Beyond Imperfections: New Structure-Property Relationships in Ceramics and Glasses

788. WE-Heraeus-Seminar

22 – 24 May 2023

at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 788. WE-Heraeus-Seminar:

This seminar focuses on structures and functionalities of extended imperfections in crystals and glasses, aiming at providing an invaluable opportunity to share up-to-date experimental and theoretical findings about a new relationship between local, intermediate, and mesoscale structures as well as macroscopic properties.

Engineering of the local imperfections like defects, impurities, and microscopically ordered regions in crystals and glasses has so far been extensively carried out to impart additional functionalities to materials, for instance, conductivity in semiconductors and luminescence in phosphors. Based on enormous experimental efforts and calculations, a fundamental understanding of local properties has been substantially developed. Recently, several exotic phenomena have been discovered in materials with microscopic heterogeneity, suggesting that the local imperfections sometimes give rise to unusual structural modulations around them in the cooperation with host matrices to induce singular functionalities, which cannot be obtained with the local imperfections nor the host matrices alone. Uncovering the hidden mechanisms behind such extended imperfections will update the fundamentals of solid-state physics and provide a new milestone for the development of novel functional materials.

Topics of this seminar range over materials synthesis and measurements, modelling, theoretical calculations, and data sciences. Moreover, we expect that structural analyses for crystals and glasses with the local imperfections having various functionalities, including dielectric/magnetic/elastic responses and their cross correlations, superconductivity, and energy harvesting/storage properties are import topics. This seminar encourages international and interdisciplinary communications between early career and experienced researchers from a viewpoint of the extended imperfections. We hope that individual inspirations and mutual collaborations born in this seminar offer a new avenue for a next-generation materials science.

Scientific Organizers:

Ass. Prof. Dr. Jens Stellhorn, Nagoya University, E-mail: jens.stellhorn@nagoya-u.jp

Prof. Hiroki Taniguchi, Nagoya University, E-mail: taniguchi@nagoya-u.jp

Prof. Kyle Webber, University Erlangen/Nürnberg, E-mail: kyle.g.webber@fau.de

Introduction

Administrative Organization:

Dr. Stefan Jorda Mojca Peklaj	Wilhelm und Else Heraeus-Stiftung Kurt-Blaum-Platz 1 63450 Hanau, Germany

Phone +49 6181 92325-11
Fax +49 6181 92325-15
E-mail peklaj@we-heraeus-stiftung.de
Internet: www.we-heraeus-stiftung.de

Venue :

Physikzentrum
Hauptstraße 5
53604 Bad Honnef, Germany

Conference Phone +49 2224 9010-120

Phone +49 2224 9010-113 or -114 or -117
Fax +49 2224 9010-130
E-mail gomer@pbh.de
Internet: www.pbh.de

Taxi Phone +49 2224 2222

Registration:

Mojca Peklaj (WE Heraeus Foundation)
at the Physikzentrum, Reception Office
Sunday (17:00 h - 21:00 hrs) and Monday morning

Program

Program *(CEST)*

Sunday, 21 May 2023

17:00 – 21:00	ARRIVAL and REGISTRATION
18:30	*BUFFET SUPPER*

Monday, 22 May 2023

08:00	*BREAKFAST*	
09:00 – 09:15	**Welcome / Opening**	
Ferroics 1 Chair: D. Meier		
09:15 – 09:55	Beatriz Noheda	**Ferroelastic Domain Walls as Memristive Networks**
09:55 – 10:35	Hiroko Yokota	**The Investigations of Polar Domain Boundary in Ferroics**
10:35 – 11:00	*COFFEE BREAK*	
Structure and Properties 1 Chair: P. Zubko		
11:00 – 11:40	Jürgen Rödel	**Dislocation-tuned Functionality in Ceramics**
11:40 – 12:10	Donald Evans	**Nanoengineering Material Properties without Changing the Bulk Symmetry or Composition**
12:10 – 12:20	**Conference Photo (outside at the main entrance)**	
12:20 – 13:30	*LUNCH BREAK*	

Program *(CEST)*

Glasses 1
Chair: S. Kohara

13:30 – 14:10	László Pusztai	**Understanding Disordered Structures by Combining Diffraction Experiments and Computer Simulations via Reverse Monte Carlo Modelling**
14:10 – 14:50	Wolf-Christian Pilgrim	**Structure Determination of an Amorphous Molecular Solid with Strong Nonlinear Optical Properties**
14:50 – 15:20	*COFFEE BREAK*	

Glasses 2
Chair: A. Zeidler

15:20 – 16:00	Matthieu Micoulaut	**Properties of Network Glasses in Relationship with Elastic Phase Transitions**
16:00 – 16:30	Benjamin D. Klee	**Reverse Monte-Carlo Modeling in Molecular Amorphous Systems**

Forest Award Talks 1
Chair: K. Hayashi

16:30 – 16:45	Taro Kuwano	**Insulation of Aliovalent-doped Rutile-type TiO2**
16:45 – 17:00	Hiromi Murashige	**Observation of the Length Selective Alkane Absorption in P4MP1 Films in the Small-angle Scattering Region**
17:00 – 17:30	*BREAK*	
17:30 – 19:00	**Poster Session 1**	
19:00	*DINNER*	

Program *(CEST)*

Tuesday, 23 May 2023

08:00	*BREAKFAST*	

Ferroics 2
Chair: H. Yokota

09:00 – 09:40	Dennis Meier	**Structure-property Relations at Charged Interfaces in Ferroelectric and Multiferroic Oxides**
09:40 – 10:20	Pavlo Zubko	**Functional Properties of Ferroelectric Superlattices with Inhomogeneous Polarisation**
10:20 – 10:50	*COFFEE BREAK*	

Structure and Properties 2
Chair: D. Evans

10:50 – 11:30	Ayako Nakata	**Large-scale DFT Calculations of Materials with Complex Structures**
11:30 – 12:00	Benedict Paulus	**XANES Simulations of Amorphous RMC Models**
12:00 – 13:30	*LUNCH BREAK*	

Structure and Properties 3
Chair: W.-C. Pilgrim

13:30 – 14:10	Kouichi Hayashi	**Elucidation of Lattice Distortion in Mn-doped ZnSnAs2 by X-ray Fluorescence Holography**
14:10 – 14:50	Tomohiro Matsushita	**Photoelectron Holography of Dopants in Crystal and Defect at the Interface**
14:50 – 15:20	*COFFEE BREAK*	
15:20 – 16:00	Matthias Muntwiler	**Measuring True Corrugation of a h-BN Nanomesh Layer**

Program *(CEST)*

Forest Award Talks 2
Chair: T. Kuwano

16:00 – 16:15	Shunta Sasaki	**Local Structure Analysis of Rare-earth Rich Borate Glasses**
16:15 – 16:30	Yuta Shuseki	**Structural Properties of MgO–SiO2 Liquids and Glasses**
16:30 – 16:45	Tomoki Nakayoshi	**Computational Study of the Effect of Active Center Reduction on the Structure of Plant-type Ferredoxin**
16:45 – 17:30	*BREAK*	
17:30 – 19:00	**Poster Session 2**	
19:00	*HERAEUS DINNER at the Physikzentrum* *(cold & warm buffet, with complimentary drinks)*	

Program *(CEST)*

Wednesday, 24 May 2023

08:00	*BREAKFAST*	

Glasses 3
Chair: B. Klee

09:00 – 09:40	Anita Zeidler	**What Can and Can't We Learn from the FSDP**
09:40 – 10:20	Ying Shi	**Medium-range Structure Characterization of Silicate Glass and its Correlation with Liquid Fragility**
10:20 – 10:50	*COFFEE BREAK*	

Glasses 4
Chair: L. Pusztai

10:50 – 11:30	Milos Krbal	**Formation of Oriented Layered Transition-metal Dichalcogenides from Amorphous Thin Films**
11:30 – 12:10	Shinji Kohara	**Order within Disorder in Glasses and Liquids**
12:10 – 12:30	**Poster Prize Awards and Closing**	
12:30	*LUNCH*	

End of Seminar / Departure

Posters

Poster List

1	Hirofumi Akamatsu	**Controlling Octahedral Rotations through Anion Modification in Layered Perovskite Oxides**
2	Ryoji Asahi	**Microscopic Origins of Enhancement of Dielectric Permittivity in Substituted and Co-doped Titanates**
3	Davi Crandles	**Localization of Vibrational Modes in High-Configurational-Entropy Rocksalt Oxides**
4	Yoshitaka Ehara	**In-situ Observation of 90°-domain Switching for Piezoelectric Pb(Zr, Ti)O3 Applications**
5	Aleksander Gurlo	**Carbon and Hydrogen Interstitials in Metals: Formation, Observation and Properties**
6	Sekhar Halubai	**Advances in the Detection of Heavy Elements in an X-ray Fluorescence Holography Using a 2D-CdTe Detector at Room Temperature**
7	Yujiro Hashimoto	**Permittivity Boosting in Nb-doped Rutile-type TiO2**
8	Shinya Hosokawa	**Changes in Atomic, Electronic, and Dynamic Structures on a Gd65Co35 Glass by Temperature Cycling Rejuvenation**
9	Antonio Iacomini	**Tuning the Electrical Conductivity in 0.67BiFeO3-0.33BaTiO3 Lead-free Piezoceramics Prepared by Mechanochemical Activation**
10	Tatsuya Kato	**Study on Relationship between Structures and High Ductility of Mg-Y Alloys by x-Ray Fluorescence Holography**
11	Neamul Hayet Khansur	**Structure-property Relationships: A-site Cations Redistribution in Complex Polar Perovskite Oxides**

Poster List

12	Koji Kimura	**In-situ X-ray Fluorescence Holography Study on Piezoelectric Material under an Electric Field**
13	Viktoria Kraft	**Influence of Field-induced Phase Transformation on the Photoferroelectric Response of Sn-doped BaTiO3**
14	Michel Kuhfuß	**Influence of Grain Size and Defects on the Electromechanical Properties of Aerosol Deposited Films**
15	Taro Kuwano	**Insulati of Aliovalent-doped Rutile-type TiO2**
16	Jonathan Isbert Link Vasco	**Inter- and Intramolecular Arrangement of Organotin Sulfide Clusters with Extreme Nonlinear Optical Properties Depending on the Organic Ligand Substitution**
17	Anh Khoa Augustin Lu	**Structural Properties of Silica Studied by Locally-averaged Atomic Fingerprints: Phase Differentiation and Applications**
18	Kenta Matsutani	**Structure of GeO2 Glass Using Neural Network Potential Molecular Dynamics - Suppression of Intermediate-range Order with Pressure**
19	Nona Mirzamohammadi	**Investigation of the Active Role of Organic Compounds in the Stabilization of Ferroelectric Polarization of BaTiO3 Thin Films Grown by rf-Sputtering**
20	Tsuyoshi Miyazaki	**Release of a Large-scale and Linear-scaling DFT Code CONQUEST**
21	Seiji Nakashima	**Structural Analysis of Electric-field-induced Strains in Mn-doped BiFeO3 Thin Films by in-situ X-ray Fluorescence Holography under Electric Field**

Poster List

22	Alex Rettie	**Disordered Electrochemical Energy Materials**
23	Felip Sandiumenge Ortiz	**Microstructure and Thickness Dependent Structure of PbZrO3 Free-standing Membranes**
24	Shunta Sasaki	**Local Structure Analysis of Rare-earth Rich Borate Glasses**
25	Alp Sehirlioglu	**CRowdsourced Materials Data Engine for Unpublished X-Ray Diffraction**
26	Takao Shimizu	**Ferroelectricity in Non-doped AlN with Wurtzite Structure**
27	Yaoguang Song	**Solution Processed Non-crystalline Thin-film Electrolytes for All-solid-state Batteries**
28	Jan Hendrik Thimm	**Simulation of Air Scattering Contributions in X-ray Diffraction Experiments on Amorphous Matter**
29	Hiroto Tomita	**Atomic Structure and Chemical State of Surface Oxide / Gallium Nitride Interface**
30	Hanna Marita Wenzel	**Structure Determination in Two States of the Amorphous Solid State Electrolyte Li7P2S8I**
31	Cuo Wu	**High-Entropy Materials for Memristive Switching Component Application**
32	Shintaro Yasui	**Ultra-high-speed Chargeable Li-ion Thin Film Batteries by Control of Solid Electrolyte Interface**
33	Žiberna	**Impact of Thermal Treatment on the Microstructure and Mechanical Properties of Aerosol-deposited Pb (Mg1/3Nb2/3) O3 – PbTiO3 Thick Films**

Abstracts of Lectures

(in alphabetical order)

Nanoengineering material properties without changing the bulk symmetry or composition

Donald M. Evans

Experimental Physics V, Centre for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, 86135 Augsburg, Germany.

Email: donald.evans@uni-a.de

The control of conductivity is critical to any electronic device. Two well-known ways to tune conductivity are via changing the chemical composition (e.g. donor/acceptor doping), or changing the macroscopic symmetry, e.g. across a metal-insulator transition. In this talk, I show two proof-of-concept approaches of how the electronic properties of a material can be tuned, without changing either the chemical composition or the symmetry of the material.

The first example focuses on ‘cheating’ bulking properties using domain walls. Specifically, I use the Mott-insulator GaV_4S_8, to show highly enhanced conductivity at structural domain walls, that form across a Jahn-Teller transition. This enhanced conductivity is attributed to strain gradients changing the distance between vanadium clusters and, as such, only appears at domain walls with large strain gradients. While highly conducting pathways are not expected in an insulator, this work illustrates how any narrow band-gap material, with large enough internal strain gradients, could form conducting pathways.

The second example takes a more chemical approach and considers how stable, nanoscale, enhancement of conductivity can be achieved without net mass transfer, net change in stoichiometry, or the build-up of spurious electric and chemical gradients. Using hexagonal-$ErMnO_3$ as an example, enhancements in conductivity can arise by functionalizing charge neutral interstitial-vacancy pairs, so called “anti-Frenkel defects”. This allows, for example, orders-of-magnitude increase in conductivity, without reducing the inherent functionality of a ferroelectric: an important steppingstone to achieving domain wall devices.

Elucidation of lattice distortion in Mn-doped $ZnSnAs_2$ by X-ray fluorescence holography

K. Hayashi[1], H. Kizaki[2], N. Happo[3], S. Hosokawa[4], M. Suzuki[5], and N. Uchitomi[6]

[1]Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan
[2]Osaka University, Suita, Osaka, Japan
[3]Hiroshima City University, Hiroshima, Japan
[4]Kumamoto University, Kumamoto, Japan
[5]Kwansei Gakuin University, Sanda, Hyogo, Japan
[6]Nagaoka University of Technology, Nagaoka, Japan

X-ray fluorescence holography has produced a lot of achievements in the local structure analysis of dopants in various materials. In the presentation, we will introduce the results of local structural analysis of Mn-doped $ZnSnAs_2$ thin film, which is room temperature ferromagnetic semiconductor. Since ferromagnetic semiconductors have both the properties of magnets and semiconductors, they are expected to be applied to next-generation devices such as spin filter in spintronics. However, ordinary ferromagnetic semiconductors are hardly applicable because of low T_c less than room temperature. Under such situations, Mn:$ZnSnAs_2$ is a promising material exhibiting room-temperature ferromagnetism. However, its origin had not been clarified. Therefore, we analyzed the local structures around the cations of Mn:$ZnSnAs_2$ using X-ray fluorescence holography.

The Zn hologram from mother material $ZnSnAs_2$ revealed that the thin film had a sphalerite structure in which Zn and Sn randomly replaced the cation sites, instead of the chalcopyrite structure that was originally assumed. In addition, we found that the As-sublattice is more disordered than the cation (Zn and Sn) sublattice.[1] On the other hand, atomic image reconstructed from the Mn hologram from 5% Mn-doped $ZnSnAs_2$ showed further distortion of the As-sublattice. This is because Mn attracts nearby As by about 0.18 Å from its original crystallographic position. Based on first-principles calculations, this Mn-As bond indicates that the As 2*p* and Mn 3*d* orbitals are spin-polarized due to *p*–*d* hybridization, and is considered to be the basis for room-temperature ferromagnetism.[2]

References

[1] K. Hayashi, et al., *J. Appl. Phys.* **119**, 125703 (2016).
[2] H. Kizaki, K. Hayashi, et al., *Phys. Rev. B* **106**, 064434 (2022).

Reverse Monte-Carlo modeling in molecular amorphous systems

B. D. Klee[1,2]

[1] *Wigner Research Centre for Physics, Konkoly-Thege Miklós út 29-33,*
1121 Budapest, Hungary
[2] *Philipps-University, Hans-Meerwein-Str. 4, 35032 Marburg, Germany*

Reverse Monte-Carlo (RMC) modeling is a technique that is widely used to extract structural information regarding disorder in crystalline and non-crystalline systems from experimental datasets.[1] This is done by computationally finding a 3-dimensional real space configuration of atoms which is in good agreement with data and other preexisting knowledge.

For molecule based systems like molecular liquids usually ab-initio and force-field based techniques (e.g. Molecular Dynamics; MD) are used to acquire structural information. Using RMC for molecular systems has been done several times in the past but is still plagued by limitations and (partly practical) problems.[2-5]

In this talk I would like to discuss the existing problems for modeling molecular non-crystalline systems, summarize previous attempts to tackle them and present the RMC approach I am currently working on.[6,7]

References

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[3] P. Jóvári, Gy. Mészáros, L. Pusztai, E. Sváb, Journal of Chemical Physics **114**, 8082 (2001)

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Order within disorder in glasses and liquids

S. Kohara

Research Center for Advanced Measurement and Characterization
National Institute for Materials Science, Tsukuba, Japan

The advent of quantum beam sources, which can generate high-flux high-energy neutrons/X-rays, and the development of advanced instrumentations make it feasible to probe atomic arrangement in disordered materials at atomistic level with a high real space resolution. A combination of quantum-beam diffraction and data-driven structural modelling such as reverse Monte Carlo enables us to study topological order in disordered materials. Recent research topics on probing the topological order in oxide glasses and liquids are introduced. Moreover, the application of advanced topological analyses to uncover the hidden topological ordering in the pair correlation is addressed. Finally, we introduce hyper-ordered glasses and liquids to discuss the relationship between diffraction peaks, topological order and hyper order in disordered materials.

Formation of oriented layered transition-metal dichalcogenides from amorphous thin films

Milos Krbal[1], Jan Prikryl[1], Vit Prokop[1], Jan Mistrik[1], Paul Fons[2], Yuta Saito[3], Igor Pis[4] and Federica Bondino[4]

[1]Center of Materials and Nanotechnologies (CEMNAT), Faculty of Chemical Technology, University of Pardubice, nam. Cs legii, 565, 530 02 Pardubice, Czech Republic

[2] Faculty of Science and Technology, Keio University, Department of Electronics and Electrical Engineering, 223-8522 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan

[3]Device Technology Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba 305-8568, Ibaraki, Japan

[4] CNR-IOM, Istituto Officina dei Materiali, 34149 Basovizza (TS), Italy

Two-dimensional (2D) transition metal dichalcogenides (TMDC) have been demonstrated to have powerful application potential [1]. In order to realize these aspirations, the synthesis of stoichiometric 2D TMDC on a large scale is crucial. One growth process compatible with large-scale growth is the solid-state crystallization of thin amorphous layers [2], a process which avoids non-stoichiometric growth. Through a combination of experimental and ab-initio studies, we will present the local structure of as-deposited amorphous and crystalline TMDC phases and their impact on the optical and electrical properties. The crystallization mechanism, investigated using molecular dynamics simulations, reveals that the 1T´phase is an intermediate phase during crystallization from the amorphous to the 2H layered phase. Our results demonstrate the strong preferential crystal growth of TMDC layers along the c-axis as substantiated by the presence of the (200) Bragg reflection, which forms immediately upon heating the amorphous phase. We will demonstrate that amorphous thin films experimentally crystallize as 2-3 layered phases in the 2H allotrope in the temperature range from 400 to 600°C and above this temperature transform to a multi-layer bulk-like structure [3]. We will further show that the ordering of quasi-two-dimensional TMDCs via solid-state crystallization can be improved by using an amorphous chalcogen-rich phase, where the gradual release of chalcogen promotes the stacking of covalently bonded triplets [4,5].

References

[1] A.V. Kolobov, J. Tominaga, Two-dimensional Transition-Metal Dichalcogenides; Springer Series in Materials Science, Springer International Publishing AG, 2016.
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[4] M. Krbal et al. Crystal Growth & Design **22**, 5, 3072 (2022).
[5] Y. Saito et al. Journal of Materials Chemistry C **10**, 10627 (2022).

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Insulation of aliovalent-doped rutile-type TiO_2

T. Kuwano, Y. Hashimoto, K. Deguchi, and H. Taniguchi

Nagoya University, Nagoya, Japan

Rutile-type TiO_2 has been known as a high-permittivity paraelectric simple oxide. Recently, doping of aliovalent elements has attracted much attention for permittivity boosting of TiO_2. For instance, colossal permittivity (CP) more than 10^4 and low dielectric loss less than 10^{-1} were simultaneously observed in (Nb+In)-doped TiO_2. Such CP is attributed to Maxwell-Wagner (MW) effect, i.e., charge accumulation at interfaces between conductive and insulative regions such as grain boundary and electrode surface. On the other hand, Nb-doped TiO_2 exhibits permittivity boosting in low-temperature region where charge carriers are frozen and hence MW effect is suppressed. In this case, the key of permittivity boosting is suggested to be a special local structure with high polarizability introduced by Nb doping. However, Nb doping also makes samples too conductive and increases dielectric loss. To use aliovalent-doped TiO_2 as a capacitor, it is critical to keep the merit of permittivity boosting with suppressing the conductivity enhancement resulting from Nb doping.

In this study, we investigated the insulation role of trivalent elements in Nb-doped TiO_2 prepared by several ways. At first, the same amount of penta- and tri-valent oxides were mixed with TiO_2 powders, and ceramics pellets of $(A^{V}_{0.5}B^{III}_{0.5})_xTi_{1-x}O_2$ were obtained by conventional solid-reaction method. In the range of x = 0.1–50%, strong MW effect was observed while low-temperature permittivity boosting was absent. At second, oxide compounds like $ScNbO_4$ were synthesized and used as starting powders. Comparing with the case of mixing simple oxides, MW effect was considerably suppressed. Given that trivalent elements compensate the excessive charge of Nb, these results indicates that the magnitude of charge compensation, i.e., the distance between doped penta- and tri-valent elements strongly depends on doping process. In addition, we found the considerable enhancement of insulation of rutile-type Nb-doped TiO_2 by post-annealing with embedded in Ga_2O_3 powder. Figure 1 shows the electric-field dependence of resistivities of Nb-doped TiO_2 annealed in Ga_2O_3 at 1200 °C for 10 h (NTO-Ga) and pristine TiO_2 sintered at 1200 °C for 10 h. The resistivity of NTO-Ga is more than two orders of magnitude higher than that of the pristine. Moreover, the electric field at which a break down was observed is also significantly enhanced. In the presentation, we will talk the details on the experimental conditions and the break-down behavior.

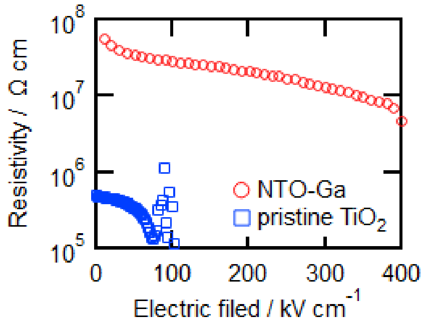

Figure 1. Electric-field dependence of resistivities of Nb-doped TiO_2 annealed in Ga_2O_3 at 1200 °C for 10 h (NTO-Ga) and pristine TiO_2 sintered at 1200 °C for 10 h.

Photoelectron holography of dopants in crystal and defect at the interface

T. Matsushita[1] **and Y. Hashimoto**[1]

[1]*Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara, Japan*

Recently, photoelectron holography has been developed to measure the atomic arrangement of dopants in crystals and that of the interface of thin films deposited on the crystals. We have installed a DA30 electron energy analyzer at SPring-8 BL25SU and have measured photoelectron holograms of dopants. By using the chemical shift of the core level, we succeeded in determining the individual atomic arrangement of multiple dopant sites [1,2]. However, DA30 had some problems such as long measurement time. Therefore, we invented a retarding field analyzer (RFA) [3,4] (Fig. 1) that achieves high energy resolution and high angular resolution, and installed it at the same beamline. This RFA enables us to measure the wide-angle photoelectron holograms (±50°) in combination with spectral measurements. For analysis, we have developed a program that enables fast peak fitting for this huge amount of data, making it possible to obtain holograms for each core level. We also succeeded in measuring the atomic arrangement of defects at the interface of insulating films on a diamond [5] (Fig. 2). In the talk, experiments, analysis, and applications will be discussed.

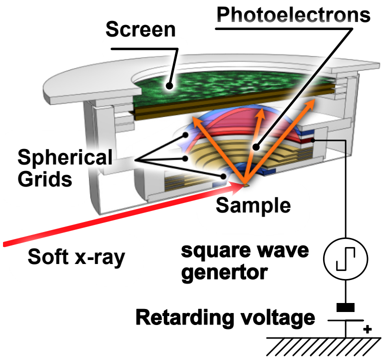

Fig. 1 Retarding field analyzer.

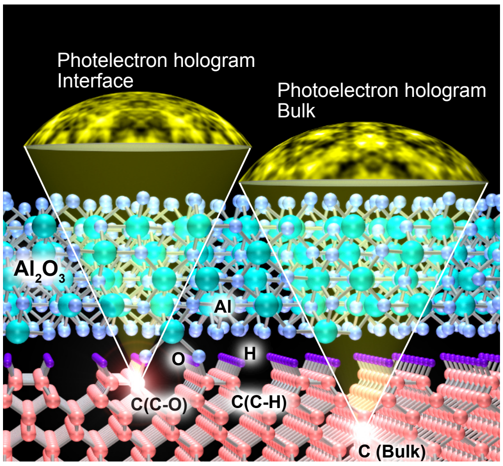

Fig. 2 Measuement of the defect structure at the insulating film on a diamond.

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[4] T. Muro, T. Matsushita, et al., J. Synchrotron Rad., **28**, 1669 (2021)
[5] M. Fujii, M. Y. Hashimoto, T. Matsushita, et al., Nano Lett., **23**, 1189 (2023)

Structure-property relations at charged interfaces in ferroelectric and multiferroic oxides

D. Meier[1]

[1]*NTNU Norwegian University of Science and Technology, Trondheim, Norway*

Oxide materials exhibit a broad range of tunable phenomena, including magnetism, multiferroicity, and superconductivity. Oxide interfaces are particularly intriguing, giving a new dimension to property engineering of functional materials. The low local symmetry at the interfaces, combined with their sensitivity to electrostatics and strain, leads to unusual physical effects, offering amazing opportunities for fundamental and applied research.

In my talk, I will discuss the unique electronic properties that arise at natural and artificially designed charged interfaces in ferroelectric and multiferroic oxides. In order to give an overview and demonstrate how structural, electric, and compositional degrees of freedom at such interfaces control the material's behavior, I will present three examples: (i) ferroelectric domain walls in hexagonal manganite single crystals, (ii) grain boundaries in ferroelectric $ErMnO_3$ polycrystals, and (iii) epitaxial heterointerfaces in multiferroic $(LuFeO_3)_9/(LuFe_2O_4)_1$ superlattices. To characterize the different types of interfaces, we perform correlated microscopy measurements, combining scanning probe microscopy, electron microscopy, and atom probe tomography. The imaging experiments provide new insight into the atomic-scale structure and chemical composition at charged oxide interfaces, clarifying the key role polar discontinuities and point defects play for their emergent physical properties.

References

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Properties of network glasses in relationship with elastic phase transitions

M. Micoulaut[1], **H. Flores-Ruiz**[2]

[1]Sorbonne Université, Paris, France
[2] Universidad de Guadalajara, Guadalajara, Mexico

Rigidity theory considers the glass network as an analog of a mechanical truss made of bars (i.e., bonds) and nodes (i.e., atoms) for which a Maxwell mechanical stability analysis can be performed. This approach can be cast into an elastic phase transition problem driven by the average coordination number $\bar{r}$ which acts as an external parameter for the transition. The latter transition is obtained between an elastically flexible underconstrained network to a stressed-rigid network that is overconstrained by atomic interactions. The locus of the transition is found when the average number of constraints per atom $n_c = 3$, the number of degrees of freedom per atom in 3D, corresponding to the well-known Maxwell isostatic criterion that furthermore provides guidance on compositional optimization of glasses. Experimentally, this transition has been detected in various glassy systems.

In the present talk, we will review the efforts that have been achieved in order to connect the molecular dynamics description of glasses to such phase transitions. We will in particular review and present results (structure, dynamics) from ab initio simulations on archetypal binary covalent chalcogenides such as Ge-Se, Ge-S and As-Se prior to some more recent efforts attempting to describe semi-metallic amorphous systems such as Ge-Sb-Te or Ge-Te that serve for data storage applications.

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Measuring true corrugation of a h-BN nanomesh layer

L. H. de Lima[1,2], T. Greber[3], and M. Muntwiler[1]

[1] *Paul Scherrer Institut, Villigen PSI, Switzerland*
[2] *Universidade Federal do ABC, Santo Andre, Brazil*
[3] *Universität Zürich, Zürich, Switzerland*

Two-dimensional (2D) materials like graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenides host a wealth of fascinating electronic properties, such as a relativistic band dispersion, topologically non-trivial band structure as well as emerging superconductivity in twisted bilayer graphene. Furthermore, their incorporation into device structures bears potential for fast, efficient electronics. The structure of two-dimensional layers is, however, often unstable and difficult to determine theoretically and experimentally. Synchrotron-based photoelectron diffraction (XPD/PED/PhD) is an excellent tool to study the atomic structure of 2D materials due to its surface sensitivity, chemical state specificity and intrinsic sensitivity to the positions of atomic cores [1]. Unlike x-ray scattering, XPD does not require long-range translational symmetry.

As an example, I will present and discuss the case of h-BN adsorbed on Rh(111). h-BN/Rh(111) forms a periodic, corrugated superstructure with a lattice constant of 3.2 nm originally called “nanomesh” due to its porous appearance in scanning tunnelling microscopy [2]. Despite numerous experimental and theoretical studies, structural details such as the corrugation amplitude and adsorption height have been difficult to determine quantitatively due to the differences in chemical and electronic environments in the strongly bound “pore” regions and the elevated “wire” regions of the corrugated structure. Using angle and energy scanned photoelectron diffraction and comparing measured data to multiple-scattering simulations we were able to determine the corrugation of h-BN nanomesh with sub-Ångström precision [3].

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Observation of length selective alkane absorption in P4MP1 films in the small-angle scattering region

H. Murashige[1], **Y. Hiejima**[2], **and A. Chiba**[1]

[1]Keio University, Yokohama, Japan
[2] Kanazawa University, Kanazawa, Japan

P4MP1 (isotactic poly(4-methyl-1-pentene)) is a semi-crystalline polymer that is used in wrapping films and trays. It has been reported as-cast P4MP1 films have pores between main chains and absorb low-molecular solvents such as alkanes. We have so far performed infrared spectroscopy (IR) and obtained results suggesting molecular selectivity; when a film is immersed in a liquid mixture of decane and hexane, it absorbs more decane than hexane.[1] However, microscopic information on the solvent absorption was lacking. For example, it is not clear whether amorphous or crystalline regions absorb more solvents. In this study, we carried out measurements of IR, small-angle x-ray scattering (SAXS) and wide-angle x-ray diffraction (WAXD), and found that both amorphous and crystalline regions absorb solvent, and also found that amorphous regions absorb more solvents than crystalline regions. We also carried out small-angle neutron scattering (SANS) using deuterated reagents. In order to distinguish the scattering by each solvent, measurements were performed with two different mixtures of solvents: a mixture of hexane(H) and decane(D) and a mixture of hexane(D) and decane(H). Here, H and D stand for natural and deuterated solvents, respectively. As a result, the SANS intensity was higher when the P4MP1 film was immersed in the mixture of hexane(H) and decane(D). This result suggests that decane(D) is selectively absorbed in the nm-scale and sub-micron range.

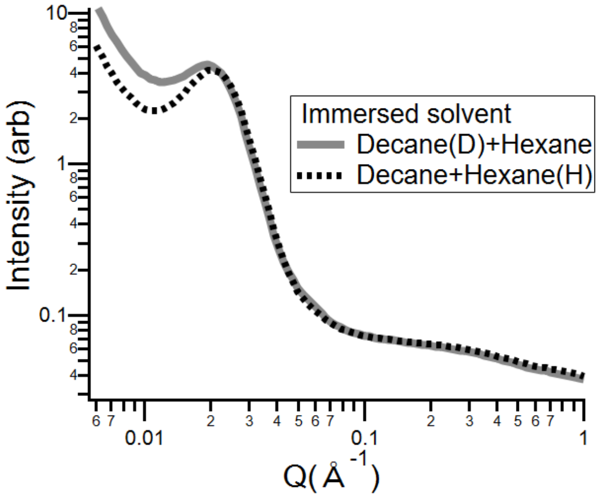

Figure 1: SANS profile of P4MP1 films immersed in a mixture of decane and hexane.

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Large-scale DFT calculations of materials with complex structures

A. Nakata[1], T. Miyazaki[1], and D. R. Bowler[2]

[1]National Institute for Materials Science, Tsukuba, Japan
[2] University College London, London, UK

First-principles density functional theory (DFT) calculation is a powerful tool to investigate the atomic and electronic structures of materials. To analyse materials with non-periodic complex structures, we often need large simulation models containing several-thousand atoms. However, DFT calculations are usually limited to study (simple) crystalline systems or clean surfaces having small unit cells with the periodic boundary condition because the conventional DFT calculation methods can treat only up to 1,000 atoms because of their high computational costs. To overcome this size limitation problem, we have developed a large-scale DFT code CONQUEST, which can treat large systems containing more than several thousands of atoms by using local orbitals and a linear-scaling (O(N)) method [1–3].

In this presentation, we will introduce our large-scale DFT calculation methods in CONQUEST and show several recent applications such as supported nanoparticle (NP) catalysts, interfaces in ferroelectric $YGaO_3$, and glass materials.

As an example of the applications, we investigated size and site dependences of atomic and electronic structures of supported Au NP catalysts. Figure 1 shows the optimizes structures of supported 2nm AuNPs with several shapes, consisting of about three thousand atoms. It was found that the larger the AuNP missing, the larger the interaction between the AuNPs and the MgO support, and the more the electronic state of the AuNPs and the MgO surface changes.

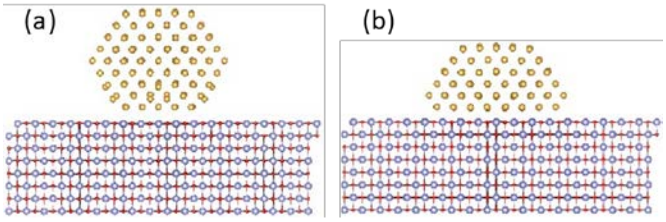

Fig. 1. Optimized structure of 2 nm Au nanoparticles on MgO(100) surface, (a) 2,901 and (b) 2,807 atoms, respectively.

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Computational study of the effect of active center reduction on the structure of plant-type ferredoxin

T. Nakayoshi[1], Y. Ohnishi[2], H. Tanaka[2], G. Kurisu[2], and Y. Takano[1]

[1]*Graduate School of Information Sciences, Hiroshima City University, Hiroshima, Hiroshima, Japan*
[2] *Institute for Protein Research, Osaka University, Suita, Osaka, Japan*

Plant-type ferredoxin (Fd) is metalloprotein containing single [2Fe–2S] cluster as the active center and mediate light-induced electron transfer from Photosystem I reaction center to various Fd-dependent enzymes in the photosynthetic process. Under physiological conditions, the [2Fe–2S] cluster mainly takes two types of redox states, *i.e.*, oxidized state ($[Fe_2S_2]^{2+}$) and reduced state ($[Fe_2S_2]^{+}$). The affinity between Fd and its target protein depends on the redox state, and the changes in affinity can be important for smooth Fd-mediated electron transfer. However, the detailed behavior of Fd in solution has not yet been fully elucidated. Therefore, molecular dynamics (MD) simulations were performed to elucidate the effect of the active-center reduction of Fd on the conformation and dynamic properties [1].

Model systems for MD simulations were constructed from our determined crystal structure of *Chlamydomonas reinhardtii* Fd (*Cr*Fd) [2]. Force-field parameters for the oxidized and reduced state of [2Fe–2S] cluster were determined using the quantum chemical calculations. The force constants for bond stretching and angle bending were directly calculated from Hessian matrices [3], and the atomic charges were determined by fitting the electronic potentials to each atom. Three independent 200-ns MD simulations were performed for oxidized and reduced forms.

Although the active-center reduction did not affect the overall structure of Fd, it did cause significant changes in the local structure around the active center. In the simulations for reduced form, the peptide bond linking Cys42 and Ser43 rotated within approximately 1 ns from the state of the simulations, due to enhanced electrostatic repulsion of the main-chain carbonyl group and [2Fe–2S] cluster. In addition, the structural changes of residues around the active site and hydrogen-bond recombination occurred in conjunction with peptide-bond rotation. These significant changes in local structure can explain the difference in affinity for the Fd-dependent enzyme between oxidized and reduced forms.

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Ferroelastic domain walls as memristive networks

Jan L. Rieck,[1,2] Davide Cipollini[2,3], Mart Salverda[1,2], Cynthia P. Quinteros[1,2], Lambert R. B. Schomaker[2,3], Beatriz Noheda[1,2]

[1]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[2]Cogni/Gron center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[3]Bernoulli Institute for Mathematics, Computer Science and AI, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
Email: b.noheda@rug.nl

Domain walls of ferroic oxides have been extensively investigated as functional defects. In particular, ferroelectric domain walls of ferroelectric oxide perovskites have shown enhanced conductivity and memristive behaviour. However, conductivity of domain walls has been mostly demonstrated at the individual domain wall level in thin layers by probing the conductivity across the layer thickness. Here we show that lateral current flow from wall to wall is also possible in these materials, therefore allowing information transfer through the domain wall network and making these systems promising for brain-inspired applications[1].

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XANES Simulations of Amorphous RMC Models

B. Paulus[1], J. Link Vasco, H. Wenzel, J. Thimm, W.-C. Pilgrim[1]

[1] *Philipps-University Marburg, Marburg, Germany*

The atomic scale structure of amorphous materials is often modeled using reverse Monte-Carlo simulations (RMC) employing experimental scattering and extended absorption fine structure (EXAFS) data as boundary conditions. [1,2] The ambiguity of the fitted experimental data and the randomness of the RMC algorithm, however, pose a problem in determining specific local structural features of the disordered system. [3] A possible way to address this issue is the simulation of the x-ray absorption near edge structure (XANES) of a variety of local atomic arrangements existing in the RMC model. Comparing the simulation results with experimental XANES data can help to evaluate the frequency of the simulated local structure in the real amorphous sample. As a test system we investigated the amorphous phases of the phase change system $Ge_{50-x}Cu_xTe_{50}$ at x = 5, 15 and 25. RMC models of these compositions were generated and XANES simulations of local structures around Ge, Cu and Te atoms were performed using the finite difference method (FDM) of the FDMNES software. [4]

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Structure Determination of an Amorphous Molecular Solid with Strong Nonlinear Optical Properties

W.-C. Pilgrim[1], J. Link Vasco[1], B. D. Klee[1,2], J. R. Stellhorn[1,3], S. Dehnen[1,4]

[1]Department of Chemistry, Philipps-University of Marburg, Germany
[2]Wigner Research Centre for Physics, Budapest, Hungary
[3]Department of Physics, Nagoya University, Japan
[4]Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany

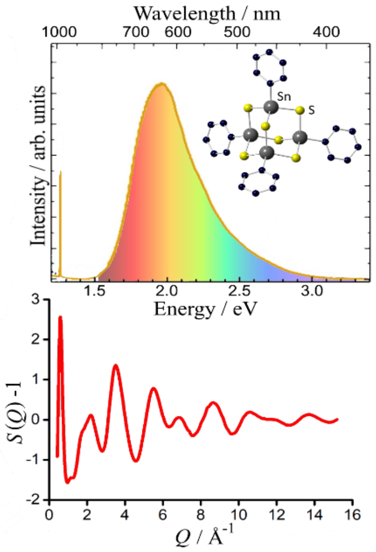

Fig. 1: X-ray structure factor (bottom) and emission spectrum (top) from IR-irradiation from a $[(PhSn)_4S_6]$ sample.

A new class of inorganic molecular clusters is presented exhibiting extreme nonlinear optical behavior when irradiated just by a simple continuous wave IR laser diode.[1] The molecular units consist of adamantane-like Sn-S clusters with organic ligands attached to the Sn atoms. The general shape is displayed in the inset of Fig. 1 for the $[(PhSn)_4S_6]$ cluster with organic phenyl-ligands. The materials are easy to synthesize, stable at air and allow great chemical variability. All of them act either as Second-Harmonics-Generators (SHG) or as White-Light-Generators (WLG), the latter provide bright white optical emissions resembling a tungsten-halogen lamp at 2900 K and retaining the beam divergence of the driving laser[2] as is exemplary shown in Fig. 1. The morphology of the substance has a significant impact on the type of response: Crystalline compounds react as SHGs while amorphous materials respond as WLGs. WLG is never observed in crystalline samples, suggesting that the effect is related to structural correlations or degrees of freedom that can exist only in disordered phases. To understand this structure-property relation and the reason for crystallization inhibition in the WLG samples, we performed a series of scattering studies on different samples using neutrons and X-rays in combination with EXAFS and analyzed the results with molecular reverse Monte Carlo simulations. The current status of our research on these SHG and WLG materials is reported, with particular attention to the observed structural differences between SHG and WLG materials.

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Understanding disordered structures by combining diffraction experiments and computer simulations via Reverse Monte Carlo modeling

L. Pusztai[1,2]

[1]*Wigner Research Centre for Physics, Budapest, Hungary*
[2] *IROAST, Kumamoto University, Kumamoto, Japan*

Reverse Monte Carlo (RMC) [1] is a simple tool for constructing large, three-dimensional structural models that are consistent with data obtained from diffraction experiments. Via random movements of particles, the difference between experimental and model total structure factors is minimized. As a result, by the end of the calculation, particle configurations become available that are consistent with the experimental structure factor(s). If the structure is analyzed further, partial radial distribution functions (prdf-s), as well as other structural characteristics (neighbor distributions, cosine distribution of bond angles), can be calculated from the particle configurations.

For the present purposes the most attractive feature of the RMC method is that it can incorporate any external information (diffraction and EXAFS data, as well as ideas based on other experimental or theoretical sources) that can be calculated directly from the coordinates of the particles. Prdf-s from molecular dynamics (MD) simulations fall into this category. In this case, if consistency with all input data is reached, then it may be stated that these input data are mutually consistent, as well as with the resulting particle configuration. If, however, some of the input data cannot be approached within their uncertainties, then it means that parts of the input data set are not consistent with other pieces of input information (see, e.g., [2] for the case of water).

Furthermore, the scheme [3] has been shown to be rather effective for creating attractive structural models of aqueous solutions of cesium halides [4] that were consistent with diffraction data and (most of) the MD-simulated prdf-s.

It is believed that the scheme [3] would also be able to serve the covalent glass community well, by combining (ab initio)MD simulation results directly with experimental structural data, via Reverse Monte Carlo modeling.

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Dislocation-tuned functionality in ceramics

J. Rödel

Materials Science, TU Darmstadt, Darmstadt, Germany

Dislocations in ceramics can serve both as barriers to thermal and electrical transport and as paths for electrical transport [1]. Exposure to light of appropriate wavelength may induce photoconductivity [2]. Just as dislocations as a one-dimensional defect can pin other dislocations, dislocations can also pin domain walls, respectively, form nuclei for domain wall formation when cooling through the Curie temperature [3].

These mechanisms rely on imprinting suitable dislocation structures into the bulk ceramic, be it a single crystal or a polycrystal. To this end we use far-field mechanical loading onto a rectangular block [4] or furnish same with a notch to obtain high-density directional structures. Simple methods entail cyclic ball loading [5], scratching or rolling on the surface. All in all, dislocation densities from 10^{12} m^{-2} to 10^{15} m^{-2} can be obtained, translating in average spacing of about 30 nm to 1 µm. Keep in mind, that naturally sintered polycrystalline ceramics or single crystals may have dislocation densities below 10^{10} m^{-2}.

I will show examples from furnishing different dislocation structures and examples from mediating electrical conductivity as well as photoconductivity.

Also, examples from pinning domain walls with unusual domain structures and huge piezoelectric coefficients will be presented.

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Local structure analysis in rare-earth-rich borate glasses

S. Sasaki[1], **A. Masuno**[2]

[1]*Hirosaki University, Aomori, Japan*
[2]*Kyoto University, Kyoto, Japan*

- Introduction

In the conventional melt quenching process, it is difficult to vitrify compositions containing high concentrations of R_2O_3 (R = rare earths). On the other hand, by using the containerless processing, it is possible to vitrify even with R_2O_3-rich compositions. R_2O_3–B_2O_3 glasses (R = rare earth element and Y) were synthesized in R_2O_3-rich compositions using an aerodynamic levitation technique[1]. In this study, the local environment around B atoms of R_2O_3–B_2O_3 glasses was investigated.

- Experimental procedure

Rare earth borate glasses were synthesized by containerless processing using an aerodynamic levitation furnace. Vibration analysis was performed by Raman scattering spectroscopy. The fraction of BO_4 units to all BO_n units (n = 3 or 4), N_4, was estimated from the ^{11}B MAS NMR spectra. The structure around the boron were estimated from ^{11}B 3QMAS NMR spectra.

- Results and discussion

Raman scattering spectra of $50R_2O_3$–$50B_2O_3$ glasses are shown in Fig. 1. It was shown that all main bands of these spectra were originated from vibrations of isolated BO_3, irrespective of a kind of R. Although the bands originated from vibrations of BO_4 did not appear clearly in the Raman scattering spectra, the peak of BO_4 was confirmed in the NMR spectra, which indicates that the N_4 value was not zero. Comparison of ^{11}B 3QMAS NMR spectra $50La_2O_3$–$50B_2O_3$ glass and $LaBO_3$ crystal suggests that the B–O bond length in isolated BO_3 in the glass is shorter and its distribution is broader than that in the crystal. The number of bridging oxygen of BO_4 in $50Y_2O_3$–$50B_2O_3$ glass was estimated to be lower than two by comparing NMR parameters with those of YBO_3 crystal.

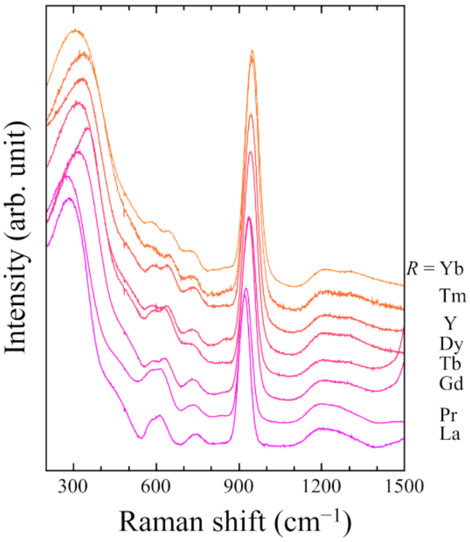

Figure 1. Raman scattering spectra of $50R_2O_3$–$50B_2O_3$ binary glasses.

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Medium-range Structure Characterization of Silicate Glass and its Correlation with Liquid Fragility

Y. Shi

Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA

Silicate glasses have no long-range order and a short-range order similar to their crystalline counter-parts. Therefore, their key structural information lies in the medium-range, represented as ring size distribution. We develop a heuristic method, named as RingFSDP[1], to extract ring structure information from the first sharp diffraction peak (FSDP) of the neutron scattering structure factor. Based on the force-enhanced atomic refinement simulations for two archetypical silicate glasses, we show that rings of different sizes exhibit a distinct contribution to the FSDP[2]. We then demonstrate that the ring size distribution of silicate glasses can be determined solely from neutron diffraction patterns, by analyzing the shape of the first sharp diffraction peak. This method makes it possible to uncover the nature of silicate glasses' medium-range order.

The medium-range structure information derived by RingFSDP method provides an insight into the structural origin of the glass transition, in particular, the sharpness of the dynamical arrest of a melt at the glass transition, defined as liquid fragility. We demonstrate that the fragility is governed by the medium-range-order structure based on a strong inverse correlation between fragility and the average medium-range distance (*MRD*) derived from the FSDP of neutron structure factor[3]. We use *in-situ* high-temperature neutron-scattering data to discuss the physical origin of this correlation. We argue that glasses exhibiting low *MRD* values present an excess of small network rings. Such rings are unstable and deform more readily with changes in temperature, which tends to increase fragility. These results reveal that the sharpness of the dynamical arrest experienced by a silicate glass at the glass transition is surprisingly encoded into the stability of rings in its network.

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Structural properties of $MgO–SiO_2$ liquid and glasses

Y. Shuseki[1] **and S. Kohara**[2]

[1]*Kyoto University, Kyoto, Japan*
[2] *National Institute for Materials Science, Tsukuba, Japan*

Introduction

The $MgO-SiO_2$ system is important in both glass science and geo science, because $MgO-SiO_2$ glass is a binary silicate glass system and enstatite (crystalline (*c*-) $MgSiO_3$) and forsterite (*c*-Mg_2SiO_4) are main components of mantle of the earth. Understanding of the structure of both glass and high temperature liquid of $MgSiO_3$ (high glass forming ability (GFA)) and Mg_2SiO_4 (low GFA) makes it possible to understand the origin of glass formation and magma ocean solidification. The status of density/viscosity measurements at the ISS, quantum beam diffraction measurements at SPring-8 and Oak Ridge National Laboratory will be reported and results of DFT-MD simulations will be discussed.

Result and discussion

Figure 1 compares the X-ray and neutron total structure factors, $S(Q)$, of glassy (*g*), liquid (*l*)-$MgSiO_3$ and Mg_2SiO_4[2,3]. It is confirmed that the $S(Q)$ of DFT−MD models reproduce experimental diffraction data. Both the $S(Q)$ of *g*,*l*-$MgSiO_3$ and Mg_2SiO_4 has a first sharp diffraction peak (FSDP) at around $Q \sim 2.0$ and 2.2 Å^{-1}. These peaks are broad and the position shifts to higher Q than those of *g*, *l*-SiO_2 ($Q \sim 1.5$ Å^{-1}), because the addition of MgO breaks down the network which is comprised by corner sharing of SiO_4 tetrahedra associated with the reduction of the cavity volume.

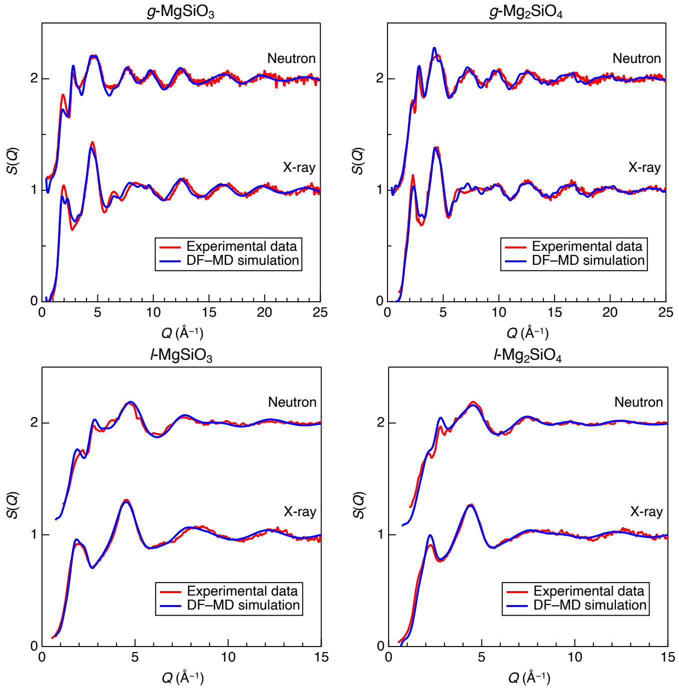

Figure 1. X-ray and Neutron total structure factors, $S(Q)$ of *g*, *l*-$MgSiO_3$ and Mg_2SiO_4. Red curve: experimental data, blue curve: DFT−MD simulation.

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The investigations of polar domain boundary in ferroics

H. Yokota[1, 2], Z. An[3], K. Kurihara[1], N. Hasegawa[1], N. Zhang[3],
M. Pasciak[4], A. M. Glazer[5,6], Y. Uesu[7]

[1] Chiba University, Chiba, Japan
[2] JST PRESTO, Tokyo, Japan
[3] Xi'an Jiaotong University, Xi'an, China
[4] Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic
[5] University of Oxford, Oxford, England
[6] University of Warwick, Coventry, England
[7] Waseda University, Tokyo, Japan

Domain boundaries in ferroics have become one of the hot research areas in the past few decades. Many unique physical properties which do not appear at domains have been reported in various materials. Among these physical properties, the existence of polarity at domain boundaries is a promising candidate for realizing a high-density memory device. Despite its attractiveness, there are not so many experimental methods to confirm the polarity at domain boundaries. We used a second harmonic generation microscope (SHGM) and successfully confirmed the polar natures at ferroelastic domain boundaries in various oxides. We applied this technique to other types of boundaries which are known as anti-phase boundary (APB). Figure 1 (a) shows the 2D image of SH wave distribution from the sample. The existence of SH-activity suggests that the APB possesses polarity. By combining with x-ray diffuse scattering experiment, we determine the internal structure of APB and it has ferri-like structure. Such internal structure allows the existence of local polarization at APB. We also applied an external stress and it turned out that the application of stress can enhance the polarity at the APB.

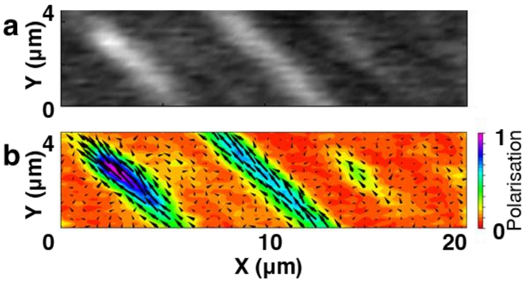

Fig.1 (a) 2D image of SH wave distribution. (b) 2D image of polarization distribution.

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What can and can’t we learn from the FSDP

<u>A. Zeidler</u> and P. S. Salmon

Department of Physics, University of Bath, Bath, UK

The structure of amorphous materials is best investigated using diffraction methods such as neutron diffraction (ND) or x-ray diffraction (XRD). Data is collected in reciprocal space, and the interpretation thereof is still a matter of debate. In this talk I will explain the occurrence or otherwise of 3 distinct peaks in the structure factors of amorphous materials and their relation to physical properties [1] (see Figure 1). Especially the first sharp diffraction peak (FSDP) has found considerable interest in recent years [2,3]. Here, I will discuss the information contained in this peak.

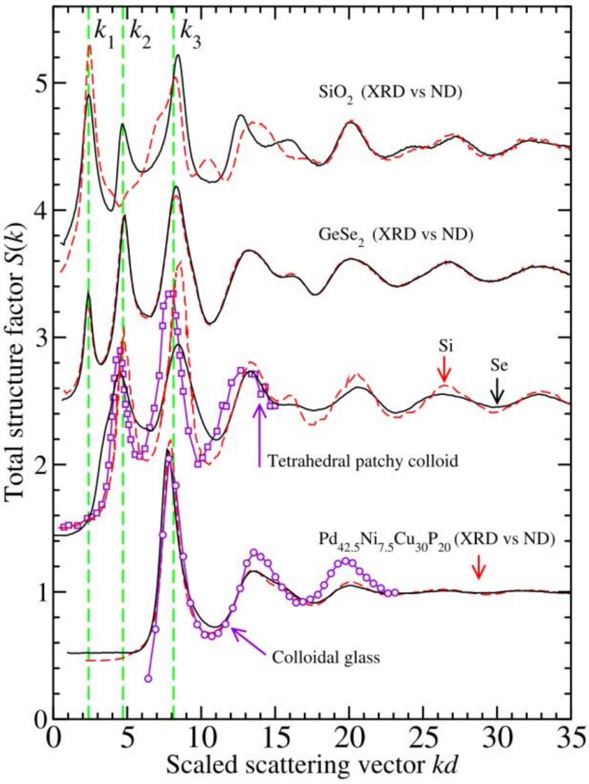

Figure 1 Total structure factors for selected glassy materials as a function of scaled scattering vector [1].

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Functional properties of ferroelectric superlattices with inhomogeneous polarisation

P. Zubko[1]

[1] *Department of Physics and Astronomy and London Centre for Nanotechnology, London, UK*

For most applications of ferroelectrics in electronics (e.g. FeRAM, FeFET or ferroelectric tunnel junctions), the coveted state is one of a stable, homogeneous polarization. However, as electronic components get smaller and the thickness of the ferroelectric material is reduced to the nanoscale, this homogeneous state becomes increasingly difficult to maintain. While this presents significant challenges for traditional device concepts, it also opens new opportunities for applications of nanoscale ferroelectrics. At the nanoscale, ferroelectrics are strongly influenced by the mechanical and electrical boundary conditions that can lead to the appearance of dense, often ordered, and sometimes highly complex nanoscale domain structures [1,2]. These domain structures have highly inhomogeneous polarization and strain distributions that are impossible to achieve in bulk materials. At the same time, they are highly susceptible to applied electric fields and stresses, giving rise to interesting properties, such large enhancements of the dielectric permittivity, antiferroelectric-like behaviour, and negative local permittivities that could pave the way to more power-efficient field effect transistors [3,4]. This talk will focus on the use of different experimental techniques to probe nanoscale polarisation structures and their contribution to the functional properties of ferroelectric superlattices—a model system for exploring nanoscale ferroelectricity.

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Abstracts of Posters

(in alphabetical order)

Controlling Octahedral Rotations through Anion Modification in Layered Perovskite Oxides

H. Akamatsu[1], **K. Ishibuchi**[1], **S. Yoshida**[1], **S. Ohno**[1], **and K. Hayashi**[1]

[1]Kyushu University, 744 Motooka Nishi-ku Fukuoka 819-0395, Japan

Controlling structural distortions is essential to induce and control physical properties due to close structure-property relationships. The rotation of coordination octahedra, which is common in perovskite-related compounds, is often controlled by cation substitution based on the tolerance factor. On the other hand, controlling by anion substitution or insertion has rarely been reported. Recently, the insertion of fluoride ions into the interlayer sites of layered perovskite oxides has been predicted by first-principles calculations to alter the octahedral rotation pattern [1].

In this study, we focus on the Ruddlesden-Popper phase $NaLaTiO_4$, which has centrosymmetric *P*4/*nmm* structure. In $NaLaTiO_4$, the coordination octahedron is not rotated, but when La is replaced by small rare earths such as Sm, the octahedral rotation is induced [2]. In order to investigate the possibility of controlling the coordination octahedral rotation by anion modification, we introduced fluorine into $NaLaTiO_4$ by a low-temperature topochemical reaction using a fluorine-containing polymer, and performed detailed crystal structure analysis of the sample. Fluoride ions are substituted with oxide ions at the apical sites of octahedra and inserted into the interstitial sites in the LaO rocksalt layers (Fig. 1). The resultant oxyfluoride exhibits octahedral rotation as observed in $NaRTiO_4$ with small rare earth *R*. The mechanism on the fluorination-induced octahedral rotations will be discussed based on our crystallochemical analysis and density functional study.

Acknowledgements: This research was supported by Japan Society of the Promotion of Science (JSPS) KAKENHI Grants Nos. JP21H05568 and JP 23H01869.

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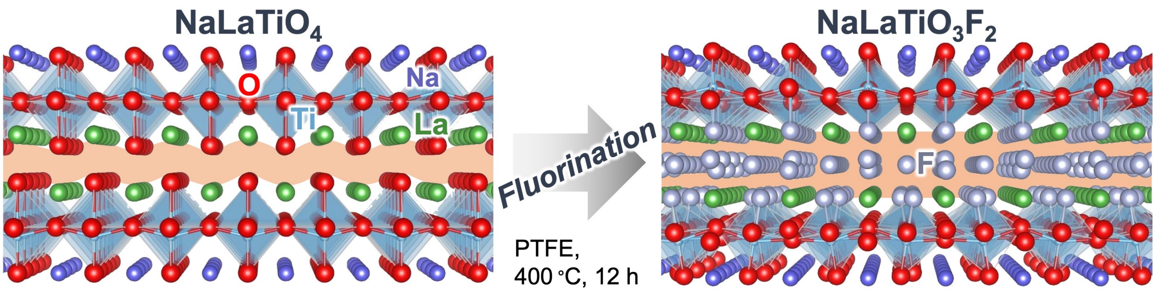

Fig. 1. Schematic illustration of topochemical fluorination of an *n* = 1 Ruddlesden-Popper phase $NaLaTiO_4$.

Microscopic origins of enhancement of dielectric permittivity in substituted and co-doped titanates

A. Kutana, Y. Shimano, and R. Asahi

Nagoya University, Nagoya, Japan

Recently, materials exhibiting colossal dielectric constants (>10^3) have been reported, suggesting that it is possible to intrinsically improve the dielectric constant of bulk crystals by controlling the local composite defect structure [1,2]. In this study, we focus on substituted and co-doped titanates to understand the correlation between the local structural feature and dielectric property through systematic calculations [3].

First-principles calculations of the dielectric constants of co-doped rutile-type oxides TiO_2, SiO_2, and SnO_2 have revealed the existence of Ti-based oxides with relatively stable and high dielectric constants (Fig. 1). To elucidate the origin of boosting in the dielectric constant, we constructed a predictive model by machine learning and investigated the correlation with the dielectric constant in detail, and found that the dielectric constant increases at a certain Ti-O bond distance (Fig. 2). Compared with the changes in dielectric constant and phonon mode in the rutile TiO_2 crystal under hydrostatic pressure, we found that the increase in dielectric constant is due to the softening of the bonds associated with the distortion of the local structure.

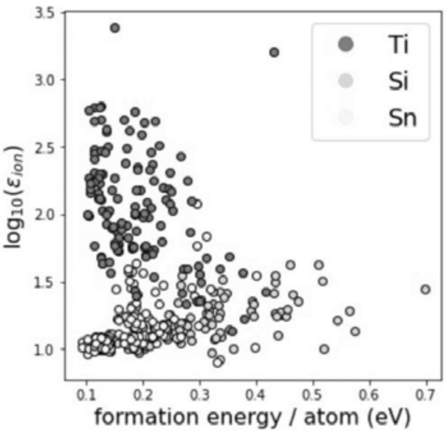

Fig. 1 Dielectric constants v.s. formation energy of doped rutiles.

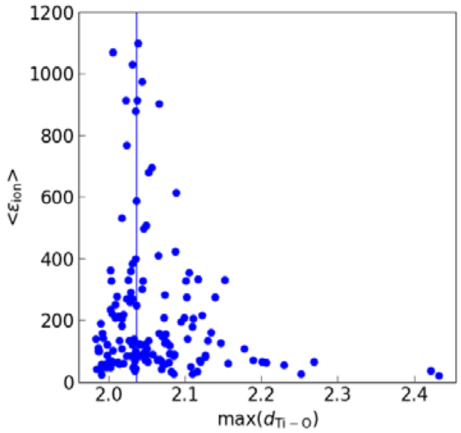

Fig. 2 Dielectric constants v.s. maximum Ti-O bonding length in co-doped TiO_2

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Localization of Vibrational Modes in High-Configurational-Entropy Rocksalt Oxides

C.M. Wilson, G. Ramachandran, T. Ashfarvoshoughi, and D.A. Crandles

Dept. of Physics, Brock University, St. Catharines, ON, Canada

X-ray diffraction shows that, if quenched to 295K from high enough temperature, the high-entropy oxide $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ (HEO) forms a single-phase rocksalt structure despite cation disorder. The material exhibits a mixture of long range order (oxygen sublattice) and disorder (random cation sublattice). In 3D materials, disorder can sometimes produce mode localization. For example, in amorphous Si, lattice dynamical calculations show that some of the phonon eigenvectors, corresponding to modes above a threshold frequency, are characterized by exponential decay.[1] Furthermore, the onset of phonon localization for mode frequencies above a high-frequency mobility edge in the Vibrational Density of states is accompanied by a participation ratio (PR)<0.1. In this work, we extend these studies to HEO using the General Utility Lattice Program (GULP). New empirical interatomic potentials (EIPs) are developed for the parent binary oxides MgO, CoO, CuO, NiO, and ZnO by fitting to experimental phonon frequencies, dielectric constants, and lattice parameters. The simulated vibrational density-of-states of the parent binary oxides are in agreement with inelastic neutron scattering data and Density Functional Theory calculations. The EIPs are uitilized in HEO by neglecting cation-cation interactions. The simulated infrared and Raman spectra of HEO are in agreement with experimental data.[2] The main result is that a smaller percentage of modes are localized in HEO than in a cluster of α-Si with a similar number of atoms. Additionally, we show that the number of localized modes increases if the ordered oxygen sublattice is disturbed by the random substitution of sulfur atoms.

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In-situ observation of 90º-domain switching for piezoelectric $Pb(Zr, Ti)O_3$ applications.

Yoshitaka Ehara[1], **Ayumi Wada**[2], **Hitoshi Morioka**[3], **Takeshi Kobayashi**[4], **Shintaro Yasui**[5,6], **Ken Nishida**[1] **and Hiroshi Funakubo**[7]

[1] *Department of Communications Engineering, National Defense Academy, Yokosuka, Japan*
[2] *Department of Innovative and Engineered Materials, Tokyo Tech., Yokohama, Japan*
[3] *Application Department, X-ray Division, Bruker Japan K.K., Yokohama, Japan*
[4] *National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan*
[5] *Laboratory for Zero-Carbon Energy, Tokyo Tech., Meguro, Tokyo, Japan*
[6] *Laboratory for Materials and Structures, Tokyo Tech., Yokohama, Japan*
[7] *School of Materials and Chemical Technology, Tokyo Tech., Yokohama, Japan*

$Pb(Zr,Ti)O_3$ [PZT] and their related materials are widely applied for microelectromechanical systems (MEMSs), such as actuators, sensors, and energy harvesters, because their superior piezoelectric properties which can directly convert the displacement into electric signal, and vice versa.(1,2) The macroscopic strain induced by an application of an electric field that consists of primally two mechanisms: (i) "intrinsic effect" lattice elongation along the polar axis and (ii) "extrinsic effect" ferroelastic domain wall motion, which is dominant in the induced strain.(3,4) The extrinsic effect in the thin film is one of the key approaches to realize the high efficiency and piezo-MEMS devices

In this work, we prepared the piezoelectric microcantilever with 1.1 μm-thick PZT active layer using by piezo-MEMS microfabrication techniques, and we observed the reversible *a*- to *c*-domain (90°-domain) switching during applying electric field clarified by using *in-situ* 2D-XRD technique. The amount of switching domain strongly depended on the thickness of Si substrate, the domain switching was suppressed about 50 % in PZT film on the 400 μm-thick Si substrate compared with the 5 μm-thick one. The piezoelectric constants of PZT films on 5 μm-thick substrate is virtually free substrate clamping effect and show the comparable constants to bulk ceramics ones. Our results suggest that the cantilever structure is one of the significant candidates for MEMS devices which require the superior piezoelectric constant.

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Carbon and hydrogen interstitials in metals: formation, observation and properties

A. Gurlo[1]

[1]*Chair of Advanced Ceramic Materials, Technische Universität Berlin, Germany*

The incorporation of hydrogen and/or carbon into the interstitial positions of metals typically does not alter their crystal structure, leading only to an expansion of the crystal lattice. The well-known example is the dissolution of hydrogen in palladium. The question arises if (and how) this effect can be used for tuning the physical and chemical properties of the corresponding systems, especially electrical conductivity and catalytic activity. Our in-situ XRD experiments with complementary electrical conductivity measurement demonstrate the effect of hydrogen and carbon incorporation for two model systems, with implications for the heterogenous catalysis and gas sensing.

The palladium-hydrogen interaction is one of the most studied systems because the high specific solubility of hydrogen in palladium is widely used in several industrial processes, for instance in membranes for hydrogen purification and hydrogen storage systems. As for electrical properties, during the adsorption of H_2 molecules hydride formation occurs and the metallic conductivity falls, until a composition of around $PdH_{0.5}$ is reached at which point the solid becomes a semiconductor. As dissolved hydrogen atoms also cause an increased scattering of conducting electrons, there is a corresponding decrease in conductivity of α-PdHx; this effect is the basis of palladium-based resistive gas sensors (chemiresistors) [1]. For carbon-nickel system, carbon in-situ generated from methane pyrolysis dissolves on the octahedral interstitials of the Fm-3m nickel nanoparticles, leading to the formation of a non-stochiometric nickel carbide with gradually increasing carbon content from core to the surface. Once the limit of solubility of carbon in nickel is achieved, the lattice contracts again due to precipitation of carbon in the form of carbon nanotubes [2].

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Advances in the detection of heavy elements in an X-ray fluorescence holography using a 2D-CdTe detector at room temperature

<u>H. Sekhar</u>,[1,2] K. Kimura,[1,2] N. Happo,[3] Y. Kubozono,[4] T. Kato,[1] J. R. Stellhorn[5] and K. Hayashi[1,2]

[1]Nagoya Institute of Technology, Japan.
[2]Super Photon Ring-8GeV (SPring-8), Japan.
[3]Hiroshima City University, Japan.
[4]Research Institute for Interdisciplinary Science, Okayama University, Japan.
[5]Department of Physics, Nagoya University, Japan.

X-ray fluorescence holography (XFH) is a non-destructive analysis method to visualize three-dimensional (3D) structural images around a specific element [1,2]. Currently, to measure, a low energy fluorescent X-ray, Si-based avalanche photodiode detector (APD) is in operation. Thus, many heavy elements, in particular palladium, rhodium, iodide and so on, are not easy to measure due to their high energy fluorescent X-rays. These elements are used in a variety of energy conversion materials such as thermo-electrical and piezo-electric materials [3,4]. In the XFH measurement, the commercially available point-CdTe detector is hard to use due to the low count rate (50,000 counts per second). To address this issue, we introduce the 2D-CdTe detector, which allows to enhance the count rate.

XFH measurements were carried out in inverse mode on a pellet β-PdBi2 sample at BL13XU, SPring-8 facility in Japan. The sample was excited to eight energies of incident X-rays from 29.5 to 33.0 keV at the interval of 0.5 keV above the Pd K absorption edge (24.4 keV). The signal was picked up through a C-shaped graphite analyser. The 2D-CdTe detector has been positioned at the focus of the graphite analyzer [3]. As the result, the counting rate for this experiment was about one million counts per second. The XFH signal measured at 29.5 KeV using point- and 2D-CdTe detectors are processed, we observed a clear standing wave (Kossel line) pattern in case of 2D- CdTe detector compare to their point-CdTe detector. From these results, we conclude that by employing the 2D- CdTe detector at ambient temperature in XFH allows to record 3D image from high-energy regime fluorescent X-rays from future energy conversion materials.

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Permittivity boosting in Nb-doped Rutile-type TiO_2

Y. Hashimoto, T. Kuwano, K.Deguchi and H. Taniguchi

Department of Physics, Nagoya University, Furo-cho, Chikusa, Nagoya, Japan

There is an increasing demand for high-permittivity dielectric materials aiming to develop capacitors of excellent electrostatic capacity that enable miniaturization of various electric devices. Ferroelectric materials like $BaTiO_3$ have so far been used for designing the high-performance capacitors. However, the capacitance of ferroelectric-based capacitors decreases under an electric field to limit their high-voltage applications. A permittivity boosting in non-ferroelectric materials is thus an important challenge.

Recently, colossal permittivity (CP) of the order of 10^4 was reported in Nb+In co-doped rutile-type TiO_2 [1]. An origin of CP was proposed to be a unique local structure called “electron-pinned defect-dipoles”, which are formed around Nb and In. This report has inspired local structure engineering of non-ferroelectric materials to develop high-performance capacitors. Several follow-up studies have clarified that the reported CP is caused by the Maxwell-Wagner effect due to a semiconducting property of the sample and the intrinsic permittivity of the co-doped TiO_2 is of the order of 10^2–10^3 [2, 3]. Despite many experimental and theoretical studies performed thus far, a mechanism of the permittivity boosting in the co-doped TiO_2 has remained an open question.

In the present study, we focused on respective roles of the co-dopants in the permittivity boosting and investigated effects of Nb-doping on the dielectric properties of the rutile-type TiO_2. Systematic dielectric measurements and structure analyses on the polycrystalline and single crystal samples have clarified a non-monotonic variation of permittivity with increasing Nb-concentration. The present results suggest that a local structure with large polarizability forms around Nb to play a major role in the permittivity boosting in the rutile-type TiO_2.

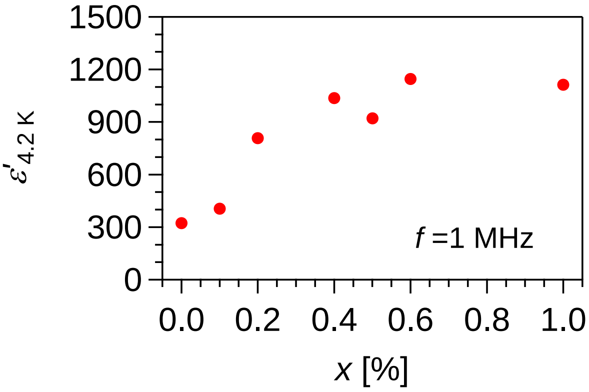

Figure 1. Dielectric permittivity at 4.2 K, $\varepsilon'_{4.2\,K}$, measured in $Nb_xTi_{1-x}O_2$ single crystals with the various Nb-concentration.

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Changes in atomic, electronic, and dynamic structures on a $Gd_{65}Co_{35}$ glass by temperature cycling rejuvenation

S. Hosokawa

[1]*Institute of Industrial Nanomaterials, Kumamoto University, 2-39-1 Kurokami,*
Chuo-ku, Kumamoto 860-8555, Japan

Rejuvenation in glasses is defined as an excitation to a higher energy state by an external stress. Ketov et al. reported a rejuvenation effect on $La_{55}Ni_{10}Al_{35}$ by a temperature cycling between room and liquid N_2 temperatures [1]. Hufnagel reviewed such cryogenic rejuvenation, and suggested that non-affine deformation must be caused on an atomistic length scale [2]. We carried out some element-selective structural experiments on a $Gd_{65}Co_{35}$ metallic glass (MG), and found distinct structural changes around both the Gd and Co atoms [3]. Subsequently, we performed photoemission and inverse-photoemission spectroscopies experiments, and found the remarkable changes in the valence- and conduction-band density of states as well as Co 3*d* core-level states by this cryogenic rejuvenation, which may be associated with the structural changes. By using inelastic x-ray scattering experiment, we have obtained the changes in the distributions of longitudinal elastic constants. In this report, we will present the structural, electronic, and dynamical changes of the $Gd_{65}Co_{35}$ MG alloy by the cryogenic rejuvenation in detail, and clarify the relationship between the cryogenic rejuvenation and atomic, electronic, and dynamic structures in this MG.

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Tuning the electrical conductivity in $0.67BiFeO_3$-$0.33BaTiO_3$ lead-free piezoceramics prepared by mechanochemical activation

Antonio Iacomini[1], Maja Koblar[1,2] and Tadej Rojac[1,2]

[1]*Electronic Ceramics Department, Jožef Stefan Institute, 1000 Ljubljana, Slovenia*
[2]*Jozef Stefan International Postgraduate School, Ljubljana, Slovenia*

Lead-based relaxor ferroelectrics, including PMN-PT, have been widely studied since 1959 for their exceptional electromechanical properties. Despite decades of research, the mechanisms behind PMN-PT ultrahigh piezoelectric properties are still being debated. Recent evidence suggests that the disorder inherent to relaxors may enhance the dielectric and piezoelectric response originating from lattice and domain-wall dynamic. However, due to the recent trend towards lead-free piezoelectric materials, PMN-PT and other lead-based relaxors must be replaced. Among lead-free ferroelectric materials, the $BiFeO_3$-$BaTiO_3$ (BFO-BT) system with the morphotropic composition (~67% BFO) is a promising candidate due to its attractive piezoelectric properties (>110 pC/N) and high Curie temperature (>400°C) [1]. However, the BFO-BT system faces two main challenges: i) heterogeneous composition with core-shell structures and secondary phases and ii) high leakage current resulting from the evaporation of Bi_2O_3 during sintering and change in the valence state of Fe cations. To overcome these challenges, defect engineering of the BFO-BT system is necessary, which requires a systematic study of the point defects in this system. This work focuses on the synthesis and point defects study of undoped and Mn-doped BFO-BT ceramics prepared by mechanochemical activation (MA). The MA method is shown to be a simple and effective way to produce high-quality BFO-BT ceramics with high densities and negligible amounts of core-shell structures and secondary phases. Additionally, point defect studies are conducted by evaluating the electrical conductivity under different temperatures (25-700°C) and O_2 partial pressures (10^{-6}-1 atm). This allows for in-situ observation of redox processes, oxygen non-stoichiometry, and defect states, particularly oxygen vacancies and p- and n-type conduction mechanism.

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Study on relationship between structures and high ductility of Mg-Y alloys by x-ray fluorescence holography

T. Kato[1, 2,*], K. Kimura[1], S. Hosokawa[3], S. Ando[3], S. Kashima[1],
Y. Hashimoto[4], N. Happo[5], T. Matsushita[5], H. Ishii[6] and K. Hayashi[1,7]
[1]Nagoya Institute of Technology, Nagoya, Japan
[2]Universite Grenoble Alpes, St Martin d Heres, France
[3]Kumamoto University, Kumamoto, Japan
[4]Nara Institute of Science and Technology, Nara, Japan
[5]Hiroshima City University, Hoiroshima, Japan
[6]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
[7]SPring-8, Kouto, Japan

In general, magnesium (Mg) is known as a low ductility at room temperature because of its own structure (hexagonal close-packed (hcp)). To improve the low ductility of Mg, the rare earth elements are mixed with Mg and made alloys. Among rare earth elements, yttrium (Y), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), cerium (Ce), and gadolinium (Gd) are usually used to make alloys. In this study, Mg-Y alloys are focused to clarify the relationship between their high ductility and their structure. The objective of this study is to analyze local structure around Y atom in a Mg-Y alloys using an x-ray fluorescence holography (XFH) analysis. The XFH experiments were conducted on a $Mg_{99.7}Y_{0.3}$ single crystal using BL12B2 beamline at the SPring-8 Synchrotron Radiation Facility, Japan. From the results of XFH experiments, it was found that a part of Y atoms was located at the ideal positions in pure Mg but others formed Y dimers in the hexagonal close-packed structure of $Mg_{99.7}Y_{0.3}$ alloys. It was considered that the dimer formation plays an important role in activating non-limited the plastic slip in the crystallographic c-direction of $Mg_{99.7}Y_{0.3}$ alloys although the crystal structure is still hexagonal by closed-packed.

Structure-property relationships: A-site cations redistribution in complex polar perovskite oxides

Gina Eyoum,[1] Kyle G Webber,[1] Neamul H Khansur[1,*]

[1]*Department of Materials Science and Engineering, Friedrich-Alexander-Universit¨at Erlangen-Nürnberg, 91058 Erlangen, Germany*

Tailoring the eletromechanical properties of a material without altering the original composition is an emerging phenomenon for the optimization of functional properties. Post-sintering thermal treatment with varying maximum temperatures, cooling rates, and atmospheres can influence the crystallographic phases, domain structures, conductivity, mechanical properties, and the temperature stability of the electromechanical properties. In this contribution, influence of annealing conditions on the funcitonal properties, structre, and defect chemistry of A-site complex polar perovksite oxides (A,'A")B_2O_6 will be highlighted.[1,2]

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In-situ X-ray Fluorescence Holography Study on Piezoelectric Material under an Electric Field

K. Kimura[1], H. Toyama[1], S. Nakashima[2], H. Sekhar[1], N. Happo[3],
H. Tajiri[4], M. Iwata[1], and K. Hayashi[1]

[1]Nagoya Institute of Technology, Japan
[2]University of Hyogo, Hyogo, Japan
[3]Hiroshima City University, Hiroshima, Japan
[4]Japan Synchrotron Radiation Research Institute, Hyogo, Japan

Piezoelectric materials can interconvert between electrical and mechanical energies. In order to understand a detailed mechanism of this behavior, it is important to elucidate structural change induced by an electric field at atomic level.

X-ray fluorescence holography (XFH) is a powerful technique to visualize three-dimensional atomic configuration around a specific element [1]. In the last decade, this technique has been applied to various ferroelectric materials [2-4] to precisely evaluate an ionic displacement at atomic level. Through these studies, it was revealed that position, shape, and intensity of atomic images sensitively reflect the ionic displacement. Therefore, in-situ XFH measurement under an electric field can be a promising technique to clarify the origin of piezoelectricity.

Figures 1(a) and (b) show photograph and schematic drawing of experimental setup for in-situ XFH under an electric field. Electrodes are deposited on both sides of the sample with the size of 5 x 5 x 0.1 mm^3. The sample this time is Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ piezoelectric material. Electric field is applied perpendicular to the surface. The incident and fluorescent X-rays can go through the electrode since its thickness is less than 100 nm. In the presentation, variation in the atomic image by applying electric field of 40 keV/cm will be discussed.

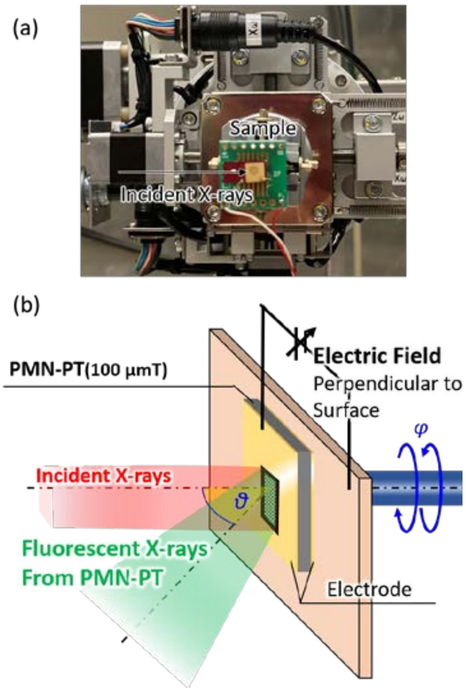

Fig. 1 (a) Photograph and (b) schematic drawing of XFH experimental setup under an electric

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Influence of field-induced phase transformation on the photoferroelectric response of Sn-doped $BaTiO_3$

V. Kraft[1], **N. Khansur**[1], **K. Hayashi**[2], **K. Webber**[1]

[1]Department of Materials Science and Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany
[2]Department of Physical Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

Meeting the increasing demand for highly efficient yet multifunctional energy conversion systems with low toxicity makes the investigation of lead-free polar perovskite oxides critical. These are possible candidates to comply with multimodal energy conversion systems requirements because of their demonstrated structural flexibility and chemical tunability. Among others, light active polar perovskite oxides, i.e., photoferroelectrics, are promising for multifunctional energy harvesting. These materials can, for example, convert mechanical energy or light illumination to electrical energy. Moreover, transforming light to strain or chemical reactions in the context of photocatalysis becomes possible for photoferroelectric materials. These coupled functional properties are achieved through a low bandgap (<3 eV) combined with switchable spontaneous polarization. Chemical tunning of B-site cations with non-d^0 metal cations are considered promising to tune the bandgap of polar perovskite oxides. Doping with Sn of the well-known ferroelectric $BaTiO_3$ has shown excellent photoferroelectric responses. In this contribution, Sn-doped $BaTiO_3$ was investigated to comprehend the influence of field-induced phase transformation and the coexistence of multiple crystallographic phases on the photoferroelectric properties. The structural and microstructural changes have been correlated to the variation in photoferroelectric properties of bandgap-tuned $BaTiO_3$.

Influence of Grain Size and Defects on the Electromechanical Properties of Aerosol Deposited Films

Michel Kuhfuß[1], Juliana G. Maier[1], Daisuke Urushihara[2], Ahmed Gadelmawla[1], Alexander Martin[2], Ken-ichi Kakimoto[2,3], and Kyle G. Webber[1]

[1]Department of Materials Science and Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU),
Martensstraße 5, 91508 Erlangen, Germany
[2]Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Nagoya, 466-8555, Japan
[3]Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Nagoya, 466-8555, Japan

Room temperature aerosol deposition (AD) is a promising method to produce thick ceramic films *i.a.* for piezoelectric vibrational energy harvesters. However, AD films exhibit a nanocrystalline microstructure, high internal stress and a high defect concentration directly after processing. This leads to an increased conductivity and decreased ferroelectric response compared to bulk samples. As the difference between the coefficient of thermal expansion (CTE) of films and substrate would cause cracks in the film, free-standing films (FSF) are produced utilizing a water-soluble sacrificial layer. Former CTE measurements of BT FSF indicate recombination of defects starting at about 120 °C. [1] For BCZT FSF this is not observed, however, the ferroelectric response increases with heat treatment temperature. Microstructure analysis with scanning and transmission electron microscopy shows grain growth with approximately Arrhenius-type behavior, but grain size is still limited compared to bulk. Therefore, spark plasma sintering (SPS) is facilitated to prepare BCZT samples with grain sizes ranging from AD to bulk. This comparison shows a direct dependence of the electromechanical properties on grain size.

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Inter- and intramolecular arrangement of Organotin Sulfide Clusters with extreme Nonlinear Optical Properties depending on the organic ligand substitution

J. Link Vasco[1], B. D. Klee[2], J. Stellhorn[3], B. Paulus[1], W.-C. Pilgrim[1]

[1]Chemistry Department, Philipps-University of Marburg, Marburg, Germany
[2] Institute of Solid-State Physics and Optics, Wigner RCP, Budapest, Hungary
[3] Department of Physics, Nagoya University, Nagoya, Japan

Light-emitting diode (LED) are well known as highly energy efficient light sources. They emit in all directions mainly in the visible spectrum without heat loss in the infrared.[1] Recently, alternative light sources with highly directional irradiation properties have been found. These Organotetrel Chalcogenide Clusters present extreme Nonlinear Optical Properties by irradiation from a continuous-wave laser diode. If the compound consists of an amorphous matrix, a broad band emission in the visible region is seen. This effect is known as White-light Generation (WLG). If the sample is crystalline, Second Harmonics Generations (SHG) takes place.[2,3] Organotin Sulfide Clusters show these characteristics. If substituted with naphtyl (Np) or methyl (Me) we observe SHG, whereas with phenyl (Ph) or cyclopentadienyl (Cp) WLG takes place.[3,4]

We performed molecular Reverse Monte Carlo simulations of these four different substituted clusters by fitting X-ray diffraction and Extended X-ray Absorption Fine Structure (EXAFS) data simultaneously. Ph- and Cp-substituted clusters show distortions of the intramolecular structure, which is suspected to suppress crystallization, whereas the intramolecular structure of Me- and Np-substituted clusters remain intact. The results of the molecular Reverse Monte Carlo simulations will be presented, as well as inter- and intramolecular arrangement of the clusters discussed and compared.

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Structural properties of silica studied by locally-averaged atomic fingerprints: phase differentiation and applications

Anh Khoa Augustin Lu[1,2], Jianbo Lin[1], Ryo Tamura[1,3], Yasunori Futamura[4], Tetsuya Sakurai[4], Tsuyoshi Miyazaki[1,4]

[1]National Institute for Materials Science (NIMS), Tsukuba, Japan
[2]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
[3]The University of Tokyo, Tokyo, Japan
[4]University of Tsukuba, Tsukuba, Japan

The rapid development of computational facilities has made possible atomic simulations of large systems. Nevertheless, complex structural properties in disordered materials remain difficult to analyze, particularly when it comes to features that span beyond the short-range order. In that respect, new methods are being developed to analyze the local environment in large systems.

In this work, we propose a methodology to capture the structural properties of silica (SiO_2), using locally-averaged atomic fingerprints (LAAF) as features, where the atomic fingerprints are atom-centered symmetry functions (ACSF) [1]. These features are projected into a low-dimensional space using a recently developed dimensionality reduction technique, the two-step locality preserving projections (TS-LPP) method [2]. By including structural information beyond the short-range order via local averaging, we have developed a TS-LPP model that properly differentiates up to eight phases of silica, including six crystals, liquid and glass. Such differentiation cannot be achieved by other methods such as principal component analysis (PCA). The atomic configurations were generated by first-principles molecular dynamics (FPMD) simulations using the CONQUEST software [3].

Two applications are discussed. Firstly, we investigate the phase transition from β-quartz to α-quartz as observed in FPMD simulations conducted under zero-pressure conditions at a temperature of 600 K. Secondly, we analyze the structural changes observed during the simulations of melt-quench processes, including the effect of pressure.

Our results indicate that structural differences in silica can be properly captured by a dimensionality reduction method with locally-averaged descriptors. In particular, this methodology could be of great use not only for silica but also for any disordered material such as metallic glasses.

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Structure of GeO_2 glass using neural network potential molecular dynamics -suppression of intermediate-range order with pressure

K. Matsutani[1], S. Kasamatsu[2] and T. Usuki[2]

[1]Graduate School of Science and Engineering, Yamagata University, Yamagata city, Japan
[2] Faculty of Science, Yamagata University, Yamagata city, Japan

In this work we focus on GeO_2 glass, a prototypical network-forming glass analogous to silica but with higher pressure sensitivity. Although changes in short-range order (SRO) under pressure are well documented [1], changes in intermediate-range order (IRO), implied by the existence of the first sharp diffraction peak (FSDP) and its suppression with pressure, are still not well understood. First-principles molecular dynamics (FPMD) has been used successfully in the past to study SRO in glasses, but its high computational cost has hindered the investigation of the IRO. We employ neural network potentials (NNPs) molecular dynamics [2] based on an interatomic potential trained to reproduce structure-energy data from FPMD calculations at a small fraction of the computational cost to tackle this issue. This enables accurate large-scale simulations of glass formation that are beyond the reach of FPMD.

To construct NNPs for GeO_2 glass, we collected training data using the standard GGA-PBE approximation. Since GGA cannot account for dispersion interactions and is known to underestimate covalency, which can be important for glass formation, we also trained on the more computationally expensive but accurate vdW-DF2-B86R and HSE06 approximations. The constructed NNPs were then used to obtain the GeO_2 glass structure through a melt-quench simulation on 3240 atoms. Figure 1 indicates that the total structure factors calculated from the obtained structures, including the FSDP, were in good agreement with experiment for the NNPs trained on GGA-PBE and HSE06, while a surprisingly significant deviation was found for vdW-DF2-B86R. HSE06 also successfully reproduces the suppression of the FSDP with pressure. On the poster, we will also discuss the topological features in GeO_2 glass using persistent homology analysis.

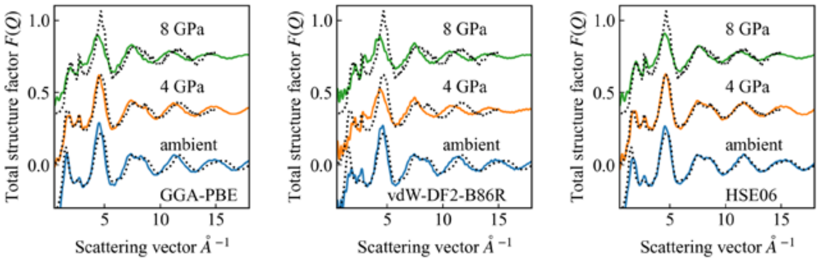

Figure 1. The obtained total structure factors at each pressure.

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Investigation of the active role of organic compounds in the stabilization of ferroelectric polarization of $BaTiO_3$ thin films grown by rf-sputtering

N. Mirzamohammadi[1], D. Pesquera[1], G. De Luca[1,2], K. Cordero-Edwards[1], G. Catalan[1,3]

[1]Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain

[2]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra, 08193 Barcelona, Spain

[3]ICREA - Institució Catalana de Recerca i Estudis Avançats, Barcelona, Catalonia, 08010 Spain

Ferroelectricity becomes unstable in thin films below a critical thickness, hampering the performance of devices such as ferroelectric tunnel junctions. Balancing kinetics and thermodynamics in the rf-sputtering deposition process, allowed us to grow 5-20 nm $BaTiO_3$ epitaxial thin films in the layer-by-layer growth mode. Piezoresponse Force Microscopy (PFM) reveals that the critical thickness for the thin films to show ferroelectric behavior lies somewhere between 10-15 nm. Also studying the switching dynamics as a function of applied bias, suggests that by applying 10 V on a 15 nm film, the critical writing speed is somewhere around 260 $\boldsymbol{\mu m/s}$. In the next step, the active role of organic 4-aminobenzoic acid (pABA) molecules, as depolarization field screening agents, has been studied for the stabilization of ferroelectric polarization in thin films below the observed critical thickness, and for the modification of writing speeds in films above the critical thickness. Our results shine new light on the possibility to use surface functionalization as a route to improve performance of ferroelectric devices.

Release of a large-scale and linear-scaling DFT code CONQUEST

T. Miyazaki[1], A. Nakata[1], D. R. Bowler[2] and L. Truflandier[3]

[1]National Institute for Materials Science (NIMS), Tsukuba, Japan
[2] University College London (UCL), London, U. K.
[3] University of Bordeaux, Bordeaux, France

CONQUEST is a large-scale and linear-scaling DFT code. Using the code, we can perform DFT calculations on very large systems containing many thousands of atoms to investigate the structural and electronic properties of large and complex materials. The code has been developed jointly by NIMS and UCL, and it is now freely available under an MIT license.

In this presentation, we present the overview of the code: theory behind the code, available pseudopotentials and PAO basis sets, the performance of the code on parallel supercomputers and so on. Some applications using the code will be also introduced.

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Structural analysis of electric-field-induced strains in Mn-doped BiFeO$_3$ thin films by in-situ X-ray fluorescence holography under electric field

S. Nakashima[1], K. Arima[1], R. Kato[1], H. Fujisawa[1], K. Kimura[2], N Happo[3], and K. Hayashi[2]

[1] University of Hyogo, Hyogo, Japan
[2] Nagoya Institute of Technology, Nagoya, Japan
[3] Hiroshima City University, Hiroshima, Japan.

In recent years, ferroelectric semiconductor which show the conductivity control of the ferroelectrics themselves by spontaneous polarization and the bulk photovoltaic effect using the anisotropy of the interband transition of carriers caused by the non-centrosymmetric crystal structure have been investigated1, 2). It is known that the conductivity of ferroelectric BiFeO$_3$ (BFO) is changed by doping a few at% of Mn. The role of Mn has been suggested by the first principles calculation, trapping oxygen vacancies near Mn to form a MnO$_5$ cluster structure3). In addition, ferroelectrics shows the inverse piezoelectric effect causing atomic displacements under an electric field. This means that crystal structure under the electric field should be clarified for clarifying the ferroelectric semiconductor properties. In this study, we aim to elucidate the functionality of the dopant-induced cluster structure in ferroelectric BFO, and clarify the behavior of this cluster structure under an external field by atomic resolution holography.

For clarify the atomic structure of the Mn-1-at%-doped BFO thin film, an inverse X-ray fluorescence holography (XFH) measurement under electric field have been performed at SPring-8 BL39XU beam line. A Pt/BFMO/Pt coplanar capacitor with the Pt interelectrode distance of 40 μm has been fabricated. The X-ray have been focused on the BFMO between the Pt electrodes with applying voltage of 175 V. The hologram patterns of Fe Kα and Mn Kα fluorescent X-rays were detected by APD. From these hologram patterns, atomic structures around Fe under the electric field have been successfully obtained. Figure 1 shows atomic images of the Bi around Fe atom indicated by circles in insets of Figs, 1(a) and 1(b) under electric fields of 0 and 44 kV/cm, respectively. The Bi atomic displacement along [111] direction can be observed, meaning larger atomic displacements of Bi by the electric fields compared to the Fe.

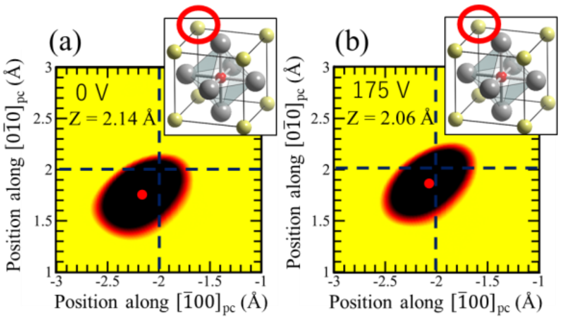

Fig. 1 Atomic images of Bi atom around Fe in Mn-doped BiFeO$_3$ thin film under (a) 0 V, and (b) 175 V application.

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Disordered electrochemical energy materials

A. J. E. Rettie[1]

[1]*Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, UK*

Static and dynamic disorder underlies function in many electrochemical energy conversion and storage materials. This is especially true in solid-state battery and thermoelectric devices, where fast ion conduction is a prerequisite for high-rate operation and correlated with favorable thermal properties respectively. Here, I will present work on a 2D superionic Ag-ion conductor, KAg_3Se_2 where the extensive disorder responsible for ion conduction was studied by X-ray/neutron scattering techniques and complementary simulations [1]. Regarding solid-state batteries, the solid electrolyte (SE) glass lithium phosphorous oxynitride (LiPON) is unrivalled in its stability to stabilize next-generation electrode materials and operate at high rates, albeit in thin film format. We used these devices to validate a mechano-electrochemical model [2], which motivated us to explore LiPON-like, glassy SEs by solution processing [3]. The structure of these new SEs is studied by X-ray pair distribution function (PDF) analysis. Finally, I will present preliminary work on 3D-delta-PDF analysis of disorder in a champion photocatalyst material: bismuth vanadate ($BiVO_4$).

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Microstructure and thickness dependent structure of $PbZrO_3$ free-standing membranes

U. Saeed[1], B. Ballesteros[1], J. Oró[2], C. Magén[3], D. Pesquera[1], G. Catalan[1] and F. Sandiumenge[2]

[1]ICN2 (Institut Catala de Nanociencia i Nanotecnologia) BIST-CSIC
Bellaterra, Catalonia 08193, Spain
[2] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)
Campus de la UAB, Bellaterra, Catalonia 08193, Spain
[3] Instituto de Ciencia de Materiales de Aragón (ICMA)Universidad de Zaragoza – CSIC,Departamento de Física de la Materia Condensada, Zaragoza 50009, Spain

Understanding size effects in antiferroelectrics (AFEs) not only poses unsolved fundamental issues, but holds strong interest in high energy-density storage applications. However, despite the strong activity and rapid emergence of exciting results in ferroelectric (FE) free-standing membranes, AFEs still remain elusive. In fact, a recently reported first experimental insight into NaNbO3 shows a complex size-induced phase evolution driven by surface effects, in line with previous theoretical work [1,2]. In particular, both theory and experiment show an intrinsic FE state below a critical thickness, above which AFE and FE orders coexist.

Here we investigate 36, 17, 13 and 8nm thick membranes of the archetypal AFE $PbZrO_3$ using planar view transmission electron microscopy, and we find evidences of structural dependence on thickness. While 36 and 17nm thick membranes exhibit ¼(1 1 0) superlattice reflections characteristic of the orthorhombic AFE state, and signs of phase mixing, in the thinnest membrane these features are absent indicating the suppression of AFE order. These results point to a behavior consistent with previous results [1,2]. In addition, our observations reveal a strong sensitivity of the crystal structure to local strain. Unexpectedly, from the microstructural point of view, these membranes exhibit a high density of threading dislocations, which contrasts with the absence of such defects in studies reported so far on FE membranes. Dislocations are of edge type with Burgers vectors [100] and ½[110]. Strain fields associated with them draw a dense polygonization pattern that could affect the resulting phase composition of the membranes.

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CRowdsourced Materials Data Engine for Unpublished X-Ray Diffraction

Yinghui Wu (PI) and Alp Sehirlioglu (Co-PI)
Case Western Reserve University
Cleveland, Ohio, USA
{yxw1650, axs461}@case.edu

Recent advances in applied data sciences allowed new approaches to develop structure-property relationships in inorganic materials and predicting (or classifying based on) properties using crystal- or micro-structure. Modern multidisciplinary materials science routinely processes scientific workflows integrating different data resources. These data resources are underutilized and sometimes tagged as ineffectual for the source problem. We propose to tackle the fundamental challenges of data-driven material science such as accessing extensive experimental data and relationship to the processing techniques of the discovered materials. Majority of machine learning models require significant number of training data that is not necessarily generated or accessible in materials research. Inspired by our past work on machine learning (ML) enabled discovery of high temperature piezoelectrics where the sparse nature of training and testing data was highlighted, we are creating CRUX, a CRowdsourced Materials Data Engine for Unpublished X-Ray Diffraction (XRD) to innovate and boost the utilization of this high-quality, unpublished material science data. The core of CRUX is a materials knowledge graph (KG), build upon the materials data and materials ontology specifically developed to capture the processing meta-data. This KG represents abstract factual knowledge from XRD datasets, answers queries, and self-evolves to recommend newly shared datasets and facilitating the feature of querying itself to help users explore the underlying materials datasets. We aim to enable a materials KG model, automatic data integration, and an exploratory query engine that support "Why" and "What-if" analysis. CRUX will enable an open, collaborative, and sustainable platform that can facilitate exchanging of unpublished XRD data and unlock new research problems (e.g., predicting solubility limits of dopants), and inspire the novel design of ML pipelines for data-driven materials science.

Ferroelectricity in non-doped AlN with wurtzite structure

T.Shimizu[1,2], K. Hasegawa[1,3], T Ohsawa[1], I. Sakaguchi[1],
and N. Ohashi[1,3,4]

[1]National Institute for Materials Science, Tsukuba, Japan
[2] Japan Science and Technology Agency, Kawaguchi, Japan
[3] Kyushu University, Fukuoka, Japan
[3] Tokyo Institute of Technology, Yokohama, Japan

AlN is one of the most popular polar materials with a wurtzite-type structure. Its simple chemical formula allows us to fabricate integrated devices at low temperature; therefore, it is widely used as piezoelectric micro-electro-mechanical systems, such as acoustic filleters. Recently, ferroelectricity in the Sc-substituted AlN with a wurtzite-type structure and its giant spontaneous polarization have been demonstrated[1]. Since the demonstration of polarization reversal with wurtzite-type structure, it is reported that various materials with wurtzite-type structure, including Mg-doped ZnO, B-doped AlN, and Sc-doped GaN, can show ferroelectricity. On the other hand, the ferroelectricity in non-doped wurtzite compound is not studied enough and only partial ferroelectric switching was reported[2].

In this study, we reported the full polarization switching in non-doped AlN films on Nb-doped $SrTiO_3$ substrate prepared by the RF magnetron sputtering method. The low-temperature deposition allowed us to observe sufficient polarization switching with remanent polarization ~ 150 $\mu C/cm^2$. This value is in accordance with the theoretical values based on first principle calculation[3, 4], indicating full polarization reversal, which is different from the previous result. The coercive field is estimated to be 8 MV/cm from the *P-E* hysteresis loop at room temperature. This value agrees with that extrapolated from the Sc concentration dependence of the coercive field. This result indicate that the ferroelectric switching is possible without any intentional substitution and lattice deformation accompanied by substitution and would give insight into elucidating the polarization switching mechanism in wurtzite-type materials.

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Solution processed non-crystalline thin-film electrolytes for all-solid-state batteries

Yaoguang Song[1], **Thomas E. Gill**[1], **Pooja Vadhva**[1], **Alexander J. E. Rettie**[1]

[1]*Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, London, UK*

Rechargeable batteries, such as the well-established lithium-ion batteries and the fast-growing sodium-ion batteries, are representative energy storage devices that can be ubiquitously used in portable electronic devices, electric vehicles and so forth. However, such batteries rely heavily on traditional liquid electrolytes which have either safety concerns due to dendrite penetration or awaiting further-improved electrochemical performance. All-solid-state batteries with non-crystalline solid electrolytes (SEs) have demonstrated enhanced safety, energy and power density compared with liquid electrolytes thus have drawn increasing attention. However, the mostly studied non-crystalline SE material, LiPON (~ 0.55 eV), features limited applicability at scale although it demonstrates higher energy density and excellent stability in Li plating/stripping (or against dendrite penetration).[1,2]

We introduce recent exploration on two types of non-crystalline thin-film SEs, Li-Al-P-O (LAPO) and Na-Al-P-O (NAPO) that can be processed by scalable method with aqueous solutions. Notably, their activation energies of hopping are comparable even lower than LiPON; this makes LAPO and NAPO more promising for commercialisation. The ionic conductivity of both types of SEs are much lower than the commercially viable regime (~10^{-6} S/cm). Studying the structure-property relationship of both types of SEs helps identify the source for the lower activation energies, thereby guiding the optimisation of ionic conductivity and eventually achieving scaling-up production.

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Simulation of Air Scattering Contributions in X-ray Diffraction Experiments on Amorphous Matter

J.H. Thimm[1], **B.D. Klee**[1-2] **and W.-C. Pilgrim**[1]

[1]*Philipps-University, Marburg, Germany*
[2] *Wigner Research Centre for Physics , Budapest, Hungary*

In structure analysis of solids by way of X-ray scattering experiments precise treatment of background intensity is usually negligible so long as crystals are probed, as their structure information is concentrated in sharp, highly intense Bragg-reflexes. In *less ordered* systems such as liquids, glasses and amorphous solids in general these sharp reflexes are absent and the scattered intensity carrying the structure information is spread continuously along the diffraction angle and mixes with the background.

In order to draw information from such scattering experiments a meticulous analysis and extensive reduction of background intensity is necessary. Accordingly great effort is undertaken to grasp and separate the various contributions to background intensity. [1]

Part of this unwanted background is intensity scattered by air, as it is not always feasible to evacuate the experimental setup. The air scattered intensity is experimentally only directly accessible in a setup without an absorbing and scattering sample present. Similarly, this intensity is not equal to the air scattering contribution in presence of a sample, e.g. due to the sample's absorption of primary intensity. Therefore it is only a crude approximation to use the measured air scattering intensity for background correction directly.

In this ongoing work, a model is derived to predict air scattered intensity in presence of the sample for a typical experimental environment at a synchrotron beamline. The model is built using the Thomson scattering equation and atomic form factors as theoretical foundation. From the experimental setup a general geometric model of the beam path is deduced. Furthermore setup-specific features in the beam path are regarded as examples that may heavily influence the measured intensity curves, most prominently the shadow of a beam stop cast onto an area detector.

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Atomic structure and chemical state of surface oxide / gallium nitride interface

H. Tomita[1], M. Uenuma[1], S. Kuwaharada[1], Z. Sun[1], Y. Hashimoto[1], M. N. Fujii[2], M. Tanaka[1], T. Matsushita[1]

[1]Nara institute of science and technology, 8916-5 Takayama-cho, Ikoma-shi, Nara, 630-0192, Japan
[2]Kindai university, 3-4-1 Kowakae, Higashiosaka-shi, Osaka, 577-8502, Japan

Gallium nitride (GaN), which is being studied for application as power electronics devices, requires improvement of the interface between the gate dielectric film and the matrix. Al_2O_3 and SiO_2 are mainly used as dielectric films in GaN-MOS structure devices, and the formation of a few monolayers of GaO_x at the interface between these and GaN has been reported[1]. Such GaO_x layers have also been observed in naturally oxidized GaN. Information on the gate dielectric / GaN interface is important for designing reliable GaN-MOS devices[2].

In this presentation, we present our recent work on surface oxide / GaN interfaces. Photoelectron diffraction (PED) experiments were performed to characterize the buried interface. PED can observe non-periodic atomic arrangements, making it powerful for analyzing local structures such as dopants, adsorbed atoms, and interfaces. Since the PED pattern is angular distribution of photoelectron emission intensity, the chemical composition can also be analyzed by scanning the energy. Using this technique, we have succeeded in extracting information on atoms at the interface that have different chemical states from those in the bulk.

To reveal the structure of the interface layer, we have developed a new PED analysis method. The structure determination was achieved by comparing the experimentally obtained PED pattern with the patterns calculated using the models considered in previous studies. In thes method, genetic algorithm (GA) is used to search for the optimal atomic arrangement (Figure 1).

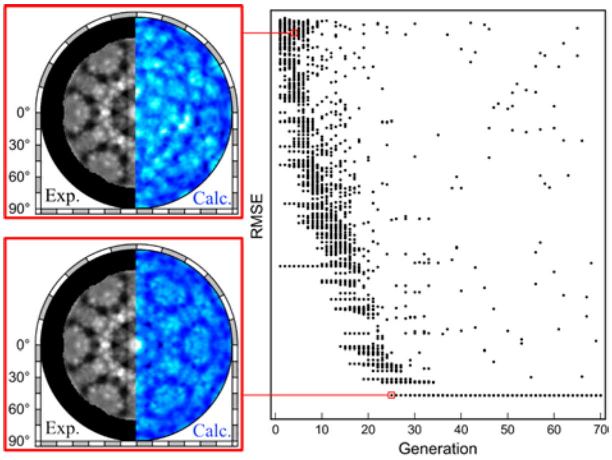

Figure 1 The process of searching for the optimal solution by GA. The pattern on the left is the PED pattern of the bulk GaN measured in the experiment (Exp.). The pattern on the right is the PED pattern calculated using the atomic structure of the generated individuals (Calc.).

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Structure Determination in two States of the Amorphous Solid State Electrolyte $Li_7P_2S_8I$

H. M. Wenzel[1] , **B. Paulus**[1], **J. R. Stellhorn**[2,3], **V. Miß**[1], **W.-C. Pilgrim**

[1] *Philipps-Universität Marburg, Marburg, Germany*
[2] *Nagoya University, Nagoya, Japan*
[3] *Hiroshima University, Hiroshima, Japan*

The novel amorphous electrolyte $Li_7P_2S_8I$ reveals an increase in Li^+ conductivity when tempered. Impedance spectroscopy shows an increase from 0.8 mS/cm to 4.6 mS/cm [1]. The tempering temperature is 10 K lower than the crystallization temperature, hence no crystallization during the tempering process is performed.

The x-ray scattering patterns of the between the non tempered and the tempered electrolyte differ significantly. This difference might be the reason for the measured increase in conductivity.

For this, x-ray scattering and EXAFS (K edge of S measured in HiSOR) measurements are obtained and analyzed in combination with Reverse Monte Carlo simulations [2]. It could be found out that the tempered state contains a longer detectable order than the non tempered state. Additionally, first results reveal an expansion in the P-S bond in the $Li_7P_2S_8I$ compound during the tempering.

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High-Entropy Materials for Memristive Switching Component Application

C. Wu[1, 2], C. Pithan[1], V. Rana[1], J. Dornseiffer[1], J. Rupp[2]

[1] *Forschungszentrum Jülich, Jülich, Germany*

[2] *Technische Universität München, München, Germany*

Email: c.wu@fz-juelich.de

Research on novel Memristive oxides is currently imminent. Deliberately enhancement of the configuration entropy may result in improved electronic performance with respect to resistive switching, especially for filamentary type memristor. Since switching events represent stochastically localized processes in space, a homogeneous distribution of cations in a highly strained lattice structure favors a reduced device variability. Also, anharmonic phonon dispersion is expected to reduce thermal conductivity facilitating the growth of filaments. A recent study demonstrated that an overall improved electronic switching performance can be obtained in thin films composed of ZrO_2-HfO_2-Nb_2O_5-Ta_2O_5-MoO_3-WO_3 deposited by PLD. [1] However, a detailed exploration regarding the mechanisms of the senary system performance has not been reported yet.

This study presents aspects of optimizing powder preparation, target fabrication, and thin-film deposition for the three binary solid solution subsystems (i) ZrO_2–HfO_2 (ii) Ta_2O_5–Nb_2O_5 and (iii) WO_3–MoO_3 as well as for the senary compositions containing all components in equimolar proportions. The general purpose is to explore the mechanism behind the high-entropy system, stability and electronic behaviors, and the influence factors of microstructure of materials, thin-film qualities, and resistive switching properties.

Powders were synthesized by three different routes: (i) Solid-state reaction, (ii) Pechini method, and (iii) Mechanochemical method. All materials were characterized regarding composition (ICP-OES), morphology (SEM & EDX), thermal stability (DTA & TGA), crystallography (XRD), vibrational modes (Raman), surface condition (AFM), bonding and defects (XPS) and sintering behavior (Dilatometry). Consolidation of 2-inch targets in diameter was conducted by Spark Plasma Sintering (SPS). All targets were characterized before thin-film sputtering. Reactive sputtering was used for thin-film preparation which were structured into devices before measuring their resistive switching response.

Results show that the binary systems $ZrHfO_4$ and $NbTaO_5$ have excellent homogeneity and achieve phase transformation (tetragonal and amorphous, respectively) while RF-sputtering and that the corresponding thin-film exhibit good current-voltage response hysteresis loop; the HE-systems introduce several percent of oxygen defect to improve filament formation; Application of the Pechini method can achieve realization high configuration entropy phases that match no recorded crystal structure and proved that Pechini process should be better for high-entropy materials preparation.

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Ultra-high-speed chargeable Li-ion thin film batteries by control of solid electrolyte interface(SEI)

S. Yasui[1], S. Yasuhara[1] and T. Teranishi[2]

[1]*Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8550, Japan*
[2]*Okayama University, 1-1-1, Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*

Li-ion battery is one of suitable energy storage, especially for mobile electronic devices and electric vehicles. Using these devices, battery life and charging time, and safety are very important. Actually, charging time is too long, for example, it takes 5 hours to fully charge in smartphone. In this case, 0.2 C is used for charging current. If higher C-rate was used, capacity cyclability is dramatically reduced. This is because SEI layer, decomposed materials of electrolyte; LiF, organic matter etc., is deposited on active materials. In this study, we have investigated the interface reaction between cathode and electrolyte using epitaxial thin film battery and bulk systems.1-6) We have tried to insert artificial SEI of high dielectric constant materials, BaTiO3, on the cathode $LiCoO_2$ epitaxial thin film. The high-rate performance and cyclability are enhanced by existence of a triple-phase interface, cathode $LiCoO_2$-electrolyte $LiPF_6$(EC:DEC=3:7)-dot $BaTiO_3$(Triple-phase interface; TPI). From the experiment, Dot BaTiO3 can eliminate SEI deposition, in other words, a robust Li-ion pass way (pure $LiCoO_2$ surface) could be set around TPI.

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Impact of thermal treatment on the microstructure and mechanical properties of aerosol-deposited $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ thick films

K. Žiberna[1,2], **M. Šadl**[1], **A. Drnovšek**[3], **G. Dražić**[4],
H. Uršič[1,2] **and A. Benčan**[1,2]

[1]*Electornic Ceramics Department, Jožef Stefan Institute, Ljubljana, Slovenia*
[2] *International Postgraduate School, Ljubljana, Slovenia*
[3]*Department of Thin Films and Surfaces, Jožef Stefan Institute, Ljubljana, Slovenia*
[4]*Department of Materials Chemistry, National Institute of Chemistry, Ljubljana, Slovenia*

Aerosol deposition (AD) is a spray coating method for producing thick films that grow by particle impact and fragmentation [1]. Deposition alone is a room temperature process, but for electromechanically active thick films, post-deposition annealing is necessary to improve their electrical and electromechanical properties. The enhancement is believed to be related to the partial release of the residual stresses in the films that were created during deposition by the high-energy impacts [2]. At the same time, the mechanical behavior of the films may deteriorate after annealing, but it is studied to a much lesser extent than the other properties [3].

In this contribution, we report the effects of annealing at 500 °C on the cross-sectional microstructure and mechanical properties of the $0.9Pb(Mg_{1/3}Nb_{2/3})O_3-0.1PbTiO_3$ thick film on stainless steel prepared using AD. These films show a significant reduction in microstrains and improvement in recoverable energy density and energy storage efficiency after annealing at 500 °C [4], but their mechanical behavior has not yet been investigated. First, we use transmission electron microscopy to reveal the dense nanocrystalline microstructure characteristic of AD films. The effects of annealing are discussed in terms of grain growth, crystallinity, and pore redistribution. We also show that the stainless-steel substrate is strongly affected by annealing. In the next step, we measure the mechanical properties of the as-prepared and annealed films using in situ nanoindentation. The hardness and Young's modulus of the films increase after annealing; both properties are discussed in terms of their distribution over the cross-sections of the films.

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