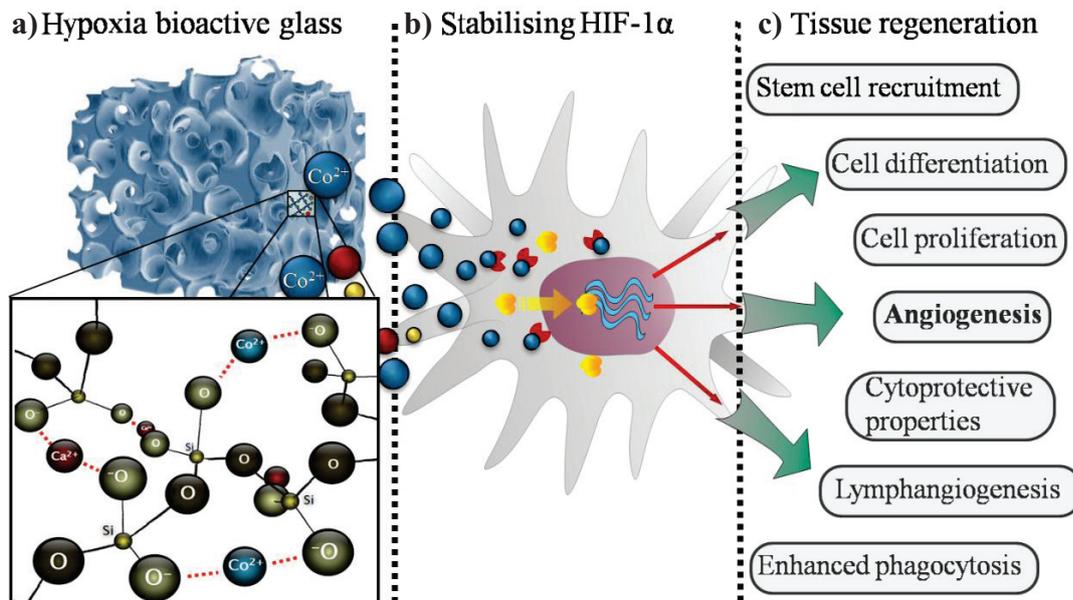


Figure 1. Regulation of the hypoxia pathway by bioactive glasses (BGs). (a) Resorbable BGs (μ CT image of a 3D gel-cast hypoxia mimicking BG scaffold) release physiologically active concentrations of cobalt ions from the silica network (Patent WO/2009/144453). (b) The cobalt ions inhibit the activity of an O₂ sensitive enzyme (PhD) thereby enabling the nuclear translocation of the transcription factor HIF-1 α and (c) causing the cell-type specific activation of hypoxia responsive element (HRE) genes associated with tissue regeneration, including new blood vessel formation. *BG μ CT image and BG structure diagram kindly prepared by Dr. J. Jones and Dr. Y. Fredholm respectively.*

Mechanical aspects in dental restorative treatment with highly filled methacrylic polymer filling materials.

Ulrich Lohbauer

Dental Clinic 1, Polyclinic of Operative Dentistry and Periodontology, University of Erlangen-Nuremberg

Clinical longevity of dental restorations is highly depending upon material, patient- and dentist related factors. Intraoral stresses like temperature, moisture and mastication influence clinical lifetimes. The adhesive interface is strained by polymerization shrinkage, cavity configuration and thermal expansion. Bond strength is markedly reduced after thermomechanical loading and retentive resin tags do thereby not contribute to bonding effectiveness.

Fracture and fatigue of resin based composites is driven by filler distribution, polymer network crosslinking and monomer conversion. The light irradiation protocol controls the degree of conversion, the build up of internal stresses and thus the mechanical properties. Failure mechanisms under cyclic fatigue conditions are controlled by slow crack growth and hydrolysis.

This talk will provide an overview on important aspects influencing the clinical lifetime of adhesively fixed dental restorations.

The role of TRIS buffer at *in vitro* testing of glass-ceramics

Dana Rohanová¹, Diana Horkavcová¹, Aleš Helebrant¹, Aldo R. Boccaccini^{2,3}

¹Department of Glass and Ceramics, Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic

²Department of Materials, Imperial College London, Prince Consort Road, London SW7 2BP, UK

³Institute of Biomaterials, University of Erlangen-Nürnberg; Germany

Biom mineralization – hydroxyapatite (HAp) forming on the surface of newly designed biomaterials is testing by using of simulated solutions. The pH near 7.4 at 36.5 °C is one of the keys of the biom mineralization. Simulated Body Fluid (SBF) is used for *in vitro* testing and the pH value is maintained by buffer TRIS (tris -(hydroxymethyl aminomethan). It is known, that TRIS buffer forms a soluble complex with Ca²⁺ ions, which suppress the deposition effect of HAp layer on the material surface. The dynamic *in vitro* tests (with continual flow of SBF around the sample) partially solve the problem of Ca and P depletion against the static arrangement tests but in the case of very soluble materials the TRIS buffer is not able to keep the pH value around the neutral level. We studied the buffer TRIS behaviour and kinetics of HAp formation in distilled water (DW), SBF with and without TRIS, TRIS solution and DMEM (Dulbeco's Modified Eagle's Medium) on the bioactive materials (glass-ceramics scaffold prepared from Bioglass®). We found that TRIS supports the solubility of crystalline phases opposite to the glassy phase of glass-ceramics and even crystalline form of HAp is formed in only TRIS solution. However, in DMEM and in SBF without TRIS, pH value was suddenly increased and the calcium carbonate and amorphous calcium phosphate were formed.

Smart Chemical Processing

Polymer-Derived Ceramic Nanocomposites (PDC-NCs): Synthesis Approaches and High-Temperature Behavior

Emanuel Ionescu,* Benjamin Papendorf, Christoph Linck,
Hans-Joachim Kleebe, Ralf Riedel

Fachbereich Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstrasse 32, D-64287
Darmstadt, Germany

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Polymer derived ceramics have been known for the last four decades and are prepared via solid-state thermolysis of preceramic polymers. They exhibit a unique combination of remarkable properties due to their covalent bonding and amorphous nature. Thus, silicon oxycarbide (SiOC) and silicon carbonitride (SiCN) based ternary PDCs have been shown to possess outstanding high-temperature properties such as stability with respect to crystallization and decomposition, oxidation and corrosion resistance as well as excellent thermomechanical properties (e.g., creep resistance up to temperatures beyond 1000 °C). Their properties are directly influenced by the chemistry and the architecture of the preceramic precursors, thus there is an enormous potential in tuning the microstructure and properties of the PDCs by using tailored polymers.

In the last two decades, the synthesis and properties of polymer-derived ceramic nanocomposites (PDC-NCs) have been studied. PDC-NCs can be synthesized via polymer-to-ceramic conversion of suitable single-source precursors, leading in a first step to amorphous single-phase ceramics, which subsequently undergo phase separation processes to furnish bi- or multiphase ceramic nanocomposites. PDC-NCs have been shown to possess intriguing properties which make them excellent candidates as structural and (multi)functional materials for applications at high-temperatures and under harsh environments.

Within this lecture, different preparative approaches for PDC-NCs as well as some of their properties will be presented. The main focus will be set on ceramic nanocomposite systems based on SiOC/MO₂ and SiCN/MO₂. Recent results concerning the relationship between the nano/microstructure of PDC-NCs and their properties will also be highlighted.

Keywords: Polymer Pyrolysis, Ceramic Nanocomposites, High-Temperature Behavior, SiCX/MO₂-based Nanocomposites (X = O, N; M = Zr, Hf).

Nanostructure, Properties and Applications of Si(B)CN Polymer-Derived Ceramics: Recent Developments

Gabriela Mera, Koji Morita, Hans-Joachim Kleebe and Ralf Riedel

Fachbereich Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstrasse 32, D-64287 Darmstadt, Germany

Polymer-derived ceramics (PDCs) are a special class of nanostructured high-temperature resistant materials which have gained a lot of attention in the last years due to their strong dependence on the preceramic polymer chemistry, ceramic nanostructure and properties. Within this framework, ternary SiCN-based ceramics are a unique class of high-temperature resistant materials, which are synthesized via pyrolysis of either polysilylcarbodiimides or of polysilazanes. Additionally, quaternary SiBCN ceramics obtained by the incorporation of boron at the molecular level into the preceramic precursors are reported to have remarkably higher thermal, chemical and mechanical (creep) stability than that of the boron-free counterparts even at temperatures beyond 2000 °C in inert atmosphere.

Herein we present the synthesis, the nano/microstructure as well as the high-temperature behavior of SiCN and SiBCN based PDC materials. Calorimetric measurements of heat of oxidative dissolution in a molten oxide solvent were used to quantify the thermodynamic stability of PDCs. The nano/microstructure characterization was performed by diffraction and spectroscopic methods (e.g. XRD and Raman and MAS NMR spectroscopy) and local analysis (i.e. HRTEM microscopy). The results emphasize the strong relationship between *chemistry* ↔ *nanostructure* ↔ *properties* ↔ *applications* of carbon-rich SiCN and SiBCN ceramics.

This work was supported by the grants funded under the MWN (Materials World Network) of the DFG and the National Science Foundation as well as LOEWE-Zentrum AdRIA (Adaptronik—Research, Innovation, Application), funded by the state of Hesse, Germany.

Advanced functional Eco-glasses prepared via spinodal-type phase separation

Yusuke Daiko, Atsushi Mineshige, Tetsuo Yazawa

University of Hyogo

Sodium borosilicate glasses show a spinodal-type phase separation to $\text{Na}_2\text{O-B}_2\text{O}_3$ and SiO_2 phases when they are heated around glass transition temperature. The ionically-bonded $\text{Na}_2\text{O-B}_2\text{O}_3$ phase is much polar than covalently-bonded SiO_2 one, and functional nanoporous, fast-ion conducting or nanocrystal-dispersed glasses can be easily obtained. Preparation and various properties are discussed based on the glass structure.

Fabrication and microstructural control of macroporous ceramics

Manabu FUKUSHIMA¹, Paolo COLOMBO² and Yu-ichi YOSHIZAWA¹

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Various microstructures were introduced in macroporous ceramic materials by employing carefully controlled processing methods. The properties and performance were strongly depending on the controlled microstructures of porous ceramics by varying pore size, pore size distribution, pore volume, pore interconnection, pore orientation and modified morphology of pore wall surface. The resulting components have a large amount of porosity ranging from 30 to 95 vol%. Four fabrication methods to control the microstructure have here been employed: (1) partial sintering method of a ceramic raw powder with or without sintering additives, acting promoted or prevented mass transfer to cause pore coarsening; (2) novel gelation freezing method to form a unique microstructure of ordered micrometer-sized cylindrical cells with unidirectional orientation which comes from the formation of ice crystal; (3) melting - blowing method of polycarbosilane preceramic polymer with blowing agent, comprised of homogenously distributed spherical cells, of pore size controlled by changing amount of blowing agent and blowing temperature; (4) decoration method of pore wall surface by 1D nanostructure via catalyst assisted pyrolysis of polysiloxane preceramic polymer. Depending on the fabrication procedure adopted, cells with an average size ranging from the submicrometer to the millimeter were obtained. Compression strength, pressure drop and filtration efficiency vary with the morphology and porosity of the porous components. All these processing routes proposed are simple, economical and versatile, and large bodies with various shapes (tubes, plates, cylinders and honeycombs) can be produced, possessing a wide range of microstructures and properties.

*Materials Design
for Energy
Applications*

The role of metal oxides in plastic electronics

Dr. Martyn A. McLachlan

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The incorporation of simple metal oxides into developing organic based electronic devices *e.g.* photovoltaics, light emitting diodes and transistors is an attractive prospect, owing to the potential low-cost but high-performance of such materials. The device performances already demonstrated by incorporation of oxides have been greeted with much enthusiasm from the research community. Added to this the range of properties available in even simple binary oxides *i.e.* transparency, electrical behaviour (conductor, insulator or semiconductor), morphological control *etc* metal oxides are considered complementary to many organic materials.

My research group are focussed on the development and understanding of chemical and physical deposition techniques for the controlled preparation of metal oxide thin films, nanoscale control of film morphology and the elucidation of structure-processing-performance relationships in a range of hybrid (oxide:organic) systems. In this presentation I will outline the wide range of research carried out at Imperial College London in the area of plastic electronics and discuss new and developing areas where metal oxides are being used to complement and improve the performance of organic devices.

Photovoltaic and Diode Effect in BiFeO₃ Thin Films Deposited on Glass Substrates with Sol-gel Method

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Multiferroic materials have attracted much attention due to their potential applications in memory devices based on magnetoelectric effect. One of the most studied multiferroic materials is BiFeO₃ (BFO). It is the only single phase multiferroic material with very high remnant polarization ($\sim 90 \mu\text{C}/\text{cm}^2$). Recently, further focus has been put on BFO for its prominent photovoltaic effect, e.g. extremely high open-circuit voltage, tunable voltage output, and huge enhanced external quantum efficiency (QE). However, all these properties were obtained in single crystal or epitaxial thin films, which limit its practical utilization due to the high cost and complicated fabrication process. The photovoltaic effect of polycrystalline BFO films deposited on Si substrates was also reported. Although the photovoltaic effect is much lower than those of bulk single crystal or epitaxial thin films, polycrystalline BFO films are still very important for solar cell applications for their low cost. Glass substrates are very cheap and have been widely used in dye sensitive TiO₂ solar cell. BFO can be deposited directly on glass substrates due to a low crystalline temperature as low as 550 °C. In our study, BFO thin films with good crystallinity were deposited on FTO glass substrates by chemical solution deposition. The deposited films have a conspicuous absorption in the blue and green light region and band gaps around 2.76 eV. The current-voltage characteristics of BFO/FTO films show a diode effect with a high rectifying ratio of 150. Good photovoltaic effect in the polycrystalline thin films was also found. The short circuit current density and open circuit voltage of the Au/BFO/FTO structure are measured to be $11.5 \mu\text{A}/\text{cm}^2$ and 0.32 V, respectively.

Acknowledgments

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Effect of conductive additives on the structural and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel

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The effect of a conductive agent on the structural and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) spinel were investigated through neutron diffraction during Li intercalation and electrochemical measurements. Differences in these properties between a conductive-carbon-containing LTO electrode and a carbon-free electrode were analyzed. The electrochemical reaction with Li transformed the white $(\text{Li}_3)_{8a}[\text{LiTi}_5]_{16d}\text{O}_{12}$ into a dark-colored $(\text{Li}_{3-x})_{8a}[\text{Li}_{x+y}]_{16c}[\text{LiTi}_5]_{16d}\text{O}_{12}$ by incorporating the inserted Li into octahedral 16c sites, and the Li in tetrahedral 8a sites was shifted to 16c sites. The occupancy of the tetrahedral 8a site varied with the existence of carbon as the conductive agent in the reacted electrode. The structural refinement results showed structural differences among the conductive agents. Without carbon as a conductive agent, the lattice parameter and cell volume of LTO decreased more notably than in the carbon-containing LTO electrode in which Li was inserted. This means that the Li occupancy of the tetrahedral 8a of the LTO electrode without carbon was less than that of the carbon-containing LTO electrode. The electrochemical results of these differently structured LTO samples were investigated in terms of the voltage profiles of their initial cycle and their subsequent cycles, and in terms of their impedance measurements.

Keywords: Lithium ion batteries; Lithium titanate; Neutron diffraction; Electronic structure

Design of Electrode materials for Lithium Rechargeable Batteries by integrating *ab initio* calculations with experiments

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Lithium rechargeable batteries have been widely used as key power sources for portable devices for the last couple of decades. Their high energy density and power have allowed the proliferation of ever more complex portable devices such as cellular phones, laptops and PDA's. For larger scale applications, such as batteries in plug-in hybrid electric vehicles (PHEV) or power tools, higher standards of the battery, especially in term of the rate (power) capability and energy density, are required. In PHEV, the materials in the rechargeable battery must be able to charge and discharge (power capability) with sufficient speed to take advantage of regenerative braking and give the desirable power to accelerate the car. The driving mileage of the electric car is simply a function of the energy density of the batteries. Since the successful launch of recent Ni-MH (Nickel Metal Hydride)-based HEVs (Hybrid Electric Vehicles) in the market, there has been intense demand for the high power-capable Li battery with higher energy density and reduced cost to make HEV vehicles more efficient and reduce emissions. However, current Li rechargeable battery technology has to improve significantly to meet the requirements for HEV applications not to mention PHEV.

In an effort to design and develop an advanced electrode material with high power and energy for Li rechargeable batteries, we approached to this in two different length scales - Atomic and Nano engineering of materials. In the atomic design of electrode materials, we have combined theoretical investigation using *ab initio* calculations with experimental realization [1-4]. Based on fundamental understanding on Li diffusion, polaronic conduction, operating potential, electronic structure and atomic bonding nature of electrode materials by theoretical calculations, we could identify and define the problems of existing electrode materials, suggest possible strategy and experimentally improve the electrochemical property. This approach often leads to a design of completely new compounds with new crystal structures. In this seminar, I will talk about olivine based multi-component electrode material study under this approach.

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*Control of Defects
and
Microstructure*

Photoluminescence properties of Eu^{3+} doped ZrO_2 nanomaterials: determination of the various sites for the localization of Eu^{3+} ions and estimation of the corresponding proportions

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The room temperature photoluminescence properties (PL) of Eu^{3+} doped tetragonal zirconia (ZrO_2) nanomaterials (xerogels, aerogels, nanocrystals prepared via a non-hydrolytic route) were measured. The aim of this study was to determine the various sites, within the ZrO_2 nanocrystals, where Eu^{3+} ions could be localized, and as well to estimate the corresponding proportions. Thus, we have developed a simple model, based on the existence of three different types of sites, whereas models dealing with only two sites are usually employed to explain the Eu^{3+} ions distribution within ZrO_2 nanoparticles:

- a first type of site (labeled site 1), corresponding to Eu^{3+} ions located at the surface of the nanocrystals, is considered. For that type of site, a short lifetime value ($\sim 0.4\text{-}0.5$ ms) of the $^5\text{D}_0$ excited state is measured, reflecting its very distorted nature (much lower coordination number, broad distribution of Eu-O lengths, ...)
- a second site (labeled site 3), corresponding to Eu^{3+} ions located in the core of the nanocrystals, is then considered. For that type of site, the environment of Eu^{3+} ions is estimated to be rather similar to that of Zr^{4+} ions in tetragonal ZrO_2 : *i.e.* a symmetric site, with a coordination number equal to 8. A rather long lifetime value is measured ($\sim 2.25 - 2.30$ ms), in agreement with the higher symmetry of the site.
- a third site (labeled site 2), still corresponding to Eu^{3+} ions located in the core of the nanocrystals, is also considered. However, for that type of site, the environment of Eu^{3+} ions is different, with a lower symmetry: the coordination number is reduced at least down to 7. Indeed, the substitution of Zr^{4+} ions by Eu^{3+} ions implies the creation of oxygen vacancies (statistically, two Eu^{3+} ions substituting two Zr^{4+} ions will create one oxygen vacancy). O atoms surrounding Eu^{3+} ions will then reorganize themselves in a less symmetric configuration than the previous one (*i.e.* site 3), explaining by this way the intermediate lifetime value measured ($\sim 1.20 - 1.45$ ms).

Taking into account everything, the overall PL intensity decay curve has been therefore fitted using the summation of three exponential decay curves. Each decay curve describes each type of site and has the following mathematical expression ($A_i \cdot \exp(-t/\tau)$), with A_i corresponds to the amplitude of the exponential decay curve and τ corresponds to the lifetime value of the $^5\text{D}_0$ excited state. The knowledge of A_i coefficients finally conducted to derive some estimation of the various proportions of Eu^{3+} ions located in each type of site.

To go further, using all the A_i and τ values, the respective PL emission spectrum of each site was extracted. In each case, the calculation of the asymmetry ratio R (defined as the ratio of the integrated intensities, $I_{5\text{D}0-7\text{F}2} / I_{5\text{D}0-7\text{F}1}$) led to logical and relevant values, compatible with our initial assumptions regarding the potential localization for Eu^{3+} ions.

Site selective spectroscopy measurements are now planned in order to fully confirm the model described here. Using such technique, it is expected to directly access the specific spectral signature for each type of Eu^{3+} ions.

Defects induced by mechanical treatment in 4H-SiC substrate

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Silicon carbide (SiC) is promising material for developing high-power, high-temperature and high-frequency electronic devices for its physical properties: wide band gap, large thermal conductivity, high melting point and high carrier mobility. Defects in SiC electronic device hamper to establish expected device performance as they degrade property, lifetime and process yield. Therefore, reducing dislocation density in 4H-SiC substrates is an urgent problem. Outstanding advancement of the crystal quality of SiC in recent years has reordered mechanical treatment a key technology. However, reports on defects induced by mechanical treatment are few. In this paper, we investigated shallow defects, which were induced by mechanical treatment, on 4H-SiC wafers. The density and the depth distribution of shallow defects on the wafers were dependent on wafer manufacturer. Most of the serious defects, such as the dislocation array, triangular stacking fault, and triangular defect, in epitaxial film were demonstrated to be caused by shallow dislocations on the surface of the wafers. Revised mechanical polishing can reduce the DA, TRSF, and TRD densities in epitaxial film.

Microstructure controlled advanced materials using templates of elastic silicone elastomer molds and colloidal crystals

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In a past decade, bottom up nanotechnology is one of hot topic in chemistry and material science field. Many approaches have been developed for new advanced materials and their applications. However, applications for ceramics and inorganic fields are limited compared to polymer science and chemistry field. In this presentation, the author will demonstrate four topics using two approaches, colloidal crystal and soft-lithography.

The first approach is colloidal crystal films assembled with sub-micron silica spheres. Here two applications, one is a colloidal crystal for harmful VOC solvents sensing. Colloidal crystal was filled with UV-curable resin precursor. After curing, the composite material enables change structural color by swelling with organic solvents. This phenomenon can be applied to a simple and low cost chemical indicator. The other application is a wide band gap material for photonic crystal device. Inverse opal photonic crystal of high refractive index of chalcogenide glass was made by all solution process ¹⁾. Here silica colloidal crystal plays a role in a template for a three dimensional microstructure. A nano-colloidal chalcogenide was spin-coating and then etched in HF acid to dissolve the silica template. Chalcogenide inverse opal structure was successfully fabricated by low-cost and low-temperature solution-based process.

The second approach is soft-lithography for inorganic materials using a polydimethylsiloxane, PDMS, elastomer molds. One application is a PDMS micro mold in capillary, MIMIC, process for colloidal suspension. Micro gas sensors were fabricated by the MIMIC technique using an ethanol suspension with a few volume per cent of SnO₂ nano-powders. The micro gas sensor enables to detect ethanol vapor by measuring the electrical resistance of the tin oxide. This MIMIC technique enables easy and simple fabrication of ethanol vapor micro-sensors in a cost-effective process ²⁾. The other application is soft imprint lithography of a bulk chalcogenide glass. A micro-pattern of cm scale surface-area are successfully imprinted into a bulk chalcogenide bulk glass at 225°C using a PDMS elastomer mold ³⁾. The patterned high refractive index of surface can be applied to optical devices, *e.g.*, diffraction gradings, photonic waveguides and optical sensors.

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Cellular ceramics

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Cellular ceramics constitute a multitude of ceramics with prominent properties (mechanical, thermal) regarding to their microstructure.

Several processing techniques yield to different microstructures and their characterisation. The focus is set on ceramic foams by replica technique, biomorphous fibrillär ceramics derived from paper and hierachical cellular ceramics using sacrificial templates. This covers a wide porosity range from 15 up to 90% porosity. This leads to different microstructures either with connecting or not connecting pore network. The effect of these microstructures on mechanical properities (strength, permeability and thermal shock) has been determined. Biomorphous fibrillar structures show an excellent thermo shock behavior after n=5 cycles of thermoshock. From permeability measurments it is determined that using sacrificial templates transformation from non connected to a interconnected pore network depends not linear to template shape and amount.

Microstructure characterisation is focused on SEM-analysis and μ CT-measurements. Regarding to μ -CT data local density distributions and anisotropy properties can be calculated. Additional structural parameters of open cellular foams and hierarchical cellular ceramics with interconnected pore network were calculated fom CT-data. Based on measured μ CT data mechanical and thermal FEM-Simulations can be preformed and linked with experimental results. The possible application of different cellular structured ceramics e.g. in automotive or energy section is shown.

2nd Symposium on Life Science

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Young Researchers

Structural basis of rhodopsin activation

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Rhodopsin is a highly specialized G protein-coupled receptor (GPCR) employed in the visual process [1]. Located in the outer segment of photoreceptor cells, rhodopsin comprises the GPCR apoprotein opsin and the photoreactive chromophoric ligand 11-*cis*-retinal. Rhodopsin is the only GPCR which contains its ligand covalently bound. In the rhodopsin ground state, the inverse agonist 11-*cis*-retinal is tethered in a central ligand binding pocket by a Schiff base to Lys-296, rendering the GPCR virtually inactive. A single photon is sufficient to isomerize the retinal into the all-*trans* configuration which triggers conformational changes in the receptor leading within milliseconds to the active metarhodopsin II state. The light-induced gain in activity towards the G protein is the largest known for the huge GPCR family. The crystal structures of inactive and active rhodopsin conformations give an idea about the switch-like behavior of rhodopsin and global protein changes associated with activation of GPCRs [1]. We solved the structure of active metarhodopsin II by soaking crystals of the active GPCR conformation with the all-*trans*-retinal agonist [2]. I will discuss the activation mechanism of rhodopsin and studies on uptake and release of retinal from its binding site [3].

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Research trends in Neurohydrodynamics

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Neurohydrodynamics is an emerging discipline in neural engineering that focuses on the role that cerebrospinal fluid hydrodynamics play in central nervous system pathophysiology. This presentation will highlight current research trends in neurohydrodynamics from an engineering perspective, starting with the pertinent anatomy and physiology. Cerebrospinal fluid is a clear Newtonian fluid with a density and viscosity nearly that of water. It surrounds the brain and spinal cord and also resides within the fluid-filled cavities of the brain. Cerebrospinal fluid flow is unique within human physiology because it exhibits a strictly pulsatile movement synchronous with the cardiac pulsation and has a net flow of nearly zero. Peak cerebrospinal fluid velocities and pressure fluctuation amplitudes are typically one or two orders of magnitude smaller than macroscale blood flow. These relatively small perturbations have made cerebrospinal fluid a historically enigmatic and difficult fluid system to study. Until the advent of flow-sensitized MRI, little was known about the flow dynamics of cerebrospinal fluid. In recent years many advances have been made in the understanding of cerebrospinal fluid system but many questions remain. In particular, abnormal cerebrospinal fluid movement has long been implicated in a number of disorders of the craniospinal system such as syringomyelia, Chiari malformation and hydrocephalus. However, an understanding is lacking of the underlying biomechanical forces that contribute to these disorders. Thus, engineers have begun to work with medical doctors to help better understand these forces with the goal to provide more objective disease assessment and improve surgical techniques. Ultimately, this work aims to improve the quality of life for the millions of people who suffer from neurohydrodynamics related disorders. This talk will elucidate what engineers have done to understand these disorders from an experimental and modeling viewpoint with a focus on the questions that engineers can help answer in the future.

Property of flavin-binding photoreceptors

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In 1990's and 2000's, various kinds of flavin-binding blue-light sensor proteins were discovered. Cryptochrome (Cry), an FAD-binding photoreceptor, was first found in plants for the inhibition of hypocotyl elongation. Crys were also found in animals and bacteria, which are involved in circadian rhythms and in the sensing of magnetic fields in a number of species. Another flavin-binding photoreceptor in plants is phototropin (Phot), which consists of two FMN-binding photoreceptive domains (LOV) and Ser/Thr kinase domain. In addition, BLUF (sensor of blue light using FAD) domain was found in photoactivated adenylyl cyclase form *Euglena gracilis* and AppA from *Rhodobacter sphaeroides*. Interestingly, unlike rhodopsins, photoreaction of flavins in Cry, LOV domain and BLUF domain are different; photoreduction, flavin-cysteine adduct formation and rearrangement of hydrogen-bonding network, respectively.

My research aim is to elucidate the control mechanisms of the photoreaction of flavin. To achieve this goal, I investigate the reaction mechanism of each protein by Fourier-transform infrared (FTIR) spectroscopy. Using FTIR spectroscopy, we are able to obtain the information of the light-induced structural changes of secondary structure (amide-I vibration), protonation states and hydrogen-bonding alteration of X-H groups (X = N, O, S), which are difficult to be obtained by X-ray crystallographic analysis.

In this symposium, I will present our FTIR studies of flavin-binding photoreceptors. For LOV domains, species dependent structural changes were highly dependent on species [1]. We first reported the FTIR spectra of a new type of Cry [2]. In BLUF domain, we recently discovered strong donation of hydrogen bond of tyrosine during photoactivation, which has never been reported [3]. Unique protein structural changes obtained by the FTIR analysis will be discussed in relation to their functions.

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Relationship between microscopic structure and intramural strain distribution in aortic tissues

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The aorta is composite material mainly comprised of cells, elastin, and collagen. It is known that these elements in the wall of aortic aneurysms was distributed heterogeneously compared with normal aortas. These heterogeneity should cause complex distribution of stress and strain, which may result in a fatal rupture. To explore microscopic dynamics of aortic rupture, I have been working on the development of techniques: observation of microstructure, application of a mechanical load to aortic specimens under a microscope, and measurement of strain distributions in the specimens. This presentation will introduce these techniques and preliminary results of correlation between microstructure and strains.

Since collagen is the toughest in the aorta, its local volume and fiber directions should be important for strength of the aorta. Since collagen is birefringent material, we established a method to get volume and direction of collagen fibers by measuring polarized light retardance and azimuth of the slow axis, respectively. An equibiaxial tensile tester were then developed. The tester can apply the mechanical loads to the specimen to mimic the mechanical environment in situ more rigorously. A metal cylinder was placed above the center of a thin-sliced specimen held with a circular metal frame. The frame was vertically elevated until specimen rupture while measuring force loaded on the frame and taking images of its deformation. These methods were applied to porcine thoracic aorta. Specimens were stretched equibiaxially during observation of collagen volume and direction. Using digital image correlation method, strain tensor was calculated locally. Finally, these techniques were applied to the porcine thoracic aorta, and strain distributions were compared with distributions of retardance and azimuth of the slow axis of collagen fibers. Normal and shear strain at rupture significantly correlated with collagen fiber volume and direction, respectively, indicating that structure of collagen fibers influenced strain distributions at rupture.

Potential of calcium silicate ceramics in biomaterial applications

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Many kinds of bioactive materials such as hydroxyapatite and Bioglass[®] have been prepared to repair bone defects. Recently, it has been focused in a new approach for investigating the biological interaction between bone and synthetic bone substitutes in the biomaterials field. Hench *et al.* suggested that bone formation on Bioglass[®] is enhanced by the stimulatory effect of silicon and calcium ions released from the material [1]. Calcium silicates are expected to be one of potential candidates for bone substitutes. It has been proposed that phosphate species stimulate the expression of protein as a key regulator in bone formation in osteoblasts [2]. We are now investigating on the preparation of new types of calcium silicate ceramics for releasing these ions over a long period of time. Tobermorite is one of crystalline calcium silicate hydrates that are synthesized by hydrothermal reaction. It has a unique structure comprising infinite double layers of Ca-O polyhedra linked on both sides to silica tetrahedral chains running along the b-axis. The stack of this assembly in the c-direction leads to formation of interlayer regions that accommodate exchangeable cations. Phosphate species was attempted to be incorporated into the tobermorite structure under the hydrothermal reaction in the CaO-SiO₂-P₂O₅-H₂O system. Tobermorite with a trace amount of phosphate species formed after the reaction. Experimental results and first-principles calculations were proposed that the phosphate species as a Ca₃(PO₄)₂ cluster with D_{3h} symmetry were incorporated into the interlayer region, to induce the distortion of the tobermorite structure.

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Tough bioactive hybrids for bone regeneration and the role of calcium

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For regeneration of bone defects, a scaffold must stimulate bone growth, dissolving as the bone regenerates. The scaffold must have an interconnected pore network. For new bone to survive, blood vessels must penetrate. Scaffolds have been developed by foaming sol-gel derived bioactive glasses. Their limitation is that they are brittle. Composites have been developed but the inorganic and organic phases tend to resorb at different rates, leading to material instability. Therefore it is proposed that hybrids that have interpenetrating networks of bioactive inorganic and tough organic components can provide the combination of toughness and bioactivity. Key to their success is that the components are covalently linked to control degradation rates and mechanical properties, e.g. sol-gel silica and enzyme degradable polypeptides. There are several key challenges in the chemistry and processing. One is how to incorporate calcium. Calcium is needed for bioactivity but when it is introduced into the sol-gel process as a calcium salt, it is only incorporated into the silica network when it is heated to $>450^{\circ}\text{C}$. This talk will describe hybrid synthesis and processing and the alternative calcium precursors and how they affect the properties of the hybrids. Calcium is also an ionic cross-linker of polymers and has contributed to the synthesis of bioactive hybrids that have the compressive strength of a glass but 30% strain to failure.

Glyco-polymers: The biomaterials with molecular recognition abilities

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Saccharides on the cell surfaces play important roles in the living systems such as cell adhesion, cell differentiation, and infection of pathogens. Though the interaction between saccharides and proteins are weak, it is amplified by the multivalency, so-called glycol-cluster effects. Polymers with pendant saccharides are known to show the large glycol-cluster effect. We called the polymers as “ glycopolymers”.

Glycopolymers have advantage of the material fabrication using polymer chemistry techniques. In our group, the glycopolymers with acrylamide backbone have been synthesized. Each glycopolymer showed the biological molecular recognition abilities based on the saccharide structure. We have reported the glycopolymers showing the molecular recognition ability with lectins, the toxin proteins and amyloid proteins. Since the molecular recognition abilities are related to the multivalency, the molecular recognition abilities were able to be controlled by precise polymerization like living radical polymerization. For example, the glycopolymers with sulfonated-glucosamine showed the inhibition activity on aggregation of amyloid beta proteins, and the inhibitory effects depended on the molecular weight of the polymers, which can be proved by living radical polymerization of glycopolymers.

The living radical polymerization enabled the facile preparation of hybrid materials with gold nanoparticle, gold substrate, glass and porous materials. The glycopolymer hybrid materials showed the specific and strong molecular recognition abilities to the target proteins. We prepared a glycopolymer with *p*-amidophenyl mannose via reversible addition fragmentation chain transfer (RAFT) polymerization. The subsequent polymer was reduced to obtain the thiol terminal polymer, and the polymer can modify the various substances based on the Au-S and maleimide-S interactions. The polymer modification provided the molecular recognition abilities to the substances, and the substances can be utilized as biosensors and protein purification materials.

*Short
Communications
on ITP Projects*

Electrophoretic deposition of bioactive glass or Biosilicate[®]/biopolymer coating

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Bioactive glasses developed during the past few decades have provided promising alternatives as materials to repair, replace or augment parts of the skeletal system. These glasses are highly bioactive and both osteoinductive and osteoconductive, and have been shown to bond within days to bone as well as to soft tissues. However, these glasses are mechanically weak and it is considered that it is difficult to use for medical products such as implants. To improve a mechanical property of bioactive glasses, the addition of biopolymer prompted us to prepare a composite material. One of the biopolymers is sodium alginate, a linear polysaccharide containing a varying composition of α -(1-4) linked D-mannuronic acid and β -(1-4) linked L-guluronic acid residues. The nature of alginate is non-toxic, low-cost and a natural degradable polymer. Therefore, we focused on bioactive glasses- or biosilicate-including biopolymer composites, because it is expected to have both enhanced biocompatibility and flexibility.

The goal of this study was to fabricate bioactive glasses or biosilicate/alginate composite coatings through electrophoretic deposition (EPD) of bioglasses or biosilicate -alginate colloidal suspension. Under an electric field, both negatively charged bioglasses or biosilicate and alginate migrate onto a positively charged anode, and are converted to a coherent biosilicate/alginate composite coating. The thickness of the prepared composite coating can be tuned by varying processing conditions such as deposition time and anode conductivity. The coating characterization after EPD was carried out by Fourier Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). The result of SEM observation revealed that the coating phase constituted bioactive glasses or biosilicate with alginate was formed on the metal substrate.

Preparation of PHA/SiV Fibermats for Bone Regeneration

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Flexible 3-D porous structure for improving good cellular attachment and supporting fitness to topographical treatment area is required for bone tissue engineering scaffold. Fibermats with large surface area and high porosity can be prepared by an electrospinning using organic polymers. Poly(hydroxyalkanoate) (PHA) is one of the biodegradable polyesters with biocompatibility. In the PHA family, poly(3-hydroxybutylate-co-4-hydroxybutylate) (P(3HB-4HB)) shows excellent flexibility. For enhancing bone regeneration, bioactivity and ion releasability are required. Ionic silicon species and calcium ions are important stimulatory agents for proliferation and differentiation of osteoblasts. In our group, 1 μm -sized spherical siloxane containing vaterite (SiV) particles, which have ability to release Si^{4+} and Ca^{2+} ions, were prepared by a carbonation process [1].

In this work, P(3HB-4HB) and SiV composite fibermats were prepared by electrospinning. Cellular attachment can be enhanced by coating the fiber surfaces with bone-like apatite. The SiV content in the fibermats is supposed to relate to their mechanical properties and bioactivity. The composite containing 30 wt% SiV showed tensile strength of 2.6 MPa and high elongation at break of over 100 %, while the composite containing 40 wt% SiV showed low elongation at break of ~ 40 %. In order to coat the fiber surfaces with bone-like apatite, the PHA/SiV composite was soaked in modified simulated body fluid (1.5 SBF). After 1 d of soaking, bone-like apatite formed on the surfaces.

Reference

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Novel Anhydrous Proton-Conducting Materials for Intermediate-Temperature PEM Fuel Cells

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An intermediate temperature proton-conducting amorphous material was prepared utilizing the reaction of zinc metaphosphate glass powders with benzimidazole. The anhydrous material, consisting of Zn-coordinated benzimidazole and benzimidazole/phosphoric acid composite groups with benzimidazole, showed almost no decrease in weight even after heating at 200°C. It showed high electrical conductivities of $\sim 0.2 \text{ mS} \cdot \text{cm}^{-1}$ at the intermediate temperatures (160 °C \sim 230 °C). The activation energy for electrical conduction ($\sim 0.9\text{eV}$) was close to that for proton transport between basic heterocycle molecules.

Effect of the Doping on Thermoelectric Properties of BiFeO₃ Bulk Ceramics

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We have been interested in a multiferroic material: BiFeO₃ as a thermoelectric material, because the material has unique character in its leakage current mechanism. [1] Based on this mechanism, it can be expected to control the high conductivity and low thermal conductivity in one material, which can achieve high figure of merit. Previously, we prepared BiFeO₃ bulk ceramic under several sintering conditions and every sample shows high Seebeck coefficient compared with other oxide as a candidate of new thermoelectric materials such as NaCo₂O₄, and La_{0.9}Sr_{0.99}Ca_{0.11}CoO₄, because of its insulating nature. Although those samples have high potentials as thermoelectric materials, the high conductivity should achieve without reducing of Seebeck coefficient. In this presentation, we investigated the effect of doping for conductivity and Seebeck coefficient of BiFeO₃ bulk ceramics.

The samples were prepared using conventional solid state reaction. The starting materials were high-purity powders of Bi₂O₃ and Fe₂O₃. La and Ca was used as doping materials. Every sample has high Seebeck coefficient. However, the relationships between the conductivity and Seebeck coefficient of the La doped sample has no tendency. It is more likely due to the un-doped sample having both oxygen and Bi deficiency. In the case of low doping sample, the conductivity is increased because of the reducing of Bi deficiency. If the amount of La doping becomes higher than that over a certain volume, the oxygen deficiency was increased or decreased. In the case of Ca doping, it showed similar behavior. Therefore, in order to achieve the sample having high conductivity and high Seebeck coefficient, it is necessary to control both the oxygen and Bi deficiency.

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Syntheses and oxide-ion conductivity of highly *c*-axis-oriented apatite-type lanthanum silicate polycrystals

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We have successfully synthesized the highly *c*-axis-oriented polycrystals of apatite-type lanthanum silicate by the reactive diffusion technique. When the $\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$ diffusion couples were isothermally heated at 1773 K – 1873 K for 5 h – 100 h, the apatite polycrystals readily produced in the form of layer at the interfacial boundaries. The annealed couples were characterized using optical microscopy, micro-Raman spectroscopy, X-ray diffractometry and electron probe microanalysis. The product layers were composed of the highly *c*-axis-oriented prismatic crystallites, with their elongation directions being almost parallel to the diffusion direction. The formation of the apatite layer was controlled by volume diffusion, the overall reaction of which is described by $(10+6x)\text{La}_2\text{SiO}_5 + (4-3x)\text{La}_2\text{Si}_2\text{O}_7 \rightarrow 3\text{La}_{9.33+2x}(\text{SiO}_4)_6\text{O}_{2+3x}$ ($0.01 \leq x \leq 0.13$). The apatite layer formed at 1873 K was characterized by the steady decrease of the *x*-value along the diffusion direction from 0.13 at the La_2SiO_5 /apatite interface to 0.01 at the apatite/ $\text{La}_2\text{Si}_2\text{O}_7$ interface. The formation of apatite at 1773 K – 1873 K was controlled by the interdiffusion of La_2O_3 and SiO_2 components within the growing apatite layer. The activation energy of this volume-diffusion process was ca. 200 kJ/mol. We have also prepared the sandwich-type $\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$ diffusion couples and heated at 1873 K for 100 h. The annealed couple was mechanically processed and the thin-plate electrolyte consisting of the highly *c*-axis-oriented polycrystal was obtained. The oxide-ion conductivity was determined from the impedance spectroscopy data at 573 K – 973 K, which steadily increased from 2.4×10^{-3} S/cm to 2.39×10^{-2} S/cm with increasing temperature. The empirical activation energy of conduction was 0.35 eV, which compares well with the calculated migration energy of 0.32 eV in a previous study. The reactive diffusion technique could be widely applicable to the syntheses of highly grain-oriented ceramics as a new facile texturing method.

Fabrication of porous zirconia with high volume fraction of closed pores formed by additives.

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A novel technique to make a porous ZrO₂ with high volume fraction of closed pores was studied. It was found that ZrO₂ sintered bodies containing small amount of impurities exhibited larger volume expansion related to the formation of closed pore when they were heated at high temperatures (1700°C, 10min, N₂). These closed pores were considered to be formed due to vaporization of impurities. Particularly, Si, Ti and P were the possible impurities to form the closed pores during heating, since the elements were mainly detected by Glow Discharge (GD) mass analysis in the ZrO₂ body having such unusual characteristics. Therefore, in this study, small amount of additives such as SiO₂, TiO₂ and/or hydroxyapatite (Ca₅(OH)(PO₄)₃) were added to 3 mol% Y₂O₃ partially stabilized ZrO₂ and then the formation of closed pores was investigated. A porous ZrO₂ with 24.6% closed pores was successfully fabricated by adding 1.0mass % of impurities and by heating treatment at 1700°C for 10min under the atmosphere of N₂. The morphology of the fabricated porous ZrO₂ bodies was investigated and formation mechanism of the closed pores was discussed in chemical thermodynamics. Furthermore the bending strength and thermal conductivity of the fabricated porous ZrO₂ were measured.

The Effect of A site Disorder on Oxygen Diffusion in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{2.5}$ Perovskite

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Materials related to BSCF are of significant interest as cathode materials for intermediate temperature solid oxide fuel cells. Therefore, various stoichiometries of these materials have been investigated. The crystal structure of BSCF is ABO_3 cubic perovskites with Ba and Sr occupying the A cation sites whilst Co and Fe occupy the B cation sites. At present, the effects of A cation ordering are not clear. This is significant because, it has recently been discovered that stated by Parfitt *et al.*, oxygen self-diffusion in $\text{GdBaCo}_2\text{O}_{5+\delta}$ is strongly dependent upon the particular A cation ordering. To understand the mechanism of oxygen migration, here we predict the effect of lattice disorder on oxygen diffusion in three related BSCF materials, each with fixed oxygen stoichiometry ($\delta = 0.5$) using molecular dynamics. Diffusion coefficients and the activation energy of the disordered structures calculated from MD simulations show reasonable agreement with experimental values. The Ba/Sr disorder parameter d ($0 \leq d \leq 0.5$) was defined for the A cation sites. When $d = 0$ this indicates that each Sr layer is fully populated with Sr, which is fully ordered. A value of 0.5 indicates that the A cation sites are randomly occupied by Sr and Ba, which is fully disordered. Large decreases in diffusion coefficients and the large increase in activation energy were observed for $d \leq 0.1$. In the Ba/Sr ordered structure, an ordered $\text{O}/\text{V}_\text{O}$ configuration is also observed. In particular, the diffusion coefficient increases and activation energy decreases are observed when oxygen occupancy in the Ba layer is close to 1. Thus, it is considered that the diffusion coefficients decreased and the activation energy increased because the oxygen sites in the Ba layer are fully occupied and oxygen migration through the Ba layer is blocked.

Investigation of the Lamination Behavior of Spinel Green Tapes for the Manufacture of Transparent Sintered Structures

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Magnesium aluminate (MgAl_2O_4) spinel is one of the attractive transparent materials due to a higher refractive index, mechanical strength, and chemical stability than glass materials. It is known that clear transparency needs more than a relative density of 99.9 % and high chemical purity. In this work, transparent spinel ceramics with a high density was produced via tape casting and lamination. This multilayer process is expected to be an advantageous route because of obtaining of homogeneous structure of the green tape and easy control of the thickness of the final sintered ceramics.

The slurries were prepared from two different commercial powders as starting materials; each is consisted of coarse or fine particles. The sintered single tape with a thickness of about 100 μm prepared from fine particles showed a relatively high density ($> 99\%$) and transparency. Also, two spinel green tapes were stacked and laminated by using hot-uniaxial-pressing (HUP) or hot-isostatic-pressing (HIP) before sintering at 1600 °C in air. The green tapes were received a compression stress above the glass transition temperature (T_g) of binder-plasticizer blends because it is expected that mass flow is occurred and interpenetration of the particles increases the density if appropriate pressure and heating are applied to laminated green tapes. In this work, the lamination in dependence of the pressing method (HUP or HIP), heating temperature (45-65 °C) and pressure (about 12-35 MPa) was investigated. The density was increased with increasing pressure at fixed temperature on the both of pressing methods. However, the sintered tape laminated by HUP was strongly curved during sintering and show no obvious improvement in the density compared to the single tapes. On the other hand, for the tape laminated by HIP, the relative sintered density achieved more than 99.5 % which is higher than the single tape. Additionally, the results of light transmission tests will be studied on the transparency of these tapes.

Preparation and Characterization of Piezoelectric Porous PZT Ceramics

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Porous piezoelectric ceramics have a great potential for many applications such as a sensor and an ultra sonic transducer. It is well known that porous structure affects mechanical and electrical properties of ceramics. In this study, piezoelectric porous PZT Ceramics were synthesized by replica technique to investigate how porous structures affect mechanical and electrical properties. Poly urethane (PU) foams which have a mean pore size of 10 and 30 ppi were used as a template of ceramics foams because the pore structure and distribution can be changed easily by designing template material. These PU foams were impregnated with a PZT slurry and were heated up to 600 °C to remove the PU. After debinding of sponges, ceramics foams were sintered at 1250 °C for 2 h. Synthesized ceramics foams showed open porosity of more than 87 %. Micro computed tomography (μ CT) scanning was also performed to investigate size and distribution of pores. Fracture strength of PZT ceramics foams was measured by compressing test. The 10 and 30 ppi sintered foams showed fracture strength of 0.29 and 0.69 MPa, respectively. In this presentation, the relationship between the rheology of slurry and coating properties of foams was discussed. The effect of pore size and pore distribution on mechanical and electrical properties was also discussed.

Sol-gel preparation of nitrogen doped zinc oxide films

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Zinc oxide (ZnO) is one of the metal oxides that have attracted considerable attention because of its low cost, non-toxicity, high stability and high efficiency. However, ZnO has a wide bandgap (3.27 eV), which only responds to a small range of the sun's energy spectrum. Thus, one of the goals to improve the optical response of ZnO is to increase its optical activity by doping a special metal element. Metal-doped ZnO nanoparticles, such as Ag, Cu, Sb, Au, As and Li, have been researched. Nevertheless, the metal doping has several drawbacks including thermal instability, deep color and potential toxicity, which are ill-suited for textiles, cosmetic and medicinal field. Under this situation, nitrogen has been regarded as the most-promising acceptor dopant because of its low ionization energy, suitable ionic radius, ease of handling, low material toxicity, and source abundance.

In this research, N-doped ZnO thin films were prepared via a sol-gel and spin-coated on glass and ITO substrates. For synthesis solution zinc acetate as Zn source and ammonium acetate as nitrogen source were used. The samples were prepared by the 3-time sol gel coating and the subsequent annealing at 300 °C for 20 minutes in air.

XRD analysis, SEM observation, and UV-vis measurement were performed on the synthesized thin films in order to characterize the constituent phases, microstructures and optical properties.

From the XRD and SEM results, ZnO was becoming amorphous with increasing N contents. In UV-vis measurement all samples had an optical transparency above 80 % in the visible range, and with increasing N contents, films became less absorbing in the wave range of 300 to 400 nm. These results indicated the bandgap reduction in ZnO by the nitrogen doping.

Evaluation of Thermal Conductivity in Porous Alumina

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A microporous ceramic membrane fabricated on a porous support substrate has been used for gas separation, and dehydration of water/alcohol mixtures at high-temperatures. The porous support substrates give mechanical strength to the membranes. Due to the intrinsic brittle nature of ceramic materials, fracture may occur due to thermal stress which is caused by a rapid temperature change. Therefore, it is important to evaluate the thermal shock resistance of the ceramic porous support substrates. In earlier study, the thermal shock resistance of the porous alumina materials for the support substrates has already been evaluated. Consequently, it has been deduced that the thermal conductivity had the most effect on the thermal shock resistance.

This work is devoted to obtaining further information on the factors controlling thermal conductivity in porous alumina. A wide range of models for the estimation of the thermal conductivity of porous materials have been proposed in the literature to take pore volume fraction into account. Using a single crystal thermal conductivity value of $35 \text{ W m}^{-1}\text{K}^{-1}$ or higher at room temperature for the solid phase, the thermal conductivity of the porous alumina could not be estimated satisfactory by these models. This is because thermal resistance of the grain boundaries has been neglected.

In this study, the thermal conductivity of porous alumina has been evaluated via measurement of the thermal diffusivity using the laser-flash technique, and the thermal resistance of grain boundaries was calculated from an analysis of the thermal conductivity-temperature data. In my presentation, the analytic results containing values of the thermal resistance of grain boundaries will be presented.

Lattice Dynamics and Raman spectroscopy study of M_2TeO_3 (M=Li, Na, K, Rb, Cs, Tl).

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TeO_2 materials have large nonlinear susceptibility, high refractive index and good transmission for visible and infrared rays with a wide range of wavelength. For these reasons, tellurites and the related compounds have received considerable attention in view of their potentials for use as nonlinear optical devices. The origin of these peculiar properties is considered to be due to their unit-structures such as TeO_4 , TeO_{3+1} and TeO_3 .

Raman spectroscopy is a very powerful method to estimate ratio of the each unit-structure of TeO_2 materials. However, the relation between the vibrational spectra and the shape of their unit-structures is not clearly understood. From the previous experimental Raman spectra data^[1], it is found that three spectra of K_2TeO_3 , Rb_2TeO_3 and Cs_2TeO_3 crystals are very similar each other and that they have a strong, single peak in the interval $780-790\text{ cm}^{-1}$. On the other hand, there is a strong band at a lower wavenumber, 730 cm^{-1} , in the spectrum of Tl_2TeO_3 crystal. The shapes of spectra of Na_2TeO_3 and Li_2TeO_3 crystal are very different from those of the other crystals mentioned above. Raman spectra of Li_2TeO_3 and Na_2TeO_3 crystals were split into two and three strong peaks, respectively, in the range from 650 cm^{-1} to 800 cm^{-1} .

In this study, we present Raman spectra and crystal structures of M_2TeO_3 (M=Li, Na, K, Rb, Cs, Tl) by using the lattice-dynamical modeling and compare these Raman spectra with experimental data. There are two main objectives in this research. The first one is to find the molecule which has a regular symmetry type TeO_3 and the second is to discuss on the reason why Raman spectra are greatly varied according to the composition of the compounds such as Li_2TeO_3 and Na_2TeO_3 .

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Small angle X-ray scattering (SAXS) analysis of mesoporous sol-gel thin films.

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Mesoporous divalent oxide materials have uniform and regular fine pores. As for mesoporous SiO₂ and TeO₂ thin films, new applications such as optical devices, gas sensors and separation membranes for SiO₂, and optical switches, optical data storages and nonlinear optoelectronic devices for TeO₂ have been expected. Moreover, it has been reported that ordered nanoporous materials are applicable to embedding another elements in their pores of mesoporous material and to forming nanoparticles within their network. However, synthesis and overall estimation of such thin films are still challenges.

In this study, SiO₂ and TeO₂ thin films were prepared by a sol-gel method with different solvents (ethanol, iso-propanol) and surfactants used to create microphase separation and mesophase templating. Films were produced by dip-coating slide glasses, cleaned with ethanol, in a stabilized sol of precursor/solvent/surfactant at a drawing rate of 2.3 mm · s⁻¹. The structures of the obtained films were then characterized by small angle X-ray scattering (SAXS). It is well known that the observation of X-ray interference is one of the most precise methods to measure the thickness of a thin film. Specular reflection of X-rays by a flat surface could be observed at glancing angle close to the critical angle. As a result, thickness of films and micelle inter-distances were simultaneously estimated from the period of the Kiessig fringes and peaks observed in the measured SAXS results. It was found that micelle ordering in TeO₂ thin film was difficult either for ethanol and iso-propanol solvent, while SiO₂ thin films successfully exhibited clear SAXS peaks especially for an iso-propanol solvent as well as small fringes corresponding to the X-ray interference. The structures of the micelle-ordered SiO₂ thin films were determined.