

CPP 15: Symposium SYCO of the divisions MM (leading), O, CPP, KFM and DS continued as topical session: Mechanically controlled electrical conductivity of oxides (joint session MM/CPP/O)

Sessions: SYCO II and III

Time: Monday 15:45–18:30

Location: H46

Topical Talk CPP 15.1 Mon 15:45 H46
Probing the properties of dislocations in SrTiO₃ through transient transport measurements — ●ROGER DE SOUZA — Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany

There is renewed interest in the interaction between oxygen vacancies and dislocations in the perovskite oxide SrTiO₃, driven by the material's possible application in devices for all-oxide electronics and for resistive switching. In my talk, I will demonstrate how transient transport experiments — comprising ¹⁸O/¹⁶O isotope exchanges and Secondary Ion Mass Spectrometry (SIMS) analysis — can be used to obtain a deeper understanding of this interaction. Having first introduced the thermodynamics of space-charge formation at extended defects, I will focus on describing experiments and simulations on various geometries: annealed single crystals, bicrystals, and polished single crystals. Finally, I will discuss how these studies allow us to arrive at a consistent description of point-defect behaviour at dislocations in SrTiO₃.

CPP 15.2 Mon 16:15 H46
Characterization of Fe:STO thin films prepared by pulsed laser deposition — ●MAXIMILIAN MORGENBESSER, STEFANIE TAIBL, MARKUS KUBICEK, ALEXANDER VIERNSTEIN, CHRISTOPHER HERZIG, ANDREAS LIMBECK, and JÜRGEN FLEIG — TU Wien, Wien, Österreich

The perovskite-type oxide SrTiO₃ (STO) is one of the best investigated materials in solid state ionics and commonly used as a model material in solid state ionics. The defect model of bulk SrTiO₃ is well understood and the conductivity of bulk samples can be tailored by acceptor or donor doping, e.g. with Fe³⁺ or Nb⁵⁺ on the Ti⁴⁺ site. However, other aspects of SrTiO₃ have not been understood so far, for example the influence of factors such as stoichiometry and strain on the conductivity which is investigated in this study.

Two different kinds of 2 % Fe-doped thin films were deposited by pulsed laser deposition (PLD). Thin films deposited from stoichiometric targets exhibit a low, intrinsic conductivity. In addition, targets with Sr overstoichiometry were used and the conductivity could be increased by four orders of magnitude. The thin films are compared to each other in regard to the structure and stoichiometry. Structural differences could be found by x-ray diffraction measures, revealing a difference in lattice parameters. The chemical composition was analyzed by means of inductively coupled plasma optical emission spectroscopy (ICP-OES) and differences in the A/B ratios could be found. A model linking the conductivity to the stoichiometry of the thin films is presented, highlighting the possible impact of cation vacancies and antisite defects on the electrical conductivity of Fe:SrTiO₃.

CPP 15.3 Mon 16:30 H46
Generation of controlled dislocation structures in SrTiO₃ and TiO₂ for elucidating dislocation impact on electrical properties. — ●LUKAS PORZ, TILL FRÖMLING, and JÜRGEN RÖDEL — Institute of Materials Science, Technische Universität Darmstadt, 64287 Darmstadt, Germany

Dislocations have been understood to alter numerous functional properties of ceramic materials, such as conductivity [Whitworth 1975]. Recently, modification of functional properties of oxide materials by dislocations receives much attention due to their various potentials for application [Szot 2018]. Especially the complex dislocation structure of naturally occurring dislocations makes investigations of dislocation effects difficult. Thus, disentangling the different effects of dislocations requires an ordered structure of the dislocations. So far ordered structures were primarily fabricated in bi-crystal interfaces which are often not comparable to natural dislocation arrangements.

We present a route to control the arrangement of the dislocations locally. Different slip systems can be individually introduced and an arrangement of all dislocations lying in the same set of slip planes was achieved. With identical line vectors, the dislocations connect two sur-

faces of a bulk sample which was shown by dark field x-ray microscopy. This well-arranged and well-understood structure of dislocations is a pre-requisite for unambiguous interpretations of detailed experiments on functional properties. The value of a controlled arrangement of dislocations is demonstrated by conductivity data along dislocation lines and across slip bands in comparison to a dislocation free reference.

45 min. break

CPP 15.4 Mon 17:30 H46
Atomic and electronic structure of wurtzite ZnO(0001) inversion domain boundaries — ●JOCHEN ROHRER and KARSTEN ALBE — FG Materialmodellierung, FB Material- und Geowissenschaften, Technische Universität Darmstadt

In a recent work [1], variations of the conductivity of ZnO bicrystal samples with (0001)|| (0001) and (0001̄)|(0001̄) orientations (inversion domain boundaries, IDB) due to the modulation of the potential barrier height at the IDB with respect to strain [2] has been demonstrated. In order to establish a more profound understanding of this behavior, a detailed characterization of the atomic structure and electronic properties of such IDBs by means of first-principles methods will be valuable. However, despite the structural and chemical variability of this system, only a few atomistic models have been studied to date [3].

In this work we comprehensively study ZnO{0001} IDBs by means of density functional theory calculations. In particular, we construct a variety of structurally and chemically different phase-pure models and identify their thermodynamic stability within the allowed range of the O chemical potential. For stable models we investigate electronic properties and their response to strain. Finally we also study the role of various dopants, commonly added in experimental bicrystal samples.

[1] P. Keil *et al.*, *Adv. Mater.* **30**, 1705573 (2018). [2] D. R. Clarke, *J. Am. Ceram. Soc.* **82**, 485 (1999). [3] S. Li *et al.*, *Phys. Status Solidi B* **255**, 1700429 (2017).

CPP 15.5 Mon 17:45 H46
Impact of internal electric field on the grain boundary barrier height of ZnO — ●BAI-XIANG XU, ZIQI ZHOU, and TILL FRÖMLING — Institute of Materials Science, TU Darmstadt

Polycrystalline ZnO ceramics with grain boundary potential barriers are important materials for surge arresters due to their non-linear current-voltage behavior, and have potential application in advanced devices. Different grain boundary barrier height models have been developed by considering the direct piezoelectric effect. However, the piezoelectric charge should not only result from the direct piezoelectric effect, but also from the inverse piezoelectric effect, which refers to the mechanical response of the material by the electric field. Due to the charges at the grain boundary, strong internal electric field can be expected, and it leads to strain change through the inverse piezoelectric effect. This strain further modifies the polarization and thus leads to additional piezoelectric charges at the grain boundary and in the depletion layer. Thus, this should also be taken into account self-consistently. For this purpose we employ both analytical model and finite-element numerical simulation to reveal the impact of internal electric field on the GB barrier height and its stress sensitivity. Results show that the piezoelectric charge induced by the internal field tends to adjust the grain boundary charge and lowers the barrier height. Furthermore, the barrier height becomes less sensitive to mechanical stress and applied voltage if the influence of the internal field is taken into account. The extended model with the inverse piezoelectric effect of the internal field allows to further elucidate their piezotronic response.

CPP 15.6 Mon 18:00 H46
Influence of cation order and strain on Na diffusion in Na₃Zr₂Si₂PO₁₂: A computational study — ●LISSETTE HAARMANN and KARSTEN ALBE — Technische Universität Darmstadt, Otto-Berndt-Str. 3 64287 Darmstadt

$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ is a solid electrolyte which is part of the Na super ionic conductor (NASICON) family. Experimentally, only Si/P lattice positions can be determined, but not the distribution of P on these sites[1]. This distribution, however, plays a crucial role for the Na diffusion. A systematic study of different cation orders is conducted using Molecular Dynamics (MD) simulations. Due to the strong correlation of diffusion in this material, the calculation of D_σ is necessary to obtain the ionic conductivity from the Nernst-Einstein equation[2]. By calculating D_σ and the tracer diffusion coefficient D_{tr} , Haven ratios are determined. Additionally, a jump rate model was developed, which allows investigation of correlation between individual jumps.

Moreover, it has been reported that doping can strongly increase the diffusivity of Na in NASICON materials[3]. In many cases, this is attributed to enlarged bottlenecks of diffusion. These doping elements, however, do not only contract or dilate the lattice structure but alter the chemical environment of the Na ions as well. In an effort to study purely the effect of mechanical deformation, the strain dependence of D_{tr} and the activation energy E_A is investigated.

[1] Boilot, J.P., *et. al.*, Journal of Solid State Chemistry **73**, (1988)

[2] Murch, G., Solid State Ionics **7**, (1982)

[3] Guin, M., Tietz, F., Journal of Power Sources **273**, (2015)

CPP 15.7 Mon 18:15 H46

The impact of mechanical stresses on the ionic conductivity

of nanoparticles — ●PETER STEIN¹, BAI-XIANG XU¹, and KARSTEN ALBE² — ¹TU Darmstadt, FB 11, FG Mechanik funktionaler Materialien — ²TU Darmstadt, FB 11, FG Materialmodellierung

Nanostructured electrodes have found wide application in electrochemical systems, for instance for lithium-ion batteries. This is due to their featuring short diffusion paths and large surface areas, allowing for comparatively fast surface reactions and transport within the slender bulk material. At this length-scale, surface stresses acting on the electrode surface induce a (non-uniform) pressure within the material, providing mechanical stabilization. As a result, nanostructured electrodes exhibit high reversible capacities and stable cycling behavior [1] as well as a higher robustness against mechanical degradation [2]. However, the surface-induced pressure field also affects the electrochemical behavior of the particle, modifying, among other things, surface reaction rates and ionic mobility.

In this contribution, we discuss the interaction of mechanical stresses with the electrochemical behavior of nanostructured electrode particles. We thereby consider ideal analytical shapes, faceted nanoparticles, and regular nanostructures such as inverse opal electrodes. We further demonstrate the impact of surface-stress-induced mechanical fields on defect thermodynamics and kinetics, chemical reactions, and phase transformations.

[1] N. Zhao et al., Pure Appl. Chem. 80:2283-2295, 2008. [2] C.K. Chan et al., Nat. Nanotechnol. 3:31-35, 2008.