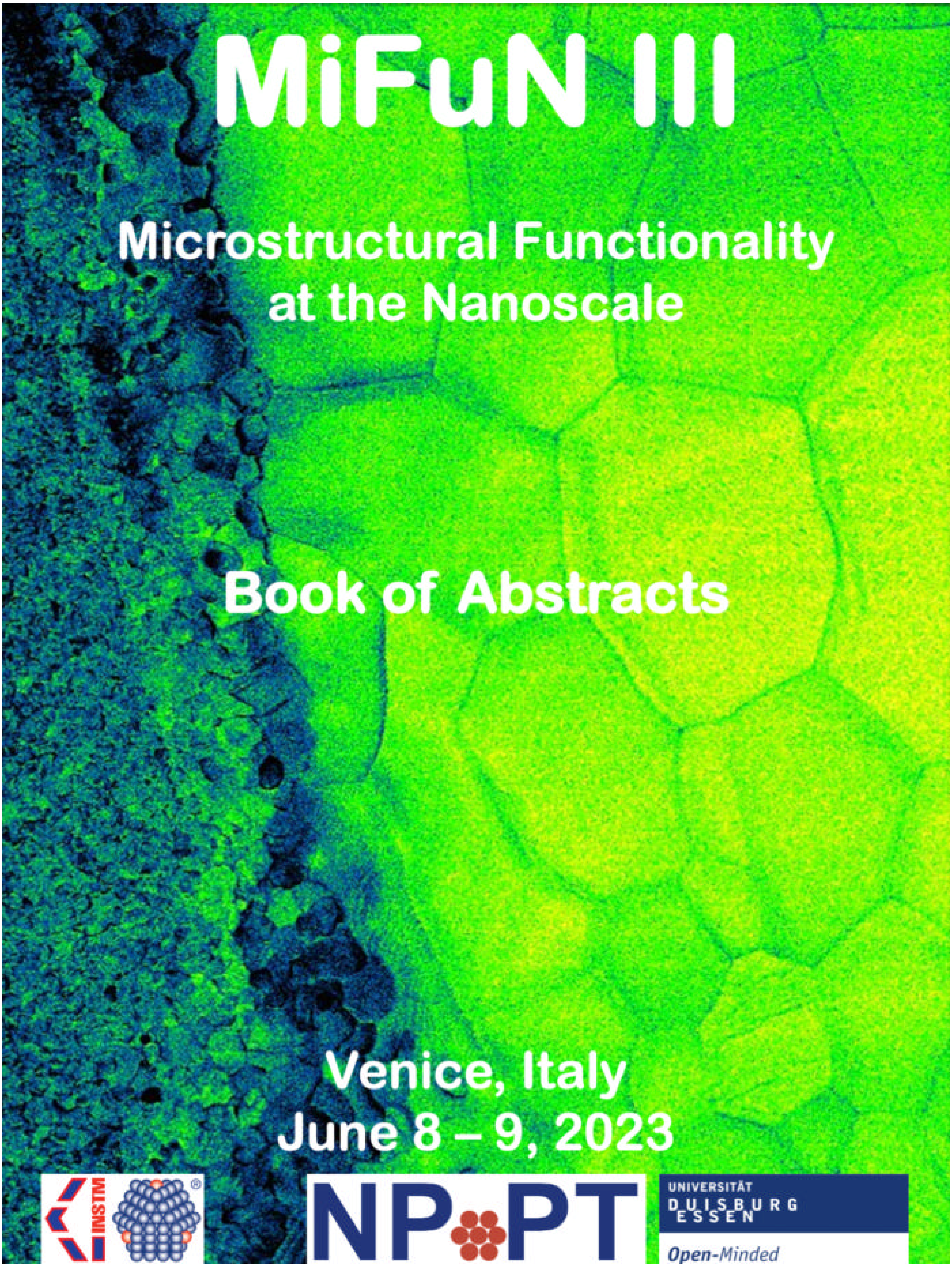

MiFuN III

Microstructural Functionality at the Nanoscale

Book of Abstracts

Venice, Italy
June 8 – 9, 2023

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Program Overview

Thursday, June 8, 2023

09:45	**Opening**	Markus Winterer
	Grain boundaries	chair: Wolf
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10:45	**Yulia Ivanisenko, Karlsruhe Institute of Technology, Germany**	
11:30	**Gregory S. Rohrer, Carnegy Mellon University, USA**	
12:15	**Oliver Diwald, Paris-Lodron University Salzburg, Austria**	
12:35	**Hyunwon Chu, Massachusetts Institute of Technology, USA**	
14:00	**Poster Session**	chairs: Anselmi-Tamburini, Wolf, Winterer
	Oxide Thin Films and Electroceramics	chair: Anselmi-Tamburini
14:45	**Nini Pryds, Technical University of Denmark, Denmark**	
15:30	**Vladimir V. Srdić, University of Novi Sad, Serbia**	
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16:10	**Mohana Veeraju Kante, Karlsruhe Institute of Technology, Germany**	
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17:45	**Timo Wagner, University of Duisburg-Essen, Germany**	
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15:50	**Magdulin Dwedari, University of Duisburg-Essen, Germany**	
16:10	**Sotiris E. Pratsinis, ETH Zürich, Switzerland**	
16:30	**Microstructural Characterization**	chair: Wolf
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18:25	**Conclusion:** Anselmi-Tamburini, Wolf, Winterer	
> 19:30	**Conference Dinner**	

Front Cover Legend / Acknowledgement
The false colored SEM image in the header displays the laser sintering track in a CuOx sample courtesy of MSc Jeldrik Schulte (NPPT, UDE).

MiFuN III

Microstructural Functionality at the Nanoscale

Venice, Italy, June 8 – 9, 2023

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MiFuN III – Microstructural Functionality at the Nanoscale

MiFuN III is the third in a series of international workshops on the time dependence of structural features at the nanoscale. It covers recent research topics with a strong impact on nanoscience and nanotechnology. Mechanisms for microstructural evolution range from the formation of defects, their transport, growth, and transformation to segregation, sintering, and cooperative mechanisms, including the controlled manipulation of grain boundaries and other microstructural elements in nanocrystalline materials. These mechanisms can lead to novel dynamic functionality, such as resistive switching or self-healing, and are also determining the lifetime of nanostructured devices such as batteries or solar cells.

June 2023

The organizing committee

Markus Winterer, University of Duisburg-Essen
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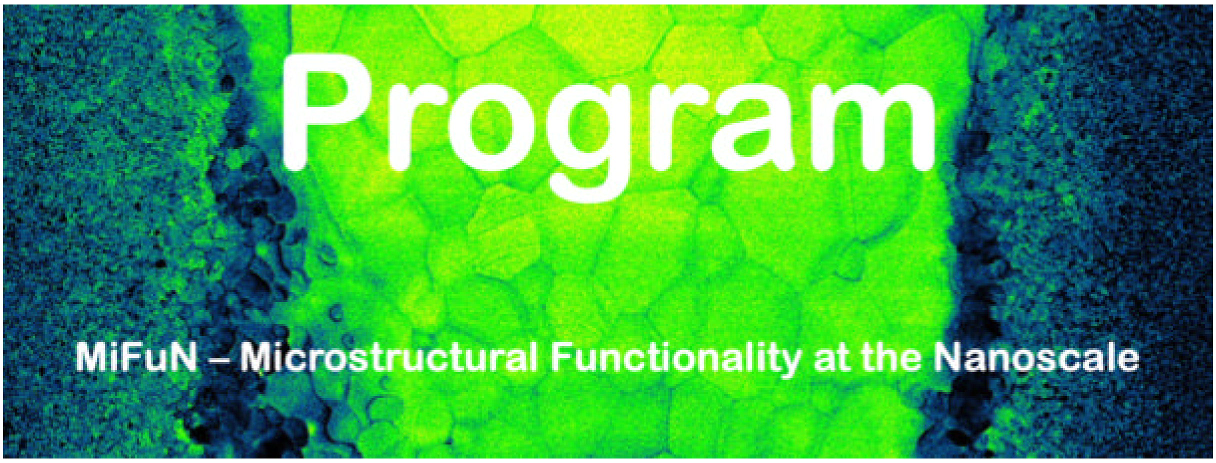

Program

MiFuN – Microstructural Functionality at the Nanoscale

Thursday, June 8, 2023

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10:45	**Yulia Ivanisenko, Karlsruhe Institute of Technology, Germany** *Influence of grain boundary segregations on mechanical properties of carbon-alloyed nanocrystalline CoCrFeMnNi high entropy alloy*	
11:05	Coffee Break	
11:30	**Gregory S. Rohrer, Carnegy Mellon University, USA** *New perspectives on grain boundary migration*	
12:15	**Oliver Diwald, Paris-Lodron University Salzburg, Austria** *Segregation engineering in metal oxide nanoparticles*	
12:35	**Hyunwon Chu, Massachusetts Institute of Technology, USA** *Designing grain boundary chemistry and transport for safe Li-garnet solid-state electrolytes*	
12:55	Lunch Break	
14:00	**Poster Session + Coffee Break**	chairs: Anselmi-Tamburini, Wolf, Winterer
	Oxide Thin Films and Electroceramics	chair: Anselmi-Tamburini
14:45	**Nini Pryds, Technical University of Denmark, Denmark** *Interfaces engineering of thin film oxides*	
15:30	**Vladimir Srdić, University of Novi Sad, Serbia** *Epitaxial $LaMnO_3$-based heterostructured thin films observed by polymer assisted deposition*	
15:50	**Alaa Alsawaf, Karlsruhe Institute of Technology, Germany** *Influence of In-doping on the electrochemical performance of multicomponent garnet-type solid electrolyte*	
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10:00	**Wolfgang Mertin, University of Duisburg-Essen, Germany** *Direct growth of graphene on semiconducting substrate via plasma-enhanced chemical vapor deposition*	
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12:15	**Maxim Sokol, Tel Aviv University, Israel** *2D* Ti_3C_2 *MXene based ceramic nanocomposites enabled by pressure-assisted sintering*	
12:35	**Lukas Engelke, University of Duisburg-Essen, Germany** *Microstructure evolution during sintering: Discrete element method approach*	
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15:50	**Magdulin Dwedari, University of Duisburg-Essen, Germany** *Can an electrical current create non-equilibrium defects ?*	
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17:45	**Shradha R. Joshi, University of Duisburg-Essen, Germany** *In situ observation of (trans-) formation of oxide nanoparticles during chemical vapor synthesis*	
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Poster Contributions

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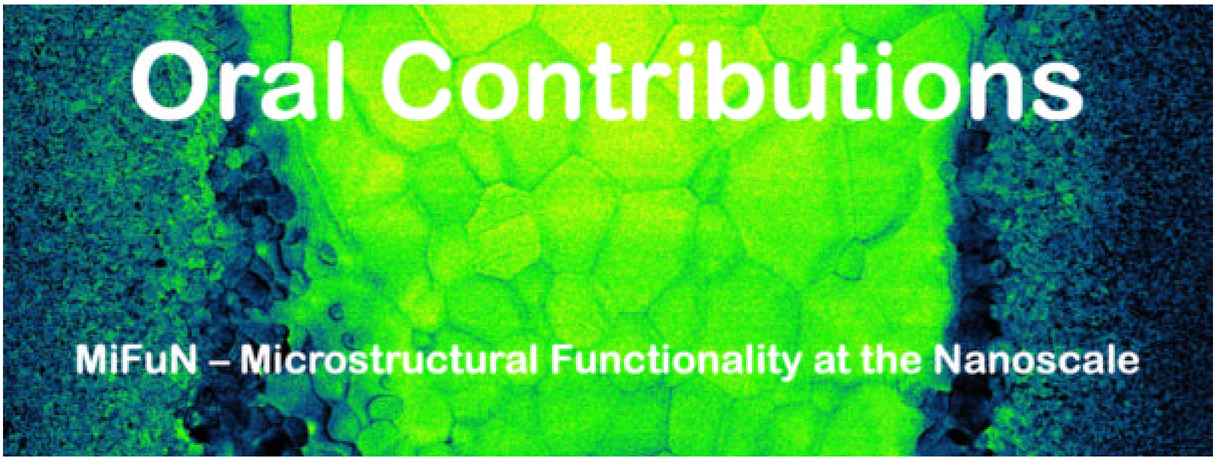
2. **Shradha Joshi, University of Duisburg-Essen, Germany**, *In situ observation of (trans-) formation of oxide nanoparticles during chemical vapor synthesis*
3. **Mohammed-Ali Sheikh, University of Duisburg-Essen, Germany,** *Synthesis and characterization of doped NaSiCON-type solid electrolytes for sodium-ion batteries from scalable spray flame synthesis*
4. **Gleb Iankevich, Karlsruhe Institute of Technology, Germany,** *Synthesis of unconventional material structures through the unique cluster ion beam deposition technique*
5. **Jeremias Geiss, University of Duisburg-Essen, Germany**, *Quantitative analysis of two-phase nanocrystalline oxides by X-ray spectroscopy*
6. **Jeldrik Schulte, University of Duisburg-Essen, Germany,** *Laser reactive sintering of complex oxides*
7. **Magdulin Dwedari, University of Duisburg-Essen, Germany,** *Can an electrical current create non-equilibrium defects ?*
8. **Shikhar Krishn Jha, Indian Institute of Technology Kanpur, India,** *Phase segmentation of steel microstructures using a deep learning algorithm*



Oral Contributions

MiFuN – Microstructural Functionality at the Nanoscale

(Abstracts in order of appearance in the oral program; presenting author in **bold)**

Grain boundary phases in metallic materials: Structure, stability and properties

Gerhard Dehm

Max-Planck-Institut für Eisenforschung GmbH, 40237 Düsseldorf, Germany

The thermodynamic concept of phase transformations of bulk materials is well established and cast into phase diagrams [1], which typically forms the basis for material and microstructure design. It is also well known that surfaces of materials can undergo phase transformations; such surface reconstructions are frequently used in semiconductor materials [2]. However, it is largely unknown in the materials community that also grain boundaries (and interfaces) can undergo phase transitions – recently called "complexions" to avoid confusion with bulk phase transitions [3]. The thermodynamic concepts for complexions have been developed over the last decades [3-5]. However, direct experimental evidence is rare as the buried structures of grain boundaries are difficult to access at atomic resolution.

In addition to growth of bicrystals, we also employed highly textured metallic thin films [6] to study the structure and possible phase transitions as a function of temperature and chemical composition in Cu and Al based alloys. We found by scanning transmission electron microscopy studies that even in the pure elemental metals grain boundary phases can coexist (Fig. 1) [7-9], although atomistic simulations of the free grain boundary energy indicate that the coexistence at ambient temperature is metastable (Fig. 1) indicating a sluggish transformation. It is also important to note that different grain boundary phases show differences in segregation behavior upon alloying (see e.g. [10]).

While there has been amble indirect evidence that grain boundary phases and their transitions influence material properties [5, 11], very little direct correlations have been realized so far. In this presentation the current state of the art in understanding grain boundary phases and their impact on properties are reported.

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[8] Frommeyer, L., Brink, T., Freitas, R., Frolov, T., Dehm, G., Liebscher, C.H. Nat. Com., **13**(1) (2022) 3331. doi.org/10.1038/s41467-022-30922-3

[9] Ahmad, S., Brink, T., Liebscher, C. H., & Dehm, G. Acta Mater., **243** (2023) 118499. doi.org/10.1016/j.actamat.2022.118499

[10] Meiners, T., Duarte, J. M., Richter, G., Dehm, G., Liebscher, C.H. Acta Mater. **190** (2020) 93-104. doi.org/10.1016/j.actamat.2020.02.064

[11] Dehm, G., & Cairney, J., MRS Bulletin, **47**(8), (2022) 800-807. doi.org/10.1557/s43577-022-00378-3

[12] Support by many colleagues, especially C. Liebscher, T. Frolov, T. Brink, T. Meiners, K. Bhat, H. Bishara, L. Frommeyer and Saba is gratefully acknowledged. Financial support was generously provided by the ERC Advanced Grant (787446-GB-CORRELATE) and by MPIE.

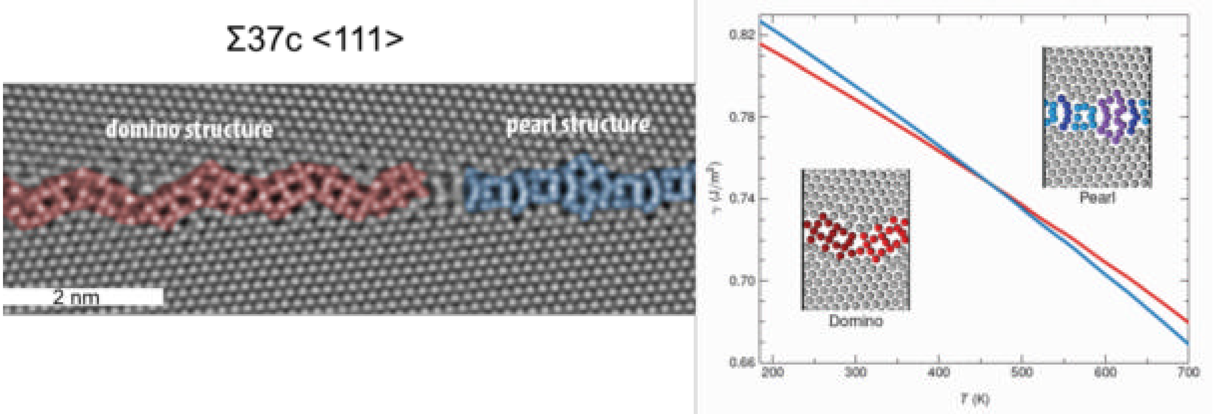

Fig. 1: Atomic resolved scanning transmission electron microscopy image of two different grain boundary motifs in a ∑37c <111> tilt grain boundary in pure Cu and the corresponding free grain boundary energy, γ, obtained by atomistic simulations as a function of temperature, T.

Notes

Influence of grain boundary segregations on the mechanical properties of carbon-alloyed nanocrystalline CoCrFeMnNi high entropy alloy

Yulia Ivanisenko[1], Yemao Lu[1,2] and Horst Hahn[1]

[1] Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
[2] Karlsruhe Nano-Micro Facility, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

Grain boundary segregations can significantly influence the mechanical properties of ultrafine grained and nanocrystalline (nc) materials, for example, they contributed to the strength enhancement of Al alloys [1,2] and stainless steel [3]. Recently, the formation of grain boundary carbon segregations in the nanocrystalline CoCrFeMnNi high entropy alloy (HEA) with reduced Cr content and with the addition of 2 at. % C processed by high pressure torsion was observed (Fig. 1a) [4,5]. This nc alloy with a grain size of 18 nm (Fig. 1b) demonstrated a record breaking strength of 2000 MPa, but was very brittle and fractured just after the onset of plastic flow [4]. However, after annealing at 200°C for one hour, the yield strength of the alloy further increased to 2300 MPa with simultaneous increase of ductility to 2 %. The microstructure investigations revealed that the mean grain size had not changed, but elemental segregation of Cr, Ni and Mn appeared at the grain boundaries. The increase of annealing temperature to 500°C led to the intensification of GB segregations and precipitation of intermetallic nano-particles, which resulted in a further increase of the yield strength to 2450 MPa, but with a concomitant decrease of ductility to 0.4%. These results show that grain boundary segregations have positive effect on the strength of nanomaterials, but may be either detrimental or beneficial for the ductility. The physical reasons and mechanisms of the influence of grain boundary segregations on the mechanical behavior of nanocrystalline HEA will be discussed.

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[3] Abramova, M. et. al Mat. Let. **136** (2014) 349; doi.org/10.1016/j.matlet.2014.07.188
[4] Lu, Y. et. al Mater. **16** (2021) 101059; doi.org/10.1016/j.mtla.2021.101059
[5] Lu, Y. et. al Adv. Eng. Mat (2022) 2201473; doi.org/0.1002/adem.202201473

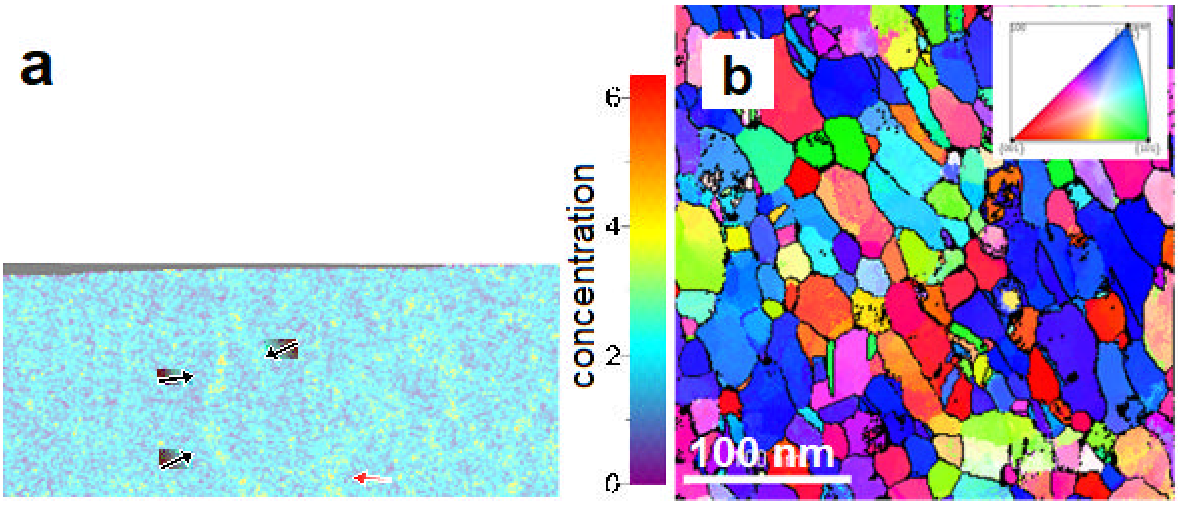


Fig. 1: Microstructure of CoCr$_{0.25}$FeMnNiC$_2$ alloy after HPT: (a) orientation maps evaluated from Automated Crystal Orientation Mapping TEM; (b) two-dimensional contour color maps of C concentration based on Atom Probe Tomography reconstruction of a slab with a thickness of 20 nm [5].

Notes

New perspectives on grain boundary migration

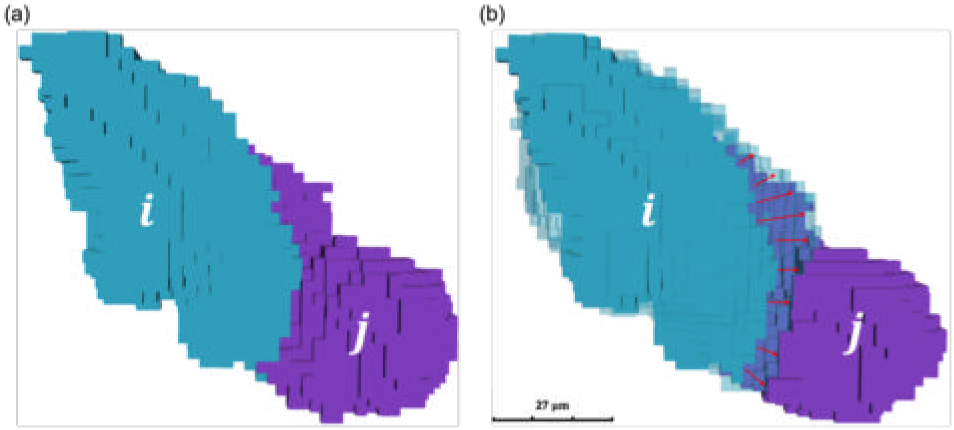
Gregory S. Rohrer and Zipeng Xu, Amanda R. Krause, and Robert M Suter

Dept. of Materials Science and Engineering, Carnegie Mellon University, 15217 Pittsburgh, PA, USA

Classical studies of isotropic grain growth in polycrystals have been based on the idea that grain boundary (GB) migration is driven by the product of the GB energy and curvature. While support for this foundational concept is certainly found in studies of bicrystals, recent experimental measurements of grain boundary migration in polycrystals using high energy diffraction microscopy contradicts this idea [1,2]. Specifically, the direction and speed of grain boundary migration in polycrystals is not correlated with curvature. As an example of this type of motion, Fig. 1 shows the migration of a grain boundary in an α-Fe polycrystal. During annealing, the boundary migrates away from its center of curvature. In addition to the curvature driven elimination of grain boundary area, a competing energy dissipation mechanism is to move or rotate boundaries in such a way that high energy boundary area is replaced by lower energy boundaries so that the average energy of the boundaries decreases. This is a previously unrecognized energy dissipation mechanism that influences grain boundary migration and might explain the absence of a correlation between grain boundary curvature and migration velocity. In this talk, recent measurements of five parameter grain boundary curvature and velocity distributions will be presented and changes in the average grain boundary energy during grain growth will be discussed in the context of grain boundary replacement.

[1] Bhattacharya A., Shen, Y.F., Hefferan, C.M., Li, S.F., Lind, J., Suter, R.M., Krill, C.E., Rohrer, G.S., Science, **374** (2021) 189; dx.doi.org/10.1126/science.abj3210.

[2] Muralikrishnan, V., Liu, H., Yang, L., Conry, B., Marvel, C.J. Harmer, M.P., Rohrer, G.S., Tonks, M.R., Suter, R.M., Krill, C.E., Krause, A.R., Scripta Mater. **222** (2023) 115055; dx.doi.org/10.1016/j.scriptamat.2022.115055.



Initial

Final

Fig. 1: An example of a grain boundary that migrates away from its center of curvature. (a) Grain i (left) and j (right) in the initial state, (b) Grain i (left) and j (right) in the final state. Grains colored by solid blue and light blue are Grain i in the initial and final states, respectively. The red arrows show the direction that the grain boundary moves.

Notes

Segregation engineering in metal oxide nanoparticle-derived ceramics

Oliver Diwald, Thomas Schwab, Korbinian Aicher, Gregor Zickler

Department of Chemistry and Physics of Materials, Paris-Lodron Universität Salzburg, 5020, Salzburg, Austria

Ion exsolution can be instrumental to engineer intergranular regions inside ceramic microstructures that are derived from nanocomposites. We explored the potential of vapor phase-grown MgO nanoparticles hosting Ba^{2+}, In^{3+} and Fe^{3+} admixtures as precursors for engineered intergranular regions. [1,2]
During annealing-induced exsolution from the nanocrystal bulk into the grain interfaces, the impurity admixtures impact grain coarsening and powder densification, effects that were compared for the first time using an integrated characterization approach. The comprehensive structural analysis with XRD and electron microscopy enabled us to draw conclusions on the structure-property-relationships that are controlled by the impurity dispersion inside the MgO grain network.

Depending on the concentration of admixed Ba^{2+} ions, isolated impurity ions either become part of low-coordinated surface structures of the MgO grains where they give rise to a characteristic bright photoluminescence emission profile around $\lambda = 500$ nm, or they aggregate to form nanocrystalline BaO segregates at the inner pore surfaces to produce an emission feature centered at $\lambda = 460$ nm.
As another example, a substantially less soft magnetic behavior was observed for samples with iron admixtures and a reduced fraction of the intergranular $MgFe_2O_4$ phase. Respective phenomenon is attributed to a nanodispersion effect describing size-dependent magnetic properties of Fe^{3+}-doped MgO ceramics.

In the case of In^{3+}-admixtures to MgO ceramics the observed decreased resistivity values by 5 orders of magnitude were rationalized by the formation of a continuous and connected $MgIn_2O_4$ path by exceeding the percolation threshold. The here presented results underline that densification of vapor phase-grown nanoparticle powders with extremely well-defined bulk and surface properties to generate ceramics can lead to a high abundance of structurally and compositionally uniform intergranular regions that emerge from the interrelated effects of segregation and grain growth.

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[2] Schwab T. et al.; ACS Appl. Mater. Interfaces **13** (2021) 25493; doi.org/10.1021/acsami.1c02931.

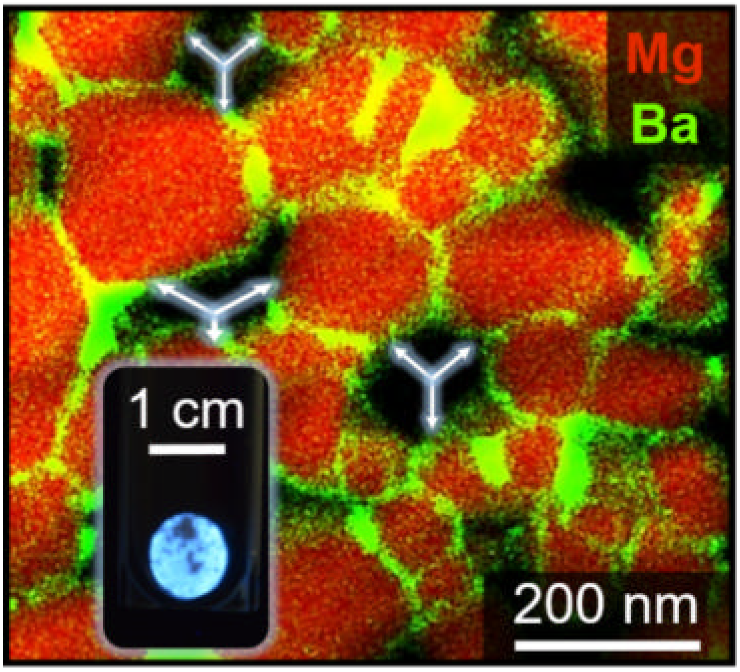

Fig. 1: Sintering-induced segregation of Ba^{2+}-ions from inside MgO host nanoparticles controls surface and interface energetics and, thus, grain coarsening and microstructure evolution. The dispersion of dopants over the intergranular region provides means to retain and adjust alkaline earth oxide (AEO) specific photoluminescence emission features from pores and outer surfaces.

Notes

Designing grain boundary chemistry and transport for safe Li-garnet solid-state electrolytes

Hyunwon Chu[1], Thomas Defferriere[1], Kunjoong Kim[2], Haemin Paik[1], Harry L. Tuller[1,], and Jennifer L. M. Rupp[1,2,3,4,]

[1] Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[2] Department of Chemistry, Technical University Munich, Garching 85748, Germany
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[4] Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Research on solid-state electrolytes has been motivated to replace flammable liquid electrolytes and improve safety and performance of Li ion cells [1]. Li-garnet LLZO ($Li_7La_3Zr_2O_{12}$) exhibits exceptional grain electrical, chemical and mechanical properties [2]. However, recent studies have shown that grain boundaries in this Li^+ conductor could play a critical role in battery degradation and failure, as the grain boundaries promote electron conduction and intervene Li^+ conduction. This results in local reduction and nucleation of Li metal, causing detrimental short circuits through the grain boundaries and limiting the maximum operating current density (known as the critical current density) [3,4]. In the pursuit of developing safe and highly-conducting electrolytes, understanding and tailoring the grain boundary and its iono-electronic properties become essential but are so far not extensively explored.

We contribute to experimental evidence corroborating that the conductivity mismatch arises from the formation of a local electric potential at the electric grain boundary. Grain boundary cores are highly susceptible to charged defect segregation, which lead to the accumulation of excess negative charges and the creation of potential barriers at the boundary cores. The core potential then engenders a depletion of ionic carriers (Li vacancies) and an accumulation of electronic carriers (holes) in the adjacent space charge zone. The carrier concentration changes in the space charge layer can explain the underlying reasons for the low ionic conductivity and high electronic conductivity of the LLZO grain boundaries. Based on the model, we design and engineer the chemistry and transport at the grain boundaries and ultimately enhance the safety and performance of LLZO electrolytes. Typically, defect segregation can be controlled by adjusting processing conditions and material composition. We discovered that the annealing atmosphere influenced the intrinsic defect equilibrium and could be tuned to suppress charge segregation at the grain boundary. Furthermore, we show that a heterogeneous donor dopant with an opposite extrinsic charge could further decrease the net charge of the grain boundary core. Both of these approaches to regulate the core potential were shown in the model electrolyte as effective to improve ionic conduction and suppress electronic conduction in Li-garnet LLZO, enabling a critical current density of 1 mA cm^{-2} in a cell-level testing.

[1] Balaish, M., Gonzalez-Rosillo, J. C., Kim, K. J., Zhu, Y., Hood, Z. D., & Rupp, J. L. M., Nat. Energy, **6** (2021) 227
[2] Kim, K. J., Balaish, M., Wadaguchi, M., Kong, L. & Rupp, J. L. M., Adv. Energy Mater. **11** (2021) 2002689
[3] Han, F., Westover, A. S., Yue, J., Fan, X., Wang, F., Chi, M., Leonard, D. N., Dudney, N. J., Wang, H., Wang, C., Nat. Energy **4** (2019) 187
[4] Liu, X., Garcia-Mendez, R., Lupini, A. R., Cheng, Y., Hood, Z. D., Han, F., Sharafi, A., Idrobo, J. C., Dudney, N. J., Wang, C., Ma, C., Sakamoto, J., Chi, M., Nat. Mater. **20** (2021) 1485

Notes

Interfaces engineering of thin film oxides

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The wide range of fascinating properties observed in complex oxide continue to attract great interest such as ferro-, piezo- and pyroelectricity. Several strategies have been employed to break the lattice symmetry and expand the range of functionalities. Here, I will show how engineering symmetry breaking offers extraordinary opportunities such as, the birth of conductivity in real-time during growth, stabilizing phases which are otherwise not stable using highly coherent interfaces and enhancing the electromechanics with interfaces. The integration of dissimilar materials in heterostructures has long been a cornerstone of modern materials science—seminal examples are 2D materials and van der Waals heterostructures. I will also briefly discuss how new methods enable the realization of ultrathin freestanding oxide films approaching the 2D limit. This collection of possibilities offers unique opportunities for a wide range of rich world and new functionality of complex oxide and their interfaces.

Notes

Epitaxial $LaMnO_3$-based heterostructured thin films obtained by polymer assisted deposition

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In magnetoelectric multiferroics, with two coupled order parameters (polarisation and magnetisation), magnetic degree of freedom can be controlled by electric field, and vice versa. However, an alternative approach is based on using femtosecond laser pulses to control both the charge and the magnetic order of materials. This phenomenon is very desirable for application in spintronics and data storage devices.

Heterostructured thin films are attractive due to their different functionality which is based on changing physical parameters by strain at the interface and their nanoscale size which follows miniaturization trends in microelectronics. Fabrication of homogeneous, high-quality epitaxial oxide thin films was reserved for physical vapor deposition methods (pulsed laser deposition, molecular beam epitaxy, sputtering, etc.) for a long period of time. However, the costs associated with the high-vacuum techniques often require more affordable techniques, such as chemical solution deposition methods.

In this work, epitaxial growth of magnetic single layer and multiferroic bilayer films by solution deposition techniques was investigated [1]. Epitaxial ferromagnetic layer, $LaMnO_3$ or $(La,Sr)MnO_3$, was prepared by polymer-assisted deposition (PAD) technique on single crystal $SrTiO_3$ (001) substrates using aqueous solution of corresponding cations stabilized with PEI and EDTA. For the bilayer films, the second ferroelectric layer, $(Ba,Sr)TiO_3$, was prepared by chemical solution deposition technique, using $BaCO_3$, $Sr(C_2H_4O_2)_2$ and Ti-alcoxide as a precursors. Structure and mechanisms of epitaxial film formation, as well as magnetic and dielectric properties of the obtained thin films were investigated.

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Notes

Influence of In-doping on the electrochemical performance of multicomponent garnet-type solid electrolyte

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Garnet-type electrolytes are one of the most promising Li-ion inorganic solid electrolytes for all-solid-state Li-ion batteries, due to their high Li-ion conductivity, stability against Li metal, and safety against flammability [1]. In this work Nb^{5+}, Gd^{3+}, and In^{3+} are doped on the Zr^{4+} site, in order to enable more Li to occupy the octahedral sites, which could increase ionic conductivity with compositions of $Li_{7-(x-y)}+zLa_3Zr_{2-x-y-z}Nb_xGd_yIn_zO_{12}$ (x = 0.8, y = 0.1, z = 0, 0.2, 0.4, and 0.6). Two synthesis methods were used to prepare the powder, Pechini method and modified solid-state reaction. Both methods have benefits such as easy and fast preparation as well as low calcination temperature compared to conventional methods. The powders were pressed and sintered at 1100 °C for 6 hours in air. X-ray diffraction (XRD) and Raman spectra demonstrated that all compositions exhibited a single phase cubic structure, and the lattice parameter increased linearity with increasing In content. It is found that LLZNbGdInO with In=0.4 has the highest room-temperature bulk ionic conductivity of 9.94×10^{-4} S cm^{-1} for the samples prepared via the modified solid-state reaction. This is one of the highest conductivities reported to date for such compositions [2]. Meanwhile, the samples prepared with Pechini method showed lower bulk ionic conductivity compared to solid-state reaction. Further investigations were performed on the chemical properties of $Li_{7-(x-y)}+zLa_3Zr_{2-x-y-z}Nb_xGd_yIn_zO_{12}$ to identify the exact chemical composition, especially the Li content, by means of ICP-OES. More investigations were performed on the properties of $Li_{7-(x-y)}+zLa_3Zr_{2-x-y-z}Nb_xGd_yIn_zO_{12}$ to identify the underlying mechanism affecting ionic conductivity.

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Notes

High entropy oxides as electrolyte for solid oxide fuel cells

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With increasing demand to reduce the carbon emissions via combustion, cleaner ways to produce energy are being explored. Solid oxide fuel cells (SOFC) are one of the cleaner ways to produce energy. Designing efficient electrolyte materials is indispensable for the development of SOFC. Typically, oxygen ion conductors are used as electrolytes in SOFC. The conduction of the oxygen ion happens through hopping through oxygen vacancies. Several material systems with oxygen vacancies have been investigated as a potential oxygen ion conductor. Yttria stabilized zirconia, ceria-based systems with fluorite structure and doped lanthanum gallate or lanthanum aluminate with perovskite structure are some of the popular oxygen ion conductors. However, one of the limitations observed in oxygen ion conductors is the contribution of electronic conductivity observed at certain partial pressures of oxygen at high operating temperatures. The existence of electronic conductivity at certain partial pressures of oxygen at a given operating temperature might result from the oxygen sublattice interaction with the measurement environment [1].

One possible way to avoid the interaction is by stabilizing the lattice oxygen at high temperatures. High entropy materials are conceptualized to be stable at high temperature due to their high configurational entropy and low formation enthalpy leading to a lower Gibbs free energy, thereby stabilizing the system. High entropy oxides were first introduced in 2015 by Rost et al. [2]. Since then, many different structures and compositions with high configurational entropy are investigated. Rare earth based high entropy oxides with fluorite structure, rare earth and transition metal based high entropy oxide with perovskite structure, transition metal based high entropy oxide with spinel and rock-salt structure are some examples of high entropy oxides [3].

In this work, we synthesize, characterize and investigate the electrochemical properties of fluorite-type and perovskite-type high entropy oxides and introduce dopants to enhance ionic conductivity and stability over a wide range of oxygen partial pressure. In our study, we observe an enhanced stability in conductivity in high entropy oxides in oxidizing condition when compared to a traditional metal oxides.

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Notes

Defect-rich and disordered materials for CO_2 utilization catalysis

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CO_2 utilization is critical for reducing the emissions of hard-to-abate energy services such as aviation, shipping, and chemical production. Advances in heterogeneous catalysis are needed to optimize the efficiency and scalability of CO_2 utilization technologies. This talk will describe our research to develop defect-rich and disordered materials as catalysts for electrochemical and thermochemical CO_2 conversions. For electrochemical conversion, we have pioneered the use of grain boundaries to create metastable active surfaces for CO_2 and CO reduction [1-5]. Using a combination scanning electrochemical cell microscopy (SECCM) and high-resolution electron backscatter diffraction (HR-EBSD), we have elucidated a structural model to explain grain boundary effects for CO_2-to-CO reduction on Au surfaces [5].

I will also discuss the prospects for exploiting grain boundary effects more broadly in electrocatalysis. An alternative to direct electrochemical reduction of CO_2 is to produce H_2 using well-established H_2O electrolysis technology and then perform the reverse-water-gas-shift (RWGS) reaction to convert CO_2 to CO.

In the second part of my talk, I will describe our development of disordered alkali carbonate (M_2CO_3) materials that are exceptionally active, selective, durable, and impurity-tolerant RWGS catalysts [6, 7]. A frontier challenge in this area is to elucidate local structure of the active alkali carbonates under operating conditions and learn how to modulate disordered materials to tune their functional properties. Carbonate-catalyzed RWGS has created new opportunities to simplify power-to-liquid systems that utilize syngas technology (Fischer-Tropsch or gas fermentation) to convert gas to liquids.

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Notes

Creating microstructures on nickel surfaces – A plasma process to enhance electrode performance for large scale hydrogen production

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As part of H2Giga, the hydrogen flagship project by the German Federal Ministry of Education and Research (BMBF), we developed a plasma treatment for industry relevant nickel plates and catalyst particles. In a common manufacturing process for electrolyzers, nickel plates or meshes are first coated with a suspension of catalyst particles. Afterwards the solvents get thermally evaporated, yielding the finished electrodes.

We developed a plasma process to enhance the characteristics of electrodes by exposing electrodes to a nitrogen plasma during manufacturing. With this treatment, we can achieve a microstructuring of the surface, thus increasing the microscopic surface area available to later electrochemical reactions. This microstructure can be seen in figure 1. We demonstrate how process parameters influence the formation of the structures on the surface.

An additional benefit of the plasma treatment is a nitrification of the nickel surface. Nickelnitride is known to be beneficial for the oxygen evolution reaction (OER). It is shown that samples treated with the developed plasma process have a notably improved electrochemical performance as measured by cyclic voltammetry and also an increased catalyst layer adhesion as measured by a custom-built cavitation erosion test. We propose an underlying mechanism for the formation of the microstructure based on nitrogen diffusion and the Kirkendall effect.

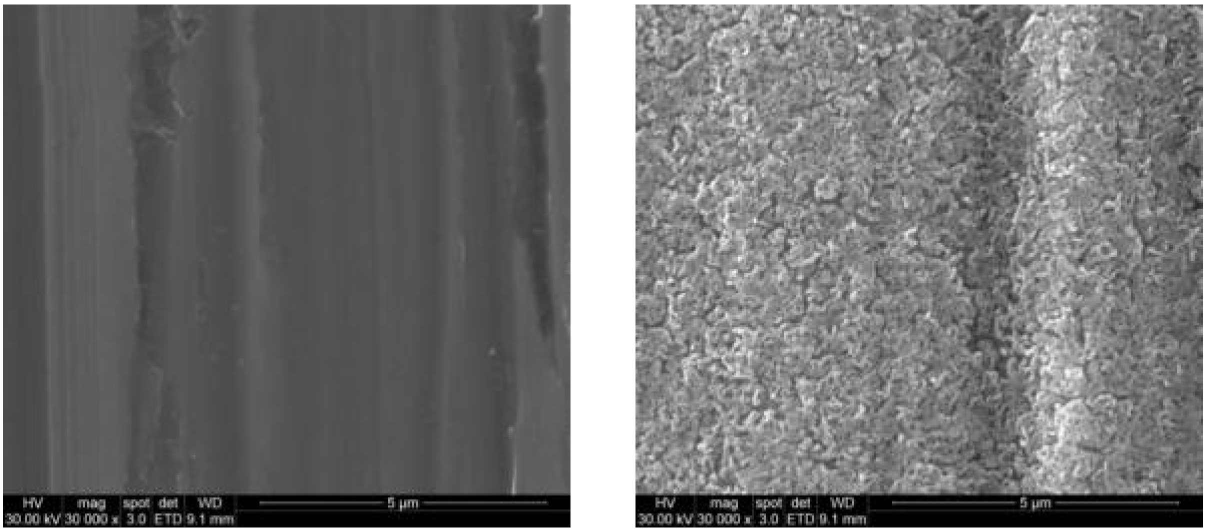

Fig. 1: SEM image of an untreated nickel surface (left) and the same surface after N_2 plasma treatment.

Notes

Quantitative analysis of two-phase nanocrystalline oxides by X-ray absorption spectroscopy

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Nanocrystalline complex oxides are widely applied as heterogenous catalysts. Among complex oxides, lanthanum-based perovskites like $LaCo_{1-x}Fe_xO_3$ exhibit excellent catalytic performance in oxidation reactions. However, the identification and elucidation of structure-activity relationships of materials with high specific surface areas is challenging due to their heterogenous disorder. The structural characterization of small lanthanum-based perovskite nanoparticles is especially challenging since synthesized samples often contain secondary phases of the corresponding transition metal oxides which may remain undetected in qualitative analyses using a single method of measurement. X-ray diffraction and X-ray spectroscopy provide a different sensitivity regarding (crystalline) phases. This may be exploited for structural characterization by combining diffraction and spectroscopy data.

We present results on small $LaCo_{1-x}Fe_xO_3$ nanoparticles (Fig. 1) generated by chemical vapor synthesis where crystal structure and phase composition are determined by Rietveld refinement of X-ray diffraction data. Based on these results, atomistic models (Fig. 2) of the crystalline phases are created and used in simultaneous refinement of extended X-ray absorption fine structure spectra from the Co, Fe and La K-edges by reverse Monte Carlo analysis. We find that the activity of the catalysts in cyclohexene oxidation is correlated to changes at the local structure level surrounding the cobalt absorber sites [1].

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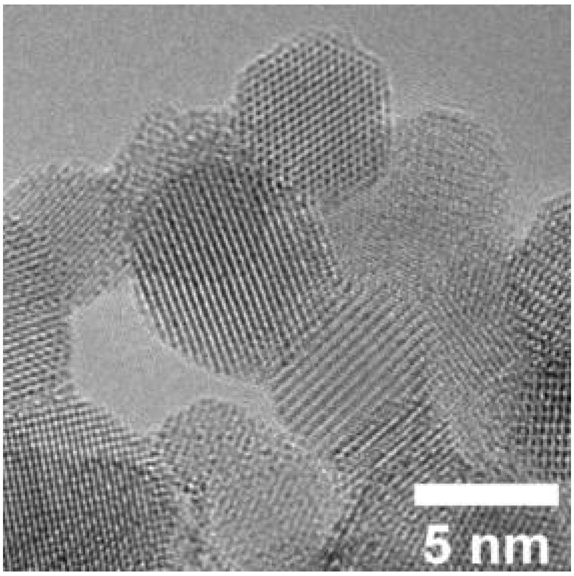

Fig. 1: TEM image of $LaCoO_3$ nanoparticles.

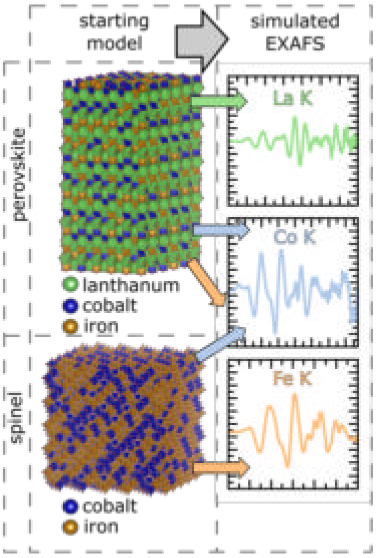

Fig. 2: Two-phase model and relation to corresponding EXAFS spectra.

Notes

Neuromorphic computing with memristive devices based on 2D semiconductors and resistive switching memories

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In-memory computing (IMC) has emerged as a promising paradigm to overcome the memory bottleneck of conventional computing systems [1]. IMC takes direct inspiration from the human brain, where information is processed by co-localized neurons and synapses. Developing brain-inspired, neuromorphic IMC systems would pave the way for a new era of artificially intelligent, autonomous agents capable of learning, classification and real-time adaptation [2]. Toward this goal, novel materials and devices should be identified to enable neuromorphic functions such as spike-based learning, integration, filtering and short-term memory over several time scales [3].

This work provides an overview of neuromorphic devices and circuits based on 2D semiconductors [4,5] and resistive switching memories [6,7]. 2D materials such as hBN and MoS_2 provide the functional switching materials for memristors and memtransistors capable of both long-term and short-term plasticity for neuromorphic synapses. In particular, Ag cation migration on the MoS_2 channel of memtransistor devices have been shown to lead to volatile switching behavior with controllable retention time for short-term synapses [4]. Charge-trap memories based on MoS_2 show extremely linear update characteristics which is useful for neural-network training accelerators (Fig. 1). In addition, the trapping/detrapping dynamics enables reservoir computing with ultra-low energy consumption thanks to the sub-threshold operation of the MoS_2 transistors [5].

Memristive devices based on metal oxides display long-term (nonvolatile) [6] and short-term (volatile) [7] potentiation and depression, thus serving a wide range of functions in neuromorphic systems. Crosspoint arrays of nonvolatile memristors can implement synaptic weights for neural network accelerators [1] and fully-memristive in-materia reservoir computing systems [6]. Volatile memristors based on dynamic Ag cation switching/recovery have been demonstrated for unconventional signal processing and brain-inspired working memories capable of activation and recall. Overall, memristive devices provide an ideal technology platform for neuromorphic systems with nonvolatile storage, low-energy consumption and high synaptic density.

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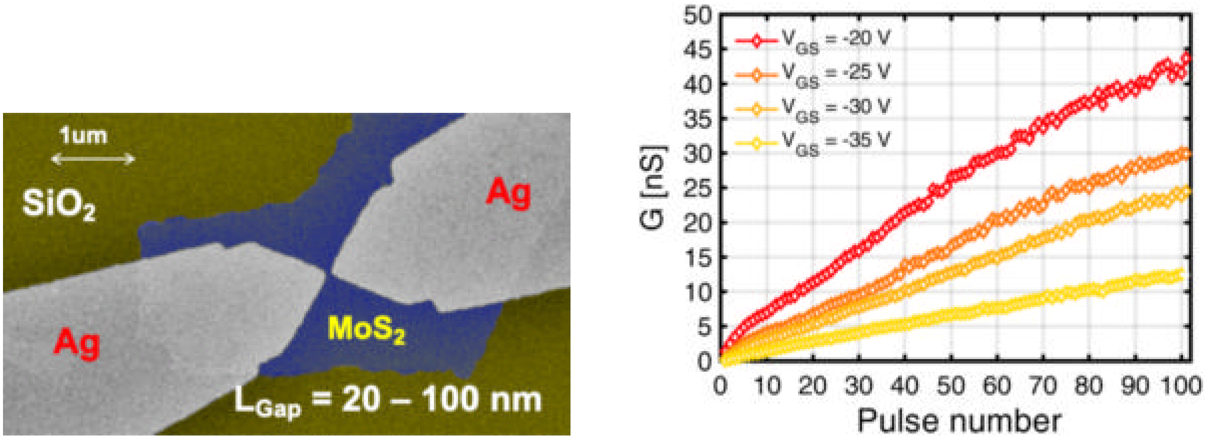

Fig. 1: MoS_2-based charge trap memory (left) and potentiation characteristics (right) demonstrating high linearity, large conductance window and ultra-low current thanks to transistor operation in the subthreshold regime.

Notes

Direct growth of graphene on semiconducting substrates via plasma-enhanced chemical vapor deposition

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Chemical Vapor Deposition (CVD) is the most common method to fabricate large scale electronic grade graphene, which is an atomically thin layer of carbon with high electrical conductivity and high optical transparency. This makes graphene attractive, e.g., as transparent conductive layers in optoelectronic devices. High-quality graphene is achieved when it is thermally grown on electrochemically polished high-quality copper foils [1]. Unfortunately, this type of graphene has to be transferred post-growth onto the target substrate via a complex, destructive and contaminating process [2]. An alternative production route is to grow graphene directly onto the semiconductor device platform. Since typical semiconductors exhibit a low or even no catalytic effect, the process requires temperatures which, in worst cases, can destroy the entire device.

To circumvent this drawback we developed a low-temperature plasma-enhanced (PE) CVD process, were a plasma is used for dissociation of the precursor instead of high temperatures. In order to study the PECVD growth mechanism of graphene on semicondutors used in optoelectronic devices we used a commercially available 4” cold wall reactor to fabricate graphene on Ge- and GaN-based devices [3-5], where graphene can be used as a transparent transport layer for high-speed photodetectors or as a transparent conductive spreading layer (TCSL), respectively. To understand the graphene growth on Ge, we investigated the PECVD growth on two different Ge surfaces, namely Ge(100) and Ge(110), for different temperatures down to 760°C and a CH_4/H_2 mixure as precusor and process gas. After 40 min growth on Ge(100) typical hexagonal shaped graphene grains with an average size of around 70 nm form, while after 8 h of growth a coverage of 41% with an average grain size of 120 nm is obtained. A hexagonal and an elongated morphology of the graphene grains on Ge(100) and Ge(110) surfaces, respectively, indicates the dominant role of substrate orientation on the shape of graphene grains [3].

For the intergration of graphene in GaN-based blue LEDs the process was modified and N_2 was used instead of the commonly used H_2 process gas in order to prevent any decomposition of the GaN surface. A growth temperature of less than 800°C results in nanocrystalline graphene on GaN surfaces, while expanding the growth time to 8 h turbostratic multilayer graphene with an average grain size of about 30 nm is observed [4, 5]. The resulting high-quality graphene electrodes show an enhanced current spreading effect and an increase of the emission area by a factor of ~8 in operating GaN LEDs.This growth process was then adapted for fabricating graphene on top of the p-AlGaN cladding layer of a deep ultraviolet (UVC) LED. After optimizing the CH_4/N_2 ratio, the growth temperature and the growth time, we obtained graphene with Raman intensity ratios of $I_D/I_G \approx 1.6$ and $I_{2D}/I_G \approx 1.4$, respectively, for a growth temperature of 670°C. The optical transparency of the as-grown graphene exceeds 90% in a spectral range from 270 nm to 800 nm and a sheet resistance of around 5 kΩ/sq was found. The UVC-LED with graphene as a TCSL shows a diode-like *I-V* behavior with a current density of approximately 0.1 mA/cm^2 at 4 V and 0.23 mA/cm^2 at 5 V, respectively. A distinct current spreading effect is observable with an emission maximum of the LED at ~275 nm.

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Notes

Interface-dominated topological transport in nanograined Bi_2Te_3

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Bismuth telluride is an excellent thermoelectric material and also belongs to the class of three-dimensional topological insulators. Therefore, charge carriers with extremely high mobility exist at the crystal surfaces. This is particularly visible in samples made of nanoparticles, provided that the nanoparticles used have sufficient surface purity. Compacted nanoparticulate bulk samples exhibit a high density of interfaces. These samples show a pronounced weak anti-localization in the low temperature transport behavior as well as a kink in the electrical resistance at about 5 K. Evaluation of the magnetotransport data using the Hikami-Larkin-Nagaoka model yields coherence lengths of up to 200 nm, which is significantly larger than the average grain size in the studied samples. Using terahertz spectroscopy, the average mobility of the surface charge carriers can be estimated to be about 1000 to 10000 $cm^2V^{-1}s^{-1}$ at room temperature. This means that good thermoelectric properties of nanoparticulate Bi_2Te_3 near room temperature are also determined in part by the existence of surface charge carriers.

Notes

Tracking self-diffusion in oxide thin films

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Self-diffusion is a fundamental physical process that, in solid materials, is intimately correlated with both microstructure and functional properties. Local transport behavior is critical to the performance of functional ionic materials for energy generation and storage, and drives fundamental oxidation, corrosion, and segregation phenomena in materials science, geosciences, and nuclear science. Here, an adaptable approach is presented to precisely characterize self-diffusion in solids by isotopically enriching component elements at specific locations within an epitaxial film stack, and measuring their redistribution at high spatial resolution in 3D with atom probe tomography (APT).

I will discuss how this versatile approach to study precisely tailored thin film samples at high spatial and mass fidelity will facilitate a deeper understanding of atomic-scale diffusion phenomena under extreme conditions. Using epitaxial Fe_2O_3 and Cr_2O_3 thin films with ^{18}O and ^{57}Fe tracers as a model system, I will demonstrate the precise measurement of the initial sharp layer interfaces, and subsequent redistribution of the isotopic tracers after annealing and/or ion irradiation. Both thermal and radiation-enhanced diffusion are quantified at moderate temperatures, revealing new insights into defect-mediated transport mechanisms. Short-circuit anion diffusion through 1D and 2D structural defects in Fe_2O_3 are also directly visualized in 3D. I will also present quantitative experimental evidence of anion intermixing over long length scales during the deposition by molecular beam epitaxy of epitaxial Fe_2O_3 and Cr_2O_3 films that incorporate ^{18}O tracers. Intermixing events suggested by molecular dynamics simulations are examined to reveal that adatoms on the film surface act to “pull up” subsurface O and cations. Subsequent ring-like rotation mechanisms involving both adatom and subsurface anions then facilitate their mixing. These intermixing mechanisms help inform a comprehensive, predictive understanding of the thin film deposition process, and may also be operant during other surface-mediated processes such as corrosion.

Notes

Laser reactive sintering of complex oxides

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UV laser sintering allows densification and microstructural transformation of granular systems. The high photon energy of an UV laser leads to resonant heating, if the energy is higher than the band gap of the irradiated material. Due to this effect, the heat load is strongly localized and for nanostructured materials temperatures up to 2000°C and extremely high heating rates are reached at laser powers as small as 80 mW [1]. Therefore, UV laser sintering is a powerful tool for material engineering, as it enables reactive sintering of binary metal oxide nanopowders to generate complex oxides with short process times [2]. It is also feasible for processing (printed) electronic components with structures in micrometer range [3].

Complex oxides exhibit many outstanding properties, for example the transparent conducting oxides (TCOs) which combine good electrical conductivity and high optical transmittance. The delafossite $Cu(Al)O_2$ is such a transparent conductive oxide with p-type conductivity [4]. TCOs are widely used in photovoltaics and opto-electronic devices like flat panel displays or solid-state lighting. However, there is a lack of p-type TCOs with high electrical conductivity impeding the production of high-performance p-n junctions. Complex oxides have shown great potential to overcome this problem.

The production of the $Cu(Al)O_2$ delafossite is a challenge, because of the complexity of the binary phase diagram of copper- and aluminumoxide. With conventional solid state reaction methods very long process times of several hours and high energy input are needed [5].

In this contribution, we will present a study of reactive UV laser sintering to generate $Cu(Al)O_2$ and their characterization.

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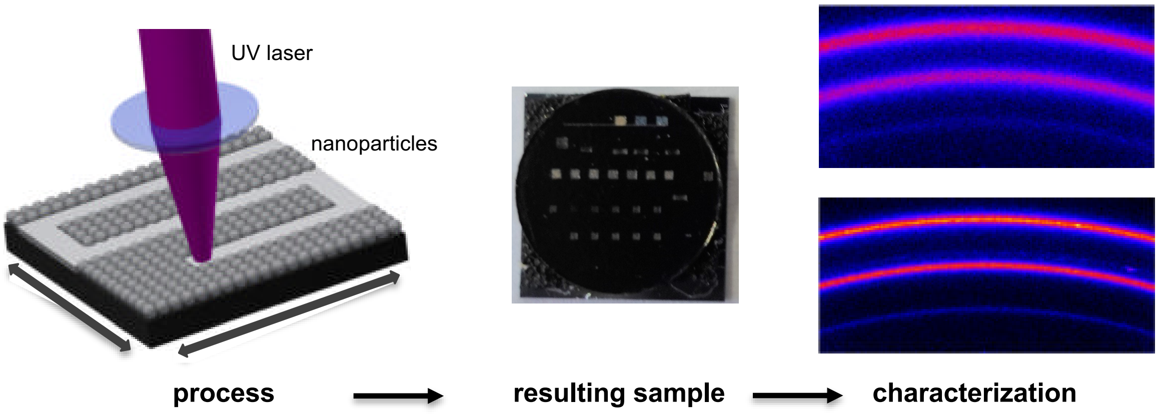

Fig. 1: (left) scheme of the laser sintering process, (middle) a pressed pellet of mixed CuO_x and AlO_x nanoparticles on which rectangularly shaped areas have been sintered with different laser parameters, (right) X-Ray diffraction images of a CuO_x sample obtained by using a microfocused X-ray beam and a 2D-detector before (upper) and after sintering (lower).

Notes

2D Ti_3C_2 MXene based ceramic nanocomposites enabled by pressure-assisted sintering

Maxim Sokol, Barak Ratzker and Or Messer

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MXene materials have gained widespread attention due to their versatility, and there is increasing interest in incorporating them into metal or ceramic matrices to create advanced nanocomposites. In this study, we present a facile approach for the production of bulk MXene/ceramic nanocomposites through the mixing of MXene with ceramic particles followed by field-assisted sintering. The $Ti_3C_2T_z$/alumina system was used as a model to investigate the effect of MXene addition on the densification behavior and properties of nanocomposites. Our results show that the presence of MXene significantly enhances the densification rate at low temperatures and leads to a homogenous distribution of $Ti_3C_2T_z$ MXene at the alumina grain boundaries (Fig. 1). The obtained $Ti_3C_2T_z$/alumina nanocomposites exhibited electrical conductivity and strong light absorption, while the hardness decreased due to weakening of the grain boundaries caused by the presence of intergranular layered MXene. Additionally, we demonstrated that using multilayered $Ti_3C_2T_z$ as a precursor can produce composites with plate-like TiC_x morphology. We suggest that the processing methods proposed in this work are applicable to metals and other widely used ceramics. MXene type, size, composition, and termination groups could be engineered and adapted to most oxides, nitrides, or carbides depending on the desired properties. This work provides a conceptual approach for utilizing the diversity and versatility of MXene in the creation of tunable advanced nanocomposites.

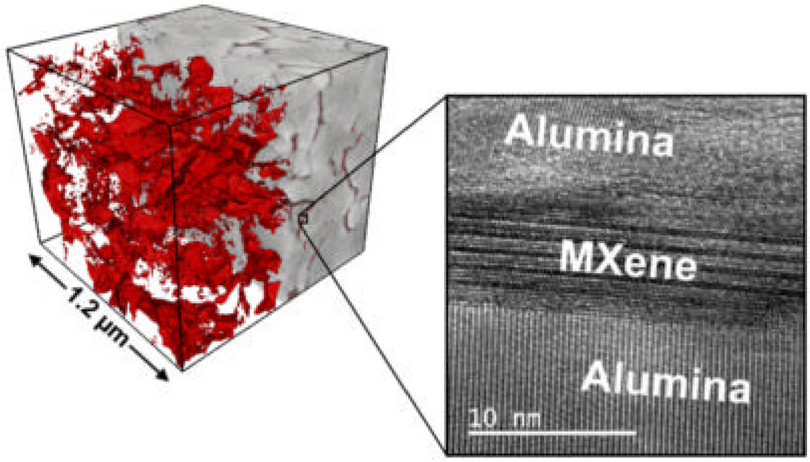

Fig. 1: FIB tomography 3D reconstruction of the MXene network and a magnified high-resolution TEM micrograph of several $Ti_3C_2T_z$ MXene layers integrated at the grain boundary between two Al_2O_3 grains.

Notes

Microstructure evolution during sintering: Discrete element method approach

Lukas Engelke, Lothar Brendel and Dietrich E. Wolf

Faculty of Physics and CENIDE, University of Duisburg-Essen, 47057 Duisburg, Germany

We present a new numerical model for the sintering of a powder of crystalline particles into a dense, polycrystalline solid. Although our method can be categorized as a Discrete Element Method, it overcomes some of the typical limitations of these methods: 1) The method derives shrinkage and grain coarsening from the minimization of the free energy. 2) By representing each grain as a truncated sphere, it takes the complex and changing shape of the grains into account to determine the thermodynamic driving forces and associated kinetic coefficients. We avoid the calculation of diffusion fields at the sub-grain scale, but validate the model by comparing the temporal evolution of a system of 4 particles with results from such a continuum model. Taking advantage of the computational efficiency of Discrete Element Methods, we simulated the sintering of polydisperse agglomerates of up to 16000 particles on a standard desktop workstation. Using material and process parameters from the literature, the model accurately reproduces experimental data on the evolution of the grain size distribution for alumina [1].

[1] Engelke, L., Brendel, L., Wolf, D.E., J .Am. Ceram. Soc. (2023); doi.org/10.1111/jace.19131

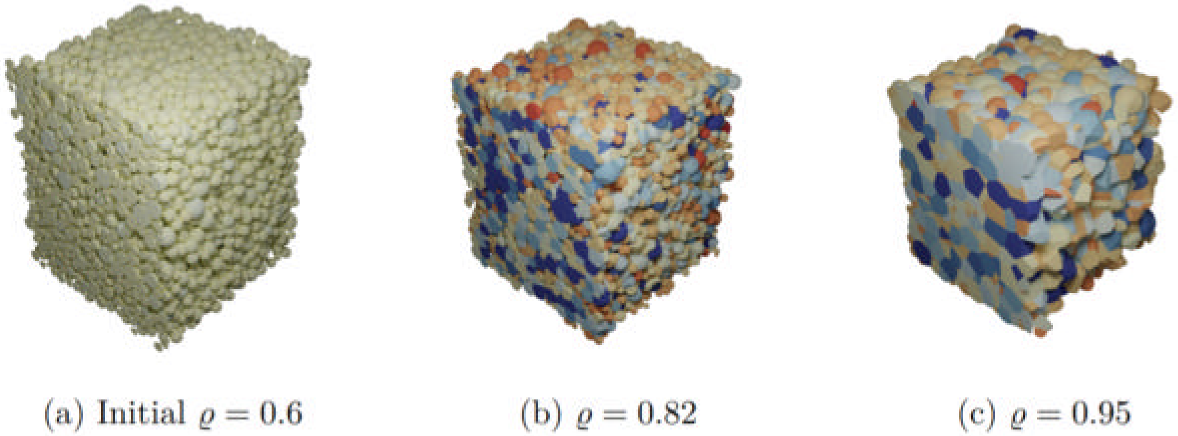

Fig. 1: Snapshots of the microstructure of sintering alumina at 1350°C. (a) Green body, (b) and (c) stages at increased relative density ρ. Left face: cut, right face: fracture surface, top face: free surface. Colors code for growth rate of grains: Blue grains grow, red grains shrink.

Notes

Diffusion at the atomic scale

Karina Morgenstern

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Surface diffusion is central to many technological processes, such as crystal growth, catalysis, sintering, etc. It influences the stability of functional, technologically important materials. Therefore, the motion of adatoms on surfaces was widely investigated and the basic mechanism of motion is quite well understood, although not completely unveiled [1]. However, it is still quite a challenge to probe the motion of slightly bigger objects, such as dimers and trimers [2-4], or even the smallest molecules.

We have used time-lapsed scanning tunneling microscopy [5] at varying temperature to follow the diffusive motion of individual molecules on metallic surface. While the motion of small molecules is comparable to that of atoms, the additional degrees of freedom of dimers and trimers of smaller molecules and that of larger molecules lead to surprising diffusivities, which we understand in conjunction with theoretical calculations. The examples discussed in this talk comprise CO [6], water [7] and phtalocyanine [8]. They demonstrate the importance of using a real-space method in understanding complex diffusion mechanisms.

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[4] Morgenstern, K.; Braun, K.-F.; Rieder, K.-H.; Phys. Rev. Lett. **93** (2004) 056102; doi.org/10.1103/PhysRevLett.93.056102.
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[8] Antczak, G.; Kamiński, W.; Sabik, A.; Zaum, C.; Morgenstern, K. J. Am. Chem. Soc. **137** (2015) 14920; doi.org/10.1021/jacs.5b08001; Antczak, G.; Boom, K.; Morgenstern, K. J. Phys. Chem. C **121** (2017) 542; doi.org/0.1021/acs.jpcc.6b11246.

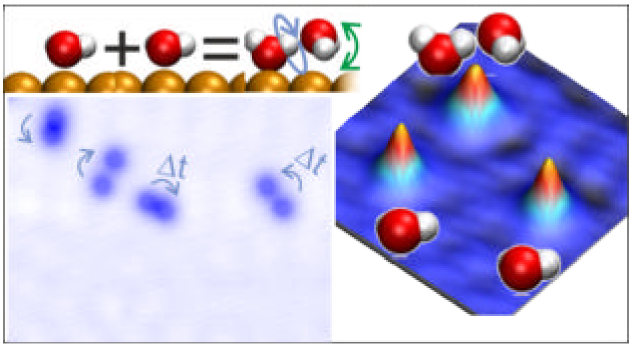

Fig. 1: Schematics of water dimer formation; motion of water molecules and 3D image of two water monomers and one water dimer.

Notes

Defect engineering via dopant-induced migration catalysis

Diego Colombara

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Since the dawn of civilization, atomic diffusion impacts the efficiency, lifetime and thermal budgets of numerous devices, from rough utensils to sophisticated artifacts. Diffusion entails the relentless interaction between atoms and defects in everyday technologies. Point and extended defects originate in crystalline solids when atoms leave their sites or fail to occupy them. Type, density and distribution of these defects control the properties of real materials, to the extent that certain defects are intentionally engineered. One way to engineer defects is via extrinsic doping, the deliberate introduction of impurities to crystalline solids during or after growth. Extrinsic doping impacts dramatically the optoelectronic, compositional and microstructural properties of materials. However, whereas doping engineering relies on established equations that describe the diffusion of dopant atoms within the matrix of a material, the effect of dopant atoms themselves on the diffusion of matrix atoms is neglected.

This study reveals that dopant atoms can alter the diffusivity of matrix atoms in Cu(In,Ga)Se_2 [1]. Specifically, Na doping in Cu(In,Ga)Se_2 is shown to enhance or impede the interdiffusion of In and Ga, depending on the relative concentration of Na and Cu. The experimental study suggests that doping a host material may enhance heteroatom diffusivities if (i) dopant migration occurs through the Frank-Turnbull mechanism and (ii) there is overlap between the (cationic/anionic) migration sublattices of dopant and heteroatom. Under such conditions a migration catalysis may occur at sufficiently low dopant concentrations, despite the decreased absolute concentration of point defects responsible for heteroatom diffusion. Hence, a mechanism of doping-assisted catalytic migration is presented (Figure 1).

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[2] Biderman, N. J., et al., AIP Advances, **6**, (2016) 055211; doi.org/10.1063/1.4950905

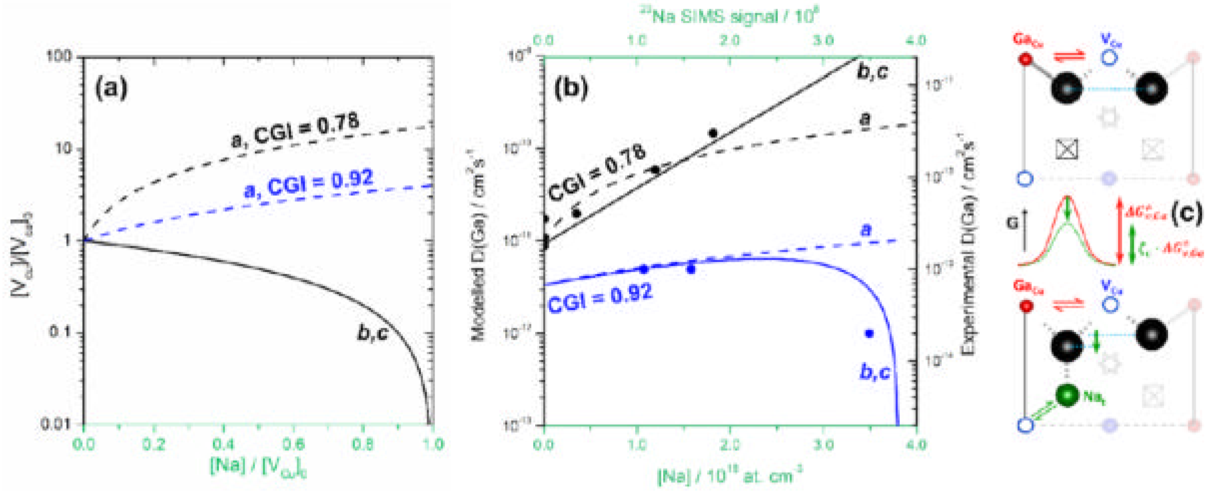

Fig. 1: Modelled dependence of gallium diffusivity on sodium concentration. (a) Relative variation of copper vacancy concentration upon sodium incorporation and (b) dependence of gallium diffusivity on sodium concentration (top abscissa) in GaAs/CInSe$_2$ libraries with Cu ratio of 0.78 (black dots) and 0.92 (blue dots). The lines are the corresponding models devised based on the theory of Biderman et al. (dashed, scenario a) [2] and proposed in this study (solid, scenarios b,c). (c) Depiction of the mechanism of scenario c: migration of gallium on copper in the absence (top) and presence of sodium (bottom) [1].

Notes

Can an electrical current create non-equilibrium defects?

Magdulin Dwedari, Lothar Brendel and **Dietrich E. Wolf**

Faculty of Physics and CENIDE, University of Duisburg-Essen, 47057 Duisburg, Germany

In a series of papers [1-3] we developed a theoretical picture, how an electrical current drives lattice vibrations out of equilibrium and hence may lead to non-thermal concentrations of interstitials and vacancies. By solving coupled Boltzmann equations for electrons and phonons, describing an electrical current with momentum transfer to the crystal lattice [1], we found a strong proliferation of short wavelength lattice vibrations. The deviation from a thermal Bose-Einstein distribution is surprisingly strong, regardless of the details of the electron-phonon matrix elements. The electrical current drives the lattice vibrations out of equilibrium.

With non-equilibrium molecular dynamics simulations [2], where a phonon mode is permanently excited with a certain rate, we demonstrated that Frenkel defects are generated in molar concentrations far above equilibrium (Fig. 1), provided three conditions are fulfilled: The phonon mode must be near the Brillouin zone edge, the excitation rate must be within a window in the TeraHertz range, and the temperature must be above the Debye temperature, but sufficiently below the melting point. We postulate that these conditions can be achieved by a suitable electrical current. The non-equilibrium molecular dynamics simulations were done for aluminum [2] and for rutile TiO_2 [3]. In the latter case, interstitial-vacancy pairs of Ti as well as of O are formed. In agreement with experiment we found that the mean-square displacements of the vibration amplitudes of the Ti and O atoms are specifically enhanced.

[1] Dwedari, M., Brendel, L., Wolf, D.E., *New J. Phys.* **24** 113039 (2022); doi.org/10.1088/1367-2630/aca11a

[2] Jongmanns, M., Raj, R., Wolf, D.E., *New J. Phys.*, **20** (2018) 093013; doi.org/10.1088/1367-2630/aadd5a

[3] Jongmanns, M., Wolf, D.E., *J.Am.Ceram.Soc.* **103** (2020) 589; doi.org/10.1111/jace.16696

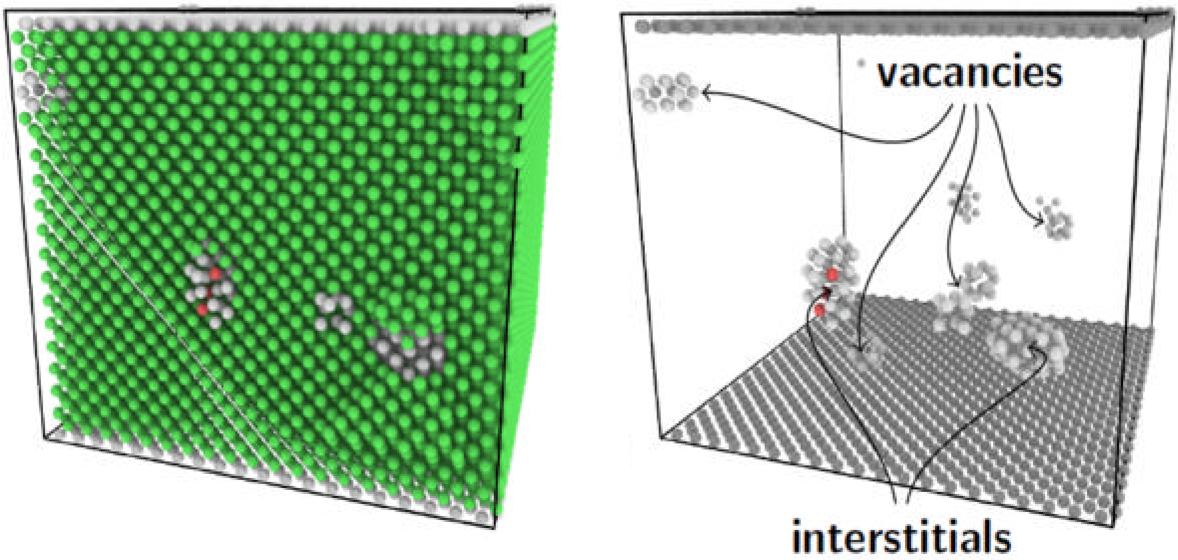

Fig. 1: Snapshot of a non-equilibrium molecular dynamics simulation of Al [2]. Green color marks atoms with a local fcc neighborhood (left panel). If these atoms are not shown (right panel), the defects can be clearly seen.

Notes

Inelastic molecular collisions and the gas mean free path

Sotiris E. Pratsinis,[1] D. G. Tsalikis,[1] V. G. Mavrantzas[1,2]

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[2] Department of Chemical Engineering, University of Patras & FORTH-ICE/HT, Patras, 26504, Greece

The mean free path (MFP) dictates when gas-phase nanoparticle transport takes place in the free molecule or continuum regime. This is crucial in process design of gas phase processes (laser, plasma, hot wall, ultrasonic and flame) in material synthesis (films and nanoparticles). For eons, the kinetic theory of gases [1] has been used to determine the MFP assuming elastic collisions between spherical gas molecules. However, is this so with what we know about molecular shape and force fields today? Having reached a state of maturity now, molecular dynamics (MD) simulations can elucidate the fundamentals of basic gas-phase (aerosol) processes that lead to understanding of natural phenomena and accelerating process scale-up, as reviewed recently [2]. Here the mechanics of gas collisions are elucidated for plain air at room temperature by thoroughly-validated atomistic MD treating O_2 and N_2 as true diatomic molecules accounting for their shape and force field, for the first time to our knowledge.
The MD simulations were conducted for 21/79 mole O_2/N_2 (air) in the NVE ensemble at 300 K & 1 atm following Zambrano *et al.* [3]. Collisions were identified by the distance between colliding molecules, as in classic kinetic theory. Treating O_2 and N_2 as hard spheres led to the straight trajectories (Fig. 1a) and collision frequencies, in perfect agreement with those from classic kinetic theory. Accounting, however, for the molecular shape and force field, trajectories were no longer straight, and collision frequencies were much higher due to the attractive part of the force field and the diatomic, thus more voluminous, shape of N_2 and O_2 (Fig. 1b) as will be shown by the respective videos.

Detailed analysis of the latter trajectories revealed that molecular collisions involve strong interactions between colliding molecules. There were instances, albeit rare, where even 3 molecules were involved in the same collision! Moreover, frequently, colliding molecules were split from each other but soon returned to collide again and again without interacting with any other molecule in between. Such collisions are termed spurious and were systematically removed from the analysis to avoid overcounting collisions. These complex collision patterns were never observed by treating O_2 & N_2 as hard spheres!

A direct result of the enhanced interactions between air molecules when these are treated as true diatomic molecules is that their MFP (calculated by three different methods: collision densities, direct averaging over the probability distribution of free paths & Hazard rates of true collisions) comes out to be considerably smaller than that from the classic kinetic theory. The new value of the MFP for air is 38.5 nm, almost 43% smaller than the currently known and widely used value in textbooks of 67.3 nm at 300 K and 1 atm. Aside from its fundamental value, such a result is significant in gas-phase synthesis of tiny (< 5 nm) nanoparticles where asymptotic (self-preserving) particle size distributions and (fractal-like) structure have not been attained yet to simplify the corresponding process design [4].

[1] Maxwell JCMA, *The London, Edinburgh, Dublin Philos. Mag. J. Sci.*, **19** (1860) 19, DOI: 10.1080/14786446008642818
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[3] Zambrano H, Walther JH & Jaffe R, *J. Mol. Liq.*, **198** (2014) 107, DOI: 10.1016/j.molliq.2014.06.003
[4] Pratsinis SE, *AIChE J.*, **56** (2010) 3028, DOI: 10.1002/aic.12478

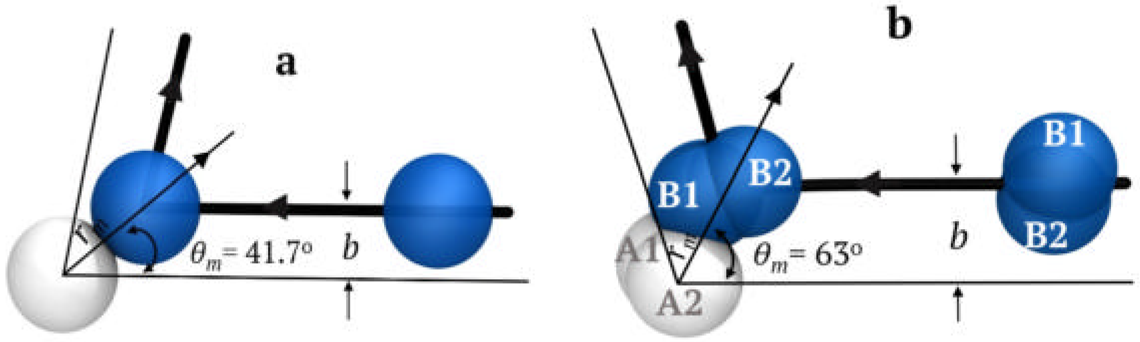

Fig. 1: Collision trajectories by a) classic kinetic theory and b) detailed accounting of attractive and repulsive forces between diatomic gas molecules (like N_2 and O_2). The reference (stationary) molecule is in white, and the colliding one in blue. The bold line shows the trajectory followed by the moving molecule before & after collision while the thin one helps to determine the collision parameter b.

Notes

Understanding nanostructure formation and transition in dry, wet and airborne hard, soft and bio matter using SAXS

Martin A. Schroer

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In order to obtain a complete understanding of the microstructure of nano-systems and their evolution, it is essential to determine it at all relevant length scales – ideally following formation and transition processes under *in situ* and *operando* conditions. A method that fulfills these requirements is small angle X-ray scattering (SAXS). SAXS does not only yield access into lengths scales from several Ångstrom up to hundreds of nanometers, but also allows probing the structural evolution by time-resolved studies under realistic formation conditions.

In my talk, I will demonstrate how SAXS can be used as a tool to explore the structure and structural evolution of various types of nano-systems (Fig 1). I will give examples how to probe structure formation and transitions in hard, soft and biological matter for different aggregation states, highlighting the broad versatility of small angle scattering.

In particular I will show how to determine local orientational order within dried thin nanoparticle films using X-ray nanobeams [1], how to monitor supercrystal formation in colloidal suspensions induced by high pressure [2], as well as how to follow nanoparticle formation in chemical vapor synthesis reactions [3]. Finally, I will show how SAXS can be used to determine the structure of biological macromolecules in solution [4] and help in the development of new pharmaceuticals, such as artificial oxygen carriers or mRNA-based vaccines.

[1] Lehmkühler, F., Schulz, F., Schroer, M.A ., Frenzel, L., Lange, H., Grübel. G., IUCrJ, **5** (2018) 254; doi.org/10.1107/S2052252518005407

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[3] Schroer, M. A., Levish, A., Yildizlar, Y., Stepponat, M., Winterer, M., Rev. Sci. Instrum., **93** (2022) 113706; doi.org/10.1063/5.0122461

[4] Schroer, M. A., Svergun, D.I. Emerg. Top. Life Sci, **2** (2018) 69; https://doi.org/10.1042/ETLS20170138

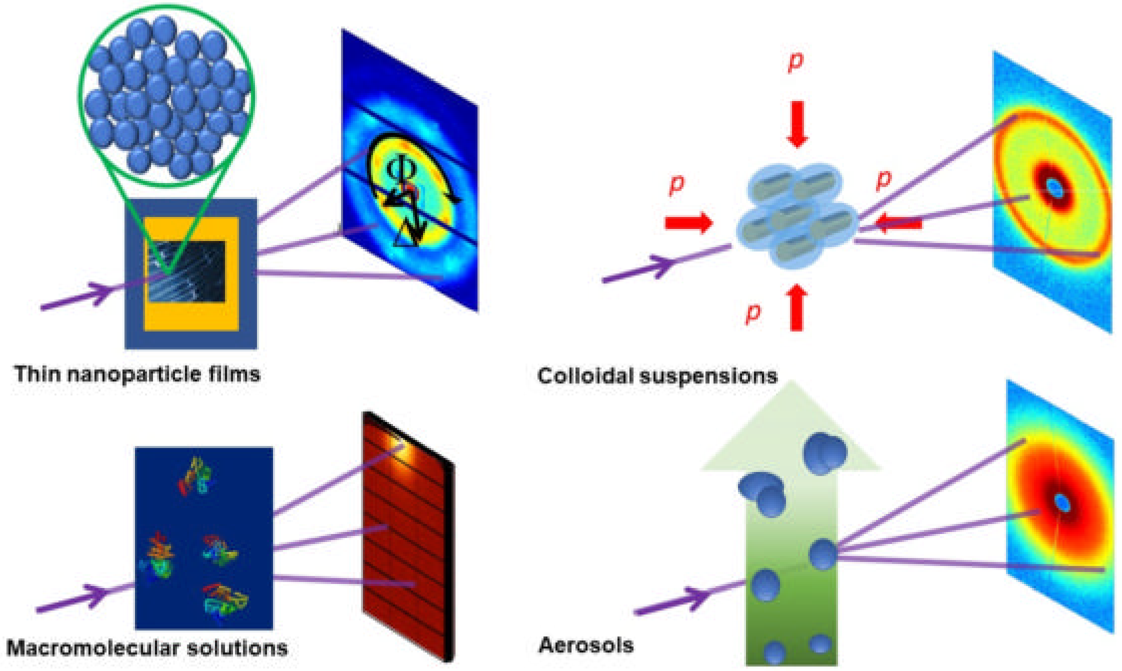

Fig. 1: The wide range of applications for SAXS to study nanostructures. Clockwise: Investigation of thin granular films using X-ray nanobeams [1], colloidal suspensions under high pressure [2], following nanoparticle formation in aerosols [3], and macromolecular solutions of proteins in solution [4].

Notes

In situ observation of (trans-) formation of oxide nanoparticles during chemical vapor synthesis

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Characteristics of nanoparticles (NPs) such as microstructure and morphology determine their physicochemical properties and thereby their application potential. Formation and transformation of NPs in Chemical Vapor Synthesis (CVS) is a dynamic process in which particle characteristics are determined by process parameters such as the time-temperature *T(t)* profile [1]. Ex situ characterization of particles may introduce artifacts during particle collection and lack direct correlation to the process. Moreover, certain NPs are intrinsically metastable due to size dependent phase transformation, oxidation, surface reaction or ageing. Detailed, reliable information about the dynamic processes and related particle characteristics are, therefore, only accessible through in situ observation.

Hence, we present results on CVS of tin oxide (SnO_2) and iron oxide (FeO_x) NPs investigated in situ using high energy X-rays at synchrotron beamlines. The key challenge in these experiments is the low number density of the particles generated in the gas phase process which is about three orders of magnitude smaller than in corresponding bulk solids. However, due to high intensity X-ray sources at contemporary synchrotron radiation facilities and modern X-ray detectors it is nevertheless possible to obtain scattering and spectroscopy data (Fig. 1 and [2]).

A novel mobile CVS reactor is designed for the in situ experiments which enables excellent control of process parameters, especially the time-temperature *T(t)* profile and oxygen partial pressure $p(O_2)$ to produce oxide NPs [2]. In situ small and wide-angle X-ray scattering (SAXS and WAXS) are used to study microstructure, morphology, phase composition and crystal structure as well as X-ray absorption spectroscopy (XAS) is performed to study electronic and local structure.

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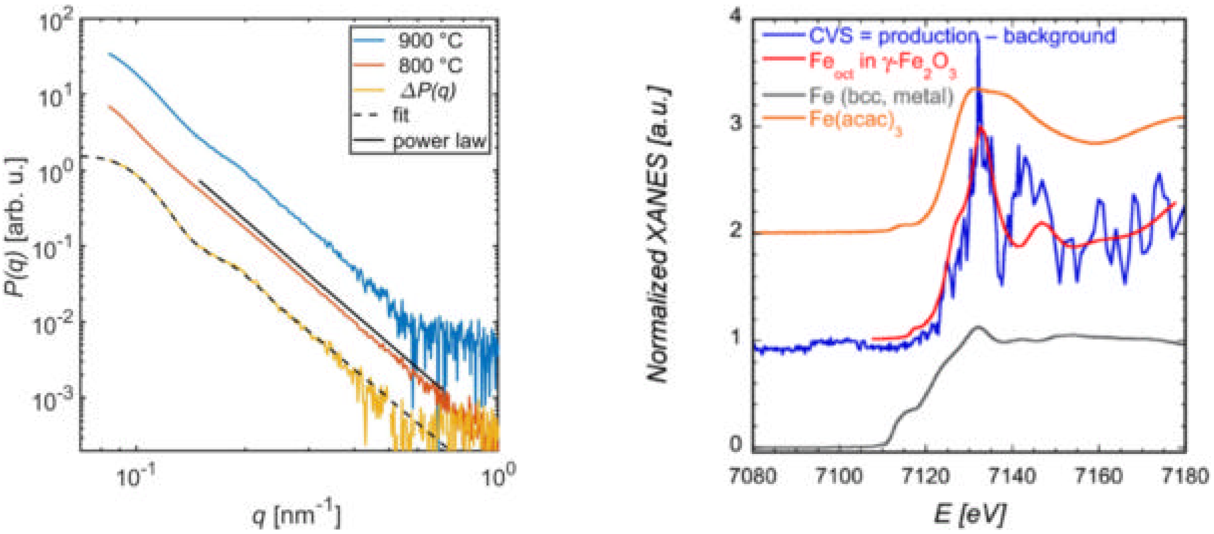

Fig. 1: SAXS scattering intensity for SnO_2 NPs (left) and XANES spectrum of FeO_x NPs (right) measured in situ during CVS [2].

Notes

Quantitative microstructural characterization using supervised machine learning

Claudia Gorynski[1], Max Frei[2], Frank Einar Kruis[2] and Markus Winterer[1]

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[2] Institute of Technology for Nanostructures, Department of Electrical Engineering and Cenide, University of Duisburg-Essen, Duisburg, 47057, Germany

The quantification of polycrystalline microstructures is critical due to the relationship between the microstructure of a material and its physical properties. At the same time, manual measurement of grain sizes consumes a lot of time and is a tedious and repetitive task. Furthermore, manual quantification creates a non-transparent bias, which impairs comparability and transferability with references. Here, we introduce a machine learning algorithm to extract several characteristic microstructural features and their distributions fully-automatically: the minimum and maximum Feret diameter d_F, the major and minor axis length of an ellipse d_E, the grain area A and circumference C, the dihedral angle Φ and the number of neighboring grains N_C. The supervised machine learning tool utilizes a two-step approach which consists of (i) a semi-automatic annotation tool, employing an off-the-shelf model to generate training data and (ii) a fully-automated neural network, using the training data to quantitatively evaluate scanning electron microscopy (SEM) images. On the basis of pure and Al-doped sintered ZnO ceramics, we trained two different networks, one for the ZnO grains at the microscale and one for precipitated $ZnAl_2O_4$ at the nanoscale. The machine learning algorithm performs well in identifying grains at the sub-micron and nanoscale, in differentiating uni-, and bimodal grain size distributions and in correctly interpreting twin boundaries and images with low contrast. The distributions of the several grain features are statistically evaluated to extract parameters characterizing the microstructure quantitatively. This versatile method enables a time-effective, less biased, consistent, and statistically more accurate grain size measurement.

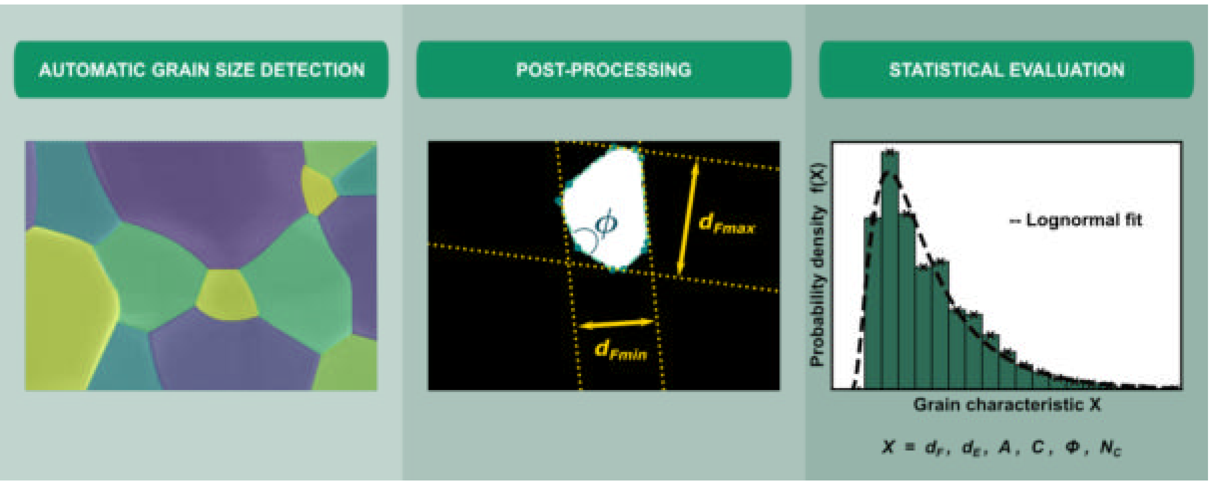

Fig. 1: Schematic illustration of the fully-automated grain size detection and microstructural feature characterization using the minimum and maximum Feret diameter d_F and dihedral angle Φ as example.

Notes

Notes

Poster Contributions

MiFuN – Microstructural Functionality at the Nanoscale

(Abstracts in alphabetical order of the presenting author’s last name; presenting author in **bold)**

List of Poster Contributions

Presenting author	Title	Abstract on page	Order number
Jeremias Geiss	Quantitative analysis of two-phase nanocrystalline oxides by X-ray spectroscopy	30	5*
Gleb Iankevich	Synthesis of unconventional material structures through the unique cluster ion beam deposition technique	64	4
Shikhar Krishn Jha	Phase segmentation of steel microstructures using a deep learning algorithm	66	8
Shradha Joshi	In situ observation of (trans-) formation of oxide nanoparticles during chemical vapor synthesis	56	2*
Jeldrik Schulte	Laser reactive sintering of complex oxides	42	6*
Mohammed-Ali Sheikh	Synthesis and characterization of doped NaSICON-type solid electrolytes for sodium-ion batteries from scalable spray flame synthesis	68	3
Max Stepponat	Designing a modular chemical vapor synthesis reactor for in situ X-ray scattering and spectroscopy	70	1
Dietrich Wolf	Can an electrical current create non-equilibrium defects ?	50	7*

*Poster contribution associated with oral presentation; order number assigns board number

(Abstracts in alphabetical order of the presenting author's last name; presenting author in **bold)**

Synthesis of unconventional material structures through the unique cluster ion beam deposition technique

Gleb Iankevich[1], Ramin Shadkam[2], Abhishek Sarkar[2], Robert Kruk[2], Horst Hahn[1,2].

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[2] Institute of Nanotechnology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Synthesis of cluster-assembled materials is a promising technique for the creation of new material structures, owing to their ability to form unique and complex configurations. It enables the precise control of synthesis parameters, allowing for manipulation at the nanoscale through controlled deposition of clusters with narrow size distribution. The physical synthesis approach to cluster and cluster-based materials, the high degree of control over process parameters, and the possibility of material co-deposition, offer significant potential for the synthesis of unique structures.

In this work, we demonstrate the advantages of the cluster ion beam deposition method for the synthesis of the unique material system. It is metastable three-dimensional nanocomposite based on a fully miscible materials, i.e., mass-selected nickel clusters embedded in a copper matrix. The compositional studies confirmed presence of the highly concentrated Ni regions and the metastable nature of the prepared samples. Additionally, we demonstrate the ability to control the physical properties by the precise control of the relative materials composition of the synthesized materials [1].

These experimental results demonstrate the wide range of opportunities that cluster ion beam deposition techniques can offer, including the creation of new types of materials that may be difficult or even impossible to achieve using conventional synthesis techniques.

[1] Iankevich, G. et al. *A New Class of Cluster–Matrix Nanocomposite Made of Fully Miscible Components*. Advanced Materials, (2022) 2208774.

Notes

Phase segmentation of steel microstructures using a deep learning algorithm

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The behavior of a material is heavily dependent on the microstructural features, such as textures, grain boundaries, phases, precipitates, composite architecture, pores, etc. Taking steel as a case study, which offers a wide range of properties based on microstructural engineering, we have developed an efficient training methodology for the segmentation of ferrite – pearlite microstructures using UNET machine learning architecture. ML is known to require a very large number of training microstructures, which are generally not available. To solve this, a novel method is proposed for circumventing the above problem by creating polycrystalline templates using 3D nucleation and growth model. Subsequently, the synthetic microstructures were populated with cropped images of pearlite and ferrite (from real microstructures) by randomly positioning on the individual grains of the polycrystalline templates. This idea could be used to produce a large number of synthetic microstructures of varying fractions and scale of the two constituents with limited numbers of starting microstructures. The UNET trained on the synthetic training set when tested on real ferrite-pearlite microstructures gave an accuracy of about 98%, which substantiates the robustness of above technique.

Notes

Synthesis and characterization of doped NaSICON-type Solid electrolytes for sodium-ion batteries from scalable spray flame synthesis

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Due to the limited availability of raw materials, sodium-ion batteries (SiB) are a viable alternative to lithium-ion batteries [1]. However, liquid-electrolyte-based SiBs have a comparably low energy density and suffer from safety issues similar to their lithium-ion-based counterparts [2, 3]. To address these issues, solid-state SiBs are a promising option and sodium super ionic conductors (NaSICON) are suitable solid electrolytes for such systems. They exhibit good mechanical properties and chemical stability, high ionic conductivity and compatibility with sodium metal based anodes enabling high energy density [4]. One of the best studied NaSICON materials is $Na_3Zr_2Si_2PO_{12}$ (NZSP) with a high ionic conductivity in the order of 10^{-4} – 10^{-3} Scm^{-1} at room temperature [5, 6]. Conventional synthesis methods of this class of materials such as solid-state reaction and liquid-phase synthesis have several drawbacks due to time-consuming process steps such as milling, high temperature sintering, precipitation, washing and drying steps to obtain the final product [7].

We present spray flame synthesis (SFS) as a new approach for the synthesis of nanosized NaSICON materials. Recent studies have shown that sintering of nanoparticular NZSP precursors offers several advantages: A high specific surface area, which increases the sintering activity, and short atomic diffusion paths, allowing high homogeneity and phase purity to be achieved at comparatively low sintering temperatures [8]. In SFS, metal salts dissolved in organic solvents are combusted resulting in fine metal oxide particles. They are characterized by transmission electron microscopy (TEM), X-Ray diffraction (XRD) and Raman-Spectroscopy for structural and morphological investigation. Elemental information is obtained via energy-dispersive X-Ray spectroscopy (EDX). Ionic conductivities of sintered NZSP pellets are measured by impedance spectroscopy.

In our approach, nanoparticles with a median diameter of around 5–9 nm are obtained. The pristine particles consist of crystalline ZrO_2, homogeneously covered with an amorphous layer consisting of the elements Na, Si, P and O. After a short annealing step for 1h at 1000°C, this mixture can be converted almost quantitatively into the desired rhombohedral NZSP phase. Moreover, aliovalent dopants were successfully added for the synthesis of $Na_{3+2x}A_xZr_{2-x}Si_2PO_{12}$ with A = Mg or Ca. Pressed pellets sintered at 1100°C for 3h to a relative density of ~92% showed - for a material sintered for such a short period of time - a surprisingly high ionic conductivity of up to 7.9×10^{-4} Scm^{-1} (Mg-doped).

In conclusion, a novel approach for the preparation of NZSP allowing the phase formation at relatively low temperatures is demonstrated. Spray flame synthesis is an elegant and promising possibility for the scalable production of solid electrolytes, which also holds great potential, especially with regard to further improvement of ionic conductivity through targeted doping.

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Notes

Designing a modular chemical vapor synthesis reactor for *in situ* X-ray scattering and spectroscopy

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Chemical vapor synthesis (CVS) is a method for the production of nanoparticles (NP) with highly desired particle characteristics such as high specific surface area and crystallinity. The properties of NP may be controlled and optimized by adjusting the CVS process parameters. In a conventional CVS process, a precursor material is evaporated and introduced into a heated, tubular flow channel under reduced pressure with the aid of a carrier gas. There, the precursor material interacts with reactants to form NP. Little is known about the actual NP formation and growth mechanisms in CVS. One way to study the formation of the nanoparticles is to use *in situ* small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS) and X-ray absorption fine structure spectroscopy (XAFS) using high-energy X-rays at synchrotron radiation facilities. For this purpose, a modular and customizable CVS reactor with the possibility of *in situ* investigation is developed.

The basic setup (Fig. 1) consists of a water-cooled vacuum vessel inside which an Al_2O_3 tube is used as a reactor. The process temperature is achieved by inductive heating. The susceptor is placed concentrically around the tube. The length of the susceptor is variable which enables a fast variation of the most important process parameter – the temperature-time profile – independent of other parameters. The vacuum vessel consists of several segments. The bottom flange contains the inlets for precursor, reactant and flushing gas and is heated or cooled depending on the precursor material. The two segments on top have feedthroughs for the HF power supply and temperature measurement using a pyrometer. The head segment provides four vacuum tight, X-ray transparent windows for the introduction and observation of hard X-rays to observe SAXS, WAXS and XAFS. The top flange has an outlet which connects the entire CVS reactor to a vacuum pump including total process pressure control (Fig. 2).
The operation of the system has been demonstrated by two proof of concept studies at DESY: The formation of tin oxide nanoparticles studied by SAXS, and the formation of iron oxide nanoparticles investigated by X-ray absorption spectroscopy (XAS) [1].

Here, we report about the design and modification of the mobile CVS reactor providing ease of operation at synchrotron radiation facilities, improved X-ray detection and providing access to other investigation methods to enable the investigation of the of nanoparticle formation and growth process in CVS.

[1] Schroer, M. A. Levish, A. Yildizlar, Y. Stepponat, M. and Winterer, M., *A versatile chemical vapor synthesis reactor for in situ x-ray scattering and spectroscopy*, Rev. Sci. Instrum. **93** (2022) 113706; doi: 10.1063/5.0122461

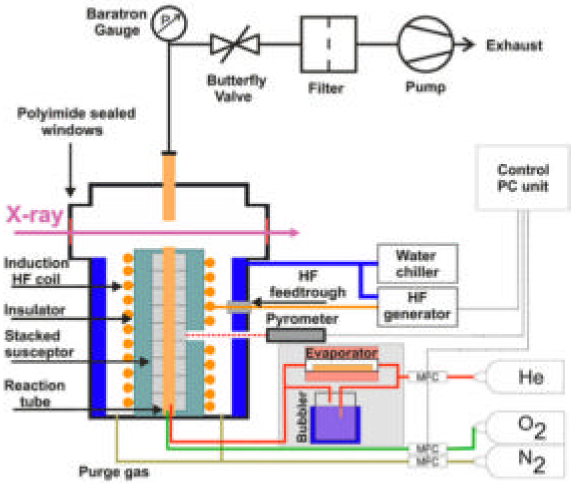

Fig. 1: Scheme of the CVS set-up [1]

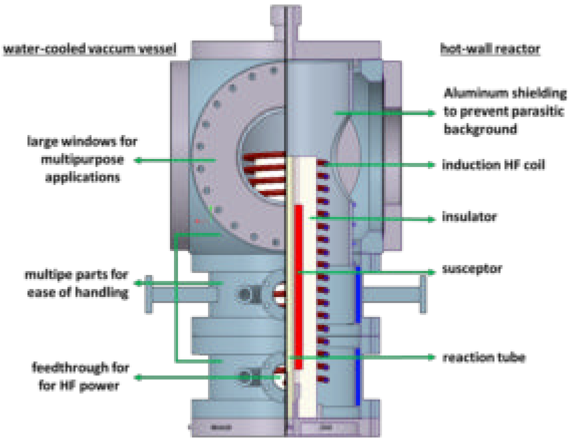

Fig. 2: Concept diagram of the improved CVS reactor

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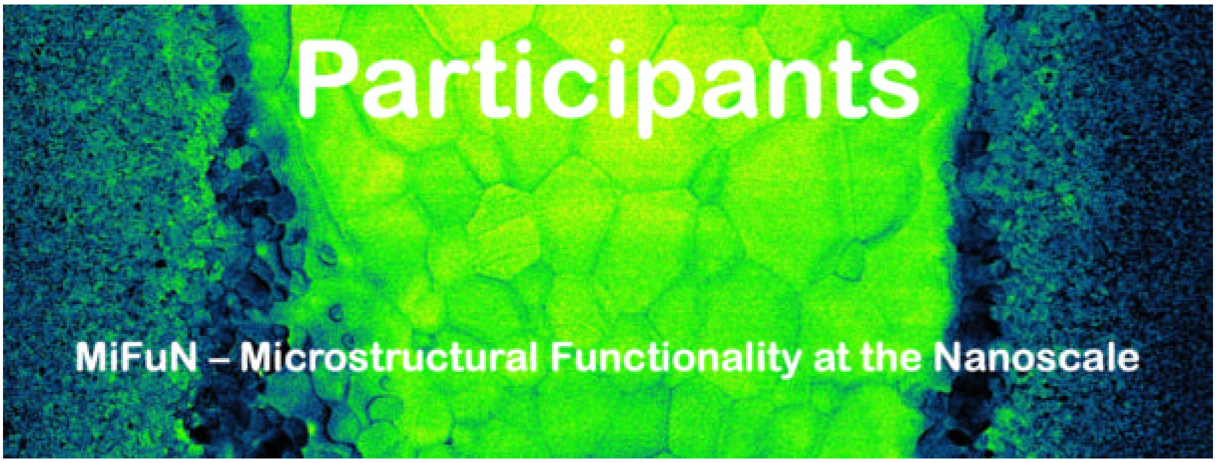

Participants

MiFuN – Microstructural Functionality at the Nanoscale

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Travel to and from San Servolo

LINEA 20 S.MARCO/S.ZACCARIA - S.SERVOLO - S.LAZZARO - S.SERVOLO - S.MARCO/S.ZACCARIA

IN VIGORE DAL 01 APRILE 2022

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S.LAZZARO	-	07:30	08:25		-	-	09:35	-	10:45	-	12:05	-	13:25	-	14:45	15:25	-	-	16:45	17:25	-	18:25	-	-	-	-	-	-	-	-
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(A) = FERMA A S.LAZZARO SOLO SU RICHIESTA DEI PASSEGGERI, MENTRE L'IMBARCO SI PUÒ PRENOTARE TELEFONANDO, ALMENO 20 MINUTI PRIMA, AL NUMERO VERDE 800845065

San Servolo


VIU Front Office
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Fondazione Franca e Franco Basaglia
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Main Entrance Hotel Reception
Conference Hall Aula Magna (1st floor)
Residential Hall
Residential Hall
San Servolo
Residential Hall
Residential Hall
Sports Grounds
Restaurant
Restaurant