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## Dean’s Office

### Staff Members

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<td>Dean of studies Materials Science:</td>
<td>Prof. Dr. Lambert Alff</td>
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<td>Dean of studies Applied Geosciences:</td>
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<td>Scientific coordinator, department and Materials Science:</td>
<td>PD Dr. Boris Kastening</td>
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<td>Scientific coordinator, Applied Geosciences:</td>
<td>Dr. Karl Ernst Roehl</td>
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<td>Secretary of department:</td>
<td>Renate Ziegler-Krutz</td>
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<td>Secretary of personnel and finances:</td>
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<td>Competence center for materials characterization:</td>
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<td>Media Design:</td>
<td>Thomas Keller</td>
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Publications of Permanent Members of the Dean's Office

[1] Weidner, Mirko; Broetz, Joachim; Klein, Andreas;
Sputter-deposited polycrystalline tantalum-doped SnO2 layers;

[2] Ruzimuradov, Olim; Nurmanov, Suvankul; Hojamberdiev, Mirabbos; Prasad, Ravi Mohan; Gurlo, Aleksander; Broetz, Joachim; Nakanishi, Kazuki; Riedel, Ralf;
Fabrication of nitrogen-doped TiO2 monolith with well-defined macroporous and bicrystalline framework and its photocatalytic performance under visible light;

Long-range superconducting proximity effect in polycrystalline Co nanowires;

[4] Ruzimuradov, Olim; Nurmanov, Suvankul; Hojamberdiev, Mirabbos; Prasad, Ravi Mohan; Gurlo, Alexander; Broetz, Joachim; Nakanishi, Kazuki; Riedel, Ralf;
Preparation and characterization of macroporous TiO2-SrTiO3 heterostructured monolithic photocatalyst;

[5] Morasch, Jan; Li, Shunyi; Broetz, Joachim; Jaegermann, Wolfram; Klein, Andreas;
Reactively magnetron sputtered Bi2O3 thin films: Analysis of structure, optoelectronic, interface, and photovoltaic properties;

[6] Stegmann, Christian; Muench, Falk; Rauber, Markus; Hottes, Martin; Broetz, Joachim; Kunz, Ulrike; Lauterbach, Stefan; Kleebe, Hans-Joachim; Ensinger, Wolfgang;
Platinum nanowires with pronounced texture, controlled crystallite size and excellent growth homogeneity fabricated by optimized pulsed electrodeposition;

[7] Rachut, Karsten; Koerber, Christoph; Broetz, Joachim; Klein, Andreas;
Growth and surface properties of epitaxial SnO2;
[8] Muench, Falk; Seidl, Tim; Rauber, Markus; Peter, Benedikt; Broetz, Joachim; Krause, Markus; Trautmann, Christina; Roth, Christina; Katusic, Stipan; Ensinger, Wolfgang; Hierarchically porous carbon membranes containing designed nanochannel architectures obtained by pyrolysis of ion-track etched polyimide; MATERIALS CHEMISTRY AND PHYSICS, Volume: 148, Issue: 3, Pages: 846-853, (2014)

Institute of Materials Science

Preface

Dear colleagues and friends,

The year 2014 was another successful period for the Department of Materials and Geo Sciences of TU Darmstadt. Details of the activities and achievements related to the individual departmental institutes, namely Materials Science and Applied Geosciences, are highlighted below.

We would like to express our gratitude to all members of the Department – the mechanical workshop staff, technical and administrative staff, students working on their diploma and bachelor theses, Ph.D. students, and postdocs – for the outstanding effort and remarkable enthusiasm they put into their work. Their outstanding engagement significantly contributed to the performance of the Department. We aim to sustain and promote the motivating and fruitful atmosphere at our institute in order to continue our commitment and success in the time to come.

Materials Science

The amount of acquired third party funding has reached a nearly constant value in the order of 10 million Euro. Presently, the total number of students (bachelor & master) in materials science amounts round about 500. The number of freshmen of the bachelor study course Materials Science in the winter semester 2014/15 reached 107 (see Figure 1).

The Materials Science and Geo Sciences Department’s Materialium Graduate School has been further developed and now accommodates 90 PhD students. The research-oriented doctorate program culminating in award of the degree of “Dr.-Ing.” or “Dr. rer. nat.” fosters an interdisciplinary integration of the various Ph.D. studies between research groups inside and outside of the Materials Science Department. During specific events, Ph.D. students present their current scientific problems and methods, providing a forum for close interdisciplinary problem solving that stimulates synergy between research groups. Professors of Materialium are committed to supporting their Ph.D. students. For instance, they strongly encourage participation at international conferences and publication in refereed research journals, which is bolstered by the high number of coordinated research programs in Materials Science at TU Darmstadt. Moreover, Materialium is a member of Ingenium, the umbrella organisation of graduate schools at TU Darmstadt.

Coordinated Research Proposals

The new proposal RESPONSE funded by the Hessian State Government started in January 2014. The scientific topic of this research program is related to “The Reduction and Substitution of Rare Earth Elements in High Performance Permanent Magnets” (RESPONSE) and is coordinated by Prof. Gutfleisch. This initiative marks the interdisciplinary approach the university is promoting and for which the Department of
Materials and Geo Science is ideal since its subjects combine various sciences like chemistry, physics, electrical and mechanical engineering.

![Graph showing the development of the number of students in Materials Science over the past 15 years.](image)

Figure 1: Development of the number of students in Materials Science over the past 15 years

Presently, the Department initiates a new Collaborative Research Center (SFB) funded by the German Research Foundation (DFG). With Prof. Albe as the coordinator, the initiative was successful with the preproposal in getting a recommendation by the DFG to submit a full proposal, which will be finally evaluated end of September 2015.

**Faculty Members and Affairs**

End of March 2014, Prof. Heinz von Seggern officially retired. However, according to an agreement with the Department, he still will be actively involved in research and teaching in Materials Science for the next few years.

In March, Dr. Kyle Webber, who run an Emmy Noether Independent Junior Research Group funded by the DFG, was appointed to Junior Professor in our Department to head the group “Electromechanics of Oxides”.
In September 2014, Dr. Jürgen Wieser was appointed as Honorary Professor at TU Darmstadt at the suggestion of the Department of Materials and Geosciences. Professor Wieser is an expert in advanced processing of polymers. His expertise will complement the research and teaching activities of Materials Science in Darmstadt which are basically focused on ceramics and metals.

After 10 years being active as Dean of Studies in Materials Science, Prof. Alff resigned from this duty. The Department wishes to thank Prof. Alff for his great efforts and engagement during his mandate. As the successor, Prof. Donner was voted as Dean of Studies in Materials Science by the faculty commission in April 2014. At the same time, Prof. Riedel was reelected as Dean of the Department.

One of the most important events for the Materials Science Division in 2014 was the start of the departmental evaluation process. Accordingly, the faculty had to prepare a comprehensive document related to the research and teaching situation in the Materials Science Division. In December 2014, the Materials Science Division was assessed by a group of reviewers in a two days lasting evaluation in our Department. At the same time the bachelor and master courses in Materials Science were evaluated by the same commission. Based on this result, the faculty will have to negotiate an objective agreement on their future research and teaching targets together with the executive committee of the TU Darmstadt in 2015.

Honours, Awards and Special Achievements

In 2014, the following precious awards were granted to faculty members of the materials science department:

Prof. Fueß received the honor of “Offizier des Ordens der Palmes Academiques“ by the French government

In December 2014, Prof. Riedel was honored with the Fellow of the School of Engineering at the University of Tokyo, Japan, in recognition of his distinguished contribution to the research and education of the above mentioned school and of his outstanding accomplishments in research and education in the field of engineering.
As usual, the annual awarding of the "MaWi Prize" formed part of the MaWi summer party. The 1st prize was awarded to Ruben Heid from the division PhM for his Diploma thesis on “Einfluss von gießtechnischen Prozessschwankungen auf das Eigenschaftsspektrum crashrelevanter Aluminium-Druckgusslegierungen;” 2nd prizes were awarded to Tim Niewelt from the division OF for his Diploma thesis about “Analyse von Defekten in kristallinem Silizium” and to Joachim Langner from the division EE for his Diploma thesis about “Ionische Flüssigkeiten als Elektrolyt, Co-Katalysator und Stabilisator in Brennstoffzellen”. The 3rd prize was awarded to Christian Lohaus for his Bachelor thesis about “Synthese verschiedener rußgeträgerter Pt-Ru-Au Katalysatoren und Untersuchung des Degradationsverhaltens.”

Social Events

As every year, our annual summer party was scheduled for middle of July, shortly before the summer break, being one of the most important social events of the Materials Science Institute.

In December 2014 we celebrated the year-end ceremony for all research groups, staff members and students, including the formal graduate celebration, where Bachelor, Master and PhD students received their certificates. The celebration including the social programme was organized by the Deanery’s team, in particular by PD Dr. Boris Kastening, Heinz Mohren, Dr. Sylvia Faßbender and our workshop team.

On the following pages, this annual report shall provide you with some further information on the most prominent research activities of the individual groups conducted in 2014.

Prof. Ralf Riedel
Dean of the Department
The Physical Metallurgy research group (PhM) in the department of materials science at TU Darmstadt, headed by Prof. Dr.-Ing. Karsten Durst, works on structure-property relationships of structural metallic materials and thin hard coatings with a focus on mechanical properties from the microscopic to macroscopic length scale. The group utilizes and develops state-of-the-art testing methods for enhanced understanding of the deformation mechanisms of structural materials. Of main interest are mechanical properties of materials under various loading conditions (uniaxial, fatigue, wear or creep), specifically those relating the macroscopic material response to the micromechanical properties at small length scales. New insights in the materials response are achieved through in-situ mechanical testing approaches, where material is mechanically loaded and monitored by microscopic or spectroscopic techniques simultaneously.

In 2014, several proposals for new test equipment were successfully acquired, summing to a total investment at PhM of more than 800,000 €. PhM is now equipped with a Keysight Nanoindenter with a tip and sample laser heater allowing for protective gas atmospheres and temperatures up to 500°C. The system is equipped with scratch test capabilities and allows max loads of up to 10 N and has already been used for both for thin film and bulk material characterization. Additionally, the group purchased two nanoindenters from Nanomechanics Inc. providing dynamic indentation testing with accurate oscillation control and a maximum load of 45 mN. One of the nanoindenters is a standalone system that is user friendly and has been successfully used in collaborations with other research groups within the department. The other nanoindenter can be used inside our new Tescan Mira 3 XMH field emission gun scanning electron microscope (FEG-SEM). The SEM features a DigiView 5 EBSD/EDX detector from EDAX and is equipped with a BSE detector providing high resolution imaging for electron channeling contrast imaging (ECCI) and a separate cooled detector allowing BSE imaging at high temperatures. In September 2014, PhM organized a symposium on “Small Scale and in-situ Mechanical Testing” at the “Material Science Engineering“, held in Darmstadt. The symposium was quite successful with five session and an international audience, discussing the latest developments in the field of micromechanics of in-situ tests in TEM, SEM, to thin layers and nanoindentation.

Current research includes steels, Al, Cu, and Ni-based alloys, a-C:H coatings, nickel-base superalloys and silicate glasses. Another important class of materials being studied are the so called ultrafine-grained or nanostructured materials, which are processed through severe plastic deformation. The material microstructure is greatly refined by these processes, leading to both strong and ductile materials. The research focuses on the deformation mechanisms and post-treatment conditions for tailoring the mechanical properties as well as residual stresses that arise during processing for different applications. Residual stresses also play a critical role in the application of hard coatings on ductile substrates. Together with corporate and academic partners, novel processing routes are being established, allowing for the design of coatings with optimized mechanical properties with respect to residual stress and contact loading conditions.
Further research at PhM includes active progress in the RESPONSE research initiative, which focuses on new permanent magnets as well as in the DFG priority program *ultrastrong glasses*.

**Staff Members**

**Head**
- Prof. Dr. K. Durst

**Research Associates**
- Dr. E. Bruder
- Dr. K. Johanns
- Prof. Dr. C. Müller

**Technical Personnel**
- Ulrike Kunz
- Claudia Wasmund
- Petra Neuhäusel
- Sven Frank

**Secretaries**
- Christine Hempel

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- Dipl.-Ing. Vanessa Kaune
- Dipl.-Ing. Thorsten Gröb
- Dipl.-Ing. Jan Scheil
- MSc. Farhan Javaid
- Dipl.-Ing. K. v. Klinsky-Wetzel
- Dipl.-Ing. Jörn Niehuesbernd
- Dipl.-Ing. Christoph Schmid
- MSc. Olена Prach
- MSc. Laura Ahmels

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- Ahmels, Laura
- Uhde, Jari
- Opitz, Tobias
- Bruns, Sebastian

**Bachelor Students**
- Schütz, Theresa
- Kowalik, Oskar
- Schmiedl, Tobias
- Grebhardt, Axel
- Zimmermann, Golo
- Schwing, Romana
- Wehling, Carlo

**Research Projects**


“Subsequent Formability of Bifurcated Profiles” in SFB 666 of the DFG “Integral Sheet Metal Design with Higher Order Bifurcations”, since 06/2013.

“New Synthesis Methods top-down” in Priority Program LOEWE “Response Ressourcenschonende Permanentmagnete durch optimierte Nutzung seltener Erden”, since 01/2014


“Influence of Glass Topology and Medium Range Order on the Deformation Mechanism in Borosilcate Glasses – a Multiple Length Scale Approach”, DFG since 07/2012

DAAD scholarship Farhan Javaid since 07/2012
“Nanomechanics of single crystalline Nickel-Base superalloys”, co-applicant in SFB Transregio 103 (Erlangen-Bochum): Super alloy Single Crystals

DAAD scholarship Elena Prach since 07/2014

iStress: residual stress analysis with the EU project EU iStress- 604646

Publications


Magnetic Hardening by Grain Refinement via Severe Plastic Deformation

T. Gröb, E. Bruder and C. Müller

Introduction

Permanent magnets are essential for our technological society especially in the field of renewable energy and as key components in electromobility. These magnets contain high amounts of rare earth elements. Because of the high demand of these elements and the export limit from China, rare earths are a strategic resource. Due to these facts, there is a great technological interest for rare earth free and reduced permanent magnets. The LOEWE research cluster RESPONSE is working on several approaches to reach rare earth free permanent magnets. One approach of the physical metallurgy at the TU Darmstadt to achieve this goal is magnetic hardening by grain refinement via “Severe Plastic Deformation” (SPD) processes.

SPD processes are mostly used to change the mechanical properties of materials. Besides the mechanical properties also extrinsic magnetic properties like the coercivity or the remanence can be influenced by these processes [1]. With decreasing grains size, the coercivity is increasing until a maximum is reached [2]. The region, where grain refinement leads to an increase in the coercivity is the ultrafine grained microstructure (UFG) of SPD processes. The magnetic properties are characterised by the shape of their hysteresis loop, measured via Vibrating Sample Magnetometry (VSM). The microstructure is determined with Electron Back Scatter Diffraction (EBSD).

The change in the coercivity by grain refinement during the Equal Channel Angular Pressing (ECAP) process

Severe Plastic Deformation (SPD) processes are used to reach a high plastic deformation in metals, which can not be reached with conventional cold working methods. These high plastic strains cause grain refinement through grain fragmentation which leads to ultrafine grained (UFG) microstructure. Besides the influence of mechanical properties with degreasing grain size, the magnetic properties are affected. This fact is used for the approach of magnetic hardening by grain refinement. For grain refinement, the ECAP process is used. ECAP is a well investigated SPD method and is based on the shear deformation of the material. The die angle in the present
investigations was 120°. 1, 2, 4 and 8 passes of ECAP were performed without back pressure using Route C. The magnetic properties were determined by a LakeShore VSM System. For the experiments, pure iron (ARMCO®) and an iron-based alloy with 17 wt% cobalt and 2 wt% chromium (VACOFLEX17) were used. Both materials were investigated in microstructure and magnetic properties for the undeformed state and after each SPD state.

Figure 2 shows the evolution of the grain boundary density. Both materials show a typical cold working behavior. At the beginning, the low angle grain boundary density (LAGB) is increasing significantly up to a grain boundary density value of 3 μm\(^{-1}\) at a strain of 2.6. For higher strains, the LAGB density of ARMCO is decreasing whereas for VACOFLEX 17 it soars through any further forming step. The high angle grain boundary density (HAGB) of both materials is increasing slightly with each ECAP pass.

Due to the ECAP process and the resulting increase in the HAGB density with each ECAP pass, there is a grain refinement in both materials. Figure 3 shows the evolution of coercivity \(H_c\) depending on the grain size.

With decreasing grain size the coercivity is increasing. ARMCO starts at low coercivity of 200 A/m with an average grain size of 42 μm. VACOFLEX17 starts at 300 A/m with an average grain size of 22 μm. After one pass of ECAP, the coercivity has increased in both cases. After 8 passes the average grain size of ARMCO has reduced from 42 μm to 8 μm. \(H_c\) has increased to 875 A/m. At the same time the coercivity of VACOFLEX17 has increased to 1750 A/m at an average grain size of 4.6 μm.

Not only the HAGB density, i.e. the grain size, effects the coercivity of the materials. The change of the magnetic behavior depends on the size of the magnetic domains and on the movement of domain walls [3]. Through the SPD process, the grain boundary density has
significantly enhanced (Figure 2). Due to the subgrainstructure, the mobility of the magnetic domain walls is hindered. For the investigated materials the average grain size, which was reached with 8 passes of ECAP by 120°, is above the critical single domain size. So the main effect in the increase of the coercivity is caused by the subgrainstructure induced by the SPD process.

Conclusions and outlook

The shown investigations offer the opportunity of magnetic hardening by SPD. It has been demonstrated, that with SPD and the resulting grain refinement during this process, the coercivity has been increased significantly. But the increase in grain boundary density is not the only microstructural change. There is no evolution of a pronounced crystallographic texture during the ECAP process by using route C. Further effects like a crystallographic texture and an elongation of grains can affect the magnetic properties as well. An elongation of grains can induce a shape anisotropy to the material [4]. Therefore, a combination of SPD process with an additional forming process like rotary swaging can induce this anisotropic magnetic behaviour and enhance the hard magnetic properties. The investigations have been performed with soft magnetic materials. The next step is to transfer these findings to a hard magnetic system to further increase the coercivity [5].

References

Borosilicate Glass Topology and Deformation Mechanisms

K. E. Johanns, P. Malchow and K. Durst

Introduction

Instrumented indentation testing provides a means of examining elastic-plastic deformation behavior in materials where more conventional testing may not be feasible. In particular, it enables local probing of small volumes and, hence, correlation of mechanical response and local structure of a material. This has generated significant interest for the study of deformation processes in macroscopically brittle glasses. While the mechanical strength of glasses (and other brittle materials) is inherently dominated by the material’s surface properties, i.e., the number and size of surface defects, it has been noted semi-empirically that the probability of local failure can be tailored via chemical composition. The notion of “defect resistance” has been introduced as a means to describe the glass’ response to a sharp contact, which may result in material compaction or indentation cracking. When the probability of indentation cracking can be reduced and/or the fracture pattern which is induced through indentation can be controlled, this would pave the way towards glasses with significantly improved resistance to surface defects. In this context, sodium borosilicate (NBS) glasses represent an especially interesting class of glasses. On the one side, they are the major group of glasses for specialty applications such as in lighting, electronic devices, biomedical substrates (and containers), labware or displays. On the other side, due to their thermomechanical properties, their mechanical performance cannot readily be improved through the conventional methods of thermal or chemical toughening. However, as has recently been demonstrated for a series of model compositions, their local deformation and cracking behavior is particularly strongly composition dependent, what provides a third lever for designing an ultra-tough glass of the borosilicate-type [1].

In this project, we consider plasticity and fracture of NBS glasses by studying their response to penetration of a sharp, three-sided pyramidal Berkovich indenter [2]. In such an experiment, observations of elastic-plastic deformation can be made along with crack initiation and subsequent crack growth [3]. As already noted, there are few other, if any, mechanical tests which provide such a broad view at the mechanical properties of a brittle material. The combination of indentation observation and analyses with spectroscopic techniques (e.g., Raman spectroscopy), can provide descriptive insights at relationships between constitutive behavior and local glass (molecular) structure.

Mechanical Properties via Indentation

Indentation deformation and crack initiation/growth are highlighted in Fig. 1. Significant differences have been found between the compositions and the cooling conditions. Furthermore, indentation testing results in Table I show that NBS1 has a greater elastic modulus, $E$, and hardness, $H$, ($E = 80.5$ GPa, $H = 7.4$ GPa) than the furnace cooled NBS2 glass ($E = 53.1$ GPa, $H = 5.8$ GPa). These results are consistent with the expected structural differences between the two compositions. The increased network modifier content of Na2O in NBS1 gives rise to greater hardness, since the added Na2O causes only partially a depolymerization of the glass structure, with sodium ions filling the voids, but also, as the composition moves away from the boron anomaly line, results in a structure with higher boron coordination, [BØ4]$^-$ charged balanced by sodium ions, and therefore
less free volume. Pile-up at the contact periphery, i.e., material that has plastically deformed up the face of the indenter, is also found to be greater for the NBS1 composition than NBS2 (fc). Evidence for this is found in ratios of pile-up height relative to total indentation depth, \( h_{\text{pile-up}}/h_{\text{max}} \), given in Table 1. Lower pile-up heights are consistent with 'anomalous' inelastic densification playing a strong role in the deformation of the NBS2 composition. The more dense NBS1 composition responds in a 'normal' way with shear driven plasticity dominating the deformation during indentation, hence increased pile-up. The respective elastic modulus to hardness ratios, \( E/H \), are 10.9 and 9.2 for NBS1 and NBS2 (fc), and while the difference is small, the larger \( E/H \) ratio of NBS1 is also consistent with greater amount of observed pile-up of material and continuum ideas of material flow during indentation.

Table 1: Experimental results on NBS glasses

<table>
<thead>
<tr>
<th></th>
<th>NBS1</th>
<th>NBS2 (fc)</th>
<th>NBS2 (qu1)</th>
<th>NBS2 (qu2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E )</td>
<td>GPa</td>
<td>80.5 ± 0.2</td>
<td>53.1 ± 0.4</td>
<td>52.7 ± 0.2</td>
</tr>
<tr>
<td>( H )</td>
<td>GPa</td>
<td>7.41 ± 0.03</td>
<td>5.79 ± 0.16</td>
<td>6.31 ± 0.05</td>
</tr>
<tr>
<td>( S^2/P )</td>
<td>GPa</td>
<td>1123 ± 60</td>
<td>615 ± 31</td>
<td>578 ± 28</td>
</tr>
<tr>
<td>( K_{\text{fc}} )</td>
<td>MPa·m(^{1/2})</td>
<td>0.48 ± 0.02</td>
<td>1.20 ± 0.10</td>
<td>0.95 ± 0.02</td>
</tr>
<tr>
<td>( h/h_{\text{max}} )</td>
<td>-</td>
<td>0.47 ± 0.02</td>
<td>0.35 ± 0.03</td>
<td>0.33 ± 0.06</td>
</tr>
<tr>
<td>( h_{\text{pile-up}}/h_{\text{max}} )</td>
<td>-</td>
<td>0.046 ± 0.004</td>
<td>0.036 ± 0.004</td>
<td>0.035 ± 0.004</td>
</tr>
</tbody>
</table>

Figure 1: Optical micrographs of Berkovich indentations in four NBS glasses, radial crack initiation probability as a function of applied load, and crack growth.
Structural Characterization via Raman Microscopy and Atomic Force Microscopy

Raman spectroscopy and relaxation anneal techniques show clear differences between the glass states when compared under nearly identical conditions (e.g., fixed indentation load, beam size, and annealing conditions). These trends are consistent with the expected differences in structure between the glass states. Indentation testing provides a unique opportunity to rapidly examine and compare elastic modulus, hardness, material inelastic deformation, crack initiation during contact, and crack growth resistance. Furthermore, the hardness, modulus, and, maybe most importantly, crack initiation resistance can be tailored with relatively small changes in composition and casting conditions.

Conclusions

NBS1 has an elastic modulus to hardness ratio, $E/H$, of $\sim 10.9$, while $E/H$ for NBS2 (fc) is $\sim 9.2$. While the two ratios are similar and well within the expected values for silicate glasses, large differences in plastic deformation during indentation were observed. It may
be that $E/H$ is not indicative, or sensitive, to changes in deformation behavior in these materials.

Densification of material can occur through elastic recovery of material around a plastically deformed volume as the indenter is unloaded (i.e., residual stress) and by structural changes during the indentation process. While the former is common to all elastic-plastic materials during indentation, the latter cause may be significant in NBS glasses, especially the NBS2 composition, due to the temperature, pressure and composition-dependence of the equilibrium between $\text{B}_3\text{O}_3$ and ($\text{B}_4\text{O}_7$)- groups, and their association on the mid-range scale.

Additional densification of the borate sub-network could be provided by the increase of connectivity with the transformation of trigonal $\text{B}_3\text{O}_3$ to tetrahedral ($\text{B}_4\text{O}_7$)- under contact pressure, as implied by the study of different cooled NBS2 glasses. A detailed study of the NBS2 composition with changes in boron coordination through heat treatments may shed light on the role of the borate sub-network on plastic flow. However, while casting conditions may influence boron coordination, they may also introduce residual stresses which play a role in indentation behavior. It may be possible to optimize the resistance to crack initiation/growth as well as densification during contact.

**Acknowledgments**

Financial support from the German Science Foundation through its priority program 1594 is gratefully acknowledged (grant no. MO1375/3-1). The authors thank A. Winterstein-Beckmann and all colleagues as the Laboratory of Glass Science at FSU Jena for the provision of glass samples and help in data evaluation. Also grateful thanks to Prof. M. Göken and the entire Department WW1 of FAU Erlangen for the support and enabling to work with their Nanoindenter and AFM equipment. Thanks also to Prof. J. Zaumseil and M. Schweiger from the Department LSP of FAU Erlangen for their support and assistance with the Raman spectroscopy.

**References**


Ceramics Group

The emphasis in the ceramics group is on the correlation between microstructure and mechanical as well as functional properties. A number of processing methods are available in order to accomplish different microstructure classes, to determine their specific properties in an experiment and to rationalize these with straightforward modelling efforts. Thus, a materials optimization is afforded which allows effective interplay between processing, testing and modelling. In particular, new lead free piezoceramics are currently being developed and mechanically tuned electrical conductivity is investigated as a fundamental new design concept.

The scientific effort can be grouped as follows:

I. **Development of new piezoceramics**
   *Prof. Dr. Jürgen Rödel and Dr. Jurij Koruza*

   In response to the recent demands for environmentally friendly piezoelectric materials for electrical and electronic applications, the principal focus of this group is the development of non-toxic piezoceramics with electromechanical performance comparable to their lead-containing counterparts.

   Among all the potentially promising candidates special attention has been given to bismuth-based materials whose properties can be effectively tailored using the so-called morphotropic phase boundary (MPB) concept. Extensive compositional research has been performed on various bismuth-based solid solution systems that contain a MPB between separating different crystal symmetries of the members. Recently, we have also started work on both KNN and BT-based lead-free piezoceramics.

   To better understand the mechanisms governing the enhancement of electromechanical properties of materials and to make our search for alternative materials more effective fundamental scientific research on model systems have been performed in parallel to the compositional investigations.

   We employ various characterization techniques such as macroscopic dielectric, ferroelectric and ferroelastic property measurements as well as crystallographic structural analyses based on synchrotron and neutron diffractions, Raman, nuclear magnetic resonance, electron paramagnetic resonance spectroscopic techniques, and transmission electron microscopy.

   We are also simultaneously establishing thermodynamic and phenomenological models which are verified by the first principles calculations. Currently, we have extensive international collaborations with eminent ferroelectric groups throughout the world.

II. **Conductivity of Oxides**
   *Dr. Till Frömling and Dr. Nikola Novak*

   Modulation of conductivity of oxide ceramics is usually achieved by doping and temperature treatment in a large oxygen partial pressure range. However, electric and ionic conductivity can also be changed by mechanical modifications. In this research group conductivity of oxide ceramics is modified by the following approaches

   a) Induction of dislocations: Dislocations are mechanically introduced into strontium titanate which can be plastically deformed even at room temperature. Changes of the electric and ionic conductivity are, amongst other methods, investigated by complex impedance spectroscopy and dc-measurements. The aim of this project is to identify the defect chemical properties of dislocation cores in strontium titanate and related materials.

   b) Altering potential barriers in piezoelectric semiconductor materials: In this project Schottky-barriers and varistor material based on ZnO are investigated as a function of applied pressure.
### Staff Members

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### Research Projects

- Processing of textured ceramic actuators with high strain (SFB 595, 2003–2014)
- Mesoscopic and macroscopic fatigue in doped ferroelectric ceramics (SFB 595, 2003–2014)
- Development of new lead–free piezoceramics (ADRIA, state funding, 2008-2014)
- Stress and strain fields in ferroelectrics (Graduate school “computational engineering” 2009-2017)
- Lead-free piezoelectric single crystals with high strain: orientation dependence, polarization rotation and morphotropic phase boundaries (DFG 2011-2014)
- Energy absorption of ZnO varistors (DFG 2011-2014)
- Ag-based electrical switches (state of Hesse / Umicore)
- Lead-free piezoceramics (Johnson Matthey)
- Fracture of bismuth-based relaxors (DFG 2014-2017)
- Complex phase diagrams in bismuth-based relaxors (AvH 2014-2016)
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Electric Field-Temperature Phase diagram in BiNaTiO₃-Based Ceramics.

Yoshitaka Ehara, Eva Sapper, and Jürgen Rödel

The enhanced piezoelectric properties observed in Bi₁/₂Na₁/₂TiO₃ (BNT)-based materials were related to the relaxor behavior found in these materials. Therefore, a considerable amount of research has been focused on the structural origin of the polarization in relaxors and the nature of phase transitions between different states of ergodicity and long-range order.[1-3] Recent developments in lead-free relaxor ferroelectrics have raised questions about the nature of field- and temperature-induced phases in macroscopically nonpolar materials as well as their ranges of stability. Therefore, the influence of electric field and temperature was investigated to establish E-T phase diagrams for BNT-xBT in compositions across the MPB and to contrast this to corresponding lead-containing relaxors. In order to reduce leakage current, of 0.5 mol% Mn acceptor doping was introduced (Mn³⁺ on the B-site) for all compositions.[4]

Ceramic samples of BNT-3BT, BNT-6BT, BNT-9BT, all doped with 0.5 mol% Mn, were produced according to a conventional mixed oxide route.[5] The P(E) hysteresis at difference temperatures are shown in Fig. 1 for BNT-3BT, BNT-6BT, BNT-9BT doped with 0.5 mol% Mn. These data show that increasing the temperature tends to lower the coercive field, while at the same time the remanent polarization decreases. Figure 2 depicts the characteristic field-dependent current density j(E) obtained at different temperatures for BNT-3BT:Mn. The curves from the first cycle, i.e., the poling cycle (Fig. 2, dotted lines) are compared with a subsequent cycle measured directly after the first one (Fig. 2, solid lines). A single peak is detected in the current density j(E) at the transition field E₁ during the poling cycle, regardless of temperature. In the subsequent cycle, E₁ is identical with E_c at 25 °C (Fig. 2(a)). With a Full Width at Half Maximum (FWHM) of 0.96 kV/mm, the peak in the j(E) curve is rather broad at this temperature. In the vicinity of T_d (Fig. 2(b)), however, a second peak is detected at E₂ indicating that the polarization reversal takes place in two steps. Furthermore, E₁ is higher in the poling cycle (Fig. 2(b), solid line) than in the following cycle (Fig. 2(b), dotted line), pointing towards a strong influence of sample history. Since these findings indicate that the polarization reversal differs from conventional ferroelectrics, the notation E₁ will be employed in the following instead of E_c. At temperatures well above T_d (Fig. 2(c)), E₂ shifts to the decreasing fields and E₁ is again at the same position in both the first and the second cycle. Furthermore, the peak width at E₁ and E₂ where polarization reversal occurs are significantly reduced. E-T phase diagrams for BNT-3BT:Mn, BNT-6BT:Mn, and BNT-9BT:Mn are displayed in Fig. 3. The insets on top of the graph show the characteristic j(E) curves for each temperature regime. Additionally, T_d determined before from thermally stimulated depolarization

![Image](Fig.1 Temperature-dependent Polarization E-field loops of BNT-3BT:Mn (a) BNT-6BT:Mn (b), and BNT-9BT:Mn (c))
current measurements (TSDC) of poled samples at zero field is shown as a reference point.[5]

All transitions displayed in Figs. 3(a)–(c) are determined from the poling cycle. The existence of a room temperature field-induced transition from the nonergodic to the induced ferroelectric (FE) state is deduced from the drastic decrease of permittivity during poling as well as from the stable remanent polarization and piezoelectric coefficient. Within the E-T phase diagram this transition line is then formed by $E_{t1}$ values from the $j(E)$ measurement. Even though above $T_d$ the remanent state is not stable anymore, an induced long-range order domain state can be inferred from the low permittivity at high field. In all compositions, the ergodic and the nonergodic state, as well as a region with a field-induced long-range order FE state were identified. The reliability of the electromechanical properties and their temperature and pressure stability are crucial requirements to developing lead-free actuators suitable for industrial applications. A 3D phase diagram (electric field, pressure and temperature: $E$-$p$-$T$) of BNT-based materials is currently under investigation, in order to give insight into the full operational range of this important lead-free material.

Fig.3 Electric Field-Temperature phase diagram of (a) BNT-3BT:Mn, (b)BNT-6BT:Mn, and (c) BNT-9BT:Mn. Transition field ($E_t$) is dependent on temperature and stability regions the nonergodic relaxor (NR) state, the ergodic relaxor (ER) state, and induced ferroelectric state (FE). Arrows indicate the direction of E-field.

References

**Electronic Material Properties**

The *Electronic Materials* division introduces the aspect of electronic functional materials and their properties into the Institute of Materials Science. The associated research concentrates on the characterization of various classes of materials suited for implementation in information storage and organic and inorganic electronics. Four major research topics are presently addressed:

- Electronic and optoelectronic properties of organic semiconductors.
- Charge transport in inorganic semiconductor devices.
- Charge transport and polarization in organic and inorganic dielectrics.
- Photo- and photostimulated luminescence in inorganic phosphors.

For novel areas of application a worldwide interest exists in the use of organic semiconductors in electronic and optoelectronic components, such as transistors and light-emitting diodes. So far, multicolour and full colour organic displays have been implemented in commercially available cameras, car-radios, PDAs, mp3-players and even television sets. Organic devices reaching further into the future will be simple logic circuits, constituting the core of communication electronics such as chip cards for radio-frequency identification (RFID) tags and maybe one day flexible electronic newspapers where the information is continuously renewed via mobile networks. In view of the inevitable technological development, the activities of the group are concerned with the characterization of organic material properties regarding the performance of organic electronic and optoelectronic devices. The major aspect deals with the charge carrier injection and transport taking place in organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs). In particular, the performance of unipolar and ambipolar light-emitting OFETs and the stability of OFETs and OLEDs are subjects of recent investigations. To conduct these demanding tasks, various experimental techniques for device fabrication and characterization are installed. Besides basic electric measurement setups, a laser spectroscopy setup used for time-of-flight as well as for life-time measurements and a Kelvin-probe atomic force microscope to visualize the potential distribution of organic devices with nanometer resolution are available.

Even though organic electronics is an emerging field especially for consumer electronics applications today's electronic devices still mainly rely on conventional silicon technology. While organic semiconductors have excellent optoelectronic properties they in general suffer from low charge carrier mobilities limiting the switching rates in organic transistors. Yet, metal oxides like ZnO, InZnO (IZO) or InGaZnO (IGZO) can bridge the gap between the high mobility semiconductors like silicon and the low mobility organic semiconductors. Using metal-organic precursors or nanoparticulate dispersions easy processing procedures like spin-coating or printing can be applied and yield rather high field-effect mobilities in the order of 1-10 cm²V⁻¹s⁻¹ for the produced thin film transistors (TFTs). Current research activities in the group concentrate on the optimization of the processing procedures especially the decrease of annealing temperatures is desired to make the processes compatible with organic substrates. Furthermore, the influence of the layer morphology and the role of the gas atmosphere for the device performance as well as stability issues are investigated.
In the field of polymer electrets current research comprises the characterization of surface charge distribution, charge stability, and charge transport properties of fluoropolymers, as well as their applications in acoustical transducers. Present investigations of charge transport and polarization in organic dielectrics are directed towards the basic understanding of polarization buildup and stabilization in PVDF and in novel microporous dielectrics. Latter are scientifically interesting as model ferroelectric polymers. Moreover, the fatigue behaviour of electrically stressed inorganic PZT ceramics is investigated. The focus lies on preventing the operational fatigue of ferroelectric devices due to cyclic and static electrical stress. The available equipment includes poling devices, such as corona and high voltage setups, and a thermally stimulated current setup to investigate the energetic trap structure in dielectrics as well as the thermal charging and discharging under high electric fields.

The field of photoluminescent and photostimulated luminescent (PSL) materials (phosphors) is concerned with the synthesis and characterization of suited inorganic compounds used as wavelength converters in fluorescent lamps and in scintillating and information storing crystals. Present work is focused on x-ray detection materials, providing improved resolution and high PSL-efficiency needed in medical imaging. In particular the storage phosphors CsBr:Eu$^{2+}$ and BaFBr:Eu$^{2+}$ are under investigation. Research is concentrated on the influence of humidity on the sensitivity of CsBr:Eu$^{2+}$. Before and after the treatment the materials are studied by means of spectroscopic methods as well as scanning electron microscopy. The exchange of water during the thermal treatment is measured in situ by thermal analysis methods. New synthesis methods for BaFBr:Eu$^{2+}$ used in commercial image plates are of interest and new synthesis routes will be tested for other storage phosphors and scintillators. On the one hand the mechanism of PSL-sensitization, which is found to be mainly due to the incorporation of oxygen and water, is investigated. On the other hand the implementation of BaFBr:Eu$^{2+}$ powders into organic binders in order to form image plates is in the focus of the work.

### Staff Members

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Research Projects

Fatigue of organic semiconductor components (SFB 595 (DFG), 2003-2014)

Phenomenological modelling of bipolar carrier transport in organic semiconducting devices under special consideration of injection, transport and recombination phenomena (SFB 595 (DFG), 2003-2014)

Polarization and charge in electrically fatigued ferroelectrics (SFB 595 (DFG), 2006-2014)

Development of organic piezo sensors (LOEWE AdRIA 26200026, 2008-2014)

Thin film dielectrics for high performance transistors (DFG, 2012-2015)

Development of gate insulators for organic field effect transistors exploiting self-assembly of block-copolymers (IDS-FunMat (EU), 2012-2015)

Piezoelectric properties of ferroelectrics (DFG, 2012-2015)

Preparation and characterization of metal-oxide field-effect transistors (MerckLab, 2009-2015)

High resolution, transparent image plates based on the storage phosphor CsBr:Eu$^{2+}$ (DFG, 2013-2015)

Metal oxide based field-effect transistors with top gate geometry (Helmholtz Virtual Institute, 2012-2017)

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*Statistical electric field and switching time distributions in PZT 1Nb2Sr ceramics: Crystal- and microstructure effects*
JOURNAL OF APPLIED PHYSICS 115, 014103 (2014)
Storage phosphors have the capability to store a two-dimensional latent image as a result of an x-ray exposure of an investigated object. X-rays are thereby partially absorbed by the investigated object and the penetrating radiation enters the image plate where it is again absorbed generating electron holes pairs, which are trapped in defects of the storage medium. The number of the locally trapped charge carriers depends thereby on the intensity of X-rays, on their energy and the intensity pattern of the radiation created by the object. This stored electrons can be stimulated by visible light (readout) and after been liberated, recombine with trapped holes producing the photo- or optically-stimulated luminescence (PSL or OSL), which can be collected by a photomultiplier. By scanning the image plate with a focussed laser the photo-stimulated light can be collected and correlated with the readout light and the corresponding electrical signal from the photomultiplier. A plot of the emission intensity as a function of the laser spot results in the x-ray image which can be displayed on a high resolution computer screen. The most relevant properties of image plates are the spatial resolution, the stimulation energy (energy of the stimulating light, which is required to reduce the PSL intensity to 1/e (37%) [µJ/mm²]) and the conversion efficiency (total PSL energy released during stimulation per absorbed X-ray dose [pJmR⁻¹mm⁻²]).

A typical resolution of a powder based commercial image plate thereby varies between 3 to 5 linepairs per millimeter (lp/mm) and present research is directed to improve this property due to urgent need e.g. in mammography where at least 10 lp/mm are necessary to image breast cancer in an early state. The strategy to increase the resolution is by reducing the scattering of the stimulating light in the storage phosphor. This can be archived by different methods: The first realized method was to add an absorbent for the stimulating light to the powder, thus preventing it to scatter too far away from the point of stimulation. The second method also commercial today is to fabricate the storage phosphor in a needle structure so that the stimulating light is reflected alongside the needles [1]. These two methods are presently used in industry to accomplish higher resolution. The more general relation between grain size and resolution as well as sensitivity is shown schematically in Figure 1. One realises that really high resolution can only be obtained for a very fine powder or for single crystalline materials where the scattering or the diameter of the laser, respectively.

Figure 4: Correlation of resolution and PSL sensitivity to grain size of a storage phosphor. Fine grained powder has a lot of grain boundaries, thus the stimulation light is scattered often in a small distance and will not travel far. With increasing grain size the scattering volume grows until the effect of too few grain boundaries becomes more important than the travelling distance between two scattering events. In the extreme of a single crystal no scattering occurs and the stimulated area is only the laser spot itself.
Therefore in the present study the grain size is varied to obtain a higher resolution. The utilized material is CsBr doped with Europium whose cubic structure allows the pressing of a transparent (low optical scattering of the stimulation light) image plate [Winch]. Unfortunately the exposure to the environment and therewith to humidity causes recrystallization and the image plate starts to turn cloudy. The conversion efficiency, however gets better the longer the image plate is hydrated. Figure 2 shows an example of a semitransparent pressed CsBr:Eu image plate. Samples using both approaches, fine grained powder and transparent pressing, are manufactured and their optical properties examined.

To determine the optical quality and resolution of the samples, a custom made readout system was designed and built. Due to the design of this scanner, image plates of different size, form and thickness can be measured. An example thereof is displayed in Fig. 3.

To quantify the resolution of the image plates the modular transfer function (MTF) is calculated using the method described by Buhr [2]. The MTF is basically the contrast ratio of alternating lines of exposed and non-exposed areas plotted as a function of the number of lines per millimeter.

Presently transparent image plates can be produced, but there is still work to be done to determine the optimal production methods and parameters and to compare these transparent image plates to non-transparent image plates made out of fine powder regarding the optical and functional properties, mainly resolution, conversion efficiency and stimulation efficiency.

References:


Surface Science

The surface science division of the institute of materials science uses advanced surface science techniques to investigate surfaces and interfaces of materials and materials combinations of technological use. For this purpose integrated UHV-systems have been built up which combine different surface analytical tools (photoemission, inverse photoemission, electron diffraction, ion scattering, electron loss spectroscopy, scanning probe techniques) with the preparation of thin films (thermal evaporation, close-spaced sublimation, magnetron sputtering, MOCVD) and interfaces. The main research interest is directed to devices using polycrystalline compound semiconductors and interfaces between dissimilar materials. The perspectives of energy conversion (e.g. solar cells) or storage (intercalation batteries) devices are of special interest. In addition, the fundamental processes involved in chemical and electrochemical device engineering and oxide thin films for electronic applications are investigated.

The main research areas are:

Electrochemical Interfaces
The aim of this research activity is the better understanding of electrochemical interfaces and their application for energy conversion. In addition, empirically derived (electro-) chemical processing steps for the controlled modification and structuring of materials is investigated and further optimized. In the center of our interest are semiconductor/electrolyte contacts.

Solar fuels
The direct solar light induced water splitting is investigated using photoelectrochemical (electrode/electrolyte) or photocatalytic (particle) arrangements. New materials, design structures, as well as interface engineering approached with advanced catalysts are investigated. The catalysts are also tested for their application in water electrolysis.

Intercalation Batteries
The aim of this research activity is the better understanding of electronic properties of Li-intercalation batteries and of their degradation phenomena. Typically all solid state batteries are prepared and investigated using sputtering and CVD techniques for cathodes and solid electrolytes. In addition, the solid-electrolyte interface and synthetic surface layers are investigated as well as composite systems for increasing the capacity.

Thin film solar cells
The aim of this research activity is the testing and development of novel materials and materials combinations for photovoltaic applications. In addition, the interfaces in microcrystalline thin film solar cells are to be characterized on a microscopic level to understand and to further improve the empirically based optimisation of solar cells.

Organic-inorganic interfaces and composites
In this research area we are aiming at the development of composites materials for (opto-) electronic applications. The decisive factors, which govern the electronic properties of interfaces between organic and inorganic materials are studied.
Semiconducting Oxides
The aim of this research area is to understand electronic surface and interfaces properties of oxides. We are mainly interested in transparent conducting oxide electrodes for solar cells and organic LEDs but also in dielectric and ferroelectric perovskites.

Surface analysis
The UHV-surface science equipment and techniques using different and versatile integrated preparation chambers is used for cooperative service investigations. For the experiments we use integrated UHV-preparation and analysis-systems (UPS, (M)XPS, LEISS, LEED), spectromicroscopy (PEEM) coupled with UHV-STM/AFM. We further apply synchrotron radiation (SXPS, spectromicroscopy), scanning probe methods (STM, AFM), and electrochemical measuring techniques. UHV-preparation chambers dedicated for MBE, CVD, PVD and (electro)chemical treatment are available.

The members of the group are involved in basic courses of the department's curriculum and offer special courses on the physics, chemistry and engineering of semiconductor devices and solar cells, on surface and interface science, and on thin film and surface technology and electrochemistry.

Staff Members

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<th>Head</th>
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<td>Guest Scientists</td>
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Research Projects

Function and fatigue of conducting electrodes in organic LEDs, SFB 595-D3 (DFG 2003-2014)
Polarization and charge in electrically fatigued ferroelectrics, SFB 595-B7 (DFG 2007-2014)
Integriertes Graduiertenkolleg SFB 595 (DFG 2008-2014)

Tunable Integrated Components for Microwaves and Optics, Graduiertenkolleg 1037 (DFG 2004-2014)

Boundary layers and thin films of ionic conductors: Electronic structure, electrochemical potentials, defect formation and degradation mechanism SFB595-A3 (DFG 2003-2014)


All Oxide PV (EU 2012 – 2014)

Inverted organic solar cells: Charge carrier extraction and interface characterization (DFG 2012- 2014)

Photoelectrochemical water splitting using adapted silicon based semiconductor tandem structures (DFG 2012 – 2015)

Coordination SPP 1613 Solar H₂ (DFG 2012 – 2015)

Joint project „PeroSol“:vacuum based thin film solar cells with novel organometal halide perovskite absorber (BMBF 2014 – 2017)

Interface engineering for the chemical and electronic passivation of group III–phosphide semiconductors to be used in highly efficient photoelectrochemical tandem cells for water splitting“ (DFG 2014 – 2017)

Publications


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| 22 | L. Dimesso, C. Spanheimer, W. Jaegermann                                | *Investigation of the LiCo$_{1-x}$Mg$_x$PO$_4$ (0 \leq x \leq 0.1) - graphitic carbon foam composites* | Solid State Sciences 30C, 89-93 (2014) doi: 10.1016/j.solidstatesciences.2014.02.011 |
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DOI: 10.1021/jp501956z

*Ultrasmall Dispersible Crystalline Nickel Oxide Nanoparticles as High-Performance Catalysts for Electrochemical Water Splitting*  
doi: 10.1002/adfm.201303600

*Highly conducting SrMoO3 thin films for microwave applications*  
doi: 10.1063/1.4896339
Properties of CH$_3$NH$_3$PbX$_3$ (X = I, Br) powders as precursors for organic/inorganic film solar cells

L. Dimesso, W. Jaegermann

In an effort to generate more cost-effective technology, the field of thin film solar photovoltaics (PV) presents a promising avenue toward high efficiency solar energy conversion. Hybrid inorganic-organic (IO) semiconductors are opening up a new insight to low dimensional PV nanostructures. They deliver a unique replacement of their inorganic and organic counterparts in advanced device structures (an example is shown in Fig. 1) and provide significant opportunity as multifunctional materials for many electronic and optoelectronic applications. Among these hybrids, self-organized low-dimensional IO structures, derived from component 3D networks of R-MX$_3$ (R-organic amine and MX-metal halide) type perovskite, have attracted much attention because of their unique crystal structures and the modified optical properties [1-3]. When the R-site in the perovskite formula, R-MI$_3$, is occupied by a monovalent cation, such as Rb, Cs, methylammonium (MA$^+$ hereafter), or formamidinium, a three-dimensional (3D) framework is obtained (as shown in Fig. 2).

Among them, MAPbX$_3$ (X = Br, I) perovskites described by Weber [4] are compounds unusual in several respects such as the color which intensifies rapidly from the reddish-orange bromide to black iodide, pointing to a charge-transfer character of the Pb-X bonds and possibly to photoconduction. Despite the widening literature on the photovoltaic use of hybrid lead perovskites [2-4], many questions, concerning their peculiar structural, electronic chemistry and material response to light induced processes, remain to be addressed. The main purposes of our research is the investigation of the structural, morphological, optical and electronic properties of the MAPbX$_3$ powders (X = I, Br) which can be used as precursors for dispersions to thin films devices. Methyl-ammonium-tri-halogeno-plumbates (II) - CH$_3$NH$_3$$^+$PbX$_3^-$, (X = Br, I) - were synthesized by a modified self-organization process [5]. The materials were prepared in concentrated aqueous solution of the acid HX which contained Pb$^{2+}$ ions [from lead (II)
Acetate] and a respective amount of CH$_3$NH$_3^+$ (by adding a 40% solution of CH$_3$NH$_2$ in water). Beautiful large crystals of size up to 1-2 mm are grown by cooling an aqueous solution from about 95-105°C to room temperature. The X-ray diffractograms of the CH$_3$NH$_3^+$PbX$_3^-$ (X = I, Br) perovskites indicate, for X = I (Fig. 3), the formation of a tetragonal structure at room temperature (space group $I\ 4/m$ or $I\ 4/mcm$) and for X = Br, the formation of a cubic structure at room temperature (space group $Pm\ 3m$) respectively. The results of the morphological investigation on the MAPbX$_3$ systems revealed the formation of single microcrystals of MAPbX$_3$ generally formed as dodecahedra, with some examples exhibiting faceting consistent with rhombo-hexagonal dodecahedra, which is a typical crystal habit of a body centered tetragonal lattice as shown in Fig. 4 for X = I as example.

The photoluminescence (PL) properties of specimens of the MAPbX$_3$ systems were measured at room temperature using an emission wavelength of 380 nm. PL emissions were observed for I- and Br-containing compounds (shown in Fig. 5a-b). The emission wavelength of MAPbI$_3$ (peak maximum at ~754 nm as in Figure 5a) is consistent with our optical absorption data [5] and supported by Stoumpos [6] providing further evidence for the direct nature of the band gap. On the other hand, the emission wavelength of the MAPbBr$_3$ (peak maximum at ~568 nm as in Fig. 5b) is consistent with our optical absorption data but it is slightly higher than the values (550 nm) reported in the literature. In the case of comparative studies between continuous thin films and nano-powdered materials, the sizes of primary particles can play a prominent role in the final properties.
The next step of our investigation has been the preparation of layers using the prepared powders as precursors. As example, 1.23 g of CH$_3$NH$_3$PbI$_3$, dissolved in different amounts of DMF, resulted in very homogeneous and stable dispersions with concentrations of 30% wt, 10% wt, 5% wt and 1% wt of MAPbI$_3$ respectively. Typically, 100 – 300 μL of the dispersion have been dropped on fluorine-doped tin oxide coated (FTO-coated) glass substrates, then deposited by spin-coating and finally thermally treated at 100 – 110°C for 5-10 minutes in order to evaporate the solvent and consequently to favor the recrystallization of the MAPbI$_3$ phase on the substrates.

The results of the morphological investigation on a typical MAPbI$_3$ layer are shown in Fig. 7a-b. The tilted SEM image (Fig. 2B) confirm the formation of a layer on the FTO glass substrate (indicated with red arrows) whereas the top view SEM image (Fig. 7A) confirm the homogeneity of the layer, however, with the presence of small hollows possibly due to the fast evaporation of the solvent during the thermal treatment.

References:

Self-driven water electrolysis by high photovoltage thin film silicon tandem cells

Jürgen Ziegler, Joachim Klett, Natascha Weidler, Florent Yang, Bernhard Kaiser, Wolfram Jaegermann

The storage of renewable energy is the major challenge for the energy revolution. Due to the volatile nature of wind and solar power a suitable storage is essential for a future reliable power supply. The conversion of sunlight to hydrogen as a solar fuel can be one way to solve this problem. One approach to accomplish this is with a photoelectrochemical cell (PEC). There are several types of PECs discussed in literature. We consider a "buried-junction" photoelectrode, which is one of the more promising cell designs for photoelectrochemical water splitting. We employ a cell provided by the Forschungszentrum Jülich consisting of a thin film silicon based tandem solar cell like it is depicted in Figure 1.

![Figure 1 Schematic of the PEC with a silicon thin film tandem cell with Pt catalyst and a RuO₂ counter electrode.](image)

In a "buried-junction" the separation of the electron hole pairs is decoupled from the chemical reaction. The tandem solar cell produces the required electrochemical potential to drive the water splitting reaction. It is connected to the two half cells, where the cathodic and the anodic reaction occur, namely the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).

We apply two types of tandem solar cell, which are prepared in the framework of this cooperation with Jülich: The first system is a stack of two amorphous silicon solar cells (a-Si:H). The second type of solar cell is a-Si:H top cell with a bottom cell made of microcrystalline silicon (µc-Si:H). The photovoltaic characteristics are depicted in Figure 2a. The a-Si:H/a-Si:H tandem cell shows a high photovoltage of 1.55 V at the maximum power.
point and achieves a photovoltaic efficiency of 9.0 %.\textsuperscript{1} In comparison the a-Si:H/\(\mu\)c-Si:H tandem cell provides a higher photo current and a higher efficiency of 10.1 %.\textsuperscript{2} The different characteristics are caused by the different band gaps of the tandem cells. This can be seen in figure Figure 2b, where the external quantum efficiency of both cells is plotted. The a-Si:H/a-Si:H tandem cell is build up of two wide band gap a-Si:H absorbers. Therefore a high photovoltage can be achieved, but sunlight with a high wavelength cannot be utilized by this cell type. A broader absorption is achieve by the a-Si:H/\(\mu\)c-Si:H tandem cell which consist of a low band gap \(\mu\)c-Si:H absorber. Hence the a-Si:H/\(\mu\)c-Si:H tandem cell can utilize more sunlight and has in principal a better chance to reach high photovoltaic efficiencies then the a-Si:H/a-Si:H tandem cell, but it suffers under a low photovoltage.

In a self-sustaining PEC for water splitting, the current which flows under short-circuit conditions, determines the efficiency. Hence the a-Si:H/\(\mu\)c-Si:H tandem cell could have an advantage to the a-Si:H/a-Si:H tandem cell, if the required photovoltage for the water splitting reaction is sufficient. Additional to the thermodynamic potential of 1.23 V, potential losses (overpotentials) arise due to the chemical reactions in the half cells of the electrochemical system. Suitable catalysts can reduce the overpotentials considerably, but they remain a major potential loss in the circuit. In Figure 3a the HER and the OER with the catalysts Pt on Ag foil and RuO\textsubscript{2}, respectively, is shown in 1 M H\textsubscript{2}SO\textsubscript{4} vs. the reversible hydrogen electrode (RHE). At a current density of 10 mA/cm\textsuperscript{2} an overpotential of 120 mV and 340 mV is required for the HER and the OER, respectively. In disregard of the electrolyte resistance a total potential of 1.23 V + 120 mV + 340 mV = 1.69 V is necessary to split water. When looking at the photovoltaic characteristics of the tandem cells it becomes evident, that the photovoltage of the a-Si:H/\(\mu\)c-Si:H cell is too low to split water without an additional bias potential. Therefore the higher absorption of this cell type has no benefit. In contrast the a-Si:H/a-Si:H cell should supply sufficient photovoltage to be used in a self-sustaining PEC. In Figure 3b a cyclic voltammogram of an a-Si:H/a-Si:H cell modified with a Pt catalyst is shown in 0.5 M H2SO4. The measurement is performed in a two electrode arrangement vs. the RuO\textsubscript{2} electrode. In this arrangement the short-circuit
condition and the working point of the PEC are at 0 V. The a-Si:H/a-Si:H photoelectrode is indeed capable of generating a photocurrent of 4.1 mA/cm² under real working conditions. Under the assumption that this current solely leads to the production of hydrogen and oxygen, a solar to hydrogen (STH) efficiency of 5.0 % is achieved. In comparison to the photovoltaic measurement the efficiency is nearly cut in half. The MPP of the photovoltaic cell is situated a slightly lower potential than the required potential of the electrochemical cell. Therefore the current density is very steep around 0 V. As a consequence a small improvement of the photovoltage or a reduction of the overpotentials can result in a drastic increase in the STH efficiency of this device.

![Cyclic voltammograms](image)

**Figure 3** (a) Cyclic voltammograms of the HER on Pt and the OER on RuO₂ in 1 M H₂SO₄. (b) Cyclic voltammogram of Pt modified a-Si:H/a-Si:H photoelectrode vs. RuO₂ in 0.5 M H₂SO₄.

Improving the catalysts morphology is our next step to enhance its active surface area, thus reducing the overpotential of the water splitting reaction. As a next step we are also investigating the substitution of the noble metal catalyst with highly active transition metal oxides like cobalt and nickel oxides to reduce the overall cost of the device.

**References:**


Advanced Thin Film Technology

The Advanced Thin Film Technology (ATFT) group works on advanced thin film deposition techniques of novel materials. The group is specialized on physical vapor deposition techniques such as pulsed laser deposition (PLD), advanced oxide molecular beam epitaxy (ADOMBE) and dc/rf-magnetron sputtering. The ADOMBE system is an in-house development and has been jointly financed by Max-Planck-Institute for Solid State Research in Stuttgart and TU Darmstadt. PLD and ADOMBE are part of a cluster system allowing for in-situ sample exchange between the different deposition methods and characterization tools. The ADOMBE apparatus is a worldwide unique thin film deposition system which is dedicated to the growth of complex oxides beyond thermodynamic equilibrium. It allows for the simultaneous deposition of six elements from electron beam sources and further elements evaporated from effusion cells. The molecular beams of each element can be individually controlled by a feed back loop using electron impact emission spectroscopy. The group is working mainly on oxide ceramics which show a stunning variety of new functional properties. Examples are high-temperature superconductors, magnetic oxides for spintronics, high-k dielectrics, ferroelectrics, and novel thermolectric materials. As a vision for future, new solid state matter can be created by building hetero- and composite structures combining different oxide materials. While present day electronic devices heavily rely on conventional semiconducting materials, a future way to create novel functional devices could be based (completely) on oxide electronics. The group uses a Rigaku SmartLab X-ray thin film diffractometer with rotating anode ("synchrotron in house"). Other characterization tools located in the Advanced Thin Film Technology group include powder X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS), high-resolution scanning electron microscopy (HREM) with light element sensitive EDX, and SQUID magnetometry. A 16 Tesla magnet cryostat allowing measurements down to liquid helium temperature has been installed. Another magnet cryostat (10 T) lowers the available temperature range to below 300 mK. This cryostat also contains high-frequency feed-throughs for electrical characterization (40 GHz). The group is also using external large scale facilities as synchrotron radiation (ESRF, Grenoble) and neutron reactors (ILL, Grenoble / HMI and DESY, Berlin) for advanced sample characterization. Throughout 2014 Lambert Alff was working also as a Dean of Studies in the faculty of Materials Science and head of the Graduate School Materialium. Lambert Alff has also worked as an elected a member of the Senat of TU Darmstadt.

Staff Members

| Head | Prof. Dr. Lambert Alff |
| Research Associates | Dr. Ewrwin Hildebrandt Dr. Soumya Ray Dr. Philipp Komissinskiy |
| Technical Personnel | Dipl.-Ing. Gabi Haindl Jürgen Schreeck |
| Secretary | Marion Bracke |
Research Projects

Novel arsenic free pnictide superconductors (SPP 1458) (DFG 2013 - 2015)

Resistives Schalten in HfO2-basierten Metall-Isolator-Metall Strukturen für Anwendungen im Bereich nicht-flüchtiger Speicher (DFG 2012-2016)

Novel oxid electrodes for all oxide varactors (DFG 2012-2014)

LOEWE-Centre AdRIA: Adaptronik – Research, Innovation, Application (HMWK 2011 - 2014)


LOEWE-Schwerpunkt RESPONSE

Publications

Photoemission and DMFT study of electronic correlations in SrMoO$_3$: Effects of Hund's rule coupling and possible plasmonic sideband
doi: 10.1103/PhysRevB.90.205131

Intrinsic versus extrinsic ferromagnetism in HfO$_{2-x}$ and Ni:HfO$_{2-x}$ thin films
doi: 10.1103/PhysRevB.90.134426

Oxygen Vacancy Induced Room Temperature Ferromagnetism in Pr-Doped CeO$_2$ Thin Films on Silicon
ACS Appl. Mater. Interfaces 2014, 6, 17496 − 17505
doi: 10.1021/am502238w

Highly conducting SrMoO$_3$ thin films for microwave applications
doi: 10.1063/1.4896339

Origin of superstructures in (double) perovskite thin films
doi: 10.1063/1.4895636
Thicknes independent reduced forming voltage in oxygen engineered HfO$_2$ based resistive switching memories
doi: 10.1063/1.4893605

High-Temperature Stability and Saturation Magnetization of Superparamagnetic Nickel Nanoparticles in Microporous Polysilazane-Derived Ceramics and their Gas Permeation Properties
ACS Appl. Mater. Interfaces, 2014, 6, 12270-12278
doi: 10.1021/am501892z

Modification of energy band alignment and electric properties of Pt/Ba$_{0.6}$Sr$_{0.4}$TiO$_3$/Pt thin-film ferroelectric varactors by Ag impurities at interfaces
doi: 10.1063/1.4885880

In-operando hard X-ray photoelectron spectroscopy study on the impact of current compliance and switching cycles on oxygen and carbon defects in resistive switching Ti/HfO$_2$/TiN cells
doi: 10.1063/1.4879678

[10] Christin M. Hamm, Lambert Alff and Barbara Albert
Synthesis of Microcrystalline Ce$_2$O$_3$ and Formation of Solid Solutions between Cerium and Lanthanum Oxides
doi: 10.1002/zaac.201300663

Towards forming-free resistive switching in oxygen engineered HfO$_2$–x
doi: 10.1063/1.4864653

[12] Lambert Alff, Philipp Komissinskiy, Aldin Radetinac, Tanju Sirman and Mehran Vafaee
The role of cationic and anionic point defects in pulsed laser deposition of perovskites
doi: 10.1088/0022-3727/47/3/034012
**Dispersive Solids**

The main research interests of the group Dispersive Solids are directed towards the development of novel strategies suitable for the synthesis of inorganic, oxidic and non-oxidic materials with properties beyond the state of the art. The materials of interest are advanced oxidic and non-oxidic ceramics with extraordinary properties in terms of thermal stability, hardness and electronic structure. Therefore, synthesis methods such as polymer-pyrolysis, non-oxidic and oxidic sol-gel methods, chemical vapour deposition and novel high pressure methods have been further developed.

The following topical issues are presently under investigation:

**Polymer-Derived Ceramics**

The thermolytic decomposition of suitable organosilicon polymers provides materials which are denoted as polymer-derived ceramics (PDCs). The main emphasis is on the synthesis and characterization of new ceramic materials in the B-C-N, Si-C-N, Si-O-C, Si-(B,C)-N and Ti-(B-C)-N systems. The structural peculiarities, thermochemical stability, mechanical and electrophysical properties of the PDCs have been investigated in a series of PhD theses and research projects. Due to their outstanding thermochemical stability as well as excellent oxidation and creep resistance at very high temperatures, the PDCs constitute promising materials for high temperature applications. Another advantage of the PDC route is that the materials can be easily shaped in form of fibres, layers or bulk composite materials. Finally the correlation of the materials properties with the molecular structure of the used preceramic polymer is elaborated.

**Molecular Routes to Nanoscaled Materials**

The aim is to develop concepts for the production of novel multifunctional inorganic materials with a tailor-made nanoscaled structure. In accordance with the so-called “bottom-up” approach, specific inorganic molecules are to be assigned to higher molecular networks and solid-state structures in the form of molecular nanotools by means of condensation and polymerisation processes.

**High Pressure Chemistry**

Ultra-high pressure techniques like laser heated diamond anvil cell (LH-DAC) or multi anvil devices have been applied to synthesise novel solid state structures which cannot be produced by other methods, for example, inorganic nitrides. Moreover, the materials behaviour under pressure such as phase transformations and decomposition can be analysed.

**Functional Materials**

Further research topics are related to the development of materials suitable for applications in the fields of microelectromechanical systems (MEMS), optoelectronics (LEDs), pressure, temperature and gas sensors as well as thermoresistant ceramic membranes for high temperature gas separation. The integration of state-of-the-art in situ and in operando spectroscopic methods is applied to understand the mechanisms responsible for sensing and catalytic properties. Advanced polymer-derived ceramics are developed for applications in the field of energy conversion and storage.
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### Research Projects


**Electromagnetic properties of nano-scaled absorption filler reinforced porous ceramics derived from single-source-precursors (China Scholarship Council (CSC), Sept. 2014 – Aug. 2017)**

**Hochtemperatur-Kriechverhalten SiOC-basierter Gläser und Glaskeramiken (DFG, May 2014 – April 2017)**


**SiHfC(N) and SiHfN(C)-based Ultrahigh-Temperature Ceramic Nanocomposites (UHTC-NCs) for EBC/TBC Applications (China Council Scholarship (CSC), Oct. 2012 - Oct. 2016)**

**Nanocomposites as anode materials for lithium ion batteries: Synthesis, thermodynamic characterization and modeling of nanoparticular silicon dispersed in SiCN(O) and SiCO-based matrices (DFG, Aug. 2010 – Dec. 2016)**

**High-Temperature Piezoresistivity in SiOC - Untersuchungen zur Hochtemperatur-Piezoresistivität in kohlenstoffhaltigen Siliciumoxycarbid-Nanokompositen (DFG, May 2013 - April 2016)**


Ternary M-Si-N Ceramics: Single-Source-Precursor Synthesis and Microstructure Characterization (M = transition metal) (China Council Scholarship (CSC), Nov. 2012 - Nov. 2015)

Molecular Routes to SiMBCN Ceramic Nanocomposites (M = Zr, HF) (China Council Scholarship (CSC), Sep. 2011 - Aug. 2015)


Investigation of interdiffusion behaviour and oxidation resistance of different protective high temperature layers on pure refractory metals (Master thesis in cooperation with DECHEMA Forschungsinstitut, Frankfurt a.M., Germany, October 2014 – March 2015)

Investigations of Polysiloxanes (Diploma thesis in cooperation with Schunk, Heuchelheim, Germany, July 2014 – March 2015)


Solid Electrolyte for Lithium-ion Battery (FAME-Master Thesis in cooperation with Energies Alternatives, Laboratoire des Matériaux pour les Batteries, CEA, LITEN/DEHT/LMB, Grenoble, France, April 2014 – Sept. 2014)


Keramische SiCN-basierte Hartstoffschichten für thermisch hochbeanspruchte Substratwerkstoffe (DFG, June 2011 - June 2014)


Preparation and high-temperature behavior of TiSi₂/SiOC ceramic composites (Bachelor Thesis, 2014)


Indium oxide (In₂O₃) under high pressure: rational design of new polymorphs and characterisation of their physico-chemical properties (DFG, since June 2009)

Publications


Nitrides are attractive materials not only in the field of fundamental crystal chemistry but also in industrial applications. In the 2000s, platinum group nitrides (PtN$_2$, OsN$_2$, IrN$_2$, and PdN$_2$) were remarkably discovered in a direct chemical reaction between platinum group elements and molecular fluid nitrogen at high pressures and temperatures.\cite{2-7} The new class of compounds attracted much attention due to the unusual crystal chemistry as well as intriguing mechanical properties (e.g., $K_0 = 428$ GPa for IrN$_2$) owing to the strong bonding interaction between noble metals and nitrogen.\cite{2-7}

However, to the best of our knowledge, there has been no experimental evidence of a successful synthesis of rhodium nitride so far, although theoretical studies suggest that rhodium is likely to form RhN$_2$ with a marcasite-type structure.\cite{8,9}

We now succeeded in the synthesis of marcasite-type rhodium nitride in a direct chemical reaction between rhodium metal and molecular nitrogen at 43.2 GPa in a laser-heated diamond-anvil cell (LH-DAC). The results are in good agreement with the theoretical prediction.\cite{8,9} We report here the details of the synthesis experiments including characterization of the product via high pressure in situ Raman and X-ray diffraction (XRD) measurements and scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis after recovering the sample at ambient conditions.

Figure 1(a) shows the XRD pattern of the sample that was measured after heating at 43.2 GPa. The details of the experimental setup are described in the Supporting Information. Several sharp reflections (labeled with Miller indices hkl) were found, in addition to the diffraction peaks that correspond to the residual rhodium metal\textsuperscript{10} and solid nitrogen.\textsuperscript{11} (b) XRD pattern of the unheated region. $N_2$ represents the solid nitrogen with a rhombohedral structure.\textsuperscript{11} (c) Simulated XRD pattern of marcasite-type RhN$_2$ at 43.2 GPa together with a schematic illustration of the crystal structure for marcasite-type RhN$_2$. Large and small balls represent rhodium and nitrogen atoms, respectively. The lattice constants and atomic positional parameters were taken from the present results and from the theoretical calculation study,\textsuperscript{8} respectively.
parameters of $a = 3.847(5) \, \text{Å}$, $b = 4.683(5) \, \text{Å}$, and $c = 2.696(6) \, \text{Å}$ (at 43.2 GPa), which is consistent with earlier predicted marcasite-type structures (space group Pnmm).\textsuperscript{8,9}

Therefore, it can be concluded unambiguously that rhodium reacted with nitrogen to form marcasite-type RhN$_2$ above 43 GPa. The presence of the new reflections was clearly identified during the decompression process to the pressure of approximately 10 GPa, while immediately after the release of the pressure the reflections broadened significantly. Although the diffraction lines of the recovered marcasite-type RhN$_2$ were rather broad with less intensity, they could be resolved, and the lattice constants could be calculated. Accordingly, the lattice parameters of marcasite-type RhN$_2$ at ambient pressure were analyzed to be $a_0 = 3.982(1) \, \text{Å}$, $b_0 = 4.858(1) \, \text{Å}$, and $c_0 = 2.834(1) \, \text{Å}$, which are close to the results of the theoretical calculations.\textsuperscript{8,9}

The fine grains of less than 100 nm in size were identified by SEM on the sample surface close to the heated regions however, the chemical composition could not be determined mainly due to the fundamental instability of marcasite-type RhN$_2$ as identified from the broadness of diffraction peaks or large amount of residual rhodium metal.

![Figure 2. Raman spectrum of the sample after being heated at 43.2 GPa, together with the theoretical prediction at 50 GPa.\textsuperscript{8} Peaks labeled I, II, III, and IV correspond to marcasite-type RhN$_2$. Intense peaks at the low-frequency region stem from solid nitrogen.\textsuperscript{12}](image)

Vibration spectroscopy analysis, combined with theoretical calculations, offers useful information on the electronic valence state and the bonding nature of nitrogen in the metal nitrides.\textsuperscript{5,6,13} Figure 2 represents the Raman spectrum of the sample that was measured after heating at 43.2 GPa. The Raman spectrum did not change even after heating for long time at 43.2 GPa. We found at least three sharp and one broad bands (denoted as I, II, III, and IV in Figure 2), and no other peaks were detected in the wavenumber region of the present study. Taking into account the results of the high pressure in situ XRD measurement, it is concluded that the Raman spectrum corresponds to marcasite-type RhN$_2$. The group theory analysis gives six active Raman modes ($\Gamma = 2A_g + 2B_{1g} + B_{2g} + B_{3g}$) for marcasite-type TX$_2$, and the Raman frequency modes are assigned with respect to the dumbbell-like X−X units.\textsuperscript{14} The vibron frequency of dinitrogen in pernitrides or molecules strongly depends on the bonding character, such as N−N ($\sim 1.4 \, \text{Å}$, $\sim 800 \, \text{cm}^{-1}$),\textsuperscript{15} N N (1.2−1.3 Å, 1300−1550 cm$^{-1}$),\textsuperscript{16−21} and N N ($\sim 1.1 \, \text{Å}$, $\sim 2400 \, \text{cm}^{-1}$).\textsuperscript{11,15} Spectroscopic approaches combined with theoretical calculations have also been applied to platinum group metal nitrides.\textsuperscript{5,6,13} Recent theoretical calculation studies reported that Pt$^{4+}$ and N$_2$$^{4-}$ are the correct electronic valence states for PtN$_2$.\textsuperscript{13}
anion $N_2^{4-}$ is isoelectronic with that of the fluorine molecule, and the N–N bond length is well consistent with the F–F bond length (1.42 Å). Moreover, the strong Raman peak (~800 cm$^{-1}$) for PtN$_2$ is well consistent with that of single-bonded polymeric nitrogen. These findings strongly suggested that dinitrogen (N–N) in PtN$_2$ exhibits a single-bond nature. In the case of rhodium pernitride, the Raman peak frequency (1100 cm$^{-1}$) characterized as dinitrogen is higher than that of PtN$_2$ and single-bonded polymeric nitrogen (~800 cm$^{-1}$), while it is lower than the frequency of 1300–1550 cm$^{-1}$, which corresponds to double-bonded nitrogen deduced from $N_2H_2$ and alkaline earth diazenides. This observation indicates that the bond length of dinitrogen in marcasite-type RhN$_2$ is intermediate between single- and double-bonded dinitrogen.

Figure 3. (a) Normalized lattice parameters and volume of marcasite-type RhN$_2$ as a function of pressure. Dashed line represents a result of the B–M EOS fitting to the present data below 21 GPa because of the discontinuity around 25 GPa as indicated by the open arrow. The EOS is extrapolated to higher pressure with $K_0 = 235(13)$ GPa and $K_0' = 5.9(1.8)$. (b) Schematic illustrations of the crystal structure of marcasite-type RhN$_2$ viewed from [010] and [001] directions. Large and small balls represent rhodium and nitrogen atoms, respectively. Rhodium atoms are coordinated by six nitrogen atoms, and each RhN$_6$ octahedra are connected by N–N units.

The elastic properties of marcasite-type RhN$_2$ are evaluated based on the high pressure in situ XRD measurements. As shown in Figure 3(a), the a- and b-axes of marcasite-type RhN$_2$ show similar compressibility between each other, while the c-axis is more compressed than the other two-axes. The order of axial compressibility is consistent with the result of the recent high pressure experiment on marcasite-type FeP$_2$. From the schematic illustration of the crystal structure viewed from different axes (Figure 3(c)), it is reasonable to assume the rotation of the RhN$_6$ octahedron in the a–b plane and the distortion along the c-axis to be the dominant compression mechanism. The alignment of N–N also plays an important role for the anisotropic axial compressibility of marcasite-type RhN$_2$. The DFT calculation suggested that bonding interactions between nitrogen and the noble metal atom (Ru and Rh) are weak, and the N–N distance in these two nitrides are shorter than that of other noble metal nitrides (PtN$_2$, OsN$_2$, and IrN$_2$). The neighboring RhN$_6$ octahedra are connected via bonded N–N. This also plays a role to block the rotation of the RhN$_6$ octahedra with the pressure, which finally results in a lower compressibility of the a- and b-axes. In contrast, the most compressed c-axis indicates that the RhN$_6$ octahedra were...
largely distorted along their equatorial direction, and the N–N seemed not to affect the compressibility along the c-axis. The pressure–volume data below 21 GPa were fitted to the Birch–Murnaghan equation of state because the discontinuity was found in the compression curve at about 25 GPa. This procedure yields a zero-pressure bulk modulus of $K_0 = 235(13)$ GPa ($K_0 = 5.9(1.8)$). Although the present data were carefully and repeatedly analyzed, the discontinuity accompanying with the volume expansion at high pressure still remained. It seems difficult to accept this behavior based on the physical points of view, and many more data points would offer a much clear conclusion. On the other hand, a new Raman peak noted as V appeared at a pressure of 28 GPa, which corresponds to the onset pressure where the discontinuity was detected in the pressure–volume data. This indicates that a change of the vibration property in the dinitrogen (N–N) might strongly correlate with the bulk compression mechanism of RhN2. The incorporation of molecular nitrogen into the lattice of RhN2 under high pressure might also expand the unit cell volume. In order to clarify these, further detailed experimental and theoretical investigations would be required. The obtained bulk modulus is 100–200 GPa lower than those of PtN2, OsN2, and IrN2 as reported in previous studies, and it is in reasonable agreement with the theoretical zero-pressure bulk modulus of $K_0 = 286$ GPa ($K_0 = 5.58$).8 The low zero-pressure bulk modulus of $K_0 = 235(13)$ GPa is due to the weak bonding interaction between metal atoms and quasi-molecular dinitrogen units in the marcasite-type structure, as proposed by theoretical studies.

REFERENCES

Stable SiOC/Sn Nanocomposite Anodes for Lithium-Ion Batteries with Outstanding Cycling Stability


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ABSTRACT
Silicon oxycarbide/tin nanocomposites (SiOC/Sn) are prepared by chemical modification of polysilsesquioxane Wacker-Belsil PMS MK (SiOC-MK) and polysiloxane Polyramic RD-684a (SiOC-RD) with tin(II)acetate and subsequent pyrolysis at 1000 °C. The obtained samples consist of an amorphous SiOC matrix and in-situ formed metallic Sn precipitates. Galvanostatic cycling of both composites demonstrate a first cycle reversible capacity of 566 mAh g⁻¹ for SiOC-MK/Sn and 651 mAh g⁻¹ for SiOC-RD/Sn. The superior cycling stability and rate capability of SiOC-RD/Sn as compared to SiOC-MK/Sn is attributed to the soft, carbon-rich SiOC matrix derived from the RD-684a polymer, which accommodates the Sn-related volume changes during Li-uptake and release. The poor cycling stability found for SiOC-MK/Sn relates to mechanical failure of the rather stiff and fragile, carbon-poor matrix produced from PMS MK. Incremental capacity measurements outline different final Li–Sn alloy stages, depending on the matrix. For SiOC-RD/Sn, alloying up to Li2Sn2 is registered, whereas for SiOC-MK/Sn Li22Sn5 stoichiometry is reached. The suppression of Li22Sn5 phase in SiOC-RD/Sn is rationalized by an expansion restriction of the matrix and thus prevention of a higher Li content in the alloy. For SiOC-MK/Sn on the contrary, the matrix severely ruptures, providing an unlimited free volume for expansion and thus formation of Li22Sn5 phase.

RESULTS AND DISCUSSIONS
Materials Characterization
The pure polysiloxanes PMS MK and RD-684a as well as the Sn(ac)2-modified polymers were investigated by FTIR spectroscopy. The spectrum of PMS MK shows absorption bands at ν = 590 cm⁻¹ (SiOC-H), ν = 768, 1278 cm⁻¹ (Si-CH3), ν = 1030 cm⁻¹ (Si-O-C) and ν = 1122 cm⁻¹ (Si-O-Si), as previously reported. The FTIR spectrum of the Sn(ac)2-modified sample shows additional absorption bands corresponding to the acetate ligands, i.e. ν = 1340, 1572 cm⁻¹ (C-O), ν = 1385 (C-CH3) and ν = 1524 cm⁻¹ (C=C). Furthermore, two new absorption bands were assigned at ν = 689 cm⁻¹ (Sn-O) and ν = 925 cm⁻¹ (Si-O-Sn).

Thus, the added Sn(ac)2 undergoes a reaction with the Si-OH reactive groups present in PMS MK (Figure 1), upon release of acetic acid and the formation of Si-O-Sn units. The formation of Si-O-M (M=metal) units upon modification of the polymer with metal alkoxides, as well as with acetylacetonates and acetates, was demonstrated previously for metalorganic precursors of other metals, e.g. Fe, Zr and Hf. The spectra of RD-684a and Sn(ac)2-modified RD-684a look very similar. Within the polymer there are neither OH nor Si-OR groups to react with Sn(ac)2 as it is the case for PMS MK. One could expect a reaction of Si-H with Sn(ac)2 upon the formation of Si-Sn units, as it is reported for the reaction of polycarbosilanes with acetylacetonates by Ishikawa et al. and shortly discussed by Ionescu et al. However, the formation of Si-metal units still needs direct
proof and thus no Si-Sn vibration could be assigned in the FTIR spectrum of the modified sample. Similar to PMS MK, the spectrum of modified RD-684a exhibits additional absorption bands related to the acetate ligands: v = 1339, 1570 cm\(^{-1}\) (C-O), v = 1380 cm\(^{-1}\) (C-CH\(_3\)) and v = 1514 cm\(^{-1}\) (C=C) and at v = 600 cm\(^{-1}\) (SiOC-H) and at v = 667 cm\(^{-1}\) (Sn-O).\(^{[5-10]}\) Although the exact reaction mechanism between Sn(ac)\(_2\) and polysiloxane RD-684a remains unclear, the important finding here is that the transformation of the modified polymer into a SiOC/Sn composite occurs comparable to that of the Sn(ac)\(_2\)-modified PMS MK.

The X-ray diffraction patterns of SiOC\(_{MK}\)/Sn and SiOC\(_{RD}\)/Sn are shown in Figure 2. Both ternary silicon oxycarbides are found to be fully X-ray amorphous as previously reported,\(^{[2,14,15]}\) whereas the Sn-modified samples exhibit the presence of metallic tin, formed in-situ upon pyrolysis. TEM analysis of both nanocomposites (Figure 3 and Figure 4) illustrates the presence of spherical crystalline Sn inclusions within the amorphous matrices. In the case of SiOC\(_{MK}\)/Sn (Figure 3) a large number of homogeneously dispersed, ultrafine Sn grains with size below 10 nm and a few ones with larger size that tend to agglomerate are found. For SiOC\(_{RD}\)/Sn (Figure 4), Sn precipitations with an average diameter of 45 nm are observed, likewise homogeneously distributed throughout the SiOC matrix. In addition a very few ones with lager diameter are present as well. For both composites, the EDS inset in the high resolution micrographs outlines the amorphous matrices as composed of Si, O and C. The Cu-signal originates from the support grid. The round-shaped Sn particles in both nanocomposites indicate that liquid tin shows a poor wettability for the SiOC matrix, as it is known for ceramics with covalent bonding.\(^{[16,17]}\) Similar features were recently found in the case of SiCN/Fe-based nanocomposites, which exhibited sphericalshaped Fe\(_5\)Si\(_3\) precipitates dispersed within a SiCN matrix.\(^{[13,18]}\)
Interestingly, the crystallization of tin oxide was not found upon pyrolysis of the modified precursors, unlike in other cases, where the modification of polysiloxanes with metal alkoxides, acetylacetonates or acetates was shown to lead to a precipitation and crystallization of the corresponding metal oxides, i.e. to the formation of SiOC/MOₓ nanocomposites (M = Al, Ti, Zr, Hf, Nb, Ta, Mn and Lu, Gd).

However, in all cases a similar behavior with respect to the polymer-to-ceramic transformation is expected, which leads in a first step to single phase-amorphous SiMOC intermediates, subsequently partitioning into amorphous SiOC/MOₓ. Recently we have shown that the phase composition and crystallization of those SiOC/MOₓ ceramics strongly
depend on the redox stability of the metal oxide towards the C-CO system. As in the investigated systems carbon is found to be present in excess, the relative stability of the systems C-CO and M-MOX determine the phase composition and the crystallization of these SiMOC materials. Zirconia, hafnia or gadolinia are stable with respect to their carbothermal reduction to metallic elements, whereas tin oxide, which is assumed to be generated intermediary upon pyrolysis of the tin acetate-modified polysiloxanes, is not stable under carburizing conditions. As tin does not form any silicides or carbides, the formation of SiOC/Sn nanocomposites is consequently related to the carbothermal reduction of SnO to Sn.

**Electrochemical Results**

Electrodes prepared from the composites were cycled by PCGA protocol in order to follow the incremental capacity as a function of the lithiation/delithiation potential and to trace the electrochemical activity of the embedded tin. Differential capacity plots for the first, second and fifth cycles are shown in Figure 5. For both samples, in the cathodic branch cycle two and five, strong and characteristic signals for Li-Sn alloying are visible: For SiOC\textsubscript{MK}/Sn at 0.64 V (LiSn) and 0.38 V (Li\textsubscript{22}Sn\textsubscript{5}) and for SiOC\textsubscript{RD}/Sn at 0.66 V (LiSn) and 0.42 V (Li\textsubscript{7}Sn\textsubscript{2}). The presence of these signals reveals the electrochemical activity of the tin phase. Note that there is a distinct difference in the detected final alloy stage between SiOC\textsubscript{MK}/Sn and SiOC\textsubscript{RD}/Sn. For SiOC\textsubscript{MK}/Sn the highest alloy phase Li\textsubscript{22}Sn\textsubscript{5} is reached, whereas for SiOC\textsubscript{RD}/Sn alloying stops with Li\textsubscript{7}Sn\textsubscript{2}. In the anodic branches, several signals for Li-Sn dealloying appear around 0.44, 0.60, 0.61, 0.70 and 0.78 V. The numerous anodic peaks indicate that dealloying occurs via multifold reactions and stages and cannot simply be considered as the reverse reaction-path of the observed alloying process.

![Figure 5. Differential capacity plot for a) SiOC\textsubscript{MK}/Sn and b) SiOC\textsubscript{RD}/Sn; first, second and fifth cycle are shown.](image-url)
The suppression of the formation of Li$_{22}$Sn$_5$ in the SiOC$_{RD}$/Sn composite is related to the restriction of the alloy expansion within the embedding matrix. The volume increase for Li$_7$Sn$_2$ only amounts 75%, as compared to Li$_{22}$Sn$_5$ resulting in less mechanical stress transference to the matrix. This lower load can be well accommodated by the soft SiOC$_{RD}$ without degradation. The stiff and fragile SiOC$_{MK}$ on the contrary, is not able to withstand the alloy expansion and thus ruptures and pulverizes during cycling. Consequently, a considerably higher volume is available for the Li-Sn expansion and the highest known Li-Sn stoichiometry Li$_{22}$Sn$_5$ is finally formed.

Table 1. Overview of the first cycle charging, discharging and irreversible capacity and coulombic efficiency (\(\eta\)) for SiOC$_{MK/RD}$/Sn and pure SiOC$_{MK/RD}$ reference electrodes.

<table>
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<th>(C_{\text{ch}}) [mAhg$^{-1}$]</th>
<th>(C_{\text{dis}}) [mAhg$^{-1}$]</th>
<th>(C_{\text{irr}}) [mAhg$^{-1}$]</th>
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<td>371</td>
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</table>

*Reference electrodes were prepared and cycled similar to the composites.*

From the elemental analysis data, a theoretical capacity for the SiOC$_{MK}$/Sn and SiOC$_{RD}$/Sn composites can be calculated, taking the mass ratio SiOC:Sn into account. For the sample SiOC$_{MK}$/Sn, the theoretical capacity of Li$_{22}$Sn$_5$ (994 mAhg$^{-1}$) and for SiOC$_{RD}$/Sn that of Li$_7$Sn$_2$ (790 mAhg$^{-1}$) is considered. The capacity contribution of the SiOC matrices is estimated from the reference electrode data (Table 1). Accordingly, the expected capacities for the composites amount 395 mAhg$^{-1}$ (SiOC$_{MK}$/Sn) and 647 mAhg$^{-1}$ (SiOC$_{RD}$/Sn). For SiOC$_{RD}$/Sn the estimation is in excellent agreement with the experimentally registered value of 651 mAhg$^{-1}$. The experimentally found higher capacity of SiOC$_{MK}$/Sn (566 mAhg$^{-1}$) can be explained by two factors: Firstly, for the calculation of the theoretical capacity of SiOC$_{MK}$/Sn composite the data found for pure SiOC$_{MK}$ was applied. However, the presence of dispersed metallic tin nanoparticles might increase the electronic conductivity and/or the availability of carbon phase within the SiOC matrix and thus increases the composite capacity in a non-linear way with respect to the calculation. A similar phenomenon was reported for mixtures of carbon-poor SiCN ceramic and graphite.$^{49,50}$ In addition the free carbon content in the sample was found slightly enhanced, providing additional Li-ion storing sites. Secondly, the higher capacity can be attributed to the partially reversible storage of less-ionic lithium species in micropores$^{[24]}$ as well as in the vicinity of SiO$_4$ units.$^{[25]}$ These reactions take place at the potential E $<$ 0.1 V giving a well pronounced peak (c.f. Figure 5a)). The lithium storage in places close to the oxygen is most probably responsible for the high first lithiation capacity (1190 mAhg$^{-1}$) but due to a strong interaction between lithium and oxygen it brings about a poor reversibility.

**CONCLUSIONS**

A new method of preparation of SiOC/Sn composite materials with outstanding stability during electrochemical insertion and extraction of lithium ions is presented. The SiOC/Sn nanocomposites were synthesized via pyrolysis of the polysiloxanes PMS MK and RD-684a modified with tin(II)acetate at 1000 °C. Upon pyrolysis, metallic Sn segregates within the SiOC ceramics, forming spherical nanoparticles of different sizes. In the case of modified PMS MK, the composite predominantly contains Sn inclusions below 10 nm, whereas for modified RD-684a an average grain diameter of around 45 nm is found. Electrochemical
measurements reveal a superior performance and cycling stability of the carbon-rich and therefore rather soft SiOC_{RD}/Sn material (C_{max} = 651 mAh^{-1} and stable), while fast capacity fading is registered for the carbon-poor and therefore stiff and fragile SiOC_{MK}/Sn composite (C_{max} = 566 mAh^{-1}, not stable). Incremental capacity measurements outlined different final lithium-tin alloy stages, strongly depending on the embedding matrix and its properties. Li_{22}Sn_{5} and Li_{7}Sn_{2} are formed in SiOC_{MK}/Sn and SiOC_{RD}/Sn, respectively. Our study emphasizes that a single-source precursor approach has two crucial advantages for synthesizing Sn-containing nanocomposites as high-performance material for Li-ion battery anode application: i) it provides the in-situ generation of Sn nanoparticles homogeneously dispersed within the SiOC host and ii) the choice of suitable single-source precursors allows for tailoring of the matrix properties (i.e. carbon-content/stress compliance), to be able to withstand the volume expansion of the Sn precipitates upon alloying with Li.

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Structure Research

In the year 2014, we setup a commercial Molecular Beam Epitaxy (MBE) system and tested it on the system Bi/Si(001). The MBE system (Riber EVA 32 R&D) is capable of evaporating three metallic sources at a time and uses a mass spectrometer for deposition control. Thin metallic samples can be grown in Ultra High vacuum and transferred, without braking the vacuum, into a small x-ray baby chamber.

We refurbished an image plate detector with onsite readout (OBI) and set up a Debye-Scherrer diffractometer. The diffractometer will be finally used together with a 6 Tesla magnet to perform x-ray diffraction experiments in a magnetic field.

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Research Projects

Magnetostriction measurements using x-ray diffraction (LOEWE-RESPONSE, 2014-2016)

Development of electrode materials for high capacitance devices (IDS-FunMat, 2013-2015)

Phase transitions in thin potassium sodium niobate films (IDS-FunMat, 2012-2015)

Influence of biaxial strain and texture on the elastic properties of Barium Strontium Titanate thin films (AvH Lab Partnership, 2013-2015)

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Bimodal domain configuration and wedge formation in tetragonal Pb[Zr1-xTix]O-3 ferroelectrics
Use of a laboratory diffractometer to perform anomalous scattering experiments on epitaxial films

Vikas Shabadi, Marton Major, and Wolfgang Donner

Alloy ordering in complex materials is always hard to detect, since different ordering schemes could lead to the same superlattice reflections. One way to distinguish between different atom types involved in the ordering is the use of anomalous scattering. Here the energy-dependence of the atomic scattering factors is used to label certain atoms in a scattering experiment. In most cases synchrotron radiation is used to tune the scattering factor, since the continuous spectrum from a bending magnet can be filtered by a Si double monochromator. In a laboratory source, the continuous bremsstrahlung is too weak to be used for monochromatization. However, the characteristic radiation can also be used in some cases to tune the scattering factors for maximum contrast.

In a recent experiment, we looked at the B-site ordering in a double-perovskite epitaxial film. In Bi$_2$FeCrO$_6$, the Fe and Cr ions might be able to arrange themselves in a long-range B-site ordering scheme, thereby modifying the magnetic behavior of this potential multiferroic. The ordering of Fe and Cr ions would lead to superstructure reflections whose intensities would be proportional to the square of the difference of the respective form factors for iron and chromium.

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**Fig. 1:** Left: (a) The real and imaginary parts of the atomic form factors of iron and chromium atoms plotted against energy of radiation. (b) The calculated value of the $|f_{Fe} - f_{Cr}|^2$ contrast plotted as a function of the radiation energy. Right: $\theta - 2\theta$ measurements of the BFCO film grown on STO (001) substrate measured along the perovskite [111] direction at two wavelengths – Co $K_{\alpha}$ and Co $K_{\beta}$.
Figure 1 (left) shows the real and imaginary parts of the form factors for iron and chromium in a range of energies that is accessible with laboratory sources. The contrast between iron and chromium scatterers in a diffraction experiment can be calculated from this form factors and is shown in fig.1 (left, b). The largest obtainable contrast can be obtained using an x-ray energy just below and above 7000 eV. These happen to be the emission energies of cobalt K\(_\alpha\) and cobalt K\(_\beta\) radiation. Therefore we set up an experiment on a four-circle diffractometer using a HOPG monochromator that was tuned to cobalt K\(_\alpha\) and cobalt K\(_\beta\), respectively.

Figure 1 (right) shows the results of two scans along the [111]-direction of a 25 nm thin BFCO film epitaxially grown on strontium titanate. In the case of an ordering scheme involving iron and chromium ions, we would expect a factor of seven difference in the relative intensities of the superlattice reflections (see fig.1 (left,b)). In contrast, the relative intensities were approximately the same for the two extreme energies. This is the proof that the origin of the observed (111) superlattice reflection can not be the ordering of iron and chromium. Instead, we propose a superstructure of oxygen octahedra tilts and/or bismuth ion displacements.

The above experiment showed the capability of laboratory x-ray sources, which can be used (albeit in rare cases) to perform experiments that were thought to be possible on at Synchrotron radiation facilities.
Materials Analysis

The Materials Analysis group participates in two of the five Research Clusters of the Technische Universität Darmstadt: New Materials and Nuclear and Radiation Science. On the one hand the group is concerned with the characterization of self-synthesized modern materials, on the other hand with effects on materials caused by exposition to detrimental influences like ion irradiation. The research aims for clarification of the correlation of materials properties and synthesis or exposition parameters, respectively, by investigation of the elemental composition and the chemical binding.

Current research topics are:

**Advanced 3-D Nanoobjects: Nanochannels, -wires, -tubes, and –networks:** In collaboration with the GSI Helmholtz Centre for Heavy Ion Research, nanoporous membranes are formed by ion irradiation of polymer foils producing latent ion damage tracks which are chemically etched to nanochannels. These ion track (nano) filters can be used for filtering particles from liquids, collecting aerosols, for gas separation, and for analyzing small (bio)molecules. In the latter case, the nanochannel walls are chemically modified so that the nanochannel sensor becomes sensitive and selective to certain molecular species. Apart from polymer-based nanochannels, anodically oxidized aluminium (AAO) is used. Filling the polymer or AAO nanochannels galvanically with metals, such as copper, gold or platinum, and dissolving the templates, nanowires are formed. Here, different metal deposition conditions are used in order to obtain monometal but also multimetal (e.g. CuCo- and CuFe) nanowires. By redox-chemical reactions, the nanochannel walls can be coated with metal or metal oxide films, such as Ni, Cu, Ag, Au, Pt, Pd, and ZnO, SnO\(_2\), TiO\(_2\), In\(_2\)O\(_3\), Fe\(_x\)O\(_y\). Thus, nanotubes can be formed. Here, different morphologies are available, ranging from smooth compact nanotube walls to nanoporous walls to rough or peaked structures. When the nanochannels are crossed, the resulting nanowires are interconnected, forming nanowire networks. Dimensions, surface topography, microstructure, and crystallinity of these nanostructures are investigated. Macroscopic properties such as thermal stability, electrical conductivity and catalytic activity are analysed. Additionally, the obtained properties are evaluated with respect to applications as sensors, for gas flow or acceleration measurements, catalysts, for chemical reactions in microreactors, or electrodes in fuel cells.

**Thin film and coating deposition and analysis:** In thin film and coating technology, the identification of chemical compounds, phases and binding conditions is of basic importance. Surface modifications and layer deposition are performed via a plasma process. With plasma immersion ion implantation (PIII) it is possible to alter several surface properties by ion implantation. Different gaseous species are used such as oxygen, nitrogen and hydrocarbons, depending on the property to be modified, e.g. hardness, wear resistance, lifetime and biocompatibility. Using hydrocarbon gases films of diamond-like carbon (DLC) are deposited. Research topics are the adhesion of the DLC films to different substrates and the influence of the addition of different elements, especially metals, to the DLC films. The films are investigated for their chemical and phase composition, microstructure, adhesion, and in relation to biological applications, tribological properties, corrosion and wear protection of metal substrates, wettability, and temperature stability. Since the PIII
technique is also suitable for complex shaped substrates, the treated substrates also include samples such as tubes, where the focus is on the treatment of their inner surfaces.

**Materials in radiation fields:** Irradiation of materials with energetic particles (protons, heavy ions) and electromagnetic radiation (X-rays, gamma-rays) may lead to degradation of the materials' properties. This happens to components in space vehicles, in nuclear facilities and in particle accelerators. Polymers with their covalent bonds are particularly sensitive towards ionizing radiation. Polymide, vinyl polymers and fiber-reinforced polyepoxides, which are components of superconducting beam guiding magnets at the future FAIR synchrotron and storage rings, oxides such as alumina which are used as beam-diagnostic scintillator screens, and semiconductor components such as CCDs are irradiated and characterized for their properties, such as polymeric network degradation, mechanical strength, electrical resistance, dielectric strength, and optical properties. Apart from basic questions on material's degradation mechanisms by energetic radiation, the investigations are used to estimate service life-times of the materials/components.

### Staff Members

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Research Projects

Preparation of lead free piezo electric thin films (LOEWE centre AdRIA 2008–2014)

Beam diagnosis and radiation damage diagnosis – Scintillator materials for high current diagnosis (BMBF/GSI 2012–2015)

Beam diagnosis and radiation damage diagnosis – radiation damage of accelerator components made out of plastics and countermeasures (BMBF/GSI 2012-2015)

Preparation of rare earth free nano rods (LOEWE Response, 2014-2016)

1D based sensors for gases and magnetic fields 1D-SENSE (BMBF, 2014-2016)

Publications


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Green Synthesis of Gold Nanotubes by Electroless Deposition

Eva-Maria Felix, Wolfgang Ensinger

In Materials Analysis group, the synthesis of one-dimensional nanoobjects, such as nanowires and nanotubes, by electroless plating is studied. By applying this special synthesis route to ion-track etched templates, nanotubes of different metals could be produced. The electroless deposition method displays a simple, yet highly versatile, wet-chemical route. This reaction is controlled by the heterogeneously autocatalyzed reduction of metal complexes on arbitrary substrates. A metastable redox pair consisting of a metal complex and a reducing agent is the core of each electroless plating solution. Due to the metastability, these components only react on catalytically active surfaces, leading to the deposition of metal films on suitable substrates. To suppress homogeneous nucleation of particles in solution a complexing agent is added. [1]

Fig. 1: Scheme of Au nanotube fabrication. [2] (1) Irradiation of polycarbonate foil with heavy ions. (2) Selective etching of ion-tracks for nanopore formation. (3) Sensitization of polymer with Sn²⁻-ions. (4) Activation with Ag⁺-ions. (5) Surface-conformal metal film deposition by electroless plating. (6) Removal of polymer template by chemical dissolution.

From the perspective of sustainable chemistry, electroless plating exhibits a number of promising characteristics. On the one hand, the plating solutions are usually based on water, depositions can be performed at ambient temperatures and require only simple equipment. On the other hand, the use of highly toxic chemicals impedes the classification of most electroless deposition processes as green syntheses. For instance, in Au plating bath formulations often the hazardous ligand cyanide is employed. Furthermore, most of the standard reducing agents, such as hydrazine, sodium borohydride, aminoboranes or formaldehydhyde are carcinogenic and toxic [1,3].

Taking the cost-efficient production advantages and modernizing the method with regard to sustainability and environmental health, one can facilitate a green synthesis of Au nanotubes [1]. The exchange of complexing and reducing agents leads to a "greener" synthesis of the nanotubes. The green synthesis is based on the environmentally benign reducing agent ascorbic acid and the complexing agent EDTA used for the fabrication of gold nanotubes in porous polymer templates. The key action to achieve well-defined nanotubes of high aspect ratio (>100) was the reduction reaction rate in order to ensure homogeneous metal deposition within the extended inner template surface. Depending on the plating time, nanotubes with porous as well as closed walls could be synthesized [1].
The porous and closed Au nanostructures (Fig. 2 A and C) were successfully implemented as sensors in the amperometric detection of hydrogen peroxide. The generally improved performance of the porous nanotubes compared to their closed counterparts was attributed to their better accessible and larger surface area (cp Fig. 3). The limits of detection of porous to closed Au nanotubes constitute 2.3 µM vs. 8.2 µM, the maxima of linear range 11.7 mM vs. 8.0 mM, response times 3.6 vs. 5.5 s, and sensitivities 770 µA mM cm$^{-2}$ vs. 360 µA mM cm$^{-2}$ [1].

References:

Experimental Simulation of Materials’ Damage by Highly Energetic Ions of Heavy Elements in Galactic Cosmic Rays

Anton Belousov, Umme Habiba Hossain, Vincent Lima, Wolfgang Ensinger

Devices operating in space, e.g. in satellites or space-based telescopes, are being hit by galactic cosmic rays (GCR). These include so-called HZE-ions, with High mass (Z) and energy (E). They consist of elements mainly of the first row of the transition metals of the periodic system of elements, such as Fe. These ions penetrate deeply into the materials and deposit a large amount of energy, typically several keV per nm range. No chemical bond can stand such energies; as a consequence, serious damage is created. Apart from structural damage, it is the generation of electrical charges which is a problem, particularly for semiconductor-based devices.

The conditions in space can be experimentally simulated by generating the HZE ions in an ion accelerator. For this purpose, the Universal Linear Accelerator UNILAC and the Heavy Ion Synchrotron SIS of the GSI Helmholtz-Centre for Heavy Ion Research can have been used.

In order to simulate the damage and the resulting change in functionality of semiconductor devices generated by HZE ions, an MOS field effect transistor chip was irradiated in operando with 500 MeV/n Tantalum ions under observation with an oscilloscope. The results show the direct influence of irradiation on the device performance parameters, such as the threshold voltage $V_{th}$, which is the minimum voltage needed for conductance between source and drain. Fig. 1 shows $V_{th}$ as a function of the number of ions. First, a considerable shift to lower values is observed. Passage of ionizing radiation leads to charge build up in the SiO$_2$/Si interface. When the chip had received about 4.4E10 ions/cm$^2$, the trend in $V_{th}$ development changed and the values started jumping. This example shows the deterioration of the device with loss of proper functionality under ion irradiation.

Apart from semiconductors, electronic devices contain polymers as electrical insulators. When they are hit by HZE-ions, their polymeric network is degraded and the polymers transform to compounds closer to graphite with progressively losing their insulating character. Due to bond breaking, small volatile molecules are cut out of the polymer. As a result, the polymer loses mass. This is shown in Fig. 2 for the aliphatic polymer polyvinylformal (PVF) which has been irradiated with different numbers (fluence) of gold...
ions in the energy range up to 11 MeV/n. It turns out that the polymer loses more than half of its mass when it has been hit by several $10^{12}$ ions per cm$^2$.

Fig. 2: left: Residual mass of polyvinyl formal as a function of number of ions; right: optical band gap as a function of number of ions [2].

Another observation is the shift in optical band gap due to formation of conjugated CC double bonds, leading to colouration and also to a reduction in electrical insulation, see Fig. 2 right side. Fig. 3 shows as an example a typical molecular degradation mechanism of PVF, with the scission of the side chain of the acetate subunit and of the acetale subunit, leading to the volatile fragments CH$_3$CHO and H$_2$CO, CO$_2$ and CO, resp.. These fragments and others, particularly hydrogen, were found with Mass Spectrometry. The resulting formation of the C=O and C=C groups was shown by Infrared Spectroscopy [3].

Fig. 3: Molecular degradation mechanism of polyvinylformal subunits polyvinylacetate and polyvinylacetale under irradiation with high energy heavy ions [2,3].

Such investigations are important for estimating both service life-times of devices in long-term space missions and of ion accelerator components, such as those of the future Facility for Antiproton and Ion Research (FAIR) which is presently being built next to GSI.

References:

Materials Modelling Division

The research of the Materials Modelling Division is focused on multi-scale modelling of defect structures in functional oxides, energy materials, nanostructured metals and glasses. We are combining electronic structure calculations with atomistic modelling methods and continuum descriptions depending on time and length scales involved. Quantum mechanical calculations based on density functional theory are used for electronic structure calculations. Large-scale molecular dynamics with analytical interatomic potentials are the method of choice for studying kinetic processes and plastic deformation. Kinetic lattice Monte-Carlo simulations are extensively used for simulations of diffusional and transport processes on extended time scales. The group is operating several HPC-computers and has access to the Hessian High Performance Computers in Frankfurt and Darmstadt.

The current research topics are:

- **Energy materials**
  - Interfaces in Li-intercalation batteries
  - Si-based anodes for intercalation batteries
  - Dislocations in CIS/CIGS absorber materials
  - High-pressure phases of nitrogen
  - Creep resistant alloys (Mo-Si-B)

- **Functional oxides**
  - Aging and fatigue of ferroelectrics
  - Lead free relaxor materials
  - Transparent conductive oxides
  - Theory of superconducting materials

- **Mechanical properties of nanostructured metals and glasses**
  - Plasticity of metallic glasses with secondary phases
  - Structure and properties of nanoglasses
  - Creep resistant SiOC-based glasses
  - Plasticity of nanocrystalline alloys

Within the Bachelor program the Materials Modelling Division is offering classes on thermodynamics and kinetics as well as defects in materials and programming techniques. In the master program we are teaching lectures on theoretical materials science, lab classes on simulation methods and several elective courses.
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Research Projects

Mikrostruktur und Stabilität von Nanogläsern (DFG AL 578/6-2, 2013-2015)

Quantenmechanische Computersimulationen zur Elektronen- und Defektstruktur oxidischer Materialien (SFB 595, Teilprojekt C1, 2007-2014)

Atomistische Computersimulationen von Defekten und deren Bewegung in Metalloxiden (SFB 585, Teilprojekt C2, 2003-2014)
Phänomenologische Modellierung von Injektion, Transport und Rekombination in Bauelementen aus organischen Halbleitern sowie aus nichtorganischen Ferroelektrika (SFB C5, 2003-2014)

Erforschung der Phasenstabilität und Niederdrucksynthese von festem Stickstoff mittels atomistischer Computersimulationen und Experimenten (DFG AL 578/3-2, 2010–2014))


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Microstructure control for thin film solar cells - Virtuelles Institut (MICO-TFSC) (HZB VH-VI-520 2012-2017)

Tailoring nanoscaled features in novel steels for high-temperature applications using ion beam modification (ODS-HiT)s) (HGFJRG-411, 2014-2016)

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* A triangulation-based method to identify dislocations in atomistic models. 

[2] Nikolaenko, Yuri M.; Kuzovlev, Y. E.; Medvedev, Yuri V.; Mezin, N. I.; Fasel, Claudia; Gurlo, Aleksander; Schlicker, L. ; Bayer, Thorsten J.M. ; Genenko, Y.A. 
* Macro- and microscopic properties of strontium doped indium oxide. 
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Plastic deformation of a porous bcc metal containing nanometer sized voids.

Atomistic simulation of tantalum nanoindentation: Effects of indenter diameter, penetration velocity, and interatomic potentials on defect mechanisms and evolution.

[6] Stukowski, A.
Computational analysis methods in atomistic modeling of crystals.
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Comparative study of A-site order in the lead-free bismuth titanates $M_{1/2}$Bi$_{1/2}$TiO$_3$.

[8] Yampolskii, S. V.; Genenko, Y.A.
Magnetic cloaking by a paramagnet/superconductor cylindrical tube in the critical state.

Low temperature heat capacity of a severely deformed metallic glass.

Surface potential at a ferroelectric grain due to asymmetric screening of depolarization fields.

Atomistic investigation on the structure–property relationship during thermal spray nanoparticle impact.
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Structure and Properties of Amorphous LiPON Electrolyte by First-Principles Simulations

Sabrina Siculo and Karsten Albe

Amorphous materials belonging to the family of Lithium Phosphorus Oxynitrides (LiPON) are increasingly popular solid electrolytes for thin-film Li-ion batteries. RF-sputtering of a lithium orthophosphate target in a nitrogen plasma leads to the deposition of amorphous glasses [1]. Besides a fairly high ionic conductivity and very low electronic conductivity, LiPON exhibits remarkable chemical and physical stability to such an extent that its use as a protective layer for cathode materials has been suggested [2]. Rationalization of the transport properties rests on a valid structural model for these glassy structures, whose simulation represents a main challenge from a computational point of view also because of their non-trivial compositions. The motivation for this study is the desire to assess the structural, electronic and transport properties of an amorphous member of the LiPON family with non-trivial composition and cross-linking.

Fig. 1: Structure of LiPON. Color code: green, Li; purple: P; red: O; light blue: N

The issue of structure prediction for a given composition is a longstanding problem even for the simplest crystalline solids. The problem is further complicated in the case of an amorphous material, as the potential energy landscape that describes the glassy region exhibits a large number of minima of varying depths. We circumvented the problem by using an evolutionary algorithm [3] to find a stable structure for a given composition and subjecting it to ab-initio simulated annealing to create disorder (Fig. 1) [4].

In this work we present the results of Density Functional Theory calculations. After characterizing the structural and electronic properties of our material, we addressed the issue of ionic conductivity by calculating the defect formation energies of neutral and charged point defects. We assume that the formation of defects is triggered by the diffusion of lithium species through the interfaces with the electrodes, and therefore we calculated defects formation energies referenced to two different Li reservoirs, namely a typical anode, metallic lithium, and a typical cathode, lithium cobalt oxide (LCO) [4]. The Fermi level
dependences of the formation energies of Li\(^{(+)}\) interstitials and vacancies for the two different Li reservoirs are shown in Fig. 2. The left panel shows that when metallic Li is considered as a lithium reservoir, excess interstitials are far more stable than vacancies across the whole band gap. Neutral interstitials are competitive species at the interface between LiPON and Li (green area) and their formation results in the chemical reduction of LiPON and the disruption of the network, compatibly with what experimentally observed [4,5]. When LCO is chosen as the lithium reservoir, vacancies are more stable than interstitials for values of $E_F$ far from the valence band edge and in particular at the Fermi level of the interface between LiPON and LCO (red area). For both reservoirs, charged defects dominate over neutral ones, as expected of an ionic conductor. The inversion of stability of Li\(^{+}\) interstitials and vacancies at the interface with metallic lithium and LCO, respectively, is consistent with the spontaneous flow of Li ions from the anode (Li) to the cathode (LCO) through the solid electrolyte during the battery discharge.

In summary, we have performed for the first time atomistic simulations of an amorphous electrolyte with non-trivial structure and composition. The investigation of the defects thermodynamics provides insights into the dominant species that govern the ionic conductivity of the material and rationalizes the experimental findings about the occurrence of side reactions at the interface with the anode.

Fig. 2: Defects formation energies as a function of the Fermi level energy with respect to metallic Li (left) and LCO (right). The VBM coincides with $E_F = 0$ and the grey areas represent the valence and conduction bands. The green and red areas locate the estimated positions of the Fermi level at the interface with Li and LCO according to Ref. [5], respectively.

References:

Developing Advanced Data Analysis Tools for Atomistic Simulations

Alexander Stukowski

Materials properties and the underlying mechanisms at the microscale are often linked to structural changes in a material and the presence, formation, or interaction of different crystal defects, for example dislocations and grain boundaries. Molecular dynamics (MD) and other atomistic modeling techniques are powerful and well-established tools to study such processes with full atomic detail and without restrictive assumptions. However, the accurate and robust identification of defects in a material is essential for understanding, interpreting, and quantifying atomic-scale processes occurring in such simulations, because the MD simulation method does not explicitly keep track of these materials features.

A related question is how to bridge atomistic descriptions of a solid with higher-level models and coarser materials descriptions. Classic continuum concepts such as strain and stress fields, or mesoscale concepts such as grain boundary networks, dislocation densities, and the geometry surface of a solid can have a different meaning or definition at the atomic level. In many cases new theoretical concepts, metrics, and the corresponding computational tools [1] must be developed to obtain such high-level information from atomistic simulations and to make it available for a treatment with classic theories – or as input to coarser materials models.

Recently, our research group developed several automated techniques, which greatly simplify the analysis of structures and processes found in molecular dynamics simulations of crystalline materials. Some of these software tools and algorithms will be presented in the following.

Dislocation Extraction Algorithm

Dislocations theory and related simulation techniques such as discrete dislocation dynamics (DDD) explicitly treat dislocations as line objects, which interact with the stress field, move, or undergo reactions according to an appropriate set of rules. However, many important effects such as split dislocation cores, nucleation, and interaction of dislocations with other defects may be difficult or impossible to incorporate in such models. Whenever microscopic details of dislocations behavior are essential, fully atomistic simulations become necessary. The so-called Dislocation Extraction Algorithm (DXA) [2], developed in our group, provides a bridge between both worlds. Starting from the atoms forming a material, it can reconstruct the three-dimensional network of dislocation lines contained in the crystal at each instant of time. In addition, it automatically determines the Burgers vector of each dislocation segment [3]. It can therefore provide a detailed picture of dislocation structures in a material and allows to measure the dislocation density – something that is not possible

Figure 6: Left: Original atomistic visualization of the plastic zone in a nanoidentation MD simulation of SrTiO₃. Right: Dislocation line structure obtained after processing with the Dislocation Extraction Algorithm.
in the original atomistic picture, because here the total dislocation length is an ill-defined quantity.

**Surface reconstruction algorithm**

Similar arguments have motivated the recent development of a computational method that can generate a geometric representation of the external and internal surfaces of a solid. The primary application of such a technique is to measure the internal surface area and solid volume fraction in molecular dynamics simulations of materials containing voids, e.g. nanoporous gold structures or consolidated nanoparticles. Because surfaces and voids can have great influence on the mechanical properties and, at the same time, are changed by the deformation of a material, monitoring the surface area, surface curvature distribution, and porosity are important analysis tools.

We have developed a parallelized algorithm [4] that constructs a closed two-dimensional manifold from the atomic positions, representing the geometric surface of a solid. The algorithm is based on the tetrahedral Delaunay tessellation and makes use of a mathematical concept known as alpha complex. The resulting surface mesh provides a well-defined means to determine the surface area and solid volume of atomistic solids with complex shapes or pore topology. Figure 7 shows surface evolution data obtained with this method for a simulated nanoporous gold structure under compressive deformation.

**OVITO – The Open Visualization Tool**

To fully leverage the capabilities of analysis algorithms like the DXA, tailored visualization tools need to be developed that provide the capability to simultaneously display, inspect, and interrelate the original atomistic data and the derived microstructure representations. Within the past years, an open source program package [5] has been developed in Darmstadt, which serves as an integration platform for various new data visualization and analysis techniques. With already several thousands of users in science and academia, the software is rapidly establishing itself as one of the standard tools in the field of atomistic materials modeling.

**References:**

Magnetic Cloaking by a Finite Size Paramagnet/Superconductor Tube in the Meissner and the full critical states

S.V. Yampolskii, Y.A. Genenko

Cloaking of electromagnetic waves as well as of static magnetic fields is one of the most intriguing effects revealed by metamaterials [1-3]. A magnetic cloak is expected to produce a dual effect: it must not distort the external field outside the cloak, thus being “invisible” for external observation, and, on the other hand, has to protect its inner area from the external field penetration. Different cloak designs have been already proposed, particularly, in the forms of multilayered [4] or bilayered [5] magnet/superconductor hollow cylinder. An essential component of the proposed hybrid cylindrical designs is the inner superconducting layer which was assumed until quite recently to be an ideal diamagnetic medium with zero effective permeability in both analytical and finite-element considerations [3, 5]. This assumption is, however, unrealistic because of (1) finite field penetration depth which can be comparable with superconductor thickness and (2) massive magnetic flux penetration followed by formation of the critical state typical of magnetic shielding applications.

We have studied theoretically static magnetic cloaking properties of a realistic bilayer paramagnet/superconductor cylindrical tube with finite thicknesses of both superconducting and magnetic constituents being in the flux-free Meissner state (Fig. 1, left) or in the full critical state (Fig. 1, right).

![Fig. 1: Cross-sectional view of a hollow superconductor cylinder in the Meissner state (left) or in the full critical state (right), covered by a coaxial cylindrical magnetic sheath and assumed to be in the cloaking regime. The vertical solid lines x=0 in the right panel denote the boundaries between the superconductor regions with negative and positive directions of the critical current. The direction of the applied magnetic field H_0 is also indicated.](image)

Let us consider an infinitely long hollow superconducting cylinder of thickness \( d_S \) and radius of a coaxial hole \( R_0 \) enveloped in a coaxial cylindrical magnetic sheath of thickness \( d_M \) with relative permeability \( \mu > 1 \). This structure is exposed to an external constant magnetic field \( H_0 \) perpendicular to the cylinder axis as shown in Fig. 1. In the case of Meissner state, the distributions of the magnetic field in the structure were found by exact solving the coupled London and Maxwell equations for superconducting and magnetic
media, respectively, supplied by the appropriate boundary conditions [6]. It was established that in the Meissner state the system with the finite penetration depth $\lambda$ of magnetic field into a superconductor never completely protects the inner region (a central hole) from the penetration of weak external field. On the other hand, a non-distorted uniform magnetic field outside the cloak can exist in a wide range of values of the permeability and thickness of the paramagnet sheath related with the other parameters of the system by equation

$$\frac{(\mu+1)^2 - (\mu-1)^2}{(\mu^2 - 1)(R_2^2/R_1^2 - 1)} = I_0(R_1/\lambda)K_2(R_0/\lambda) - K_0(R_0/\lambda)I_2(R_0/\lambda),$$

(1)

where $R_1 = R_0 + d_S$ and $R_2 = R_0 + d_M$. In particular, cloaking feature is exhibited for both cases of thick and thin superconductor layers. At the same time, the magnetic moment of such a bilayer tube vanishes under the cloaking conditions (1) (as well as all higher multipole moments) making this object magnetically undetectable. Furthermore, initial penetration of magnetic flux into a superconductor in the form of single vortices produces rather small paramagnetic moment of the system, thus breaking the perfect cloaking only slightly.

With further increase of applied field, magnetic flux enters the superconducting constituent through the superconductor/magnet interface and, according to the Bean concept of the critical state, induces shielding currents of density $j_c$ in the regions of flux penetration. At fields $H_0$ equal or higher than the field of full flux penetration in the superconducting constituent,

$$H_{fp} = H_{fp}^0 \left[1 + \frac{(\mu-1)(2\mu-1)}{6\mu} \frac{R_2^2 - R_1^2}{R_1^2} + \frac{12\mu}{R_1^2 R_2^2} \right]$$

(2)

(here $H_{fp}^0 = (2j_c/\pi)(R_1 - R_0)$ is the same field for an unshielded superconductor cylinder), the superconductor layer is completely penetrated by the magnetic flux, i.e., is in the full critical state (see Fig. 1, right). It was established that in this case the magnetic field outside the cloak remains undisturbed at applied field $H_d$ determined by equation

$$\frac{H_{cl}}{H_{fp}^0} = \frac{4\mu}{3(\mu^2 - 1)} \frac{R_1^2 + R_2^2 + R_0^2}{R_2^2 - R_1^2}.$$

(3)

Notice that this is qualitatively different from the case of cloaking in the Meissner state, where the cloaking conditions were field-independent. The calculated typical dependence of $H_{cl}/H_{fp}$ on the relative permeability $\mu$ and on the thickness $d_M$ is shown in Fig. 2 for the case of $d_S = R_0$. At the same time, under the cloaking conditions (3), the magnetic moment of the bilayer structure vanishes (as well as all higher multipole moments) making this object magnetically undetectable as in the case of cloaking in the Meissner state. And finally, when the applied field equals to the field of full flux penetration, such a system also completely protects the inner region (a central hole) from the penetration of the external field, thus revealing in this case cloaking in its ideal, “dual” form. At higher applied fields, the central hole of the structure is never protected from the magnetic flux penetration.
Fig. 2: The dependence of the ratio $H_{cl}/H_{fp}$ on the relative permeability $\mu$ and on the thickness $d_m$ of the magnet sheath for the thickness of superconductor layer $d_S = R_0$.

Thus, both features of cloaking and of complete magnetic undetectability by a paramagnet/superconductor cylindrical structure, realized in the Meissner state, can be reestablished by increase of an applied magnetic field to a certain value in the range of the superconductor full critical state. These results are expected to hold also for low frequency ac fields as is generally the case for superconducting shielding.

References:

Finite-element simulations of hysteretic ac losses in a magnetically coated superconducting tubular wire subject to an oscillating transverse magnetic field

Y.A. Genenko, H. Rauh, S. Kurdi

Cylindrical heterostructures made up of superconductor and paramagnet constituents find use in various technological applications, power transmission cables involving second-generation high-temperature superconductor multistrand wires and electromagnetic coils based on coated conductors or bulk MgB₂/Fe filaments playing a prominent role thereby. The combined magnetic shielding properties of these kinds of constituents render beneficial effects like a reduction of hysteretic ac losses or an enhancement of the (field-dependent) critical current, to name just a few. Given specific material characteristics and geometries, coaxial superconductor/paramagnet heterostructures may even disclose the exceptional hallmarks of magnetic cloaks.

Although multistrand wires and electromagnetic coils are obviously exposed to transverse magnetic fields, only few works seem to have addressed the electromagnetic behaviour of tubular superconductor/paramagnet heterostructures in oscillating applied magnetic fields. An elaborate numerical study of the shielding properties of such heterostructures, for example, assumes a nonlinear current-voltage characteristic of the superconductors and a reversible field-dependence of the permeability $\mu$ of the magnetic constituents, apart from including the field-effect on the critical current density $J_c$. Hence, configurations with the paramagnet layers placed outside the superconductor constituents exhibit much stronger shieldings than those with the respective layers placed inside. Significant progress exemplifies a theoretical analysis of the electromagnetic response of a cylindrical tubular wire, an infinitesimally thin superconductor constituent subject to an oscillating transverse magnetic field. In a description where the superconductor is delineated by the sheet current $J$, with a (field-independent) critical value $J_c$, the profiles of the magnetic field, the field of first penetration of magnetic flux and the hysteretic losses that ensue pave the way towards research on the electromagnetic behaviour of tubular heterostructures embracing superconductor as well as paramagnet constituents. We here extend this ansatz for a coated superconductor tubular wire, with a coaxial paramagnetic support, by making recourse to Bean’s model of the critical state and carrying out a finite-element analysis.

Let us first define the magnetostatic problem by considering a cylindrical superconductor/paramagnet heterostructure of bilayer geometry, viz. an infinitely extended type-II superconducting tubular wire of radius $R$ and thickness $d$ on an outer paramagnetic support of respective thickness $D$, buffered by an infinitesimally thin non-magnetic layer in between, and subject to a transverse magnetic field with strength $H_a$. We choose dimensions that second-generation coated conductors typically display, i.e. $R=5mm$, $d=2\mu m$ and $D=250\mu m$, understanding that the paramagnetic support is delineated by a finite permeability $\mu$. Since $d << R$, we ignore spatial variations of the induced current on a length scale less than $d$ and, for mathematical convenience, regard the superconducting tube as infinitesimally thin too, so that its physical state can be characterized by the sheet current $J$ alone. In conformity with Bean’s model of the critical state duly adapted to the geometry of the tube for a polar orientation of the applied magnetic field, magnetic flux penetrates from both equatorial sides of the tube into two cylindrical segments, of angle $2\gamma$,
where the sheet current $J$ equals the constant $J_c$; flux-free regions prevail in the polar segments of the tube, where the normal component $H_n$ of the magnetic field disappears. For an oscillating applied magnetic field with amplitude $H_a$, the penetration of magnetic flux and the consequential dissipation of energy, per cycle and unit length of the tube, $U_{ac}$ can be determined by resorting to the quasistatic approach.

Fig. 1 illustrates the distribution of the magnetic field around the magnetically coated superconducting tubular wire for a fixed permeability and three progressive values of the amplitude of the applied magnetic field. At $H_a/H_c=2.0$, the interior of the wire is completely shielded from the magnetic field by the paramagnetic support on top of the superconducting tube: the lines of the magnetic field are refracted at the wire's outer surface and guided around inside the paramagnetic support (Fig. 1(a)). As the amplitude of the applied magnetic field is increased to $H_a/H_c=3.0$, magnetic flux starts to enter the superconductor constituent tangentially from both equatorial sides, threading two cylindrical segments of the tube, with refraction of the lines of the magnetic field at the wire's inner surface too, before the interior of the wire accommodates the flux (Fig. 1(b)); an effect which, for $H_a/H_c=4.0$, gets more pronounced still, exhibiting intensified refraction towards the poles (Fig. 1(c)). The paramagnetic support thus always plays a prominent role in the distribution of the magnetic field. Its shielding capacity defines an effective, reduced field, $H_\mu$ that acts on the wire’s superconductor constituent.

![Fig. 1: Lines of the magnetic field around the superconducting tubular wire coated with an outer paramagnetic support of relative permeability $\mu/\mu_0=10$, when the normalized amplitude of the applied magnetic field (a) $H_a/H_c=2$, (b) $H_a/H_c=3$ and (c) $H_a/H_c=4$. The support together with the tube is indicated by black contour lines.](image)

The variation of the half-angle of flux-penetration with the amplitude of the applied magnetic field, depicted in Fig. 2(a) for a range of values of the permeability, confirms these traits: penetration of magnetic flux sets in at $H_a/H_c=\pi/2$, like for an isolated superconducting tube, with a monotonic rise and a tendency towards saturation in a fully flux-filled state, as the amplitude of the applied magnetic field augments. Increasing the permeability to account for a paramagnetic support results in a duplication of this course, yet rescaled to higher values of the amplitude of the applied magnetic field. Similar traits
recur in the variation of the hysteretic ac loss with the amplitude of the applied magnetic field shown in Fig. 2(b). The known threshold for the onset of the hysteretic ac loss appears, followed by a sharp monotonic rise with a turn to a shallow maximum, given a vacuum environment. Increasing the permeability to model a paramagnetic support thus yields a shift to higher values of the amplitude of the magnetic field, but also a considerable reduction in strength. It should be noted that these results can be calibrated to high accuracy against the expressions

\[ \gamma = \gamma(H_\mu/H_c) \quad \text{with} \quad H_\alpha/H_\mu = 1 + 0.048 \left( \mu/\mu_0 - 1 \right) \]

and

\[ U_{ac}/H_\alpha^2 = 8\pi\mu_0 R^2 \gamma \left( H_\mu/H_c \right) \quad \text{with} \quad \log \lambda_\mu = -0.325 \log^2 \left( \mu/\mu_0 \right), \]

the chosen values of the geometrical parameters of the wire implied, making recourse to the functional dependences \( \gamma(H_\alpha/H_c) \) and \( f(H_\alpha/H_c) \) deduced for the isolated superconducting tube, either from analytical theory or numerical analysis.

**Fig. 2:** Dependence of (a) the half-angle of flux penetration \( \gamma \) and (b) the normalized hysteretic ac loss \( U_{ac}/H_\alpha^2 \) on \( H_\alpha/H_c \), the normalized amplitude of the magnetic field applied to the magnetically coated superconductor tubular wire, in the computationally accessible regimes, for four different values of the relative permeability of the outer paramagnetic support \( \mu/\mu_0 \) identified on the curves. The full triangles, squares and circles elucidate the scaling properties of the respective physical observables; the dashed lines represent analytical results for the isolated superconducting tube.

In conclusion, our finite-element simulations reveal a spectacular shielding effect of an outer paramagnetic support in a tubular superconductor/paramagnet heterostructure subject to an oscillating transverse magnetic field, with a possible reduction of hysteretic ac losses by orders of magnitude, depending on the magnetic permeability and the amplitude of the applied magnetic field.
Physics of Surfaces

Physical properties of surfaces and interfaces are relevant in nearly all areas of science and engineering. The fundamental interactions between surfaces, the surrounding fluid and small objects in the fluid play an important role, for example in biology, biotechnology, mechanical engineering, or petroleum geology. The common research question can be expressed as “How does the interplay between physical surface properties, surface and interface chemistry, and fluid flow affect the entire system?”

We follow an interdisciplinary approach focusing on physical, chemical and biological properties of surfaces. The connection between surfaces and fluids is of particular interest because it is essential in many technological systems. Our research portfolio targets at a better understanding of the interplay between surface patterning (morphological and chemical) and modification with the fluid flow. Experimental methods such as microscopy, microfluidics, or spectroscopy are essential tools.

Staff Members

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Research Projects

Smart Interfaces (DFG 2010-2014)
Bioborides (DFG 2012-2014)
Wetting of DLC Coatings (Industry 2012 – 2015)
Wafer cleaning (Industry 2012 -2016)
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[1] Controlling Polymerization Initiator Concentration in Mesoporous Silica Thin Films
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[4] Preparation of Ag-containing diamond-like carbon films on the interior surface of tubes by a combined method of plasma source ion implantation and DC sputtering
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   JOURNAL OF PHYSICAL CHEMISTRY C Volume: 118 Issue: 9 Pages: 4656-4663 Published: MAR 6 2014
Surface versus Volume Properties on the Nanoscale: Elastomeric Polypropylene

Agnieszka Voss, Robert W. Stark, Christian Dietz

Recent developments in the synthesis of smart polymeric materials that allow for the modification of various mechanical properties have triggered remarkable scientific and economic interest. A prominent example from the broad field of polymers is that of thermoplastic elastomers, also known as thermoplastic rubbers, which are often used in high-impact plastics, pressure-sensitive adhesives and polymeric foams. To better understand the relationship between the internal structure and the macroscopic material behavior, it is essential to quantify the composition and mechanical properties with nanometer resolution, not only on the surface but also in the bulk material. Polypropylene is a thermoplastic material, and its elastomeric properties depend on the crystallinity of the polymer. Polypropylene with a high degree of crystallinity is an important structural material with outstanding properties, this is, low-cost production, low weight, and high tensile strength, and is widely used in the machinery and automotive industries as well as in electrical and civil engineering. The elastomeric properties of the material thus can be tuned by balancing the content of atactic and isotactic polypropylene in the semi-crystalline polymer. For full property mapping, various advanced AFM techniques have been proposed to simultaneously acquire the surface topography and maps of the nanomechanical properties of polymeric materials, but atomic force microscopy measurements are inherently restricted to the surface. Thus, the volume must be inspected in a layer-by-layer manner to obtain the structural and mechanical information within the material. 

Figure 1. Mechanical surface properties of an unetched ePP sample measured via quantitative nanomechanical mapping: (a) Approach (blue) and retract (red) curve of a single force versus separation measurement. The derived physical quantities are highlighted in the graph. (b) Topography image. The bright areas correspond to the crystalline regions of the polymer, whereas the dark areas correspond to the amorphous regions. (c) Corresponding error map for the feedback loop maintaining a constant peak force of 8 nN during imaging. (d) Elasticity map of ePP derived from a DMT model fit. The crystals appear bright due to their high stiffness. (e) Adhesion map of ePP. Please note the inverted contrast. The force necessary to separate the tip from the amorphous regions is greater than the adhesion force on crystalline regions. (f) Map of the energy dissipated between the tip and the sample surface during one oscillation cycle. The determined cantilever/tip properties were $k = 6.6 \, \text{N/m}$ and $R = 8 \, \text{nm}$.

bulk of a sample. This nano-tomographic information is of particular interest for semi-crystalline polymers because not only the nanomechanical properties but also the number, shape and spatial arrangement of the crystalline component contribute to the macroscopic elasticity and the material strength.

In this work, we use the peak-force-tapping mode to correlate the morphology of elastomeric polypropylene (ePP) with quantitative mechanical properties, such as elasticity, adhesion, and dissipation. Successive etching provides these physical properties for the layers located beneath the surface. This combination allowed an unprecedented nanomechanical characterization of the volume morphology of elastomeric polypropylene. The diversity of the mechanical properties of elastomeric polypropylene, which were derived pixel-wise from the force-versus-distance data, as illustrated in Fig. 1(a), is illustrated in Fig. 1(b)-(f). In the topographical image (Fig. 1(b)), two distinctive regions are visible, which can be allocated to the crystalline (bright) and amorphous portions (dark) of the semi-crystalline polymer. The root mean square (rms) roughness of the surface was approximately 4.0 nm. Fig. 1(c) shows the corresponding error map (peak-force error) for the feedback loop maintaining a constant peak force of 8 nN during imaging. The elasticity map (Fig. 1(d)) reveals the elastic modulus of the crystalline and amorphous regions as 154 ± 10 MPa and 91 ± 2 MPa, respectively. Local maps of adhesion and energy dissipated between the tip and the polymer sample are visualized in Fig. 1(e) and 1(f), respectively. The adhesion values for the crystals were 9.6 ± 0.9 nN, and the adhesion in the amorphous regions was 12.8 ± 0.4 nN. The respective values for the dissipation were 0.8 ± 0.2 keV on the crystals and 2.3 ± 0.3 keV on the amorphous regions. Note that the contrast in these images is inverted compared with that of Figs. 1(b) and (d) due to the higher adhesion and dissipation values measured on the amorphous portions compared with the crystalline portions of the polymer. Peak-force tapping also allows for the quantification of the sample deformation of the polymer surface. In contrast to the elasticity, adhesion, and dissipation values, we found significant differences between deformation values provided by the Nanoscope software and the values we manually extracted from single force curves. Please refer to the supplementary data to compare the deformation maps for different sample depths. However, the absolute values of these maps have to be treated with caution.

The morphology exhibits similarities to the bundled flowerlike structure at a later stage of crystallization, as described by Schönherr et al.

Our specimen showed a higher density of crystals at the surface than that of Schönherr et al. due to the higher content of [mmmm]-pentade of the polymer used in this work (36%). In addition, our samples were measured 1 week after preparation, when most of the isotactic polymer chains are expected to be in the crystal phase. The surface roughness of 4 nm is a consequence of the difference in the sample deformation/indentation due to the applied load of the tip between the crystalline and amorphous regions (see supporting information). This suggests that the sample surface is rather flat, and the measured roughness is mainly tip-induced instead. The localized DMT modulus measured on the amorphous portions of ePP was on the same order of magnitude as the values previously reported by Gracias et al. using tips with large radii of curvature (1 µm). The surprisingly low DMT modulus measured on the crystalline regions, however, can be explained by the presence of a thin amorphous layer covering the surface of the crystals.

Considering the geometric tip-sample convolution and the widths of single crystalline lamellae of 14 nm in the \(\alpha\)-modification and 7 nm in the \(\gamma\)-modification, the lateral resolution of the local elasticity map is striking because extremely thin crystalline connections (~15 nm; see red arrow in Fig. 1(d)) are visible in the DMT modulus image.
The high adhesion force and dissipated energy measured on the amorphous phase compared with those of the crystalline portions can be ascribed to the viscous properties of an amorphous polymer in the non-glassy state.\textsuperscript{22}

In summary, the combination of peak-force tapping and layer-by-layer etching of elastomeric polypropylene permitted us to find a thin amorphous layer on top of a freshly prepared film as well as regions of structural defects in the crystalline component of the material, which also appeared in the volume of these films. This inhomogeneity measured on the nanoscale can affect the mechanical stability of polypropylene on the macroscopic scale. The technique presented in this work can be applied to other classes of material and provides a basis for full quantitative nanomechanical tomography when combined with nanotomography.\textsuperscript{11}

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Joint Research Laboratory Nanomaterials

The Joint Research Laboratory Nanomaterials was established in the year 2004 as a joint project between the Institute for Materials Science (Technical University of Darmstadt) and the Institute of Nanotechnology (INT) at the Karlsruhe Institute of Technology (KIT). Its research focuses on the synthesis and characterisation of nanoparticles, nanoparticulate layers, nanoporous as well as dense nanoscale materials. Special interest lies in the determination of correlations between synthesis, interface and bulk properties and the macroscopic functional and structural properties. An important building block is the understanding of the surface, grain boundary and size effects on the physical material properties, which can be significantly different from classical crystalline bulk materials. Since a couple of years, the research has focused on energy materials (batteries, fuel cells). In addition, (reversible) topochemical reactions (chemical and electrochemical) are also under investigation, allowing for the tuning of material properties.

The materials of interest (nano- and microcrystalline powders) are produced by a variety of techniques, ranging from gas phase processes (chemical vapour synthesis (CVS) over aerosol based techniques (nebulized spray pyrolysis, NSP) to solid-state reactions (SSR). Additionally, a variety of techniques are available for the preparation of thin films: spin coating and different modifications of the chemical vapour deposition process (CVD).

A multitude of methods is available and in constant use for the characterisation of the as-synthesized powders and thin-films as well as their properties, among them X-ray powder diffraction, low-temperature N\textsubscript{2} adsorption, dynamic light scattering, low and high temperature impedance spectroscopy and cyclic voltammetry.

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Guest Scientists

B.Sc. Klaudia Kantarowska, Poznan University of Technology, Poland

Research Projects


Investigation of non-equilibrium phonon populations in biased metallic single-walled carbon nanotubes (DFG OR 262/1-2, 2011-2014)


Helmholtz Portfolio, Elektrospeicher im System – Zuverlässigkeit und Integration (325/20514659/NANOMIKRO, 2012-2014)

Förderung durch Mittel des Helmholtz Institut Ulm (2010-2014)

Publications

Nebulized spray pyrolysis of Al-doped Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolyte for battery applications, SOLID STATE IONICS, 263 (2014) 49.


CO$_2$-Laser Flash Evaporation as Novel CVD Precursor Delivery System for Functional Thin Film Growth, CHEMICAL VAPOR DEPOSITION, 20 (2014) 152.

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Advances in Battery Materials and Technologies

Oliver Clemens, Ruzica Djenadic, Miriam Botros, Christoph Loho and Horst Hahn

Lithium-ion batteries are the fastest growing and widely used type of batteries. Most of today electronic devices use batteries containing liquid electrolyte facing safety issues (e.g. dendrite growth, leakage, and flammability). Therefore, development of a Li-ion conducting solid electrolyte is a main focus of current battery research which potentially will lead to a safe all-solid-state battery. Additionally to the safety improvement, solid electrolytes offer stability over a broad electrochemical potential as well as a large temperature range. There are already several solid electrolyte materials with Li-ion conductivities equal or higher than liquid electrolytes, however, they are not stable over a wide potential range. The main challenge is to produce a material which will combine all of the mentioned properties.

Nebulized spray pyrolysis followed by consolidation and sintering was used for the first time to prepare ultra-fine grained ceramics of Al-doped garnet-based Li$_{7-3x}$La$_{2}$Zr$_{2}$Al$_{x}$O$_{12}$ (x = 0 – 0.25) (LLZO), which is a good candidate to replace the existing liquid electrolytes. The structural changes from the tetragonal (x = 0), via a mixture of the cubic and the tetragonal (x = 0.07, 0.10) to the cubic modification (x = 0.15 – 0.25) were observed (Figure 8a). Despite their low relative density preliminary ionic conductivities of the LLZO ceramics (Figure 8b), were found to be 1.2·10$^{-6}$ S cm$^{-1}$ and 4.4·10$^{-6}$ S cm$^{-1}$ for tetragonal and cubic LLZO at room temperature (Figure 8c), with activation energies of 0.55 eV and 0.49 eV, respectively. Further sintering optimization (i.e. use of spark plasma sintering) would reduce porosity and consequently improve conductivity of LLZO ceramics.

In addition to the above mentioned advantages, solid state electrolytes allow for battery miniaturization. The use of a liquid electrolyte in a thin-film battery may lead to leakage problems upon bending of the thin-film battery, which is the reason why solid state electrolytes are the material of choice. In order to build a complete all-solid-state thin-film Li-ion battery, the deposition of anode, cathode and solid state electrolyte thin-films has to be established. Recently, CO$_2$-laser flash evaporation was introduced as a novel precursor delivery system for a chemical vapor deposition (CVD) process. This so-called CO$_2$-laser assisted chemical vapor deposition (LA-CVD), shown in Figure 2, allows for the highly controlled growth of multicomponent, functional thin-films. The capabilities of LA-CVD were shown by means of LiCoO$_2$ thin-films, which showed reasonable electrochemical
performance as cathode material. The deposition of the solid state electrolyte LLZO thin-films was already successful, but needs further optimization.

Figure 9. Schematic illustration of a novel CVD precursor delivery system using CO2-Laser flash evaporation (LA-CVD).

Apart from advances in the field of lithium ion battery technologies, first results could be obtained in the field of new intercalation based fluoride ion batteries. This type of battery was first demonstrated by Fichtner et al., who used conversion type electrode materials M/MF₃ (M = e. g. Bi, Fe), i. e. materials which suffer from an entirely reconstructive structural change on charging/discharging. Although so far not reversible, we could show that a fluoride ion battery type setup (see Figure 10a) can be used to intercalate fluoride ions into perovskite type compounds, which was exemplarily shown on anion deficient BaFeO₂.₅ for the charging reaction. The successful intercalation was demonstrated by comparison to chemically fluorinated BaFeO₂.₅ by means of X-ray diffraction (see Figure 10b).

Figure 10. (a) Schematic illustration of the cell setup used for the electrochemical fluorination of BaFeO₂.₅, (b) Rietveld analysis of the BaFeO₂.₅ containing active electrode material after charging against CeF₃ to 4 V.
References:


Mechanics of Functional Materials

The research at the Division of Mechanics of Functional Materials is focused on the constitutive modeling and the simulation of functional materials and systems, for instance ferroic materials and lithium-ion battery electrodes. These materials are characterized by a coupling of multiple physical fields at a variety of length-scales. Their macroscopic responses depend on the microstructure and its thermodynamic kinetics. The main features of our research therefore include coupled fields (e.g. mechanical, electrical, chemical), microstructural evolution, mesoscopic material properties, and homogenization. Primary tools of our research are continuum models and Finite Element numerical simulations. Novel concepts such as phase-field models or Isogeometric Analysis are regarded to an increasing extent in our work.

Phase field simulation of the domain structure of ferroelectric ceramics

Ferroelectrics are widely applied as actuators, sensors, and memory devices due to pronounced dielectric and piezoelectric properties. One of the most distinguishing features of ferroelectrics is that they have different spontaneous polarization states. If an electric field is applied, switching between these states is possible and cycling loading of a specimen gives rise to nonlinear hysteretic behavior. Domain walls in ferroelectrics are transition areas between two domains with different polarization states. Three kinds of 180° domain walls are usually considered: "up-down", "head-to-head" and "tail-to-tail“. These domain walls are electrically neutral, positively charged, and negatively charged, respectively. Bound charges at domain walls however generate large electric fields, making the corresponding domain structure unstable.

There is significant effect of semiconducting properties on domain configurations in ferroelectrics, especially in doped materials. We formulated a phase field model and performed simulations for ferroelectrics with space charges due to donors, acceptors and electronic charge carriers. These show that head-to-head and tail-to-tail domain configurations in ferroelectric samples are both energetically favorable and stable due to screening by electrons or holes. The role of donors, acceptors and electronic charge carriers in the domain structure’s stabilization can hence be investigated in a quantitative way.

Simulation of the electrocaloric effect of relaxor ferroelectrics

Ferroic cooling has an attractive potential for the reduction of energy or material consumption. Solid state refrigeration using materials with a significant electrocaloric effect (ECE) is a viable alternative to concepts based on the magnetocaloric effect. We aim at investigating the underlying physics of the ECE, utilizing the tools of simulation. Through application/removal of an electric field on ferroelectrics under adiabatic conditions, the dipoles' alignment in the material, and hence the entropy, changes. In order to keep the total energy constant, the temperature must change in order to accommodate this change in entropy. By this means, the temperature variation can be obtained.

In order to investigate the ECE in both ferroelectrics and relaxor ferroelectrics, we proposed a lattice-based model consisting of a phase-field-type potential energy and a thermal energy. By combining the canonical and microcanonical ensemble, the ECE be evaluated directly rather than indirectly through the Maxwell relation. The random fields are
incorporated into the electrostatic energy to mimic the relaxor behavior. This shows that the temperature-induced polarization change is moderate in the presence of random fields, in contrast with the sharp change in conventional ferroelectrics. Our results also demonstrate that the freezing temperature is lowered by random fields, while it is promoted by the domain wall energy. Similarly, in presence of random fields the ECE peak is shifted to lower temperature and the peak value drops. The domain wall energy influences the ECE in an opposite fashion: here the peak appears at higher temperature and the peak value increases. Finally, it is exposed that the ECE increases in three different stages with the strength of the applied external field rather than in a simple linear manner.

Simulation of diffusion introduced stresses in the Lithium-ion batteries via Isogeometric Analysis
Mechanical degradation of the active material has been identified as one of the root causes of the degradation of Lithium-ion batteries, which can be observed macroscopically as a gradual fade of the batteries' capacity. The understanding of the damage processes in the electrodes' particles and their influence on the mechanical-electrochemical properties is hence of utmost importance.

The coupled electrochemical-mechanical processes in individual electrode particles are described by continuum mechanics and higher-order Finite Element procedures based on the concept of Isogeometric Analysis. Their application is motivated by higher-order gradient/coupling terms arising from the thermodynamics of the problem; it allows for stable implementation of the governing equations as well as for a unified treatment of diverse particle shapes and electrode geometries.

In addition to large deformations of certain electrode materials, in situ TEM observations have revealed the coexistence of lithium-poor and lithium-rich phases in the electrode particles during charge and discharge, which suggests that the concentration of Li-ion does not change gradually but experiences a gap at a certain interface. In order to capture this behavior, a Cahn-Hilliard phase-field model is currently developed that regards not only the chemical aspects of the phase separation and diffusion, but also viscoplastic effects.

Phase field modelling of ferromagnetic materials
Owing to their ferromagnetic property and magnetic-mechanical coupling, ferromagnetic materials find wide industrial application, for instance in magnetic data storage, sensors and actuators, transducers, or microelectromechanical systems. Viable applications and reasonable design of devices based on ferromagnetic materials are highly dependent on the fundamental understanding of these materials' microstructures. For materials with only ferromagnetic orderings, magnetic domains play a critical role in determining both their macro- and microscopic properties. If the magneto-mechanical coupling in the magnetostrictive materials is considered, a mechanical scheme for tailing the properties becomes possible. Ferromagnetic shape memory alloys (FSMAs), which possess both ferroelastic and ferromagnetic orderings, can produce large strains under an external magnetic field due to the martensitic phase transformation. By virtue of the coupling between the ferroelastic and ferromagnetic orderings, the ferroelastic martensitic variants can be manipulated by a magnetic field, whereas the ferromagnetic domains are sensitive to mechanical loading. Uncovering the evolution of these microstructures in the above-mentioned ferromagnetic materials is prerequisite for a deep understanding and control of
the microscopic mechanism and macroscopic properties. In our group, we focus on the phase field modeling towards this eternal goal.

**Continuum modeling and numerical simulation of multicrystalline materials**
The investigation of the hardening behavior and texture development in polycrystalline materials is of high interest to scientists. Experimental results show an intrinsic size-dependent response of such materials along with inhomogeneous plastic flow on the microscale level. The existence of boundary layers thereby plays an important role. Their influence on dislocation movement can be diverse, depending on, for instance, the misorientation of the adjacent grains. Study and prediction of these behaviors require incorporation of atomistic slip systems, gradient description and length scale parameters into the conventional plasticity models.

In the current study, a well-defined gradient crystal plasticity model is employed in order to investigate the size-dependent strengthening behavior and orientation gradient in a large-grain thin-sheet metal under mechanical loading. The constitutive description is an extended crystal plasticity model based on the microscopic force balance and is consistent with thermodynamic laws. Here, the free energy comprises two parts: a hyperelastic description for large-deformation compressible material and a function of dislocation densities via Peach–Koehler forces conjugate to corresponding glide directions. A non-local plastic flow rule in the form of partial differential equation is introduced, which incorporates energetic and dissipative gradient strengthening as well as latent hardening in a multi slip-system crystal. The proposed constitutive model is implemented in the FEM software ABAQUS via a user-defined element subroutine, where displacement components and dislocation densities are treated as nodal degrees of freedom.

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### Research Projects

- Phase-field simulation of ferroelectrics with defects (Project in DFG-SFB 595, 2012-2014)
- Simulation of the electrocaloric effect of relaxor ferroelectrics (Project in DFG-SPP 1599, 2013-2015)
- Isogeometric simulation of diffusion-induced stress in Lithium-ion battery electrodes (Project in GSC CE, 2013-2015)
Phase-field modeling of ferromagnetic materials (Project in LOEWE Response)

Continuum modeling and numerical simulation of the hardening behavior and the texture development of sheet metal under large plastic deformation (DFG-SFB 666, 2014-2016)

**Publications**

[1] Yi, Min ; Xu, Bai-Xiang :
A constraint-free phase field model for ferromagnetic domain evolution .  

[2] Zuo, Yinan ; Genenko, Yuri A. ; Xu, Bai-Xiang :
Charge compensation of head-to-head and tail-to-tail domain walls in barium titanate and its influence on conductivity .  

[3] Zuo, Yinan ; Genenko, Yuri A. ; Klein, Andreas ; Stein, Peter ; Xu, Baixiang :
Domain wall stability in ferroelectrics with space charges .  

[4] Stein, P. ; Xu, B. : 3D Isogeometric Analysis of intercalation-induced stresses in Li-ion battery electrode particles .  

[5] Schmitt, Ljubomira Ana ; Schrade, David ; Kungl, Hans ; Xu, Bai-Xiang ; Mueller, Ralf ; Hoffmann, Michael J. ; Kleebe, Hans Joachim ; Fuess, Hartmut :  
Bimodal domain configuration and wedge formation in tetragonal Pb[Zr1–xTix]O3 ferroelectrics .  

[6] Wang, Min-Zhong ; Xu, Bai-Xiang ; Gao, Yang :  
On the assumptions of the generalized plane stress problem and the Filon average .  
In: Acta Mechanica, 225 pp. 1419-1427. ISSN 0001-5970 [Article], (2014)

[7] Xu, Bai-Xiang ; von Seggern, Heinz ; Zhukov, Sergey ; Gross, Dietmar :  
An internal-variable-based interface model for the charging process of ferroelectrets .  
Phase field modelling of microstructure and switching dynamics in ferromagnetic materials

Min Yi and Bai-Xiang Xu

A continuum constraint-free phase field model is proposed to simulate the magnetic domain evolution in ferromagnetic materials. The model takes the polar and azimuthal angles ($\vartheta_1, \vartheta_2$), instead of the magnetization unit vector $m$ as the order parameters. In this way, the constraint on the magnetization magnitude can be exactly satisfied automatically, and no special numerical treatment on the phase field evolution is needed. The phase field model is developed from a thermodynamic framework which involves a configurational force system for $\vartheta_1$ and $\vartheta_2$. A combination of the configurational force balance and the second law of thermodynamics leads to thermodynamically consistent constitutive relations and a generalized evolution equation for the order parameters ($\vartheta_1, \vartheta_2$). The 3D finite element implementation of the constraint-free model is straightforward and, compared to the constrained model, the degrees of freedom are reduced by one. The model is shown to be capable of reproducing the correct damping-dependent switching dynamics, and the formation and evolution of domains and vortices in ferromagnetic materials under the external magnetic or mechanical loading. Particularly, the calculated out-of-plane component of magnetization in a vortex is verified by the corresponding experimental results, as shown in Figure 1.

![Figure 1](image)

Fig. 1 (a) Initial (top) and equilibrium (bottom) magnetization configuration in a free-standing sample. (b) The contour plot of $m_1$ in the equilibrium state. (c) Comparison of the measured and the calculated (c) $m_2$ along the line $CC'$ and (d) $m_1$ along the line $DD'$. Both $CC'$ and $DD'$ go through the vortex core in (b).

The mechanically induced switching dynamics in nanomagnets is studied by the constraint-free phase field model. Depending on the geometry of the nanomagnets, there exist two distinct switching modes: one is the coherent mode where the magnetization vector remains homogeneous during the switching, and the other is the incoherent mode where heterogeneous magnetization distribution occurs. For the application of nanomagnets-based logic and memory devices, the coherent mode is of great interest. Results show that a deterministic $180^\circ$ switching can happen if mechanical loading is removed once the magnetization rotates to the largest switching angle $\vartheta_m$, as shown in Figure 2. The switching time decreases with the magnitude of the applied strain. In addition, the $180^\circ$
switching under a combination of magnetic field and mechanical strain is also investigated. Simulations demonstrate that an optimum additional strain to reduce the switching time is around 0.2%. This work provides a foundation for the study of mechanically driven/assisted nanomagnets-based logic and memory devices.

Fig. 2 Mechanical loading history and temporal evolution of magnetization components during the 180° switching.
The Functional Materials (FM) Research Group’s main research interests are permanent magnets, and magneto caloric materials. The group works in close collaboration with the Project Group for Materials Recycling and Resource Strategy at the IWKS Fraunhofer Institute in Hanau, a group of which Prof. Gutfleisch is also chair.

2014 has been an exciting year for the FM Group with the start of the LOEWE funding from the Land Hessen to the RESPONSE project. This is a research program investigating the possibilities of Rare Earth reduced and free permanent magnets and involves several groups from the Material Science, Chemistry, and Mechanical Engineering Departments at TU Darmstadt. This is a vitally important research area needed for sustainable and environmentally-friendly technology development, and is an area where the FM Group is an international leader.

2014 has been a year of expansion for the FM Group. Whilst continuing with our current academic and industrial collaborations (for example the DRREAM, ROMEO, and REFREEPERMAG projects), the group has grown in size to include 8 postdoctoral researchers, a support team of 5 technical and administrative staff, 16 postgraduate students and more than 10 undergraduates.

This year has also been a strong year for publications. We have published more than 20 peer reviewed papers in various international journals listed in this document. The group has also been represented at international conferences. These included Intermag 2014 (Dresden) where Prof. Gutfleisch was the publication chair, Dr. B Kaeswurm was an Editor, Thermag 2014 (Victoria, Canada) where Prof. Gutfleisch was a member of the advisory board, and REPM2014 (the Rare Earth and Future Permanent Magnets and their Applications meeting in Annapolis, USA). Prof Gutfleisch will bring REPM to Darmstadt in 2016. The FM group has attended national meetings such as the annual DPG meeting in Dresden. Together with European Innovation Partnership (EIP) on Raw Materials our Group hosted the "Raw Materials University Day" in May 2014 at TU Darmstadt. The aim was to create awareness amongst undergraduate and graduate students of all disciplines about resource efficiency and working opportunities in the raw materials sector. Speakers from academics, industries and politics informed and discussed with about 200 students. The DGM-Fachausschuss Funktionsmaterialien was constituted also in May in Darmstadt with a workshop on „Phase change materials and tuneable properties” with well-known invited speakers.

We have also strengthened our international reputation through international collaborations, receiving visitors from Japan, the USA, and Europe for both short and long term stays. In addition to the groups research activities the FM Group has increased its contribution to teaching at the Department of Material Science. We now offer 3 lecture and 3 practical courses:

<table>
<thead>
<tr>
<th>Lecture Courses</th>
<th>Practical Courses</th>
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<tr>
<td>Material Science for renewable energy systems (M.Sci. in Energy Science)</td>
<td>Wärmeleitung (FPI)</td>
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<tr>
<td>Prof. Gutfleisch, Dr. Kaeswurm, Prof. Jaegermann*, Dr. Mankel*</td>
<td>Prof. Gutfleisch, Helbig, MSci,</td>
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</table>

* indicates a co-author.
This year another highlight for the group was a 3 day internal seminar in Grasellenbach. This was an opportunity to discuss our work in an informal setting and take part in team building exercises in the Bergstrasse countryside.

### Staff Members

**Chair**
- Prof. Dr. Oliver Gutfleisch

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- PD Dr. Michael Kuzmin
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- Ms Adjana Eils
- Mr Andreas Taubel
- Mr Tarini Mishra
- Mr David Brand
### Publications

<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s)</th>
<th>Title</th>
<th>Journal</th>
<th>Year</th>
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</table>


Temperature dependent Dy diffusion processes in Nd-Fe-B permanent magnets

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\textsuperscript{2} Vacuumschmelze GmbH & Co. KG, 63412 Hanau, Germany
\textsuperscript{3} Fraunhofer IWKS Project Group for Materials Cycles and Resource Strategy, 63450 Hanau, Germany

Nd-Fe-B permanent magnets have been coated with 0.6 wt.% Dysprosium and annealed at various temperatures to study the impact of the temperature dependent Dy diffusion processes on both the magnetic properties and the microstructure (figure 1). When optimum annealing conditions are applied the Dy processed magnets with initial coercivity of about 1100 kA/m yield coercivity increases which can exceed 400 kA/m without a significant reduction of the remanent magnetic polarization.

![Figure 1](image)

Figure 11: (a) Room temperature coercivity $H_c$ of bulk samples after diffusion treatment for 6 h at 600°C \( \leq T_a \leq 1050°C \) and (b) corresponding remanent polarization $B_r$. The coercivity and remanence of annealed reference samples without Dy – coating and the average $H_c$ and $B_r$ in the initial state prior to the annealing treatment are indicated for comparison.

The improved stability against opposing magnetic fields can be observed up to a depth of about 3 mm along the diffusion direction restricting the application of the Dy diffusion process to either thin magnets or magnets with tailored coercivity gradients (figure 2). While in the proximity of the Dy – coated surface, each grain has a Dy enriched shell with a Dy – content of around 6 at.\%, the Dy concentration decreases exponentially to about 1.8 at.\% after a diffusion depth of 400 µm and to about 1 at.\% after a diffusion depth of 1500 µm, as was found with WDX and STEM EDX, respectively (figure 3).
Figure 2: Dependence of the switching field variation $\Delta H_s$ on the distance $d$ to the Dy coated lateral surface of samples after a grain boundary diffusion process at $700^\circ C \leq T_a \leq 1000^\circ C$ for 6 h and of one sample in the initial state without diffusion process. Note that for better visibility, the error bars of $\Delta x = +/- 300 \mu m$ and $\Delta H_s = +/- 40 kA/m$ are not indicated.

In the vicinity of the Dy – coated surface, the mechanism of the Dy – shell formation is attributed to the melting/solidification of a heavy rare earth rich intermediate phase during high-temperature annealing. This is based on the observation that a constant Dy concentration over the width of the shells was found. Also an epitaxial relation between Dy – poor core and Dy – rich shell was observed by EBSD. This finding is supported by results obtained with Kerr microscopy.

Figure 3: Depth profiles of the Nd and Dy concentration after Dy – diffusion treatment at 900°C for 6 h. Each data point was obtained from a WDX measurement in a Dy enriched shell.

Acknowledgement

The authors would like to thank Dr. T. Woodcock for help with the EBSD analysis. Financial support from the Federal Ministry of Education and Research (BMBF) via the PerEMot project (No. 03X4621A) is gratefully acknowledged.

This work has been published: K. Loewe, C. Brombacher, M. Kätter, O. Gutfleisch, Temperature-dependent Dy diffusion processes in Nd-Fe-B permanent magnets, Acta Materialia, 83 (2015) 248-255.
Large reversible magnetocaloric effect in Ni-Mn-In-Co

T. Gottschall, K. P. Skokov, B. Frincu and O. Gutfleisch

The number of publications related to magnetic refrigeration drastically increased after the discovery of the giant magnetocaloric effect. There are only few material families showing a first-order magnetostructural transition near room temperature being mostly based on rare earth elements like Gd-Si-Ge and La-Fe-Si. Besides the Fe2P-type materials, Heusler alloys are among the most promising rare earth free magnetic refrigerants. Unfortunately, a large thermal hysteresis is typically observed in Heusler compounds, which has negative impact on a cyclic operation. In this work, we comprehensively investigate the hysteretic behavior of Ni-Mn-In-Co, showing ways and means to partially overcome the thermal hysteresis problem which allows to achieve large reversible magnetocaloric effects.

We report on the high irreversible adiabatic temperature change of -8K in a magnetic field change of 1.95 T in the Heusler compound Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2} showing a first-order magnetostructural transition which is visible in Fig. 1. Due to the large thermal hysteresis of 10 K, this high $\Delta T_{ad}$ cannot be obtained in a cyclic way but still the reversible magnetocaloric effect amounts to -3K (cyclic operation plotted in the inset) - an unexpectedly high value which compares to the $\Delta T_{ad}$ of La(Fe, Si, Co)$_{13}$. In order to reveal the nature of this high reversible magnetocaloric effect, in-situ temperature dependent optical microscopy of minor loops of thermal hysteresis has been done. An example of the martensite formation after different cooling cycles is shown in Fig. 2.

This research has received funding from funding from the DFG SPP 1599 and has been published: T. Gottschall, K.P. Skokov, B. Frincu, O. Gutfleisch, Large reversible magnetocaloric effect in Ni-Mn-In-Co, Applied Physics Letters, 106 (2015).

![Fig. 1: Different presentation of the field induced temperature change plotted together with the magnetic phase diagram (martensite start $M_s$, martensite finish $M_f$, austenite start $A_s$, and austenite finish $A_f$). The inset shows the reversible behavior under cycling.](image1)

![Fig. 2: Optical microscopy images of the initial sample in austenite state at room temperature (a), at low temperature in pure martensite state after first (b), second (c), and third (d) cool down.](image2)
Ion-Beam Modified Materials

Our research activities concentrate on processes related to high-energy heavy ions and their interaction with solids. The different topics cover destructive processes leading to radiation damage as well as using ions as structuring tool to fabricate tailored nanopores and nanowires. Ion beams used in this field have typically kinetic energies in the MeV to GeV range and are produced at large accelerator facilities such as the GSI Helmholtz Centre for Heavy Ion Research. During the last year we focussed on radiation-induced degradation of material candidates suitable for components to be used in high dose environments. This includes, various carbon based materials as well as molybdenum-carbide graphite (Mo-Gr) composites specifically developed for high-energy physics applications. This latter material shows a very promising combination of thermal, electrical, and mechanical properties for application in beam protection elements for high-power accelerators. Irradiation experiments were performed at the linear accelerator UNILAC of GSI using Au ions of about 10% velocity of light. The analysis of beam-induced modifications was performed by means of Raman Spectroscopy, X-ray diffraction, scanning electron microscopy and nanoindentation.

Nanotechnology with energetic ions benefits from the fact that each individual ion generates a nanometer wide damage trail along its trajectory. By selective chemical etching, the damage along the ion track is converted into an open high-aspect ratio channel. Because of the low threshold for track formation and for track etching, most commonly polymer films (typical thickness 10-30 µm) such as polycarbonate or polyethylene terephthalate are used. To modify the pore wall of track-etched nanochannels, e.g. for better wettability or controlled size reduction, we applied the rather new technique of atomic layer deposition (ALD). Layer by layer, shape-conform coatings of nanochannels were successfully performed with SiO2, TiO2 or Al2O3 as coating material.

Track-etched nanopores were also filled galvanically with different materials. By dissolution of the polymer membrane nanostructures are obtained which are of great interest for various applications due to their extremely high surface to volume ratio. We investigated e.g. plasmonic properties of Au or AuAg alloy nanowires. By selectively dissolving the silver component, highly porous nanostructures are synthesized and studied by infrared spectroscopy (see report below). By performing irradiations under tilted beam incidence from different angles, nanowire networks were fabricated. Given by the high degree of interconnections, they show excellent mechanical stability. Other nanostructures we synthesized were Bi-compound nanowires for thermoelectric applications as well as for testing properties of nanostructured topological insulators. Ion-track based semiconducting nanostructures are considered as excellent model systems to reach higher efficiencies for harvesting solar-energy via water splitting.

Staff Members

<table>
<thead>
<tr>
<th>Head</th>
<th>Prof. Dr. Christina Trautmann</th>
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<tr>
<td>PhD Students</td>
<td>Dipl. Ing. Loic Burr</td>
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<td>M. Sc. Janina Krieg</td>
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<td>Dipl. Ing. Michael F. Wagner</td>
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</table>
Bachelor Students

Ben Heider  Philipp Bolz  Christoph Reimuth  Pascal Simon

Research Projects

Fabrication of Bi-based nanowires and their characterisation with respect to thermoelectric properties (FIAS 2011-2014)

Fabrication of semiconducting nanowires using the ion track technology (Beilstein Institute, 2012 – 2015)

Fabrication and controlled surface functionalisation of mesoporous SiO2 materials and ion-track nanochannels (DFG, Forschergruppe (FOR 1583), 2011-2014)

Radiation hardness of carbon stripper foils under high current UNILAC operation (BMBF, Verbundforschung, 2012 – 2015)

Radiation hardness of carbon-based components for the future FAIR facility (GSI, 2012-2015)


Publications


Localized surface plasmons (LSP) are collective electronic oscillations on the surface of a nanoparticle that are excited by the electromagnetic field of light. They are promising candidates for sensing applications, such as surface enhanced Raman spectroscopy and infrared spectroscopy since they exhibit very high nearfield enhancement on the nanoparticle surface [1]. For molecules attached to a nanoparticle, these field enhancements result in intensified molecular signals in the corresponding spectra, if the wavelength of the surface plasmons is tuned to the vibrational one [2,3]. It has recently been shown that spherical porous nanoparticles exhibit excellent tunability of the resonance wavenumber and intensified local electric fields in the visible and near-infrared wavelength range that can be efficiently used for surface enhanced Raman spectroscopy (SERS) [4].

In this project, we analysed the plasmonic properties of smooth and porous Au nanowires by infrared (IR) spectroscopy. While spherical nanoparticles have a resonance wavenumber that is located in the visible spectral range, for nanowires with length of few µm the resonance is shifted to the middle infrared regime. We have used IR spectroscopy to investigate the plasmonic characteristics of the dipolare LSP mode in this wavelength range. These results are of great importance for further applications of the wires as substrates for surface enhanced infrared spectroscopy (SEIRS). Our nanowires were prepared by electrochemical deposition of gold into the pores of ion-track etched polymer templates [5]. 30 µm-thin polymer foils were irradiated with swift heavy ions at the linear accelerator UNILAC at GSI Helmholtz Center. Each ion creates a damage trail along its trajectory consisting of broken polymer chains and other defects. By wet-chemical etching each ion track is transformed into an open nanochannel. To prepare a cathode for the electrochemical deposition process, a thin Au layer was sputtered on one side of the foil. This layer was reinforced to obtain a stable layer by electrodeposition of Cu. Subsequently, the nanowires were electrodeposited in the nanochannels in a three-electrode configuration applying a potential of 1.1 V vs. Ag/AgCl reference electrode. As electrolyte we used 50 mM KAu(CN)₂ for the Au wires and 50 mM KAu(CN)₂ and 50 mM KAg(CN)₂ to grow AuAg alloy nanowires. Both electrolytes contained an amount of 0.25 M Na₂CO₃. A platinum coil served as anode.

After dissolution of the polymer, the nanowires were released from their backlayer by ultrasonification in dichloromethane and drop cast on a diamond substrate with lithographically attached Au grid for localization of the nanowires. The Au wires were annealed for 30 min at 200 °C. Finally, both types of wires were immersed into nitric acid for 3h. While the Au wires maintain their smooth morphology, the Ag content in the AuAg wires is dissolved resulting in porous wires consisting mainly of Au with a very small
amount of 5-10 % of Ag [6]. Figure 1 shows representative scanning electron microscopy (SEM) images of smooth and porous nanowires on a Si substrate that were prepared according to the described protocol.

![Figure 1: SEM image of a porous (a) and smooth (b) Au nanowire with very similar length of about 1 µm and diameter of about 100 nm.](image)

Microscopic infrared spectroscopy of our nanowires was performed at the synchrotron light source Soleil. We recorded relative transmission spectra using an IR beam polarized parallel to the longitudinal wire axis. The contribution of the substrate was considered by recording reference spectra of the bare substrate and a subsequent normalization. In Figure 2, the resonance wavelength determined from the transmission spectra are shown as a function of the nanowire length for smooth (black symbols) and porous (red symbols) nanowires. For the smooth nanowires, it is well known that the resonance wavelength is shifted to higher values with increasing wire length [7]. Our data nicely confirms this relationship for wires of length between 1300 and 2200 nm. For porous wires, our data also reveals increasing resonance wavelengths with nanowire length. However, the resonance is clearly red-shifted for a porous nanowire compared to a smooth nanowire of the same length due to the increased damping.

Finally, Figure 3 shows exemplarily relative IR transmission spectra corresponding to three smooth nanowires with length 1560 nm (red), 1680 nm (green) and 1930 nm (blue). All wires are coated with a 5-nm thin layer of CBP (4,4′-bis(N-carbazolyl)-1,1′-biphenyl) as test molecule for SEIRS measurements. The vibrational bands of this molecule are marked by vertical black lines. For the longest wire, the vibrational modes are detected between 1230 and 1603 cm$^{-1}$, while for the shortest wire only the vibrational modes between 1450 and 1603 cm$^{-1}$ are enhanced. Our data clearly show that fine tuning of the nanowire parameters is necessary to enhance specific molecular vibrations.

In conclusion, our measurements demonstrate that the resonance wavelength of a nanowire is tunable not only by its dimensions, but also by its surface morphology. Here a resonance shift of about 1000 nm is found for the porous wires with same dimensions as the smooth ones. For SEIRS, fine tuning of the nanowire parameters is important to efficiently enhance specific vibrational modes of the analyte. Further investigations to compare SEIRS enhancement of smooth and porous nanowires are ongoing.
Figure 2: Resonance wavelength versus nanowires length for smooth (black) and porous nanowires (red).

Figure 3: Relative transmission spectra for three nanowires coated with CBP with length L of 1560 nm (red), 1680 nm (green) and 1930 nm (blue). The dashed horizontal lines mark the vibrational modes of CBP.

References:
Molecular Nanostructures

The Joint Laboratory for Molecular Nanostructures has been established in 2011 to enhance the cooperation between the Institute for Nanotechnology at the Karlsruhe Institute of Technology (KIT) and the Institute of Materials Science at the Technische Universität Darmstadt. The research focus of the laboratory is on nanocarbon materials, in particular on carbon nanotubes and graphene. Carbon nanotubes and graphene are made of a single layer of covalently bonded carbon atoms. The electrical, optical, chemical and mechanical properties of these molecular nanostructures are outstanding, which is why CNTs and graphene are considered as important new materials for high speed electronics, optoelectronics, sensing, coatings, material reinforcements and other potential applications. The motivation of the Joint Laboratory is to gain new and important insights into carbon nanomaterials for enabling future applications. In 2013 funding for a Fourier-Transform Photocurrent-Spectromicroscope using a Supercontinuum-Lightsource has been provided by the German Science Foundation, the Institute of Materials Science and the President of the Technische Universität Darmstadt. The system has been commissioned in 2014 and is used to study the optoelectronic properties of materials and functional devices.

Staff Members

<table>
<thead>
<tr>
<th>Head</th>
<th>Prof. Dr. Ralph Krupke</th>
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<tr>
<td>Secretaries</td>
<td>Renate Hernichel</td>
</tr>
<tr>
<td>Master Students</td>
<td>Adnan Riaz (KIT)</td>
</tr>
</tbody>
</table>

Publications

[1] Michael Engel, Frank Hennrich, Ralph Krupke
Klein, Schnell, Hell
Physik in unserer Zeit 45 (2014) 243, 10.1002/piuz.201401364

Photocurrent Imaging of Semiconducting Carbon Nanotube Devices with Local Mirrors

[3] Wenshan Li, Feliks Pyatkov, Simone Dehm, Benjamin S. Flavel, Ralph Krupke
Deposition of Semiconducting Single-Walled Carbon Nanotubes using Light-Assisted Dielectrophoresis
Photocurrent Spectroscopy of (n,m) Sorted Solution-Processed Single-Walled Carbon Nanotubes
ACS Nano 8 (2014) 9324, 10.1021/nn503278d

[5] Daniel D. Tune, Adam J. Blanch, Ralph Krupke, Benjamin S. Flavel, Joseph G. Shapter
Nanotube film metallicity and its effect on the performance of carbon nanotube–silicon solar cells

Fabrication of carbon nanotube nanogap electrodes by helium ion sputtering for molecular contacts

Waveguide-Integrated Light-Emitting Carbon Nanotubes
Advanced Materials 26 (2014) 3465, 10.1002/adma.201305634

Projects

Waveguide-Integrated Light-Emitting Carbon Nanotubes

Svetlana Khasminskaya¹, Feliks Pyatkov¹,², Benjamin S. Flavel¹, Wolfram H. Pernice¹ & Ralph Krupke¹,²

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Photons propagating at the speed of light and outpacing electrons are the fastest carriers of information possible. For this reason a large proportion of mid- and long-distance electrical communication connections have been replaced by fiber optics in the last years. [1] The next evolutionary step will be the replacement of short-distance electrical connections by optical waveguides, which will thereby enhance on-chip data transfer rates, for example between processor and memory. [2] In order to achieve this goal the development of optical modules with large numbers of input and output channels will be required. Furthermore, on-chip generation of light will be needed to overcome foreseeable limitations in scalability and reproducibility. The then required level of integration will exceed the capacity of conventional integrated optical circuits [3] and will necessitate the use of waveguides with tight modal confinement, as well as the co-integration of active components. Since the beginning of the field it has been a challenge to couple light into nanoscale photonic waveguides. The current state-of-the-art solution is to launch light from external sources, such as lateral microcavity lasers, [4] vertical cavity surface emitting lasers, [5] or microdisc lasers, [6] into the photonic waveguides using fiber-coupling techniques. [7,8] These hybrid solutions, however, require sophisticated multilevel nanofabrication processes for producing the lasers, which is in marked contrast to comparably simple photonic waveguide processing techniques. Furthermore, tight alignment tolerances for the orientation of the waveguide with respect to an optical fiber core make such an approach unfeasible for large numbers of input/output ports. In this work we demonstrate efficient coupling of light emitted from an electrically-stimulated carbon nanotube into a photonic circuit by integrating a CNT with its long axis perpendicular to a photonic waveguide. We use electric-field assisted placement of solution-processed carbon nanotubes into pre-patterned structures containing the photonic waveguide, couplers, Mach-Zehnder structures and electrical wiring. Our approach allows for contacting multiple devices in parallel as a key step towards carbon based optical interconnects.

All the devices in this study consist of three basic components: carbon nanotubes, nanophotonic waveguides with coupler gratings, and metallic contacts. The device fabrication was performed in three steps. At first, 60 nm thick metal contacts with a gap of 1 μm were formed on a doped Si-wafer with SiO₂ (2 μm)/Si₃N₄ (0.2 μm) top layers, using electron-beam lithography and subsequent metal evaporation. Then, 500 nm wide waveguides terminated with focusing grating couplers were defined with electron beam lithography and formed by thinning 100 nm of the Si₃N₄ layer in between the metal contacts by reactive ion etching. Optimal etching parameters for obtaining the nominal etching depth in combination with minimal surface roughness were identified using reflectometry, scanning electron microscopy and atomic force microscopy.
Finally, single-walled carbon nanotubes were deposited in between the metal contacts and onto the waveguide by dielectrophoresis from an aqueous dispersion. Use of CNT based material enables us to employ nanotube solutions with high uniformity and sufficient CNT content for efficient contacting of many devices in one single deposition step, which is thus a procedure also suitable for waferscale fabrication. The dielectrophoretic force thereby ensures precise alignment of the nanotubes with the nanotube axis perpendicular to the direction of the waveguide, which guarantees optimal coupling of the emitted radiation into the underlying optical circuitry.

Fig. 1: Waveguide-coupled carbon nanotube light emitter. (a) Schematic cross-sectional view of the multilayer device structure (not to scale). The central waveguide is etched into the Si$_3$N$_4$ layer and runs along the x-axis. The carbon nanotube is in contact with the Au/Cr metal and the waveguide, and aligned with the y-axis. (b) False-colored scanning electron micrograph showing two metal electrodes (yellow) and a photonic waveguide (purple), bridged by a single-walled carbon nanotube. The inset shows the indicated region at higher magnification. Carbon nanotubes appear as thin white lines. (c) CCD-camera image of a device under electrical bias. Light emission is observed from the carbon nanotube emitter (E) and from the terminating coupler gratings C1 and C2, both connected with (E) through the waveguide (not visible). Superimposed is a grayscale image of the sample under external illumination to reveal the position of the electrodes. Scale bar 50 μm. (d) Sequence of carbon nanotube emission spectra recorded at (E) with increasing electrical power dissipation. The data is fitted with a Planck spectrum modulated by substrate induced interference fringes. The fit-parameter temperature is given for every curve.

The direct, near-field coupling of light from an electrically driven carbon nanotube into a waveguide, as opposed to the traditional far-field fiber coupling of an external light source,
opens up new opportunities to produce compact optoelectronic systems. Considering the wide range of different, structure dependent emission spectra of semiconducting and metallic carbon nanotubes and the continuing progress in the sorting of specific nanotubes, it seems possible to use nanotubes with specific emission lines in the near future. The use of electrically triggered on-chip nanotube emitters for signal transmission through extended waveguides and interferometers shown in this work provides the basis for next-generation nanoscale interconnects that can be seamlessly integrated with passive silicon photonic technology. While the emitters are operated at high currents in this work leading to incandescence, in contrast, tailored electroluminescent emission within the range of the CCD detector will be possible by employing CNT material with an S11 peak at shorter wavelengths. Alternatively extending the detecting window of the camera into the technologically relevant NIR-range could reveal electroluminescence at low current levels where thermal radiation is expected to be absent. This mode of operation will then enable to use tailored spectral emission in nanophotonic circuits by using a suitable type of carbon nanotube.

References:

Electromechanics of oxides

The group of J.-Prof. Kyle G. Webber focuses on the functional properties of oxides through combined experimentation and simulation. Of particular interest is the influence of external mechanical, electrical, and thermal fields on ferroelectricity and ionic conduction and the role of field-induced phase transitions. Together, macroscopic constitutive behavior and in-situ structural studies are used together to elucidate the microstructural processes responsible for the observed phenomena.

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Virginia Rojas

**Guest Scientists**  
Prof. Dr. George Rossetti

Research Projects

- Mechanical Compliance at Phase Transitions in Lead-Free Ferroelectrics (DFG 2011 – 2014)
- The Influence of Mechanical Loads on the Functional Properties of Perovskite Oxides  
  (DFG Emmy Noether Programme 2013 – 2018)
- The effect of electric field-induced phase transitions on the blocking force in lead-free 
  ferroelectrics (DFG SFB595/D6 2013 – 2014)

Publications

[1] **By: Wang, Zhiyang; Webber, Kyle G.; Hudspeth, Jessica M.; et al.**  
*Electric-field-induced paraelectric to ferroelectric phase transformation in prototypical polycrystalline BaTiO3*  
*APPLIED PHYSICS LETTERS* Volume: 105  Issue: 16  Article Number: 161903  Published: OCT 20 2014

[2] **By: Ehmke, Matthias C.; Schader, Florian H.; Webber, Kyle G.; et al.**  
*Stress, temperature and electric field effects in the lead-free (Ba,Ca)(Ti,Zr)O-3*  
*piezoelectric system*  
*ACTA MATERIALIA* Volume: 78  Pages: 37-45  Published: OCT 1 2014
Determination of the True Operational Range of a Piezoelectric Actuator
JOURNAL OF THE AMERICAN CERAMIC SOCIETY Volume: 97 Issue: 9 Pages: 2842-2849 Published: SEP 2014

[4] By: Brandt, David R. J.; Acosta, Matias; Koruza, Jurij; et al.
Mechanical constitutive behavior and exceptional blocking force of lead-free BZT-xBCT piezoceramics
JOURNAL OF APPLIED PHYSICS Volume: 115 Issue: 20 Article Number: 204107 Published: MAY 28 2014

Identification of crystalline elastic anisotropy in PZT ceramics from in-situ blocking stress measurements
JOURNAL OF APPLIED PHYSICS Volume: 115 Issue: 17 Article Number: 174102 Published: MAY 7 2014

[6] By: Seo, Yo-Han; Koruza, Jurij; Bencan, Andreja; et al.
Simultaneous Enhancement of Fracture Toughness and Unipolar Strain in Pb(Zr,Ti)O-3-ZrO2 Composites Through Composition Adjustment
JOURNAL OF THE AMERICAN CERAMIC SOCIETY Volume: 97 Issue: 5 Pages: 1582-1588 Published: MAY 2014

[7] By: Zhang, Hailong; Jo, Wook; Wang, Ke; et al.
Compositional dependence of dielectric and ferroelectric properties in BiFeO3-BaTiO3 solid solutions
CERAMICS INTERNATIONAL Volume: 40 Issue: 3 Pages: 4759-4765 Published: APR 2014

[8] By: Khansur, Neamul H.; Groh, Claudia; Jo, Wook; et al.
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[10] By: Dittmer, Robert; Jo, Wook; Webber, Kyle G.; et al.
Local structure change evidenced by temperature-dependent elastic measurements: Case study on Bi1/2Na1/2TiO3-based lead-free relaxor piezoceramics
JOURNAL OF APPLIED PHYSICS Volume: 115 Issue: 8 Article Number: 084108 Published: FEB 28 2014
[11] By: Franzbach, Daniel J.; Seo, Yo-Han; Studer, Andrew J.; et al. 
*Electric-field-induced phase transitions in co-doped Pb(Zr1-xTix)O-3 at the morphotropic phase boundary* 
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[12] By: Tan, X.; Young, S. E.; Seo, Y. H.; et al. 
*Transformation toughening in an antiferroelectric ceramic* 
ACTA MATERIALIA Volume: 62 Pages: 114-121 Published: JAN 2014

[13] By: Groh, Claudia; Franzbach, Daniel J.; Jo, Wook; et al. 
*Relaxor/Ferroelectric Composites: A Solution in the Quest for Practically Viable Lead-Free Incipient Piezoceramics* 
ADVANCED FUNCTIONAL MATERIALS Volume: 24 Issue: 3 Pages: 356-362 Published: JAN 2014
Mechanical stability of polar defects in ferroelectric perovskites

Florian Schader and Kyle G. Webber

Perovskite oxides are an important material class due to their numerous functional properties. One of the central advantages of the simple ABO$_3$ structure is the ability to significantly alter the functional properties with relatively small amounts of aliovalent and isovalent substitutions. Often, in the case of ferroelectric materials, aliovalent transition metals or rare-earth ions are selected that occupy either an A- or B-site, resulting in the formation or elimination of oxygen vacancies for charge compensation. Acceptor-doping with lower valence ions leads to the formation of oxygen vacancies ($V_O$), which has been shown to electrically “harden” the ferroelectric, [1] i.e., increase the electrical poling field and decrease the piezoelectric response, and result in aging. [2] These effects correspond closely to the development of an apparent internal bias electric field that depends on the concentration content as well as the thermoelectrical history of the sample. [3, 4] Studies on acceptor-doped (Fe$^{3+}$) Pb(Zr, Ti)$_3$O$_3$ (Pb(Zr$_{0.52}$Ti$_{0.48}$)$_{0.09}$Fe$_{0.01}$O$_3$) have also demonstrated the formation of nanodomains and increasing rhombohedral content in comparison to undoped materials. [5] Although donor-doped ferroelectrics are less understood, it is generally agreed that the observed enhancement in electromechanical properties and decreased electric poling fields may empirically be correlated with the decreased oxygen vacancy content, the formation of A-site vacancies, and changes in B-site valance. [1] This facilitates increased domain wall motion and, therefore, increased extrinsic contributions to the electromechanical properties.

Despite the importance of perovskite ferroelectrics and the number of investigations, there has been little work on the mechanical stability of polar defects. Understanding the role of mechanical fields on acceptor-doped ferroelectrics is important, as many applications apply mechanical loads during operation. There is, unfortunately, little experimental data available on the influence of mechanical stress on acceptor-doped perovskite ferroelectrics. Previous characterization of the macroscopic electromechanical and stress-strain behavior has shown that uniaxial compressive stress can result in ferroelastic switching [6, 7] as well as field-induced phase transitions in polycrystalline PZT. [8] Therefore, the primary aim of this work is to investigate role of stress on donor and acceptor-doped Pb(Zr, Ti)$_3$O$_3$ through the characterization of the stress- and temperature-dependent direct piezoelectric response.

Experimental Methodology

Materials

The samples used in this study are widely used, industrial important and commercially available soft and hard PZT, which are both near the morphotropic phase boundary on the tetragonal side. These terms soft and hard are loosely used here and only exemplify the observed constitutive behavior; both materials are substituted with multiple cations, some of which can act as an acceptor or donor depending on the site location and oxidation state. Replacing Ti/Zr with lower valence ions on the B-site is most often referred to as acceptor doping although this is more correctly described as chemical substitution. The soft PZT material (PIC151, PI Ceramic GmbH, Lederhose, Germany) has the following composition: Pb$_{0.99}$[Zr$_{0.45}$Ti$_{0.47}$]$_{0.92}$[Ni$_{0.38}$Sb$_{0.67}$]$_{0.08}$O$_{3}$. The hard PZT (PIC181, PI Ceramic GmbH,
Lederhose, Germany) has the following composition

\[
Pb_{1.00}[(Zr_{0.47}Ti_{0.48}Mn_{0.33}Sb_{0.32}Nb_{0.33})_{0.05}]_{1.00}O_{3.0}\]  

\(Mn^{2+}\) acts as an acceptor-dopant on the B-site, whereas \(Nb^{5+}\) is a donor dopant.

**Experimental Procedure**

Cylindrical samples of 5.8 mm diameter and 6 mm height were produced by core drilling and grinding from an as-sintered block of material. After machining, the samples were electroded with a sputtered thin layer of platinum. Prior to testing, all samples were annealed at 450 °C for 30 min. Measurement of the temperature- and stress-dependent longitudinal direct piezoelectric coefficient \(d_{33}\) was performed on a screw-driven load frame (Z030, Zwick GmbH & Co.KG, Ulm, Germany) fitted with a heating chamber (SV800, Thermal Technology GmbH, Bayreuth, Germany) and custom-built equipment capable of applying small mechanical impulses at various frequencies. The load frame applied the global bias uniaxial compressive stress, while an integrated piezoelectric stack actuator (P-025.80, PI Ceramic GmbH, Lederhose, Germany), positioned in series with the sample and controlled by a LabVIEW program, partially unloaded the sample with a sinusoidal mechanical signal. During testing a load amplitude of ±0.5 MPa was used. The small signal direct piezoelectric coefficient was calculated from the measured amplitudes of stress and polarization in a frequency range between 50 mHz and 240 Hz with an accuracy of better than ±0.2 pC/N.

**Results**

The direct piezoelectric coefficient of the soft and hard compositions was determined during uniaxial compressive loading and unloading in the frequency range between 50 mHz - 240 Hz and is shown in Fig. 1. The arrows indicate the direction from lower frequencies to higher frequencies. The soft material displays a significantly larger \(d_{33}\) value, 550 to 600 pC/N, depending on frequency, in the poled state without applied stress. In contrast, the hard PZT composition has a \(d_{33}\) of 250 to 280 pC/N over the same frequency range. The lower piezoelectric response of hard PZT is due to the decrease in domain wall mobility and a subsequent decrease in the intrinsic contribution. [9]

With an increasing compressive stress, the piezoelectric response of the soft PZT is found to monotonically decrease above approximately -25 MPa, which is related to the first deviation from the linear elastic behavior (Fig. 1a). This point is where ferroelastic domain reorientation begins and is defined as the onset stress \((\sigma_0)\). As the external compressive stress reorients domains parallel to polarization direction, the average piezoelectric response of the polycrystal decreases. This effect continues until saturation, where no additional domains are available to be switched. In comparison, the hard PZT displays a considerably different response to the applied compressive stress (Fig. 1b); namely, an initial increase in \(d_{33}\) until -75 MPa, followed by a decrease and subsequent saturation. A similar increase in \(d_{33}\) with compressive stress in Fe\(^{3+}\)-doped PZT has been previously observed, although this study only applied bias stresses up to -80 MPa and, therefore, did not observe the subsequent decrease. [10] The initial increase is proposed to be due to the presence of an internal bias field, created by the high temperature poling procedure. At elevated temperature, the mobility of polar defects increases, [11] which allows for their orientation in the polarization direction. Upon field cooling, the polar defects remain in the oriented state (aligned in the direction of applied electric field) and are frozen in at room temperature, where their mobility is significantly decreased. As the applied bias stress increases, the electrostatic and mechanical forces work antagonistically and result in an
increase in the piezoelectric response through enhanced domain wall motion. Further increases in the mechanical load see a shifting of this balance and a mechanical clamping of domains.

The stress-dependent experimental results (Fig. 1) indicate that compressive stress can reduce the apparent internal bias that is caused by the ordered orientation of polar defects. Through the increase in temperature, the influence of stress on the polar defect should increase with the increasing thermally activated mobility of such defects. Soft PZT displays a reduced $d_{33}$ value at room temperature and a gradual decrease with increasing temperature. Hard PZT, however, clearly shows a two-step switching process with the first decrease occurring at ~40 °C. Importantly for applications, this limits the thermal operating range of such materials when a compressive stress is applied. Above approximately 150 °C, the rate of decrease in $d_{33}$ drops and the subsequent $d_{33}(T)$ behavior matches well that observed in soft PZT. In addition, the high temperature frequency dispersion is also reduced with a bias stress of -100 MPa. This two-step switching step is proposed to be due to the reorientation of the polar defects with the application of a bias stress. At lower temperatures, the mobility of the polar defects is low enough that they are not significantly influenced by the stress. However, as the temperature and the mobility increase, they can reorient, which is the origin of the first step. Because they are mechanically clamped, the frequency dispersion at higher temperatures also decreases. Eventually, the material loses the spontaneous polarization and the $d_{33}$ reduces to zero.
Fig. 2: Temperature-dependent direct piezoelectric coefficient for soft (a), (b) and hard (c), (d) PZT with a bias compressive stress of -5 MPa and -100 MPa.

The present findings indicate that compressive stress reduces the intrinsic forces generated by electrostatic ordering of charged defect population. This resulted in the presence of a two-step switching in hard PZT with increasing temperature that was rationalized to be due to the increasing mobility of the charged point defects, most likely oxygen vacancies. These data, however, cannot directly determine whether the observed behavior is due to the direct influence of stress on the polar defects or the indirect reorientation of ferroelastic domains. Further stress-dependent electron paramagnetic resonance measurements are required in order to directly address this.

References:

The center for collaborative studies (Sonderforschungsbereich) has been awarded by the Deutsche Forschungsgemeinschaft in 2002 to TU Darmstadt and is centered in the Department of Materials and Earth Sciences with important contributions from the Department of Chemistry as well as the Mechanical Engineering Department of the University of Karlsruhe. The center was renewed in 2006 and again in 2010 and is now in the third and final four-year funding period. It is comprised of a total of 19 projects and financial resources for the current four-year period of about 8 Mio. €. The center has an active guest program with guests visiting from 2 days to 3 months. In 2008, an integrated graduate school was also implemented with graduate students visiting from other Universities for time frames between 1 to 12 months. The collaborative research center SFB595 will be closing by the end of 2014 after twelve years of operation. Finally an International Symposium on Electrical Fatigue in Functional Materials was on September, 15th-18th 2014 at the Cliff Hotel on Rügen island directly at the German side of the Baltic sea. The meeting brought together international experts on ageing and fatigue in ferroelectrics, ionic conductors and organic semiconductors. The workshop presented invited talks and contributed posters by active and former members of SFB595, international guests and partners from industry. It provided ample of time for scientific discussions. For specific information, please contact either the secretary of the center, Mrs. Gila Völzke, or the chairman of the center, Prof. Karsten Albe.

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Electrical fatigue in functional materials encompasses a set of phenomena, which lead to the degradation of materials with an increasing number of electrical cycles. Electrical cycling leads to both reversible and irreversible currents and polarisations. Ionic and electronic charge carriers interact with each other and with microstructural elements in the bulk as well as at interfaces (grain boundaries and domain walls) and interphases (electrode/electrolyte). This in turn causes local changes in the distribution of electric currents and electric potentials. As a consequence local overloads and material degradation ensues and leads to irreversible loss of material properties. This material degradation can lead finally to mechanical damage as well as to dissociation reactions. The basic phenomena of electrical fatigue are not yet understood on a microscopic level. A key feature of the center is therefore the steady comparison between theory and experiment. This is utilized to find the physico-chemical origins of electrical fatigue as well as to develop strategies for new materials and improved material combinations. The
materials of interest are ferroelectrics, electrical conductors (cathode materials for lithium batteries and transparent conducting oxides) and semiconducting polymers. The goal of this center of excellence is the understanding of the mechanisms leading to electrical fatigue. An understanding of the experimental results is supported by concurrent materials modelling which is geared to encompass different time and length scales from the material to the component. In the third phase next to a quantitative modelling the development of fatigue-resistant materials and in the case of ferroelectrics, lead-free piezoceramics, is of particular focus.

Projects:

Division A: Synthesis

A1
P.I.: Prof. J. Rödel
Topic: Manufacturing of textured ceramics actuators with high strain

A2 [ended 2010]
P.I.: Prof. M. J. Hoffmann
Topic: Manufacturing and characterization of PZT-ceramics under dc loading

A3
P.I.: Prof. W. Jaegermann
Topic: Boundary layers and thin films of ionic conductors: Electronic structure, electrochemical potentials, defect formation and degradation mechanisms

A4
P.I.: Prof. R. Riedel
Topic: Novel functional ceramics using anionic substitution in oxidic systems

A5
P.I.: Prof. M. Rehahn
Topic: Synthesis of semiconducting model polymers and their characterization before and after cyclic electric fatigue

Division B: Characterization

B1 [ended 2010]
P.I.: Dr. R.-A. Eichel
Topic: EPR-Investigations of defects in ferroelectric ceramic material

B2 [ended 2010]
P.I.: Dr. A. G. Balogh
Topic: Investigations of the defect structure and diffusion in ferroelectric materials

B3
P.I.: Prof. H.-J. Kleebe / Prof. W. Donner
Topic: Structural investigations into the electrical fatigue in PZT
B4
P.I.: Prof. H. Ehrenberg
Topic: In-situ investigations of the degradation of intercalation batteries und their modelling

B7
P.I.: Prof. H. v. Seggern / Prof. A. Klein
Topic: Dynamics of electrical properties in fatigued PZT

B8
P.I.: Prof. Christian Hess
Topic: In situ characterization of intercalation batteries using Raman spectroscopy

B9
P.I.: Prof. Gerd Buntkowsky / Dr. Hergen Breitzke
Topic: Characterization of structure-property relationships of functional materials using solid state NMR

Division C: Modelling

C1
P.I.: Prof. K. Albe
Topic: Quantum mechanical computer simulations for electron and defect structure of oxides

C2
P.I.: Prof. K. Albe
Topic: Atomistic computer simulations of defects and their mobility in metal oxides

C3 [ended 2010]
P.I.: Prof. R. Müller / Prof. W. Becker
Topic: Microscopic investigations into defect agglomeration and its effect on the mobility of domain walls

C5
P.I.: Dr. Y. Genenko / Prof. H. v. Seggern
Topic: Phenomenological modelling of bipolar carrier transport in organic semiconducting devices under special consideration of injection, transport and recombination phenomena

C6
P.I.: Jun. Prof. B. Xu
Topic: Micromechanical Simulation on Interaction of Point Defects with Domain Structure in Ferroelectrics

Division D: Component properties

D1
P.I.: Prof. J. Rödel
Topic: Mesoscopic and macroscopic fatigue in doped ferroelectric ceramics
D3
P.I.: Prof. A. Klein
Topic: Function and fatigue of conducting electrodes in organic LEDs and piezoceramic actuators

D4
P.I.: Dr. A. Gassmann / Prof. H. v. Seggern
Topic: Fatigue of organic semiconductor components

D5 [ended 2011]
P.I.: Prof. W. Jaegermann
Topic: Processing and characterization of Li-ion thin film batteries

D6
P.I.: Dr. Kyle G. Webber
Topic: The effect of electric field-induced phase transitions on the blocking force in lead-free ferroelectrics

Division T: Industry transfer

T1 [ended 2013]
P.I.: Prof. H. Ehrenberg
Topic: In operando investigations of fatigue of commercial battery types using neutron tomography and diffraction

T2
P.I.: Prof. M. Hoffmann
Topic: Influence of PbO stoichiometry on microstructure and properties of PZT ceramics and multilayer actuators

T3
P.I.: Prof. H. Ehrenberg
„in operando“ studies on Li(Ni,Co,Mn)O2 cathode materials (NCM) using local and global methods for structure analysis – modification and fatigue of materials

Integrated Graduate school

MGK
P.I.: Prof. A. Klein
### Diploma Theses in Materials Science


### Bachelor Theses in Materials Science


[7] Alexander Valentin Brabänder; *Einfluss der Hydrierungsparameter auf die mechanischen Eigenschaften von La1,06Fe11,6Si1,4 im Massivmaterial*, 26.08.2014

[8] Sabrina Angelika Brehm; *Optische Emissionsspektroskopie an Lichtbogenplasmen*, 30.08.2014


[14] Lorenz Hagelüken; Stromlose Abscheidung von 1D Gold-Nanostrukturen auf 3D Makrostrukturen, 22.08.2014

[15] Stefan Hawel; Grenzflächenuntersuchungen an Zinkoxid (ZnO) - Einkristallen, 05.08.2014

[16] Ben Heider; Fabrication of gold nanocones in a triode field emission configuration, 31.10.2014


[18] Jennifer Honselmann; Analyse der Schichtbildung Chrom(III)-haltiger Aluminium-Passivierungen, 05.08.2014


[21] Benjamin Juretzka; Stromlose Abscheidung von superhydrophoben, mikro- und nanostrukturierten Silberoberflächen durch Halogenidzusatz, 13.05.2014

[22] Timo Kaiser; Nutzung nanostrukturierter Silberschichten zur Abscheidung von Ag-DLC-Schichten auf der Innenseite eines Rohres, 04.11.2014

[23] Oskar Kowalik; Einfluss der Prozessparameter auf die Struktur und die mechanischen Eigenschaften lasergeschmolzener Stähle, 08.07.2014


[26] Frank Löffler; Bestimmung von Tripplett-Niveaus und Abklingzeiten von Emissionsschichten, 05.03.2014

[27] Tobias Simon Maisch; Eddy Current Testing of wires made of Platinum alloys, 12.05.2014

[28] Corinna Müller; Nahordnung in BNT und BNT-BT, 06.05.2014
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[6] Elke Barbara Flegel; Molecular Dynamics Simulations of Liquid Phase Crystallized Silicon, 31.07.2014


[8] Richard Günzler; Untersuchung des Einflusses von Ta2O5- und Bi2O3-Pufferschichten auf die dielektrischen Eigenschaften von Ba0.6Sr0,4TiO3-Dünnschichtvaraktoren, 25.02.2014


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[1] Thorsten Bayer; Einfluss injizierter Ladungen auf Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-Dünnschichten: Elektrische und dielektrische Charakterisierung und Simulation des Ladungstransports, 10.09.2014


[7] Christine Jamin; Constrained Sintering of Patterned Ceramic Films on Stiff Substrates, 09.05.2014


[9] Jan Hans Kaspar; Carbon-rich Silicon Oxycarbide (SiOC) and Silicon Oxycarbide/Element (SiOC/X, X=Si, Sn) Nano-Composites as new Anode Materials for Li-Ion Battery Application, 04.07.2014


[13] Saima Nasir; Stimuli-Triggered Ionic and Molecular Transport through Track-Etched Nanopores, 03.11.2014


[17] Eva Sapper; *Lead-free (1-x)(Bi1/2Na1/2)TiO3-xBaTiO3: The impact of relaxor characteristics and induced long range order on piezoelectric properties*, 25.07.2014


[20] Sebastian Siol; *Quasistatische und transiente Oberflächenpotentialverteilungen organischer Feldefekttransistoren*, 02.10.2014


[22] Clemens Wall; *Mangan- Nickel- und Cobaltverbindungen als Konversions-elektrodenmaterialen für Lithium-Ionen-Batterien*, 31.01.2014


[24] André Leo Wolz; *Nanostrukturierte PEM-Brennstoffzellenelektroden aus alternativen Materialien*, 06.06.2014

[25] Jiadong Zang; *High-temperature dielectrics based on relaxor ferroelectrics*, 06.05.2014
**Mechanical Workshop**

The mechanical workshop of the Institute of Materials Science is designing, manufacturing and modifying academic equipment for a broad range of projects. In the year 2014 the workshop was involved in the following major projects:

- Components for Evaporation System for Rotated Fibre Substrates
- UHV-preparation chambers dedicated for MBE, CVD, PVD, PLD and (electro)chemical treatment
- Components for six-circle diffractometer
- Design and manufacturing of a protection chamber for x-rays with up to 150keV photons
- UHV baby chamber for x-ray diffraction experiments

**Staff Members**

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**Electrical Workshop**

The electrical workshop of the Institute of Materials Science was involved in the following projects:

- Maintenance and repair of various academic equipment like the Electron Probe Micro-Analyzer (EPMA), Secondary Ion Mass Spectrometry (SIMS), sintering furnace, Transmission Electron Microscopy (TEM), X-Ray powder Diffractometer (XRD) and Molecular Beam Epitaxy (MBE)
- Design and development of electronic components for specific research projects like temperature control unit, data logging, power controller, high voltage amplifier, high voltage power supply, measuring amplifier, high temperature furnace for impedance measurements
- Development of testing software (V-Basic / LabView / i-Tools)

**Staff Members**

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Institute of Applied Geosciences

Preface

Many of today’s major societal challenges are, to a large extent, geoscientific origin. The efficient management of water as well as other geo-resources, the securing of our future energy demands, or the understanding of the effects of the anthropogenic alteration of global cycles are vital for the future development of our society.

The Institute of Applied Geosciences at the TU Darmstadt has continued its efforts to focus research activities as well as its educational program on our key activities in Water – Energy – Environment. In 2014, most research groups of the institute participated in a LOEWE initiative UrbanH2O together with colleagues from the IWAR of FB 13. The audit in March 2014 was highly successful and the project was scientifically top ranked. Unfortunately, the political decision process led not to a funding of this project.

The Hydrogeology group organized the Kick-Off meeting of the FP7 project MARSOL that they coordinate. It took place in February 2014 in Darmstadt with 40 colleagues from 7 countries attending. In this project alternative water resources are used to increase water availability in the water scarce Mediterranean countries. The project has a high international visibility and will help to further establish water as a one of the key activities of our Institute. The group is also active in international cooperation. They started to implement a PhD program in Hydrogeology at the Mekelle University in Ethiopia. There is an urgent need for experts in water resources management especially in the water troubled countries in Northern Africa. In the first batch, 5 Ethiopian PhD students have been selected that will spend part of their time in our Institute.

In the focus of the 9th deep geothermal energy forum, held by the research group of Prof. Ingo Sass on September 30th 2015 at the Institute of Applied Geosciences, were presentations of the recent Hessian deep geothermal energy power plant projects and the medium deep geothermal potentials in the urban areas of Hesse as well as preliminary results of recent research projects.

In 2014, our revised consecutive Bachelor and Masters program ‘Angewandte Geowissenschaften’ has been successfully accredited by the accreditation agency ASIIN and the new curriculae could start in the winter term 2014/15. Basically, we kept the orientation of the study programs but the structure of the modules was homogenized and the sequence of lecture through the study became more visible. Moreover, the master students can select between two key aspects: Applied Geology (Angewandte Geologie) and Environmental Geochemistry (Umweltgeochemie). The master program turned out to be highly attractive for external applicants who make up ca. half of all master students. The main reason is the specific applied focus in geosciences in Darmstadt which is among few in Germany.

Also the international master course TropHEE increasingly attracts students. Since 2013 the amount of students has doubled and ca. 50 students are enrolled in total. They are from 29 (!) different countries, in particular from developing countries in Africa and Asia. However, also students from South America, the USA, New Zealand, and eastern Europe take part in the course. Every year DAAD awards 5 to 6 scholarships to TropHEE and support the course also financially.
Again, we could donate 6 Deutschlandstipendien to excellent students. In the winter term 2014/15 the IAG hosted 332 Bachelor, 87 master, and 55 TropHEE students. Together with diploma and PhD students, the total number was 515 students. Of those, 32% are female.

On December 05, 2014, we organized for the first time a celebration for our graduates, where their Diploma, BSc or MSc thesis was briefly introduced. All students received a small item which should serve as a nice memory of this very special event in their scientific career.

The Institute is very grateful for the intensive help in organizing this event, in particular, Gabriela Schubert (left in picture), Melanie Werner and Astrid Kern; without their continuous support during the run-up of the planned celebration, we would not have had such a positive response from our alumni.

On October 31, 2014, we organized a symposium for Prof. Dr. Dietrich Schumann on the occasion of his 80th birthday. Prof. Schumann was an active member of the institute in the field of paleontology from 1974 to 2000. Prior to the symposium, Prof. Schumann invited us to the Landesmuseum to see this famous fossilized rudist reef from Oman. We stayed there for more than one hour while Prof. Schumann explained all details of the original of this particular reef and how he finally managed to transport this natural treasure to Darmstadt.

As it is a long standing tradition in Geosciences to conclude the academic year with the ‘Barbara Fest’, all faculty, staff and students got together to discuss the events of the year as well as the future in a very friendly and positive atmosphere. Due to the high number of freshmen, the welcome ceremony of the new students, who were baptized during this event, was rather crowded but, finally, everyone was finally officially accepted as a new member of the Institute of Applied Geosciences.
Physical Geology and Global Cycles

In the solar system, Earth is a unique rocky planet with an ocean and an atmosphere. It is inhabited by bacteria since about 4 billion years and by higher life – plants and animals – since ca. 600 million years. Organisms, air, water, and rocks are interconnected in a never ending cycle of matter and energy: The Earth System.

The crustal plates of Earth are driven by radioactive heat. This causes creation of new crust at mid-oceanic ridges at rates of several centimeters per year. On the other side, plate margins become subducted into the mantle again or fold up vast mountain ranges, like the Alps and the Himalayas, combining rocks of very different origin. During subduction the basaltic crust is partially melted, generating more felsic magmas which rise to form plutons and to cause lines of andesitic volcanoes such as occurring around the entire Pacific Rim. This is called the endogenic cycle of rocks.

At the same time Earth receives solar radiation which moves air and water in gigantic cycles around the planet. Specifically the water cycle causes the denudation of mountains by mechanical erosion and the leveling of plains by chemical weathering, the latter aided tremendously by vegetation and its CO₂-input to soils. This is called the exogenic cycle of rocks.

This exogenic cycle is increasingly impacted by mankind. The radiation balance of the atmosphere has been upset by the emission of carbon dioxide, methane, and other trace gases. Earth is warming. Industrially produced chlorinated hydrocarbons have risen to the stratosphere, weakening the protective ozone layer. Dust from traffic, industry and agriculture produces reagents which alter air chemistry, causing unprecedented interactions with the marine realm, vegetation and even rocks through acidification, excessive deposition of nutrients and salts. Dry and wet deposition of anthropogenic (i.e. produced by humans) particles can be measured world-wide. The population explosion caused the intensification of agriculture and an alarming loss of topsoil while reducing the extent of natural ecosystems at the same time. Artificial fertilization of soils causes wide-spread nitrate pollution of shallow ground waters. Urbanization alters the water cycle above and below ground. Local leakage of chemicals impacts soil, rivers and ground water. Civil engineering causes alterations in almost all rivers world-wide, and even coastal oceans show increasing eutrophication, siltation and ecosystem changes in the water column and in their shallow sediments. Scars left by mining of minerals and fossil energy are visible everywhere and cause increasing problems. Throughout the globe man has changed the rate of natural processes. He spreads ever further into the landscape, utilizing regions and building in areas which are not suitable for construction, considering their natural risks. Thus, damage of natural catastrophes rise each year, endangering the world insurance system. These processes and their consequences are topics in Environmental Geology.

Understanding Global Change and accepting the responsibility of mankind to conserve the planet and its resources for future generations are prerequisites for ensuring a sustainable development. The division of Physical Geology and Geological Cycles at the Institute for Applied Geosciences addresses questions important to environmental geology both in the present and in the geological past.
Staff Members

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**PhD Students**  
Ingo Bauer  
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**Diploma Students**  
Sven Philipp

**Student research projects**  
Jan Will, Christopher Henze

Research Projects

- 3D Scanning of caves and speleogenetic process studies
- Pyroducts (Lava Tunnels) in the Kahuku Ranch area, Hawaii Volcanoes National Park
- Desert Kites in the Harrat of Jordan
- Dekapolis Tunnel, a presumably >100 km long Roman aqueduct system in Northern Jordan
- Tectonic structure of the southern boundary of the Harz Mountain and its development since the Permian

Publications

1. **Kempe, S. (2014):**  

2. **Kempe, S. (2014):**  

3. **Schleusener, F., Kempe, S., Dirks, H., Rausch, R., & Göbel, P. (2013):**  
CaCO_3 Precipitation in Multilayered Cyanobacterial Mats: Clues to Explain the Alternation of Micrite and Sparite Layers in Calcareous Stromatolites.

Józef Kaźmierczak 1,*, Tom Fenchel 2, Michael Kühl 2, Stephan Kempe 3, Barbara Kremer 1, Bożena Łącka 4 and Krzysztof Małkowski 1

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Marine cyanobacterial mats were cultured on coastal sediments (Nivå Bay, Øresund, Denmark) for over three years in a closed system. Carbonate particles formed in two different modes in the mat: (i) through precipitation of submicrometer-sized grains of Mg calcite within the mucilage near the base of living cyanobacterial layers, and (ii) through precipitation of a variety of mixed Mg calcite/aragonite morphs in layers of degraded cyanobacteria dominated by purple sulfur bacteria. The δ^{13}C values were about 2 ‰ heavier in carbonates from the living cyanobacterial zones as compared to those generated in the purple bacterial zones. Saturation indices calculated with respect to calcite, aragonite, and dolomite inside the mats showed extremely high values across the mat profile. Such high values were caused by high pH and high carbonate alkalinity generated within the mats in conjunction with increased concentrations of calcium and magnesium that were presumably stored in sheaths and extracellular polymer substances (EPS) of the living cyanobacteria and liberated during their post-mortem degradation. The generated CaCO_3 morphs were highly similar to morphs reported from heterotrophic bacterial cultures, and from bacterially decomposed cyanobacterial biomass emplaced in Ca-rich media. They are also similar to CaCO_3 morphs precipitated from purely inorganic solutions. No metabolically (enzymatically) controlled formation of particular CaCO_3 morphs by heterotrophic bacteria was observed in the studied mats. The apparent alternation of in vivo and post-mortem generated calcareous layers in the studied cyanobacterial mats may explain the alternation of fine-grained (micritic) and coarse-grained (sparitic) laminae observed in modern and fossil calcareous cyanobacterial microbialites as the result of a probably similar multilayered mat organization.

References:

Published in: Life 03/2015; 5(1):744-769. DOI: 10.3390/life5010744
Fig.: A schematic presentation of the artificial mat zonation (in vertical section), with examples of most characteristic calcium carbonate morphs precipitated in micritic (left column) and sparitic (right column) layers. Scale bars: (a) 5 μm, (b) 1 μm, (c) 1 μm, (d) 100 μm, (e) 10 μm, (f) 10 μm, (g) 10 μm, (h) 10 μm, (i) 3 μm, (j) 20 μm, (k) 2 μm.
Hypogene limestone caves in Germany, geochemical background and regionality

Stephan Kempe

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Germany exhibits a very diverse geological history. Thus a large number of stratigraphically, petrographically and tectonically different carbonate and sulfate rocks exist that have been subject to karstification. Possible “agents” (sensu Klimchouk) of hypogene karstification fall into three principally different processes: (i) water rising because of buoyancy (either thermally or concentration induced), (ii) in-situ oxidation of siderite, according to:

\[ 4\text{FeCO}_3 + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{FeO(OH)} + 4\text{HCO}_3^- + 4\text{H}^+ \quad (1) \]

or (iii) rising gases (CO\(_2\), H\(_2\)S or CH\(_4\) ), whereby hydrogen sulfide and methane could be oxidized according to:

\[ \text{H}_2\text{S} + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \leftrightarrow \text{H}^+ + \text{HSO}_4^- \quad (2) \]

and

\[ \text{CH}_4 + \text{O}_2 \rightarrow 4\text{H}^+ + \text{CO}_2 \quad (3) \]

yielding acids to dissolve limestone.

Germany has a complex geology featuring large tracts of Devonian, Carboniferous, Permian, Triassic, Jurassic and Cretaceous carbonates and sulfates. The Devonian and Carboniferous rocks have been subject to the variscian orogeny with intensive folding. Permian and Mesozoic rocks have been subject to gradual uplift and fracturing and, in the south of Germany, to Alpine orogenic thrusting. If applying the most pertinent epigene versus hypogene morphological characteristics (see Table) it becomes evident that hypogene caves occur in many different areas of Germany, often side-by-side with clearly epigene caves.

Table comparing epigene versus hypogene morphological features.

<table>
<thead>
<tr>
<th>Evidence for</th>
<th>Epigene</th>
<th>Hypogene</th>
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<tbody>
<tr>
<td>General layout of cave</td>
<td>Linear, tributary, cave of substantial longitudinal extent</td>
<td>Maze, isolated cavities, cave passages limited to a small area</td>
</tr>
<tr>
<td>Entrances</td>
<td>Former ponors or springs</td>
<td>No natural entrance or cave opened accidentally by erosion</td>
</tr>
<tr>
<td>Shape of rooms</td>
<td>Canyons, waterfall pits, seepage shafts, or phreatic round or oval</td>
<td>Large chambers interconnected (if at all) by narrow passages, shafts, passages of rough cross-section</td>
</tr>
<tr>
<td>General wall morphology</td>
<td>Meandering passages, erosion pots, scallops</td>
<td>Ceiling cupolas, solutional ceilings, solution cups, sloping side walls</td>
</tr>
<tr>
<td>Wall roughness</td>
<td>Smoothed and polished walls</td>
<td>Walls irregular with pockets, harder seams protruding, fossils exposed</td>
</tr>
<tr>
<td>Sediments</td>
<td>Allochthonous or autochthonous gravel, sandy material</td>
<td>Fine grained, autochthonous sediments</td>
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For many areas, the agents of hypogene speleogenesis must remain unclear. This applies for most caves in the Paleozoic limestones of the Rhenish Schist Massif. Only the Iberg/Harz caves seem to be a clear case; here the world-wide highest concentrations of siderite weathering-induced caves occur. The large cavities discovered recently in the Blauhöhlen System and some of the deep pit caves in the Swabian Alb may have their explanation in volcanic CO₂, having emanated from some of the 355 pipes of the Swabian volcanic field. Most striking is the high concentration of hypogene caves in the Franconian Alb. Many of them occur in a small area while other areas are devoid of larger caves. Here the tectonic situation suggests that fractures could have taped reservoirs of either sulfide or methane from below. The finding of goethitic crusts in the Bismarckgrotte may indicate that rising anaerobic gases could have been involved.

References:

Hydrogeology

The Hydrogeology Group focuses on three main research areas, (I) the fate of organic contaminants in the environment, (II) the development of novel methods to remediate soil and groundwater contaminations, and (III), on water resources management from a local to a regional scale. In all three research areas externally funded projects are currently running, some as part of larger joint projects with national and international partners.

The Kick-Off meeting of our EU FP 7 project MARSOL (Managed Aquifer Recharge as a Solution to Water Scarcity and Drought) was held in Darmstadt in February. 40 of our partners from southern Europe and Israel attended this meeting and were excited to start with this project that is tackling the severe water problems these countries are facing. Over the year field sites have been implemented and first results have been presented in several conferences and journals.

We also started two projects in international cooperation with Bangladesh and Ethiopia. In Bangladesh the main focus is sea water intrusion into coastal aquifers due to overpumping of groundwater. The study area is Cox's Bazar, were a booming touristic sector is using large amounts of fresh water. In Bangladesh we are developing, with funding of DAAD, a PhD program focusing on Hydrogeology. Already 5 PhD students have been hired by the Ethiopian partners at Mekelle University that are co-supervised by us.

Staff Members

<table>
<thead>
<tr>
<th>Head</th>
<th>Prof. Dr. Christoph Schüth</th>
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<tr>
<td>Research Associates</td>
<td>Dr. Laura Foglia</td>
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<td>Rainer Branolte</td>
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<tr>
<td>Secretary</td>
<td>Pamela Milojevic</td>
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Research Projects

MARSOL - Managed Aquifer Recharge as a Solution to Water Scarcity and Droughts (EU-2013-2015)
RADAQUA - Pilotstudie zur Einschätzung erhöhter Radionuklidkonzentrationen in Grundwässern der Arabischen Halbinsel und Nord-Afrikas (BMBF 2013-2014)

Prozessorientierte Untersuchung zum Nitratabbauvermögen der Grundwasserkörper im Hessischen Ried (HLUG: 2012-2014)

Heavy metal contamination of surface water and groundwater resources in the industrial area of Dhaka City, Bangladesh (BMBF-IPSWAT, 2011-2014)

Detection of oil spills and water contamination in the Kirkuk area, Irak, using remote sensing data (DAAD 2011-2014)


Institutional Partnership for the Establishment of a PhD Program in Hydrogeology at Mekele University, Ethiopia (DAAD 2014-2018)

**Publications**


MARSOL – Managed Aquifer Recharge as a Solution to Water Scarcity and Drought

Christoph Schüth, Laura Foglia, Annette Wefer-Röhl, Karl-Ernst Röhl

The Mediterranean basin is one of the most sensitive regions of the world with respect to the likely climatic changes that are predicted as a result of human activities. According to the latest IPCC projections, average temperatures are expected to increase by 3.5°C by the end of the century and precipitation could decrease on average by more than 10%, with a larger decrease in summer and in the more southern areas. Despite the uncertainties in projections, the anticipated reduction of renewable water resources can be as high as 50% within the next 100 years hitting regions that already suffer from water scarcity and droughts. In addition, the Mediterranean coastal zone represents already one of the most densely populated regions in the world with currently 180 million inhabitants, and 250 million expected by 2025 due to strong population growth. This will increase the demand for food, energy and other natural resources, putting additional stress on the diminishing water resources. As a further consequence, the deterioration of fresh groundwater resources due to intensive use of fertilizers in agriculture, pollution by industrial activities, or overexploitation of coastal aquifers resulting in seawater intrusion is already a reality.

At the same time, large water quantities are lost to the Mediterranean Sea as surface runoff and river discharge, discharge of treated and untreated wastewater, or as discharge of excess water from various sources during periods of low demand. These alternative water sources in principal can be used to increase water availability in general and in periods of high demand, and therefore improve water security. The main factors hindering the effective use of such waters are related to concerns about water quality, the lack of sufficient low cost intermediate storage options, and a lack of confidence in available concepts such as Managed Aquifer Recharge (MAR).

Storing water in aquifers during times of excess can help address water scarcity challenges experienced in many parts of the Mediterranean Basin. In principal, large storage capacity is available in shallow aquifers, either due to thick unsaturated zones or due to already depleted water resources in overexploited aquifers. In addition, water quality can be improved due to chemical and biological reactions during transport of the infiltrated water through the unsaturated and saturated zone, and by infiltrating waters for hydraulic control, e.g. to prevent seawater intrusion. Therefore, MAR, together with Soil-Aquifer-Treatment (SAT) systems and Aquifer Storage and Recovery (ASR) could be the key Water Resources Management (WRM) tool for tackling water scarcity in Southern Europe, the Mediterranean, and in water scarce regions worldwide by linking water reclamation, water reuse and water resources management.

In the MARSOL project we will: (1) review, evaluate and expand the worldwide available scientific and experimental knowledge on MAR, (2) demonstrate the feasibility and efficiency of MAR in combating future water scarcity threats in the Circum-Mediterranean area using unique DEMO sites, and (3) develop innovative solutions that can be generally applied to arid and semi-arid regions. For this, the MARSOL consortium combines the expertise of consultancies, water suppliers, research institutions, and public authorities ensuring high practical relevance and market intimacy.

A total of 8 field sites in 6 countries with a variety of running MAR facilities, or MAR facilities that are ready for operation, will ensure a coverage of the broad spectrum of
potential water sources and MAR technical solutions that are available (Fig. 1). The operators of all field sites will offer a tailored information and training program on their respective sites for different stakeholders to demonstrate the potential of MAR for a variety of targets and under a variety of boundary conditions ensuring dissemination, public awareness and commercial exploitation.

![Field demonstration sites of the MARSOL project and training activity at the Menashe site in Israel.](image)

**Fig. 1:** Field demonstration sites of the MARSOL project and training activity at the Menashe site in Israel.

The main objective of MARSOL is to demonstrate that MAR is a sound, safe and sustainable strategy that can be applied with great confidence. With this, MARSOL aims to stimulate the use of reclaimed water and other alternative water sources in MAR and to optimize WRM through storage of excess water to be recovered in times of shortage or by influencing gradients. Widespread application of MAR can help address water security problems to stimulate economic development, improve public health and well-being, and maintain ecological functions and biodiversity. The use of MAR technologies can substitute the need for other, more energy-intensive water supply options, such as seawater desalination.

MARSOL’s main output will be a powerful knowledge base of existing field applications of MAR technologies for addressing different societal challenges related to water availability. The effectiveness, efficiency and sustainability of existing MAR technologies will be demonstrated, including operation, maintenance and monitoring procedures. Examples include different water sources, ranging from treated waste water to desalinated seawater and various technical solutions e.g. infiltration ponds, injection wells, river bed scarification, and hydraulic barriers against seawater intrusion. The pros and cons of each technology will be assessed systematically, and compared to alternative solutions. Economic costs and benefits of MAR options for the various economic sectors will be quantified. Causes of public concern or acceptance of MAR will be examined and proven ways to enhance public acceptability (e.g. through education and transfer of knowledge, evaluation of best practices) identified. Governance frameworks (laws, policies, institutions, etc.) that enhance the prospects of successful implementation of MAR will be proposed. Finally, guidelines will be developed for MAR site selection, technical realization, monitoring strategies, and modelling approaches to offer stakeholders a comprehensive, state of the art and proven toolbox for MAR implementation.

MARSOL, a FP 7 project with 21 partners, is coordinated by the Hydrogeology Group at TU Darmstadt. It started in December 2013 and will run for three years.
Engineering Geology

Engineering Geology is a branch of geology that deals with the characterization of soil, rock and rock masses for the location, design, construction and operation of engineering works. Typical tasks relate to foundation of roads and buildings, but also to underground excavations like tunnels and caverns. The special focus of the Engineering Geology group at Technische Universität Darmstadt is on reservoir geomechanics, i.e., the application of rock mechanics as well as of techniques for stress and fracture characterization to depth of up to 5 km. In particular, numerical (finite element) models are used to predict the corresponding subsurface conditions prior to drilling operations. Such predictive tools are of great value not only for the optimal exploration and efficient use of hydrocarbon and geothermal reservoirs, but also for CO₂ sequestration sites as well as radioactive waste repositories.

The present research activities of the group comprise several case studies applying geomechanical modeling techniques to oil and gas reservoirs in the North German basin and the Rhine Graben area as well as to a demonstration site for subsurface storage of CO₂ in Australia (see Abstract 2 for details). In addition, large-scale surface outcrops serving as analogs to subsurface reservoirs are investigated. These studies utilize a terrestrial laser scanner for rapid detection of fractures and their geometrical and statistical properties (see Abstract 1 for details). One of these natural laboratories is located in the Spanish Pyrenees and allows for a comprehensive analysis of fault-and-thrust structures at a reservoir scale.

Research activities of our group won special recognition as Dr. Karsten Fischer received the Georg-Hunaeus award of the Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle (DGMK). He left soon after his PhD to work at the Schlumberger Reservoir Geomechanics Centre of Excellence in the UK. We wish him all the best for his future career.

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                        M.Sc. Dennis Laux
                        Dipl. Geol. Christoph Wagner

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                  M.Sc. Bastian Weber

M.Sc. students:   Sebastian Kurka
                  Stefan Wewior
                  Benjamin Schmitz
Research Projects

Prediction of tectonic stresses and fracture networks with geomechanical reservoir models (DGMK Projekt 721, ExxonMobil, GDF SUEZ, RWE Dea)

PROTECT - PRediction Of deformation To Ensure Carbon Traps (BMBF)
Building and populating geomechanical reservoir models – a case study from the Upper Rhine Graben (GDF SUEZ)

LIDAR-based analysis of fracture networks (PhD thesis)
Fracture prediction in fold-and-thrust belts – a worked example from the southern Pyrenees (PhD thesis)

 Publications


Laux, D., Henk, A., 2014: 

Wagner, C. & Henk, A., 2014: 

Weber, B., Henk, A., and PROTECT Research Group, 2014: 
Incorporation of spatial variations in elastic rock properties in geomechanical reservoir models. GEOTECHNOLOGIEN-Statusseminar, 23.-24.06.2014, Leipzig.

Weber, B. & Henk, A., 2014: 

Weber, B., Henk, A., and PROTECT Research Group, 2014: 
Incorporation of spatial variation in elastic rock properties in geomechanical reservoir models – workflow and application to the CO2CRC Otway project. Abstract volume CO2CRC Research Symposium, Tourquay, Australia.
Geomechanical reservoir models for tectonic stress prediction – workflow and case studies

Henk, A., Fischer, K & Aruffo, C.M.

Detailed knowledge of the tectonic stress field is crucial for the optimal exploration and use not only of conventional and unconventional hydrocarbon reservoirs, but also for deep geothermal reservoirs, carbon capture and storage (CCS) projects as well as underground mining and nuclear waste repositories. Any reliable stress prediction is hindered by the observation that the magnitude and orientation of the stress field can vary significantly – not only in time, but also in space. Such spatial stress variations comprise all scales, i.e., from the scale of lithospheric plates down to the grain-scale. On the reservoir- and fault block-scale, the local stress field can be influenced by faults and different mechanical properties of lithologies. The resulting variations in stress magnitude and/or stress orientation are commonly referred to as stress perturbations and give rise to a unique, reservoir-specific stress pattern. Thereby, local stress fields can deviate by up to 90° in orientation and several tenth of Megapascal (MPa) in magnitude from regional trends.

The state of stress in the subsurface can be determined by various methods, but all these stress data rely on wells as stress is commonly measured either downhole under in situ conditions or in experiments on core samples. However, stress information is frequently required already prior to drilling, e.g., for planning of horizontal well trajectories. Any pre-drilling prognosis has to incorporate the specific reservoir geometry regarding faults and lithological boundaries as well as the specific rock mechanical parameters and the far-field stresses. Integration of all this information for a quantitative analysis can only be achieved with a numerical model. In the following we present a general workflow to build and calibrate such geomechanical reservoir models. Subsequently, two case studies are used to test the workflow and illustrate its value in the real world. Case study I describes a field-scale (35 x 30 km) model of an intensively faulted gas reservoir in Northern Germany where numerous well data are available to compare model predictions to stresses actually observed. Case study II deals with a former gas reservoir in Australia which is now used for CO₂ injection. This model is smaller (8 x 5 km) but comprises the entire overburden of the reservoir up to the earth's surface.

The main focus for both case studies is set on the spatial variations of the present-day tectonic stress field resulting from faults and contrasts in mechanical rock properties. As these models reveal insights into the local in situ stress distribution prior to production, they also provide a refined input for further modeling work like flow simulations (considering stress-dependent permeabilities) and hydro-mechanically coupled models addressing the future reservoir behaviour due to pore pressure changes during production or injection. The ultimate goal of our work is the development of a tool for a reliable stress prediction based primarily on seismic and only sparse well data.

A major outcome of the project is the development of a comprehensive workflow for building and calibrating geomechanical FE models. It considers the reservoir-specific subsurface geometry as well as the mechanical stratigraphy and incorporates existing faults as distinct planes of weakness by using 2D interface elements. This allows for addressing...
the stress state and movement behavior of the modeled faults in addition to the tectonic stresses within the fault blocks. Computing time and resolution are optimized by using two different load frames in combination with the cut-boundary displacement method to incorporate the regional stress field. During a calibration phase modeling results are compared to stress data actually observed in borehole data. Thereby, poorly constrained input parameters are iteratively modified within reasonable limits until a satisfactory fit between calculated and measured stresses is achieved. This validated model can then be used for stress predictions in undrilled parts of the reservoir or along planned well trajectories.

The workflow is applied successfully to two case studies. They demonstrate that even geometrically complex structures with numerous faults can be transferred to a FE model for tectonic stress analysis. In particular, case study I, for which abundant calibration data is available, indicates that more than 80% of the observed stress data can be satisfactorily reproduced by the numerical model. Case study II illustrates that the approach is not restricted to the reservoir itself but can incorporate the entire overburden for borehole planning and fault stability analyses, for example. These case studies also demonstrate the general potential of geomechanical models for reservoir- to fault block-scale stress predictions. This offers a wide range of applications not only for hydrocarbon exploration and production, but also for other stress-related applications in the fields of deep geothermal energy, carbon capture and storage (CCS), underground mining as well as nuclear waste disposal.
Geothermal Science and Technology

Geothermal Energy is defined as the heat of the accessible part of the earth crust. It contains the stored energy of the earth which can be extracted and used and is one part of the renewable energy sources. Geothermal Energy can be utilized for heating and cooling by applying heat pumps as well as it can be used to generate electricity or heat and electricity in a combined heat and power system.

The field of Geothermal Science has natural scientific and engineering roots. Geothermal Science connects the basic knowledge with the requirements of practical industry applications. Geothermal Science is in interdisciplinary exchange with other applied geological subjects such as hydrogeology and engineering geology and therefore is a logic and proper addition to the research profile of the Technische Universität Darmstadt.

The broad implementation of geothermal energy applications and the utilization of the underground as a thermal storage will help to reduce CO₂ emissions and meet the according national and international climate protection objectives. Furthermore, the utilization of geothermal energy will strengthen the independency on global markets and the utilization of domestic resources. Geothermal Energy will be an essential part of the decentralized domestic energy supply and will contribute an important share of the desired future renewable energy mix.

Regarding the worldwide rising importance of renewable energy resources, Geothermal Science is one of the future's most important field in Applied Geosciences. In 2009, the industry-funded Chair for Geothermal Science and Technology was established at the TU Darmstadt – the first foundation professorship in energy science of the university.

The Chair of Geothermal Science and Technology deals with the characterization of geothermal reservoirs, starting from basic analyses of thermo-physical rock properties, which lead to sophisticated calculation of the reservoir potential of distinct rock units. Reliable reservoir prognosis and future efficient reservoir utilisation is addressed in outcrop analogue studies world-wide. Organisation of a highly qualified geothermal lab and experimental hall (TUDA HydroThermikum) started already in 2007 and was continued in 2014. Field courses and excursions in 2014 focused on geothermal energy in New Zealand, Germany and Austria.
## Staff Members

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<td>Dipl.-Geol. Stefan Knopf, Krebs und Kiefer Ingenieure, Karlsruhe</td>
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Research Projects

Geothermal Reservoir Analogs in Foreland Basins – „Malvonian“ (DAAD 2014 – 2016)


Entwicklung von wartungsarmen PEHD-Filterelementen für oberflächennahe geothermische Brunnenanlagen (Deutsche Bundesstiftung Umwelt (DBU) 2011 – 2015)

Machbarkeitsstudie „Machbarkeit und Nutzung von tiefer geothermischer Energie am Flughafen Frankfurt“ (FRAPORT AG 2010 – 2014)


Quantitativer Einfluss des Wasserhaushalts, der Umwelttemperatur und der geothermischen Kennwerte auf die Wärmeableitung erdverlegter Starkstromkabel (E.ON Innovation Center Distribution und Bayernwerk AG 2012 – 2015)


### Publications


Testing procedure for the assessment of the influence of cyclic freeze-thaw-stresses on borehole heat exchanger grouts

Hauke Anbergen, Ingo Sass

In Germany the borehole heat exchanger is the most common application for shallow geothermal systems. It is used for domestic heating coupled with a ground source heat pump system. During periods of extensive heat extraction freezing and thawing of the grout of the borehole heat exchanger might occur. This can affect the sealing properties of the grout. Consequently legal authorities require that grouting materials have to be resistant against freeze-thaw-cycles. However, there is no standardized procedure to test freeze-thaw-resistance of geothermal grouts.

Due to broad experiences in cyclic freeze-thaw-tests for concrete and natural stones, most previous grout tests relied on testing procedures for these materials. The procedures focus on the assessment of mechanical properties such as compressive strength or the loss of weight caused by frost. However, these tests do not follow the in-situ boundary conditions for geothermal grouts and also neglect to take into account the theoretical models of freezing-processes. To address these shortcomings a testing procedure was developed that simulates the downhole in-situ conditions as confining radial earthpressure, freezing and thawing direction from the inside to the outside, and saturated conditions. The hydraulic conductivity can be measured in axial flow direction. Thus statements according to the susceptibility of grouts against cyclic freezing and thawing stresses can be made. The theoretical models and the implementation of the testing procedure will be discussed.

Time- and temperature dependency of grouting materials was investigated and thus four criteria for a valid testing procedure were formulated:

1) The hydraulic conductivity of the system grout / probe has to be assessed.
2) The systems’ hydraulic conductivity has to be assessed after a freely selectable number of freeze-thaw-cycles.
3) The specimen must remain under defined pressure conditions inside the testing device during the whole procedure.
4) The specimens must be frozen radially from inside out, simulating in-situ conditions.

The specimens were designed in true portions to a real borehole heat exchanger. They are composed of an axial polyethylene pipe and a surrounding grout body. Thus the systems’ hydraulic conductivity is considered.

Several grouts were tested and the procedure was implemented in different geotechnical laboratories with different infrastructures. Therewith procedural independency with regard to laboratories or locations was proven. Tests with pure components of grouts were executed in order to proof the variability of the procedure. A testing series with a high number of freeze-thaw-simulations showed the general hydraulic behavior of froststressed grouts. Tracer tests underpinned the need of the assessment of the system hydraulic conductivity.

Temperature during the freeze-thaw-simulations was logged and validated experimentally and numerically. Therefore a plug-in was developed for the finite element method software.
FEFLOW. The plug-in enables FEFLOW to simulate phase change processes considering the temperature dependent material properties while including latent heat effects.

Based on tests conducted the following conclusion can be made:

- The system hydraulic conductivity is higher than hydraulic conductivity of the bulk material;
- the difference is of a magnitude around two;
- the increase of the system hydraulic conductivity due to cyclic freeze-thaw-stresses depends on the type of grout material;
- the first freeze-thaw-stresses cause the heaviest increase in hydraulic conductivity.

As the testing device is similar to the dimensions of regular hydraulic conductivity test and due to its handling, the procedure can be easily implemented into any geotechnical laboratory. Thus the testing procedure can contribute to quality assurance for shallow geothermal systems.

Fig. 1: Closed Measurement Cell (left: schematics; right: foto)
Sedimentary rocks cover about 75% of the earth’s surface and host the most important oil and water resources in the world. Sedimentological research and teaching at the Darmstadt University of Technology focus on applied aspects with specific emphasis on hydrogeological, engineering and environmental issues. One key issue in this context is the quantitative prediction of subsurface reservoir properties which is essential in modelling of regional groundwater hydrology, oil and gas exploration, and geothermal exploitation. However, also basic sedimentological research is carried out, e.g. the use of sediments as archives in earth history to reconstruct geodynamic, climatic and environmental processes and conditions in the past. To predict groundwater movement, pollutant transport or foundations of buildings in sedimentary rocks a detailed knowledge about the hydraulic, geochemical or geotechnical properties is needed which often vary about several magnitudes. This kind of subsurface heterogeneity can be related to distinct sedimentological patterns of various depositional systems. In addition, changes of depositional systems with time can be explained by specific controlling parameters e.g. changes in sea level, climate, sediment supply and are nowadays described by the concept of sequence stratigraphy. The research in applied sedimentology also includes modelling of erosion and sediment transport and its implication for the management of rivers and reservoirs with the help of GIS.

For any subsurface management a quantitative 3D model is a prerequisite, either related to water and geothermal energy or to gas, oil, and CO₂ storage. Together with the groups of Prof. Schüth (Hydrogeology), Prof. Sass (Geothermics), and Prof. Henk (Engineering Geology) the sedimentology group focuses on detecting the large to meso-scale sedimentary architecture and permeabilities of sedimentary reservoir rocks in order to achieve an optimized subsurface management of water and renewable energy resources. In 2014, the sedimentological research groups participated in the LOEWE initiative UrbanH₂O together with colleagues from the IWAR of FB 13. This program was designed to receive funding for this kind of joint research in water resources. The audit in March 2014 was highly successful and the project was scientifically top ranked. Unfortunately, the political decision process led not to a funding of this project. Dr. Hornung received a grant from Shell to analyse small-scale heterogeneities of porosities and permeabilities of sedimentary rocks and their link to microfacies patterns.

To detect subsurface heterogeneities at a high resolution, the sedimentology group hosts a georadar equipment for field measurements. This geophysical device is composed of various antennas and a receiver unit. Sophisticated computer facilities are provided to process the data and construct real 3D subsurface models. The group shares their equipment and facilities with the Universities of Frankfurt (Applied geophysics), Tübingen (Applied sedimentology), Gießen, Bonn, the RWTH Aachen and industrial partners. These institutions founded the Georadar-Forum which runs under the leadership of Dr. Jens Hornung (http://www.georadarforum.de/). Thanks to funding via a DFG research grant and recently by the Hochschukpakt we could invest into a shear wave measuring unit, which will extend our abilities for subsurface surveys down to several hundred meters and through materials, weakly penetrable by electromagnetic waves. Here we cooperate with the Leibniz Institute for Applied Geophysics in Hannover and the University of Hamburg. For quantification of reservoir properties a self-constructed facility for permeability
measurements of soil and rock materials exists which is further developed. This lab is also fundamental to geothermal research. The industrial project with Shell enabled us to design and construct a scanning device for automatized petrophysical screening of rocks. This device was constructed in 2014 and is planed to start its operation in 2015. This unique scanning device provides a new dimension in petrophyiscal surveys of rocks on the extended lab scale and its development was also embraced by industrial partners. On the other hand, it well suits as a training facility for students and offers new possibilities for bachelor theses.

In 2014, the group still participated in the DFG Research Unit RiftLink (http://www.riftlink.de/) whereas the two European Research Groups within the EUCORES Programme (TOPOEurope, SedyMONT) were completed. The topic of these research projects are in the context of earth surface processes and palaeoenvironmental reconstructions. Here still two funded PhD theses were running in 2014. The research activities in Saudi Arabia in cooperation with the GIZ (Gesellschaft für International Zusammenarbeit), the UFZ (Umweltforschungszentrum Halle-Leipzig), and the Ministry of Water and Energy of Saudi Arabia (MOEWE) also were completed, however, a report workshop together with the ministry in January 2014 opened new perspective for further cooperation. In April 2014, a new proposal was submitted to MOEWE and awaits decision for funding. Anoter outcome is the acceptance of a 3 years DFG proposal in order to elucidate the provenance of the widespread sandstones on the Arabian Peninsula and Ethiopia.

Based on previous work of the group several research initiatives are running at the moment, e.g. past environmental pollution in Central Europe as reconstructed from lake sediments, Mesozoic palaeoenvironmental evolution in NW China (initiative together with University of Bonn and Jilin University, China), and high-resolution palaeoclimatic studies in Messel and similar maar lakes (DFG). Janguang Zhang continued his PhD with a Chinese grant. Dr. Dorthe Pflanz quitted our grouped after receiving a position at the Landesanstalt für Umwelt in Bavaria, but she is still active in publishing results of her stay in Darmstadt about loess deposits in southern Hessia.

Prof. Hinderer is continued to be the representative of the German-speaking sedimentologists (Section of Sedimentology in Geologische Vereinigung and SEPM-CES) and co-organized the DGG-GV conference in Frankfurt 2014. In this context he participated in the process to merge the two geological societies in Germany, the DGG and GV to the new joint society DGGV – Deutsche Geologische Gesellschaft – Geologische Vereinigung e.V. He kept on being a member of the editorial board of the International Journal of Earth Sciences.

**Staff Members**

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<tr>
<th>Head</th>
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Research Projects

Linking source and sink in the Ruwenzori Mountains and adjacent rift basins, Uganda: landscape evolution and the sedimentary record of extreme uplift: Subproject B3 of DFG Research Group RIFT-LINK “Rift Dynamics, Uplift and Climate Change: Interdisciplinary Research Linking Asthenosphere, Lithosphere, Biosphere and Atmosphere” (DFG HI 643/7-2).

Monitoring of soil water content with ground penetrating radar (PhD thesis).

Climatic and tectonic interplay in central Asian basins and its impact on paleoenvironment and sedimentary systems during the Mesozoic (PhD thesis, Chinese funding).

Provenance of Paleozoic clastic sediments and reasons for radioactive anomalies in groundwaters on the Arabian Platform (PhD thesis, partly GIZ funding)

Paleozoic source to sink relationship around the northern Trans-Gondwana Mountain Belt (East Africa, Arabia) (PhD thesis, DFG HI 643/13 together with Universität Göttingen)

Periglacial eolian sediments in southern Hessia, their chornology, and their genesis (Diploma und BSc theses and preparation of a DFG project)

2-D heterogeneities of poroperm, ultrasonic and resistivity on sub-meter scale (Diploma und BSc theses, funded by Shell)

Publications


New palynology-based astronomical and revised 40Ar/39Ar ages for the maar lake of Messel (Germany)

Olaf K. Lenz, Volker Wilde, Dieter F. Mertz, Walter Riegel

The Upper Rhine Graben is the prominent central segment of the Cenozoic Central European Rift System. Initial crustal weakness along the incipient Upper Rhine Graben is indicated by Paleogene phreatomagmatic volcanism sometimes leaving behind isolated sinks where sedimentation started prior to the onset of major rifting and graben formation. The best known of about half a dozen isolated occurrences of Paleogene sediments on the Sprendlinger Horst which flanks the Upper Rhine Graben to the northeast, is Messel. As most of them it represents the filling of a maar structure.

A continuous core from Messel revealed a complete reference section of the Eocene lake deposits (Messel Formation), including 90 m of clastic lake sediments overlain by 140 m of the classical “Messel oil shale”, a continuous succession of finely laminated bituminous claystones. The lamination was caused by annual algal blooms in the meromictic lake forming light layers alternating with the dark layers of the terrigenous background sedimentation (Lenz et al., 2010). These oil shales provide a unique high-resolution archive for palaeoenvironment and palaeoclimate of a time interval of ~640 ka during the Paleogene. The character of the annually laminated sediments allows studies at an unprecedented resolution within the most recent greenhouse period on Earth.

As a consequence of orbitally controlled changes of the vegetation in the vicinity of the lake (Lenz et al., 2011) the lacustrine laminites can now be astronomically tuned. The correlation is based on the eccentricity amplitude modulations of the regional pollen rain and their correlation to the astronomical La2010a/d solutions in combination with a revised ⁴⁰Ar/³⁹Ar plateau age between 48.26 and 48.11 Ma ± 0.22 Ma (2-sigma) for the eruption at Messel (Lenz et al., 2015). This allows for the first time the exact correlation of a Paleogene lacustrine sequence to the marine record. The Messel oil shale therefore becomes slightly older than previously assumed and includes the Ypresian/Lutetian boundary which moves the base of the European Land Mammal Age (ELMA) Geiseltalian (MP 11) into the Lower Eocene. Astronomical tuning in combination with refined radioisotopic ages now enables to establish an independent chronostratigraphic framework for Paleogene terrestrial records and their correlation to the marine realm. Furthermore, astronomical tuning of Messel reveals that higher amounts of pollen from “wet” and thermophilous plants indicate increased precipitation and slightly higher temperatures during a well expressed eccentricity minimum.
Fig. 1: Upper part of core “Messel 2001” and new chronostratigraphic ages based on astronomical tuning and recalculated 40Ar/39Ar ages. Depending on astronomical dating using the La2010a solution or the La2010d solution, the boundary Lower/Middle Eocene (Ypresian/Lutetian) is placed in the middle (~59 m depth) or in the upper part (~30 m depth) of the MMF (based on the new age of 47.8 Ma for the GSSP of the Lutetian/Ypresian boundary (Molina et al. 2011; Cohen et al. 2013)).

References
Geo-Resources and Geo-Hazards

When the group was founded in 2001 it was named “Geo-Resources and Geo-Hazards”, as the first in Germany, based on the experience of the chair holder that geology becomes more and more important for societies and its decision makers while these normally have big difficulties to understand the 3 to 4-dimensional aspects of this discipline. As a consequence, the group used the increasing possibilities of electronic data processing, especially the techniques of GeoInformationSystems and 3D-modelling to translate the geoscientific knowledge especially in the surroundings of urban areas. In the following years model areas in southern Hesse, the Ebro Basin and Belo Horizonte in Brazil have been analysed.

During the years expert knowledge was gained, transferred in courses to students and deepened by BSc, MSc and doctoral theses. Among the German geological institutes this is a unique feature, recognized as well by an external group of experts who evaluated the institute. After the retirement of Andreas Hoppe end of March and the leave of Rouwen Lehné in October to the Geological Survey of Hesse, the institute tries consequently to maintain these capabilities by building a GeoInformationGroup led by Rouwen Lehné who will continue to give courses for the students and to develop projects which address topics and methods mentioned above.

Staff Members

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<td>Thomas Schmitz (MSc)</td>
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Research Projects

Focus was still laid on the analysis and evaluation of geopotentials in the surroundings of urban areas as well as on hazards based on mass movements. Tools to achieve these goals were GeoInformationSystems (GIS) and 3D modelling (GOCAD).
Hannah Budde continued to elaborate a 3D model for the Rhein-Main area in cooperation with the Hessian Geological Survey (HLUG). Ina Lewin elaborated a high resolution model of Quaternary sediments in a test area east of the Odenwald and investigated the water exchange between a dredging lake and a groundwater well in cooperation with the local water distributor (ZVG Dieburg).

3D modelling of the Quaternary of the Northern Upper Rhine Graben was intensified by Rouwen Lehné. Together with HLUG, he also started, together with a number of graduate assistants, a GIS supported data base on geo-hazards in Hesse.

Distribution and quality of geopotentials in Estonia (i.e. oil shale and black shale) have been investigated with GIS and GOCAD techniques by Rouwen Lehné and master students in co-operation with the Estonian Land Board.

Rouwen Lehné served as speaker of the Section Geoinformatics within the German Geological Society (DGG).

Andreas Hoppe initiated and led together with Rouwen Lehné an interdisciplinary project seminar about the possibilities to use some parts of the many artificial lakes in the northern part of the Upper Rhine Graben for solar energy. He served as Chief Editor of the ZDGG (German Journal of Geology) and evaluated in February the education in geology and mineral prospecting at the University of Ust-Kamenogorsk in Kazakhstan. In March he was invited speaker of the Akita University in Tokyo and in Akita. He continues lecturing at the universities of Darmstadt and Freiburg im Breisgau (where he was appointed as honorary professor).

### Publications

Land-use impact and nitrate analysis to validate DRASTIC vulnerability maps using a GIS platform of Pablillo River Basin, Linares, N.L., Mexico. – Int. J. Geosci. 5: 1468-1489 (doi 10.4236/ijg. 2014.512120).


The research group of Prof. Hans-Joachim Kleebe is active in the field of Geomaterial Science (formerly Applied Mineralogy) and explores the formation/processing conditions, composition, microstructure and properties of natural minerals and in addition of material science relevant compounds. The study of the latter material group focuses on both basic science questions and potential industrial applications. Research activities include a comprehensive characterization of natural and synthetic materials, their performance for example at elevated temperature, local chemical variations as well as tailored synthesis experiments for high-tech materials.

The experimental studies comprise the crystal chemistry of minerals and synthetic materials, their crystal structure, phase assemblage and, in particular, their microstructure evolution. The microstructure variation (e.g., during exposure to high temperature) has an essential effect on the resulting material properties, which is true for synthetic materials as well as for natural minerals. Therefore, the main focus of most research projects is to understand the correlation between microstructure evolution and resulting material properties.

An important aspect of the Fachgebiet Geomaterial Science is the application of transmission electron microscopy (TEM/STEM) techniques for the detailed micro/nano-structural characterization of solids. STEM in conjunction with spectroscopic analytical tools such as energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) are employed for detailed microstructure and defect characterization down to the atomic scale. High-resolution imaging of local defects in addition to chemical analysis with high lateral resolution is similarly applied to natural minerals as well as to high-performance materials.

Recent research projects involve topics such as fatigue of ferroelectrics, defect structures in Bixbyite single crystals (and their corresponding exaggerated grain growth), morphology of \( \text{In}_2\text{O}_3 \) nanocrystals, ultra-hard materials such as boron suboxide, transparent polycrystalline ceramics (LiF-doped Mg-Al spinel), interface structures in polycrystals, high-temperature microstructures, fatigue of ferroelectrics, and the study of biomineralisation and biomaterials.

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<tr>
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<td>Dr. Ana Ljubomira Schmitt</td>
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<td>Dr. Michael Dürrschnabel</td>
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<td>Dr. Ingo Sethmann</td>
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**PhD Students**

- Stefania Hapis
- Cigdem Özsoy Keskinbora
- Marc Rubat du Merac
- Mathis M. Müller
- Katharina Nonnenmacher
- Michael Scherrer
- Ekin Simsek
- Dmitry Tyutyunnikov
- Carolin Wittich
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- Sven Schild
- Leoni Wilhelm

**Technical Personnel**

- Bernd Dreieicher

**Secretary**

- Angelika Willführ

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**Research Projects**

- **Polymer-derived SiCO/HfO₂ and SiCN/HfO₂ Ceramic Nanocomposites for Ultrahigh-temperature Applications,** SPP-1181 (DFG 2009-2014)

- **Structural Investigations of Fatigue in Ferroelectrics,** SFB-595, detailed TEM Characterization of Lead-Free Ferroelectrics (DFG 2007-2014)


- **Investigation of the Atomic and Electronic Structure of Perovskite-Multilayer-Heterojunctions** (in collaboration with the MPI Stuttgart, Prof. P. van Aken)

- **Phase Developments and Phase Transformations of Crystalline Non-Equilibrium Phases** (in collaboration with the MPI Stuttgart, Prof. P. van Aken)

- **Microstructure Characterization and Correlation with Corresponding Properties, in particular Hardness und Fracture Toughness, of Boron Suboxide Materials** (DFG 2012-2015)

- **Microstructure Characterization of Polycrystalline Transparent Mg-Al-Spinel Samples; The Effect of LiF Doping** (Industry 2012-2014)

- **Microstructure and Defect Control of Thin Film Solar Cells** (Helmholtz Virtual Institute 2012-2018)

- **Hydrothermale Umwandlung von porösen Ca-Carbonat Biomineralen in antibiotische und antiosteoporotische Ca-Phosphat-Knochenimplantat-Materialien mit eingelagerten Mg-, Sr-, Zn- und Ag-Ionen** (DFG 2014 – 2016)
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<td>10</td>
<td>J. Kaspar, M. Graczyk-Zajac, S. Lauterbach, H.-J. Kleebe, and R. Riedel</td>
<td>&quot;Silicon oxycarbide/nano-silicon composite anodes for Li-ion batteries: Considerable</td>
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[20] M. Zakhozheva, L.A. Schmitt, M. Acosta, W. Jo, J. Rodel, and H.-J. Kleebe, "In situ electric field induced domain evolution in Ba(Zr_{0.2}Ti_{0.8})O_3-0.3(Ba_{0.7}Ca_{0.3})TiO_3 ferroelectrics," Appl Phys Lett, 105 [11] (2014).
In situ Electric Field Investigations on Lead-free Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_{3-x}$(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$
Piezoceramic

Marina Zakhozheva, Ljuba Schmitt and Hans-Joachim Kleebe

The evolution of ferroelectric domains in the lead-free Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_{3-x}$(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT-xBCT) piezoelectric ceramic was investigated in situ under an applied electric field using transmission electron microscopy (TEM). Poling induced reversible multi- to single-domain state transformation has been monitored for a large variety of compositions. For all studied materials, this transformation occurs with the appearance of an intermediate nanodomain state at moderate poling fields. According to our results, under high poling fields a single-domain state vanishes and multiple domains reappear within the grains. Upon further cycling switching between two different multi-domain states occurs. For all investigated BZT-xBCT compositions no sign of the electric-field-induced structural changes have been detected using the selected area electron diffraction (SAED) patterns, which are devoid of the reflection splitting or any detectable changes during electrical poling. The extrinsic contribution to the piezoelectric properties is found to dominate in the BZT-xBCT piezoceramic.

Figure 1. In situ TEM bright field images of the BZT-0.3BCT along the [1-53]c zone axis at (a) zero field, (b) 0.66 kV/cm, (c) 1.33 kV/cm, (d) 2 kV/cm, (e) 0.66 kV/cm, (f) zero field, (g) -2.66 kV/cm, (h) -14 kV/cm, (i) -20 kV/cm. The direction of poling field is indicated by arrows.
Using in situ TEM allowed for the first time to show the formation of a unique single-domain state in BZT-0.5BCT during electrical poling [1]. This single-domain state formation was associated with enhanced piezoelectric properties in the system. Nevertheless, such single-domain state was also reported for the rhombohedral BZT-0.3BCT and therefore is not an exclusive characteristic of the PPT composition. Most of the studies mainly concentrate on the BZT-xBCT composition around the PPT region [1-4], because of its outstanding properties. However, to fully understand the structure property relationship, the domain morphology evolution should be investigated in a broad compositional range. A composition dependent in situ electric field induced microstructure evolution in lead-free BZT-xBCT system could be verified. Strain and polarization measurements as a function of electric field are consistent with the in situ electric field TEM findings. The microstructure evolution in the BZT-xBCT system correlates well with the macroscopic data, since maximum values in saturation and remanent polarization for PPT compositions correspond to the miniaturization of domains. For instance, the higher coercive field for tetragonal BZT-0.6BCT (Fig. 2 (c)), is correlated with the high poling fields required to induce the single domain state in comparison with rhombohedral and PPT compositions. Enhanced values of maximum and remanent strain for BZT-0.4BCT and BZT-0.52BCT compositions, which locate near to the (R – O) and (O – T) PPT areas in the phase diagram, respectively, coincide with reduction in the domain size. A sharp decrease in these values for the BZT-0.45BCT can be attributed to the presence of an orthorhombic structure far from phase boundaries. The domain evolution as a function of an applied electric field in lead-free BZT-xBCT piezoelectric showed a multiple-domain state (A) → nanodomain state → single-domain state transformations, which occurred in all compositions studied. Further increase in poling field leads to the multiple-domain state (B) formation, which can be associated with strain incompatibility between neighboring grains under the electric field. SAED patterns did not reveal any detectable changes during the poling process. Domain wall motion during electrical poling is a sign of a high extrinsic contribution to the piezoelectric response in all studied lead-free BZT-xBCT compositions. Stresses are suggested to determine the domain configuration evolution under the field.

References

Electron Beam Nanosculpting of Kirkendall Oxide Nanochannels

Leopoldo Molina-Luna and Hans-Joachim Kleebe

The nanomanipulation of metal nanoparticles inside oxide nanotubes, synthesized by means of the Kirkendall effect, is demonstrated. In this strategy, a focused electron beam, extracted from a transmission electron microscope source, is used to site-selectively heat the oxide material in order to generate and steer a metal ion diffusion flux inside the nanochannels. The metal ion flux generated inside the tube is a consequence of the reduction of the oxide phase occurring upon exposure to the e-beam. We further show that the directional migration of the metal ions inside the nanotubes can be achieved by locally tuning the chemistry and the morphology of the channel at the nanoscale. This allows sculpting organized metal nanoparticles inside the nanotubes with various sizes, shapes, and periodicities. This nanomanipulation technique is very promising since it enables creating unique nanostructures that, at present, cannot be produced by an alternative classical synthesis route. In summary, a novel manipulation strategy of Cu nanoparticles inside Kirkendall copper oxide nanotubes has been demonstrated. This strategy is based on the control of the thermally activated local diffusion of Cu ions inside the nanotube using an e-beam extracted from a TEM source.

Figure 1: Electron energy-loss spectroscopy showing the impact of the e-beam on the chemical state of an oxide nanotube created by the Kirkendall effect. (a) High-angle annular dark field (HAADF)-STEM micrograph of an oxide nanotube containing a nanoparticle created by irradiation using an e-beam; the dashed red circle represents the e-beam spot, whereas the yellow and the black rectangles represent the two regions analyzed by spatially resolved EELS in combination with STEM. (b) EELS spectra of a hollow tube area composed of cuprous oxide (region 1). (c) EELS spectra of a tube area containing a nanoparticle (region 2); Cu and Cu2O EELS references are plotted in red and cyan, respectively. (d, e) Evolution of the Cu L3/L2 ratios (the raw data are plotted in black, and the deconvoluted ones are in red) on going from the inner side toward the extremity of (d) region 1 and (e) region 2.
The migration of Cu ions was found to be governed by the surface diffusion mechanism occurring on the inner walls of the nanotube. The directional diffusion of Cu can be achieved by controlling the chemical state of the different regions surrounding the particles. This manipulation technique allows the creation of nanoparticles with various sizes, shapes, and spatial distributions that are confined inside an oxide nanochannel. Copper has been selected as the model system in this study, but this strategy can also be applied to other metals such as iron. In the case of ferromagnetic metals, this nano-scale manipulation strategy could be ideal for the fabrication of novel magnetic nano-objects. The main limitation of the reported nano manipulation strategy appears to be that it works better for particles with relatively large interparticle distances (>100 nm), limiting the ability to control finely the coupling between magnetic nanoparticles. This limitation is mainly related to the relatively large e-beam spot size (50 nm) used in this study. One way to overcome this drawback is by decreasing the e-beam spot size, which allows reducing the size of the locally heated area.

References

Electron Crystallography

Electron crystallography uses electron radiation to characterize the structure of matter by imaging, diffraction and spectroscopy from fully crystalline over highly disordered to amorphous materials. One of the most potential tools for solid state investigation in the nano regime are transmission electron microscopes (TEM). Apart from imaging techniques in parallel illumination, scanning methods, based on a sequential data collection, are becoming more and more popular.

The scientific approach of this group lies mainly on the development of electron diffraction techniques. A new method was invented, Automated Diffraction Tomography (ADT), consisting of a new data collection concept and applicable to nano particles down to a size of some tens of nanometer. Using ADT, nearly kinematical 3D electron diffraction data can be collected from a selected nano crystal being suitable for „ab-initio“ structure solution, i.e. based only on electron diffraction data. In contrast to high resolution imaging this approach is applicable even to material highly sensitive to the electron beam (e.g. drugs, MOFs, zeolites, hybrid materials).

Application as well as development of the above described ADT method has a high demand for cooperation within the Materials- and Geosciences but also with other departments such as chemistry, mathematics and informatics.

The new tomographic approach can be run on different transmission electron microscopes and can be learned from scratch in a reasonable time. Thus it is suitable for teaching purposes not only directly associated with electron crystallography but as well for basic understanding of crystallographical concepts.

Structure determination of highly crystalline nano particles has been established even for complicated structural features. Therefore the focus of the development in this group has moved on to the analysis of additional scattering potential originating from splitted atomic positions, channel ions, templates in zeolites and solvate molecules. A quantitative approach to describe disordered structures is under development. The use of total scattering approaches (e.g. pair distribution function PDF) successfully applied to X-ray data is planned to be established for electron diffraction.

Prof. Kolb started to build up the group in the Institute of Applied Geosciences in November 2012. In addition she has been assigned as Equal Opportunities Officer.

Staff Members

**Head**                             Prof. Dr. Ute Kolb

**Diploma Students**                Angela P. Moissl (MSc)

**Secretary**                       Angelika Willführ
Publications


[7] M. Koch-Müller, E. Mugnaioli, D. Rhode, S. Speziale, U. Kolb, R. Wirth, Synthesis of quenchable high-pressure form of magnetite (h-Fe₃O₄) with composition Fe₁(Fe₂+0.75Mg₀.₂₆)₂ Fe₂(Fe³+3 0.70Cr₀.15Al₀.11Si₀.04)₂O₄, American Mineralogist, 99 (11-12) 2405-2415 (2014).


Noncentrosymmetry of human tooth hydroxyapatite

_Ute Kolb and Etienne Brès_

Due to the sophisticated growth mechanisms, human calcified tissues (bones and teeth) present a hierarchical architecture over several length scales, tuning each tissue to its specific biological function. Mechanical properties are optimized and adapted to stress (e.g., femurs for bending strength or teeth for wear resistance). The microscale of calcified tissues is made up of nanocrystals arranged and oriented in specific fashions. The atomic structure of human calcified tissue nanocrystals (tooth enamel, dentine, and bone), determined by X-ray diffractometry,

IR and Raman spectrometry, and thermal decomposition, is very similar to that of hydroxyapatite (HA: [Ca(2)\textsubscript{6}Ca(1)\textsubscript{4}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2}]). The HA structure can be described as a column of OH\textsuperscript{−} ions, located on the 6\textsubscript{3} screw axis parallel to the c axis and surrounded by two equilateral Ca(2) atom triangles directed in opposite directions, perpendicular to the c axis and separated by a distance of c/2. The mirror plane in the HA P6\textsubscript{3}/m structure is preserved by a statistical positioning of the OH\textsuperscript{−} ions above and below the Ca(2) triangles (Figure 1 right, a). OH\textsuperscript{−} ions can be shifted by the presence of interstitial F\textsuperscript{−} and O\textsuperscript{2−} ions, or H\textsubscript{2}O, or by direct substitution of CO\textsubscript{3}\textsuperscript{2−} ions on the 6\textsubscript{3} axis. When this is observed over several unit cells, the hexagonal P6\textsubscript{3}/m symmetry is reduced to the monoclinic P2\textsubscript{1}/b symmetry (Figure 1b). In this structure, the mirror plane is transformed into a glide plane and the a or the b parameter is doubled. Hexagonal and monoclinic domains can coexist simultaneously in the same single crystal.

The HA structure of macroscopic crystals is centrosymmetric as shown by X-ray diffractometry with a statistical occupancy of 50% for the OH\textsuperscript{−} positions above and below the Ca(2) triangles. This structure has been assumed also for human enamel and dentine nanocrystals. Up to now, there has not been any direct proof of the structure of HA nanometric crystals of biological calcified tissues. Herein, we investigate human single hydroxyapatite crystals (enamel and dentine) by convergent-beam electron diffraction (CBED) and automated electron-diffraction tomography (ADT). The CBED pattern shows the absence of the mirror plane perpendicular to the c axis leading to the P6\textsubscript{3} space group instead of the P63/m space group considered for larger-scale crystals, this is confirmed by ADT. This experimental evidence is of prime importance for understanding the morphogenesis and the architectural organization of calcified tissues. In the case of hydroxyapatite (tooth enamel, Figure 1) it was possible to determine the absence of a centre of symmetry, important for the orientation of enamel nanoparticles in tissue directly with ADT data.
Figure 1: Left) Dark-field scanning transmission electron microscopy image of an enamel crystal; b) convergent beam electron diffraction of zero-order Laue zone pattern oriented along the [11-20] zone axis; c) ADT data viewed along b*; d) ADT data viewed along c*. Right) hydroxyapatite (HA) structures: a) 2x2 HA unit cells with random positions of OH- groups above and below the Ca(2) triangles (space group P6_3/m); b) 1x1 HA unit cell with alternated OH-positions (space group P2_1/b); ADT structure: c) 2x2 HA unit cells with ordered OH-positions above the Ca(2) triangles (space group P6_3). OH- groups are shown as big red spheres; PO_4^3- groups as violet tetrahedral structures; Ca atoms as green spheres.
Total-Scattering Pair-Distribution-Function of Organic Material from Powder Electron Diffraction

Ute Kolb and Tatiana Gorelik

In order to investigate structural features of amorphous material it is often necessary to perform a pair-distribution function (PDF) analysis. This approach is getting more and more accepted for X-ray diffraction but is seldom applied based on electron diffraction data. This work demonstrates that PDF analysis can be carried out on organic and organometallic compounds from powder electron diffraction data. Different experimental setups are demonstrated, including selected area electron diffraction and nanodiffraction in transmission electron microscopy or scanning transmission electron microscopy modes. The methods were demonstrated on organometallic complexes (chlorinated and unchlorinated copper phthalocyanine) and on purely organic compounds (quinacridone). The PDF curves from powder electron diffraction data, called ePDF, are in good agreement with PDF curves determined from X-ray powder data demonstrating that the problems of obtaining kinematical scattering data and avoiding beam damage of the sample are possible to resolve.

In total, 50 pairs of diffraction/image pairs were collected from each sample. This approach not only maximizes the counting statistics while minimizing beam damage, but increases the powder statistics (the number of crystallites that are averaged to obtain the integrated diffraction pattern) in a natural way. Based on the corresponding images these pairs could be classified into: (i) diffraction patterns from the material, (ii) diffraction patterns from the carbon film only. The patterns from the carbon film were averaged and used for background estimation. All diffraction patterns from the material were summed together, likewise for all the background diffraction patterns, and these integrated images were used for further processing.

After the patterns were centered by the gradient of the central beam, several patterns from different parts of the sample, as described above, were averaged in order to increase the signal-to-noise ratio owing to the counting statistics and to improve the powder average. Averaged patterns were then azimuthally integrated and normalized by a number of 2D pixels into each bin of constant Q-value. The integration procedure was done by a home-written program and produced integrated intensity versus Q.

The high Q-range accessible in principle in the TEM, and the sensitivity to light atoms, means that ePDF may become a powerful method for nanostructure characterization. The maximum values of Q obtained here were modest, and future work will also be invested in protocols for collecting data in TEMs over wider ranges of momentum transfer. Potential advantages of ED derived PDFs are that they can be obtained from small quantities of material, and material in special geometries, such as in the form of a thin film. While they are not currently straightforward to obtain, this may be remedied in the future with special attachments to microscopes coupled with dedicated software for data collection and reduction.
Figure 1: Diffraction data of chlorinated Cupperphthalocyanine: a) red curve: X-ray (Mo-Kα1), blue curve: electron diffraction data collected with transmission electron microscopy/nanodiffraction mode, green curve: electron diffraction data collected using scanning transmission electron microscopy/nanodiffraction mode both after azimuthal integration and with the x axis converted to Q, respectively; b) Comparison of the electron pair-distribution function (ePDF:blue line) with a simulated pair-distribution function (PDF:red line) from the known crystal structure.
Electron Crystallography School – Introduction to Electron Diffraction Tomography

Ute Kolb

In the tradition of Electron Crystallography Schools, started in Erice (Sicily) in 1990 and held since then in different European countries, a school with a focus on electron diffraction tomography took place in Darmstadt (Germany) on 7.4.-11.4.2014. The school organized by the group of Prof. Ute Kolb covered the basic concepts of electron diffraction and imaging, new ways of data acquisition using different upcoming tomography methods in reciprocal space as well as procedures for structure solution. 9 Lecturers provided theoretically morning lectures and 5 Lecturers gave practical afternoon courses using different transmission electron microscopes at the Technical University in Darmstadt.

42 students (15 woman and 27 men) from 16 countries all over the world (Belgium, Denmark, Germany, Greece, Israel, Italy, Mexico, Netherlands, Poland, Russia, Slovakia, Spain, Sweden, Switzerland, Turkey, USA) participated in the school many of whom contributed their own research for discussion in the poster session.

We are grateful for the support provided by the national and international associations of Crystallography (International Union of Crystallography IUCr, European Crystallographic Association ECA, Deutsche Gesellschaft für Kristallographie DGK), and Microscopy (European Microscopy society EMS).
Technical Petrology with Emphasis in Low Temperature Petrology

Petrology is devoted to study the genesis and the mineralogical evolution of a rock with a specific bulk composition at various physical and chemical conditions. The scientific and educational fields of this branch within the applied geosciences are based on crucial knowledge in magmatic-, metamorphic-, hydrothermal petrology, mineralogy, structural geology, tectonophysics, geothermal geology, sediment petrography, thermodynamics/kinetics and geochemistry.

Technical Petrology aims to assess the physical and chemical properties of natural or synthetic rocks for applied purposes at various physical and chemical conditions (e.g. pressure, temperature, chemical composition). The Technical Petrology group is in particular devoted to study the low temperature domain. These low temperature studies serve as an aid to qualify and quantify processes occurring in hydrocarbon prospecting, geothermal system, and geodynamic study.

The principal motivation of our Low-Temperature Petrology research group is to understand and to quantify low temperature petrologic processes. For this purpose, an effort is addressed to innovate new tools to calibrate and to model the metamorphic P-T-Xd-t conditions in low-grade rocks. A multidisciplinary approach is necessary because crystallization and recrystallisation are not obvious at low temperature. Hence, our work links field and experimental petrology, analytical methods, thermodynamic and kinetic modelling. Similar approaches are easily applied in archaeometry in order to characterise a range of firing temperatures and to describe recrystallisation processes of starting clay material. Opposite to prograde diagenetic to metamorphic processes, presented working philosophy is employed to describe the reverse cycles of destruction and weathering of rocks and the formation of clays and techno soils.

The main research interests of the Technical Petrology Group are focussed on the following topics:

Clay Mineralogy

- The application of Kübler Index and other clay mineral parameters to determine a grade of diagenesis and incipient metamorphism.
- Development of Geothermobarometers based on the reaction kinetics in the reaction progress and aggraduation of clay minerals to micas. These can be used in orogenic researches, sediment basin analyses, hydrocarbon exploration, and geothermic prospections.
- Improvement of methods related to hydrocarbon exploration.
- Improvement of methods related to the low-grade metamorphism characterisation.
Stability of clay barriers

Natural bentonite is considered as a suitable candidate for buffer material required for the underground disposal of high level radioactive waste (HLW). Repositories of HLW are commonly representing multibarrier systems. The host rock is an important barrier and so is clay used as backfill and buffer, that is the interface between the canister with the radioactive waste and the host rock. Backfill material is considered as a safety barrier in the emplacement tunnel. There are a number of concepts for the future disposal of HLW in underground repositories. They are based on the use of "multi-barrier" systems made up of two basic factors: an engineered barrier and host rock. The engineered barrier comprises metallic container ("canister") containing vitrified nuclear waste or spent nuclear fuel. The metallic containers could be made of iron or copper. These are placed in underground caverns within host rock (e.g. shale, granite or salt), which constitutes the natural geological barrier. Our research focuses on concepts of different countries of using iron metallic castor and salt, crystallized rock or claystone rocks formations as host rock and bentonite acts as buffer and backfill materials. The main question for this type of scenario is, will bentonite be stable or not? In order to examine this question as well as to evaluate the long term safety of the repository, it is necessary to consider the stability of the buffer and backfill components by laboratory testing and theoretical modelling. Different smectitic rich clay and bentonite in the worlds are examined with the aims are followed:

- Stability of chemical structure and geotechnical parameters of smectite rich clays/bentonite in contact with groundwater, cement and Fe leachate from concrete and Fe-canister of multi barrier systems.
- Kinetics dissolution of smectite rich clays/bentonites under HLW-repository conditions.
- Natural Fe-rich clays as potential natural analogues to buffer alteration processes, driven by the presence of Fe and high alkaline groundwater in system.

Low-Temperature Petrology s.l

Orogen and palaeogeothermal researches in foreland basins of the Alps, Vosges, Dinarides, Carpathians, Stara Planina (Bulgaria), Balkanides, Variscides of the Bosporus and Turkey.

A broad analytical spectrum must be applied in low-temperature petrology due to very small grain-size. Technical Petrology group maintains a Microscopy Laboratory (CCA coal-reflection microscopy, MPV coal-reflection microscopy, fluorescence microscopy, transmitted light microscopy). The former XRD laboratories (Clay and XRD Laboratory and a research XRD Laboratory) had to be moved and merged with the awkward geochemical laboratory. The ICP-AES, TOC, AOX and gas chromatography together with the Organic Geochemical Laboratory was closed in 2012. A non-completed refurbishment of the Geoscience Institute forced us to accept an adverse decision. A XRF laboratory (Wave-dispersive BRUKER S8-Tiger) is maintained together with the groups of Chemical Analytics and Environmental Mineralogy.
Due to the adjournment of the refurbishment of the building and the infrastructure the situation did not change since 2012. On photographs of the laboratories the iniquitous situation depended on development is documented on the Web page to testify the need to get back ideal working conditions. In 2014 the negative development in rejected funding continued. The economic situation declined again and evaluation criteria of the faculty forced the need to cut an assistant position and thus some parts of the infrastructure of the technical petrology group had to be closed (Experimental Coal Petrology, Coal Petrology, Archaeometry and part of the instrumental analytics). The rebuke against the head is a concealed and perfidious way to erode scientific licence and freedom of research causing damage on the ambitious content in education of the specialism. It is to point out that the coal petrology research associate (position being cut in 2013 due to employment rules for research associates - 12 years of temporary engagement) Dr. Ronan Le Bayon and the head were honoured by The Society of Organic Petrology (TSOP) with five reference papers on the society homepage, also the appointment as convenors of a coal petrologic session on the GeoFrankfurt 2014 and as guest editors. A strong misfit between the evaluation at the university and the reputation in the coal community is evident. The reduction of the wide research base in Germany will cause future damages in sciences.

**Staff Members**

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<tr>
<td>Head</td>
<td>Prof. Dr. Rafael Ferreiro Mählmann</td>
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<td>Research Associates</td>
<td>Dr. Lan Nguyen-Thanh</td>
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<td>Technical Personnel</td>
<td>Dr. Norbert Laskowski</td>
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<td>Secretary</td>
<td>Astrid Kern</td>
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<td>BSc-MSc Students</td>
<td>Tobias Necke and Sascha Kümmel</td>
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**Research Projects**

Kübler Index standardization. Cooperation with Greifswald University (D) and the working group of the MECC 2014.

Temperature determination between 50 and 270 °C through fluid inclusion microthermometry and vitrinite reflectance values in the external parts of the Central Alps. Cooperation with Basel University (CH) and RWTH Aachen (D).

Reliability of very low-grade metamorphic methods to decipher basin evolution: case studies from basins of the Southern Vosges (NE France). Cooperation with LaSalle Beauvais Geosciences Department, (F), Geoscience Australia Resources Division (AU).

Low-grade study on the thermal evolution of wairarapa area, North Island, New Zealand. Cooperation with LaSalle Beauvais Geosciences Department, (F), UMR 8217 Géosystèmes,
bâtiment SN5, University of Lille (F), University of Picardie Jules-Verne (F), GNS Science (NZ).


The Zlatitsa para-series group, a new Palaeozoic lithostratigraphic member determined in the Kashana section at the southern Stara Planina mountain range (Central Balkanides, Bulgaria). Cooperation with the Universität Freiburg (D), Université de Genève (CH), University of Sofia "St. Kl. Ohridski" (Bg).

Characterization of Fe-smectites from Nui Nua clay, Thanh Hoa province, Viet Nam and its alteration potential considering for HLW repositories. Cooperation with the Ernst-Moritz-Arndt-Universität, Greifswald (D), Hanoi University of Science (Vietnam), Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Braunschweig (D), Vietnamese Academy of Science and Technology.

Fossil Multiphase Normal Faults - Prime Targets for Geothermal Drilling in the Bavarian Molasse Basin. Cooperation with the University of Alberta (Canada), GeoTec Consult, Markt Schwaben (D), Loske Geosciences, Essen (D), GFZ - Helmholtz Centre Potsdam (D), Exorca, Grünwald (D).

Determination of rock maturity using vitrinite like bituminite kinetics. A field and laboratory study including liptinite and vitrinite reflectances. Implications for prospection and engeneering geology in meta-sedimentary rocks. Cooperation with GFZ - Helmholtz Centre Potsdam (D). The project was finished in 2014 without funding and the results by the usual route to be published.

Conversion mechanism of bentonite barriers. Cooperation with the Ernst-Moritz-Arndt-Universität, Greifswald (D), Hanoi University of Science (Vietnam), Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Braunschweig (D). The project will run from 01.01.2015 to 30.09.2017.

**Society activities**

The head was appointed member of the Scientific Program Committee at the 68th International Committee for Coal and Organic Petrology (ICCP) Meeting, Potsdam 2015, Germany.

The head and Ronan Le Bayon have been conveners with Ralf Littke at the GeoFrankfurt 2014 Conference, Earth System Dynamics (GV, DGG). Session A09: “Organic petrology, organic geochemistry and mineralogy in basic research and applied geosciences”. Frankfurt, Germany.
The head was convener with Laurence N. Warr and chairperson at the 7th Mid-European Clay Conference (MECC14). Session 5: “Clay minerals in diagenetic and low temperature metamorphic environments” including a round table about the "Kübler Index - standardisation“. Dresden, Germany.

The head was member of the Scientific Program Committee at the 9th European Coal Conference. Gliwice, Poland.

The head was elected reviser of the Swiss Society of Mineralogy and Petrology (SSMP).

**Publications**


Correlation of vitrinite like bituminite reflectance with vitrinite reflectance in various geological settings: A tool for determining organic matter maturation level

Rafael Ferreiro Mählmann & Ronan Le Bayon

Introduction

With the growing interest in oil and gas shales, organic petrology and geochemistry as well as mineralogy are again in the focus of interest of sedimentary basin research. In particular, high levels of diagenesis reaching the early stage of metamorphism have become economically more interesting than in the past. Shales are also important as potential storage sites for (nuclear) waste and as cap rocks for natural and artificial gas accumulations in the subsurface. Furthermore, there is a growing interest in coal-anthracite raw material prospection. Petroleum production now moves more and more into complex tectonic settings and into areas with high fluid pressure, especially at passive continental margins with deep burial shelf conditions. Fast sedimentation, under-compaction, over-pressured poor fluids, thermal anomalies and abnormally low thermal conductivities have a strong influence on organic matter maturity. In these settings, pressure can play an important role in maturation, especially if fast tectonic load in orogenic settings prolongs low conductivity conditions hindering thermal steady state advection and if strong tectonic forces cause cleavage. In these settings, a combination of parameters including organic geochemical, organic petrological, and clay mineralogical parameters can be of advantage.

Anthracites and hard coals in inverted basins as well as bituminite hosted ore deposits often contain unexpected, high amounts of gas. Contact metamorphism without release of hydrocarbons can lead to high over-pressure. The prediction of gas in internal orogenic settings is also of interest for large tunnel constructions and forces the need of basis research. A refined and sophisticated modelling will have considerable economic benefit and increase security precaution. For prospection of hydrocarbons empirical and kinetic based models will allow to predict hydrocarbon quantity and composition including secondary cracking-products. Due to the increased demand in fertilizers, pharmaceutics, petrochemical products and carbonaceous materials a precise prediction of properties of the mostly small deposits is a pre-requisite for the success.

Specific research interest

Vitrinite reflectance (VR) is a useful and reliable parameter to monitor the level of organic matter maturation from the immature stage to graphite. Additionally, VR is a useful and essential tool in modeling the temperature–maturation time path followed by huminithe/vitrinite-bearing sedimentary and meta-sedimentary terranes throughout their geological history. VR pressure (P) dependence (Le Bayon et al. 2011, 2012) can not be ignored, but no equation fit to be used for the moment employing P as a VR-controlling variable (Ferreiro Mählmann, 2001). Such modeling enables to reconstruct the geological history of sedimentary and metamorphic terranes, to improve geothermal prospection, hydrocarbon exploration and gas-blow prediction in the tunnel construction. The usefulness of VR for such crucial purposes evidently depends on the presence of huminite/vitrinite (i.e.
Type III organic matter) phytoclasts in the geological terranes. However, pre-late Silurian to Devonian rocks and many organic-rich marine rocks (e.g. sapropelic sediments) lack of huminite/vitrinite particles. Furthermore, vitrinite is sparse in carbonate sediments.

However, the presence of bituminite (including exsudatinite, migrabitumen and pyrobitumen) in rocks lacking of Type III organic matter is shown to provide a valuable aid via its reflectance (vitrinite like bituminite reflectance – VlBR, and/or bituminite reflectance - BR) to fulfill the above-described tasks, that VR enables. This study presents a relationship between BR/VlBR and VR for various types of geodynamic setting and over the largest possible range of maturation level so that VlBR may be used as a substitute for VR.

Whereas the effort to correlate VlBR with VR is not novel, it is the first time that such VR/VlBR(BR) correlations are established for various frequent geodynamic contexts. The investigated geological contexts are:

(1) sedimentary basins (e.g. the Saar, Ruhr Pennsylvanian, Texas and Petrosani basins);

(2) metasedimentary terranes occurring as inverted basins in orogenic belts (e.g. from the Subalpine-Molasse, Helvetic, Austroalpine and Danubian nappe systems) and having suffered from very low to low grade metamorphism (from anchizone to greenschist facies);

(3) metasedimentary terranes (e.g. slates and schists from the Franciscan and Alpine belts) that were subducted at anchizone to blueschist facies conditions; and

(4) metasedimentary terranes suffering from contact metamorphism. Together, the frequent geological settings are referred and most of the earth geothermal conditions and heat fluxes considered.

At least VR and BR comparisons with mineralogical calibrations and temperature estimations have to be discussed. Frequently VR is used for palaeo-temperature calibrations in low grade metamorphic settings. Depending from the P-T conditions a sub-division of diagenesis, sub blueschist facies and sub-greenschist facies will be proposed (Fig. 1).
References


Effects of chemical structure on stability of smectites in short-term alteration experiments

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Bentonites are suitable candidates as buffer and backfill materials in HLW-repositories. An objective of these investigations was to explore the idea that bentonites have a specific dissolution potential (by “rate of alteration”-experiments). The “rate of alteration” experiments were carried out as overhead-shaking batch experiments. Well characterized bentonites (9 from API-standard series, 12 from the BGR-collection and 4 others) were investigated in contact with deionized water (liquid/solid-ratio = 10/1) and with NaCl 1N solution (liquid/solid-ratio = 4/1) for 30 days. XRD and TEM – EDX measurements were the major analytical techniques applied in this research. FT-IR and XRF analyses were used as additional tools for the characterization of the structure and composition of the smectites.

Numerical description of the degree of alteration by Δ%S by TEM-EDX

a. Using of Mineral Formulae with focus on the tetrahedral composition (Si-amount)

b. Calculation of smectitic layer (S%) by Środón et al. (1992)

\[
S\% = 100.38 \times (4 - IVSi)^2 - 213 \times (4 - IVSi) + 109.4
\]

(%S: proportion of smectitic layer; IVSi: Si in tetrahedral sheet)

c. Calculation of degree of alteration (Δ%S )

\[
\Delta%S = S\%_{\text{experiment}} - S\%_{\text{origin}}\quad (\Delta%S > 0:\text{ smectitization};\; \Delta%S < 0 \text{ “illitization”})
\]

After the mineralogical characterization of original samples and of the reaction products of these experiments different degrees of alteration were recognized. Each approached smectite has shown a specific dissolution potential. This potential was identified by degree of “illitization” or smectitization for each sample (proofed by TEM-EDX, FT-IR) Figure 1, 2A. Bentonites with illite-smectite mixed layer phase in the original material have shown commonly smectitization. It seems that such mixed layer phases can buffer dissolved Si.
Figure 1. Smectitization and illitization caused by the (60 rpm + NaCl) experiment (left). Empirical determination of impact by (A) initial interlayer cations $\Delta$XII and (B) initial octahedral cations $\Delta$VI on specific dissolution potential, $\Delta P$, for experimental series: 60 rpm + NaCl. Note: $\Delta = \Delta$XII + $\Delta$VI; the diameter of the circles is related to the measured decrease of smectitic layer ratio, %S, between the original and treated smectites.

The following parameters were identified as driving forces for the mentioned specific dissolution potential: (i) original distribution of Al, Fe and Mg in octahedral sheet and (ii) Na/(Ca+Mg)-ratio in cationic composition of interlayer space.

Increasing octahedral Fe- and Mg-amounts are promoting a faster dissolution of smectite. Two types of dissolution behavior were identified for 21 different bentonites. High Na amount in interlayer space has acted in some cases as stabilizer (type A) (Fig. 2B). In other cases Ca+Mg-cations in interlayer space stabilized the aggregates (Fig. 2C). These two groups are characterized by specific composition of octahedral sheet (Fig. 3A) and by a specific signature in FTIR-spectroscopy (Fig. 3B).

The Al-Fe ratio in the octahedral sheet influences the stability of the interlayer:

a. $\text{Al}_{\text{oct}} > 1.4$ and $\text{Fe}_{\text{oct}} > 0.2$ (per $\text{OH}_2\text{O}_{10}$) favour delamination of quasicrystals. The swelling pressure increases by a co-volume process between the delaminated layers with higher numbers of quasicrystals for Na-dominant population of the interlayer space (Laird, 2006). The microstructural components including both small and large particles and parts of them have a very small ability to move and undergo free rotation. Such Na-montmorillonites are considered as stable phases and have only a low specific dissolution potential. They are „Sleepers“.

b. $\text{Al}_{\text{oct}} > 1.4$ and $\text{Fe}_{\text{oct}} < 0.2$ or $\text{Al}_{\text{oct}} < 1.4$ and $\text{Fe}_{\text{oct}} > 0.2$ (per $\text{OH}_2\text{O}_{10}$) promote demixing of monovalent and divalent interlayer cations (Laird, 2006). In the case of Ca and Mg-dominant interlayers, quasicrystal can break at Na-bearing interlayers and help to maintain the quasicrystal structure. Such Ca and Mg-montmorillonites can be also be taken as „Sleepers“, because of their low specific dissolution potential.
Specific degree of alteration ($\Delta S_{\text{total}}$) of bentonites.

Notes: $\Delta S_{\text{XII}}$ - impact of interlayer cations on stability of smectite; $\Delta S_{\text{VI}}$ - impact of octahedral cations on stability of smectite; $\Delta S_{\text{Total}} = \Delta S_{\text{XII}} + \Delta S_{\text{VI}}$ - specific dissolution potential of smectite

- $\Delta S_{\text{total}} > -20\%$ ("Sprinter")
- $\Delta S_{\text{total}} = -5\% \rightarrow -20\%$ (Intermediator)
- $\Delta S_{\text{total}} < -5\%

It is assumed that the original composition of octahedral sheet is representing mainly the pH-environment during the formation of the smectite clay and therefore it serves as a geological fingerprint.

Figure 2: Smectitization and illitization caused by the (20 rpm + NaCl) experiment (A) and group A (B), group B (C) and specific dissolution potential ($\Delta S$) of bentonite classified by short-term alteration experiments (table below)
The specific dissolution potential of MX80 determined by “rate of alteration” experiments has shown in figure 2 comparable values to degree of alteration in tetrahedral sheet of “clay/iron-interaction” experiments. This observation indicates that the results of specific dissolution potential form “rate of alteration”-experiments could be transferred to processes in the “clay/iron-interaction”-experiments. An Excel-based tool has been developed in order to estimate the specific dissolution potential and expected Si-precipitation of any bentonite. This tool can be used for the preselection of possible suitable bentonites for long-term stable barriers in repositories.

References
Environmental Mineralogy

Environmental mineralogy focuses its research on the characterization of individual aerosol particles by electron beam techniques (high-resolution scanning electron microscopy, transmission electron microscopy, environmental scanning electron microscopy).

We study individual aerosol particles in order to derive the physical and chemical properties (e.g., complex refractive index, deliquescence behavior, ice nucleation) of the atmospheric aerosol. These data are of great importance for modeling the global radiation balance and its change due to human activities.

We are also interested in studying particle exposure in urban environments and at working places. As aerosol particles may have adverse effects on human health, the knowledge of the particle size distribution and the chemical and mineralogical composition of the particles is of prime importance in order to derive the exact mechanisms of the adverse health effects.

In addition, we also investigate particles as carriers of pollutants into Nordic and Arctic ecosystems.

Our research is carried out in cooperation with the following national and international partners: Max Planck Institute for Chemistry in Mainz, Institute for Atmosphere and Environmental Sciences (University of Frankfurt) Institute for Atmospheric Physics (University of Mainz), Institut für Steinkekservierung (IFS) in Mainz, Institute for Meteorology and Climate Research (Karlsruhe Institute of Technology), Institute for Tropospheric Research in Leipzig, Institute of Atmospheric Physics (German Aerospace Center DLR) in Oberpfaffenhofen, Paul Scherrer Institute (Laboratory of Atmospheric Chemistry) in Villigen (Switzerland), National Institute of Occupational Health (STAMI) in Oslo (Norway), and the Norwegian University of Life Science (NMBU) in Ås (Norway).

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Research Projects

Environmental scanning electron microscopical studies of ice-forming nuclei (DFG Forschergruppe INUIT).

Electron microscopy of long-range transported mineral dust.

Source apportionment of rural and urban aerosols.

Sources of soot at work places (National Institute of Occupational Health, Oslo, Norway).

Influence of traffic on the surface of monuments.

Particle and organic pollutant emissions of coal burning in the Arctics.

Publications


Long-range-transported Saharan dust in the Caribbean – an electron microscopy perspective of aerosol composition and modification

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From June to July in 2013, the Saharan Aerosol Long-range Transport and Aerosol-Cloud-Interaction Experiment (SALTRACE) was performed in the Caribbean. Airborne aerosol sampling was performed onboard the DLR Falcon aircraft in altitudes between 300 m and 5500 m. Ground-based samples were collected at Ragged Point (Barbados, 13.165 °N, 59.432 °W) and at the Cape Verde Atmospheric Observatory (Sao Vicente, 16.864 °N, 24.868 °W). Different types of impactors and sedimentation samplers were used to collect particles between 0.1 µm and 4 µm (airborne) and between 0.1 µm and 100 µm (ground-based). Particles were analyzed by scanning electron microscopy and energy-dispersive X-ray microanalysis, yielding information on particle size, particle shape and chemical composition for elements heavier than nitrogen. A particle size correction was applied to the chemical data to yield better quantification. A total of approximately 100,000 particles was analyzed. For particles larger than 0.7 µm, the aerosol in the Caribbean during the campaign was a mixture of mineral dust, sea-salt at different aging states, and sulfate (Figure 1). Inside the Saharan dust plume – outside the marine boundary layer (MBL) – the aerosol is dominated by mineral dust. Inside the upper MBL, sea-salt occurs as minor component in the aerosol for particles smaller than 2 µm in diameter, larger ones are practically dust only. When crossing the Soufriere Hills volcano plume with the aircraft, an extremely high abundance of small sulfate particles could be observed. At Ragged Point, in contrast to the airborne measurements, aerosol is frequently dominated by sea-salt particles (Figure 1). Dust relative abundance at Ragged Point has a maximum between 5 µm and 10 µm particles diameter; at larger sizes, sea-salt again prevails due to the sea-spray influence. A significant number of dust particles larger than 20 µm was encountered. The dust component in the Caribbean – airborne as well as ground-based – is composed of mainly silicates and minor amounts of Ca-rich and Fe-/Fe-Ti-rich particles (less than 10 % of dust fraction). The composition of the silicates indicates a major contribution of kaolinite (Al/Si atomic ratio between 0.6 and 1) and a minor contribution of quartz and feldspar particles. The inter-sample variation of the dust composition is generally low, pointing to a very thorough mixing from differently-composed Saharan sources. The temporal evolution of aerosol composition at Ragged Point shows a variation in dust abundance, but strong isolated events could not be identified. An airmass change induced by the passing by of a hurricane, however, is visible in sulfate abundance and their composition (Figure 2). Pronounced internal mixing of dust and sulfate or dust and sea-salt is very rare (up to 1 %
of particles in the airborne samples), but a slight increasing tendency with decreasing altitude was found. In the lower MBL at Ragged point, dust/sea-salt mixtures are more frequent (in the same abundance range as pure dust particles). A first conclusion from the data set is that dust aging with respect to internal mixtures does not happen during the long-range transport across the Atlantic Ocean, but rather at the end during the down-mixing of mineral dust into the Caribbean MBL.

Figure 1: General composition development for Eastern (Cape Verde) and Western (Barbados) North Atlantic Ocean. SAL = Saharan Air Layer, BL = Planetary Boundary Layer.

Figure 2: Sulfate composition of single particles (0.7 µm < d < 8 µm) with respect to their cation composition (x and y axis) and their ageing (anion composition, color scale). RPE_20, 04 and 09 were collected during maritime conditions, RPE_26 and 30 show Barbados island influence. At Cape Verde, high amounts of sulfate and magnesium are detected in the aerosol.
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