International Symposium on Electrical Fatigue in Functional Materials

15.9.-18.9.2014 • Sellin • Rügen • Germany

Welcome

With great pleasure, we welcome all participants of the „International Workshop on Electrical Fatigue in Functional Materials“.

This event will bring together experts in the area of ferroelectrics, organic semiconductors and ionic conductors to share their most recent results on electrical fatigue mechanisms.

We are looking forward to the presentations given by our invited speakers and by members of the SFB 595. The scientific program will cover various aspects of studies on fatigue including characterization of structural and functional properties, preparation and synthesis of new materials and modelling.
We hope that the wonderful setting at the Baltic Sea will stimulate active discussions and help to create new ideas for future research.

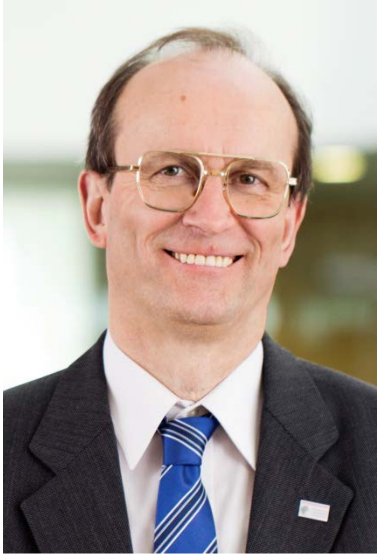
This workshop is also the closing event of the collaborative research center SFB 595 that started in January 2003. During the 12 years of operation we have seen a number of important scientific achievements, which will be in part highlighted during the coming days. We are also very happy that many international colleagues, who were collaborating with us over the years, join us for this event in Sellin.

Moreover, we welcome among the participants of this workshop all members of the various review committees, who devoted their time and closely followed our research activities over the years. We are also much obliged to the DFG representatives, who were excellent partners during all stages of our research center and also take part at this workshop.

Finally, we want to thank Gila Völzke for organizing this event and for being the administrative brain of the SFB 595 over the years.

We wish you all an enjoyable and most stimulating meeting.

The coordinators of the SFB 595



SFB 595

Deutsche
Forschungsgemeinschaft
DFG

Karsten Albe

Prof. Dr. Karsten Albe

Jürgen Rödel

Prof. Dr. Jürgen Rödel

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Time schedule

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K	–	Keynote speakers	(60 min.)
I	–	Invited speakers	(30 min.)
O	–	Overview report	(30 min.)
T	–	Talk	(15 min.)

Divisions of SFB 595					
A	–	Synthesis	T	–	Transferprojects
B	–	Characterizing			
C	–	Modelling			
D	–	Component Properties			

Sunday, September 14th

	Check In and Welcome Buffet

Monday, September 15th

8:45 AM	Opening	Karsten Albe		

Ferroelectrics I

9:00 AM	K 01	Mark Hoffman	Effect of Relaxor-Ferroelectric Transitions on Fatigue of BNT-based Lead-free Piezoceramics	
10:00 AM	O 01	Jürgen Rödel	Developing Lead-Free Piezoceramics	
10:30 AM	Coffee			

Ferroelectrics II

11:00 AM	T 01	Wolfgang Donner	Static and Dynamic Disorder in Ba-doped Bismuth Sodium Titanate	B3
11:15 AM	T 02	Pedro B. Groszewicz	Lead-free BNT-xBT relaxor ferroelectrics characterized by ^{23}Na NMR	B9
11:30 AM	T 03	Melanie Gröting	Structure-Property Relationships in the Relaxor Ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$	C1
11:45 AM	T 04	Marina Zakhozheva	Reversible multi- to single domain transition in $Ba(Zr_{0.2}Ti_{0.8})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$ ferroelectrics under poling conditions	B3
12:00 PM	I 01	Philippe Ghosez	Interplay between lattice, spin, orbital and charge orders in bulk and layered ABO_3 perovskites	
12:30 PM	Lunch			

Batteries I

2:30 PM	I 02	Hirokazu Munakata	Design and Fabrication of all-solid-state rechargeable lithium batteries using ceramic electrolytes	
3:00 PM	T 05	Magdalena Graczyk-Zajac	New insights into understanding of irreversible and reversible lithium storage within SiOC and SiCN ceramics	A4
3:15 PM	T 06	Christian Hess	In Situ Raman Diagnostics of Intercalation Batteries	B8
3:30 PM	T 07	René Hausbrand	Surface science investigations of electrode-electrolyte interfaces in Li-ion batteries	A3
3:45 PM	T 08	Sabrina Sicolo	Structure and Properties of Amorphous LiPON Electrolyte by First-Principles Simulations	C1
4:00 PM	I 03	Alois Kuhn	Sodium insertion properties of titanates and related materials as negative electrodes for Na-ion batteries	
4:30 PM	Coffee			

Fatigue and Ageing

5:00 PM	I 04	Akira Ando	Degradations of Dielectric ceramic materials	
5:30 PM	T 09	Eva Sapper	Aging in of Fe-doped (1-x)$(Bi_{1/2}Na_{1/2})TiO_3$-$xBaTiO_3$ piezoelectric ceramics	D1
5:45 PM	T 10	Feng Chen	Fatigue free in epitaxial KNN films	
6:00 PM	I 05	Xiaoli Tan	In situ TEM Study on the Aging and Fatigue of Piezoelectric Ceramics	
6:30 PM	O 02	Yuri Genenko	Aging and fatigue in ferroelectrics: experimental results and current understanding	
7:00 PM	-/-			
7:30 PM	Dinner			
9:00 PM	Poster			

Tuesday, September 16th

OLED I

9:00 AM	K 02	Roland Schmechel	Electrical Engineering with nanostructured materials: Examples from Photovoltaic and Thermoelectric	
10:00 AM	O 03	Heinz von Seggern	Electrical fatigue of polymer light-emitting diodes based on *poly* (*p*-phenylene vinylene) derivatives: a comprehensive approach	
10:30 AM	Coffee			

OLED II

11:00 AM	I 06	Katja Stegmaier	Status, Technology and Challenges in OLED Development	
11:30 AM	T 11	Nicole Vilbrandt	Poly(*p*-phenylene vinylene)s – Highlights of 12 years of research within the SFB 595	A5
11:45 AM	T 12	Sergey Yampolskii	Self-consistent description of charge-carrier injection at a conductor/organic semiconductor interface: extension to the case of a degenerate semiconductor	C5
12:00 PM	O 04	Andreas Klein	Do TCOs contribute to electrical fatigue of organic light emitting diodes?	
12:30 PM	Lunch			

Afternoon Program

2:30 PM	Excursion
7:30 PM	Dinner

Wednesday, September 17th

Batteries II

9:00 AM	K 03	Claude Delmas	An overview of the behaviour of layered oxides in lithium and sodium batteries	
10:00 AM	O 05	Helmut Ehrenberg	Investigations on fatigue of Li-ion batteries	
10:30 AM	I 07	Rüdiger Eichel	High-power, high energy-density lithium ion batteries – impact of atomic-scale processes on electrochemical performance and cyclic aging	
11:00 AM	Coffee			

Point Defects

11:30 AM	I 08	Paul Erhart	Polarons in oxides and halides	
12:00 PM	T 13	Mareike Hohmann	Transparent Conducting Oxide Electrodes	D3
12:15 PM	T 14	Karsten Albe	Point defects and surfaces of transparent electrodes studied by electronic structure calculations	C2
12:30 PM	Lunch			

Ferroelectrics III

2:30 PM	I 09	Tor Grande	On the electrical conductivity and point defects in $BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ materials	
3:00 PM	T 15	Yinan Zuo	Phase field simulation of domain structure in ferroelectrics with semiconducting feature	C6
3:15 PM	T 16	Wolfgang Rheinheimer	Influence of Lead Oxide Stoichiometry Microstructure and Characteristics of PZT Ceramics and Multilayer Actuators	T2
3:30 PM	T 17	Jurij Koruza	True Operational Range of Piezoelectric Actuators	D6
3:45 PM	T 18	Shunyi Li	Interfaces of Ferroelectrics	B7
4:00 PM	Coffee			

Ferroelectrics IV

4:30 PM	I 10	Nina Balke	Investigation and Manipulation of Domains on Small Length Scales in Ferroelectric Materials: Limits and Opportunities	
5:00 PM	T 19	Na Liu	Core-shell domain structure investigation of lead-free incipient piezoceramics by piezo response force microscopy	
5:15 PM	T 20	Martin Blömker	(Co-)doping of lead-free $Bi_{1/2}Na_{1/2}TiO_3$–$Bi_{1/2}K_{1/2}TiO_3$-based piezoceramics	A1
5:30 PM	Concluding Remarks			
7:30 PM	Gala Dinner			

Thursday, September 18th

	Departure

General information

Scope

The International Symposium on Electrical Fatigue in Functional Materials will bring together international experts on ageing and fatigue of ferroelectrics, ionic conductors and organic semiconductors.

The meeting will be on **September, 15th-18th 2014** at the Cliff Hotel on Rügen island, directly at the German side of the Baltic sea.

The workshop will present invited talks and contributed posters by active and former members of SFB 595, international guests and partners from industry. It will provide ample of time for scientific discussions.

The meeting is organized by the DFG funded collaborative research center SFB 595 at TU Darmstadt, which will be closing by the end of 2014 after twelve years of operation.

Venue

The five star Cliff Hotel Rügen is situated in a biosphere reserve directly at the Baltic Sea with a 1.5 kilometer long and sandy beach.

A gigantic view either to the sea or on the back to the Selliner See is provided. A lift brings you down from the Cliff Hotel to the private beach. Alternatively, you can enjoy the 25m long indoor swimming pool.

The region invites for swimming, hiking, cycling and a lot of other outdoor activities.

After the hotel was built 30 years ago as a resort for the officials of former eastern German government, by now everything in the hotel has changed. But the extravagance, the favorable position and the amazing view remain the same till today.

Local Organizers

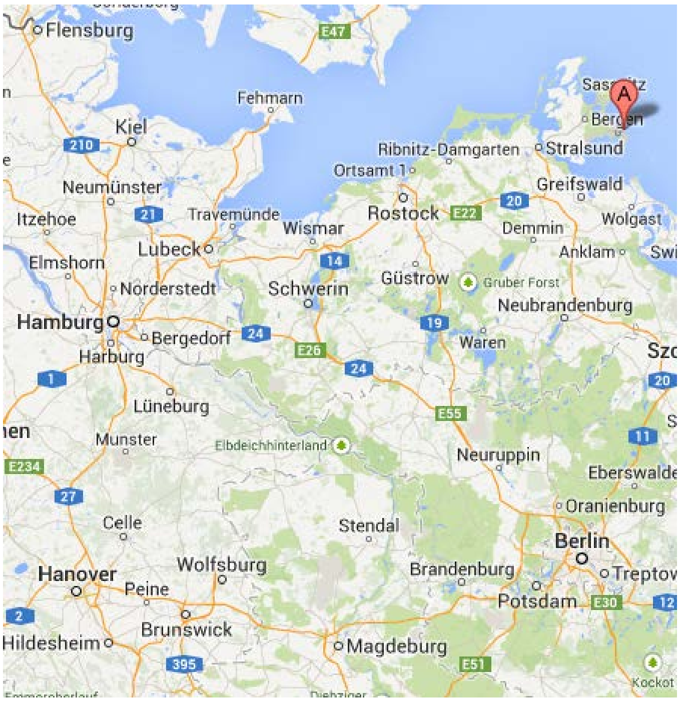
Prof. Dr. Karsten Albe
Coordinator SFB 595

Gila Völzke
Secretary SFB 595

Directions

Rügen island can be reached by plane via the airport Rostock/Laage and shuttle service to Rügen (approx. 60 min). From Hamburg and Berlin there are also direct train connections to Binz/Rügen.

In addition, we will organize group transportation by train or bus on Sunday, September 14th 2014, from Darmstadt and Frankfurt to Sellin.



Excursion program for Tuesday, September 16th 2014:

On Tuesday afternoon you have the choice of two excursions:

1. With the historic train “Rasender Roland” we will go to “Jagdschloss Granitz”.
   A guide will give you detailed information about this historical building, which exists since 1846.

   http://ruegensche-baederbahn.de/fahrplaene.html
   http://ruegensche-baederbahn.de/home.html
   http://www.jagdschloss-granitz.de/

2. The bus brings you to the Center of the National Park with his famous “Kreidefelsen”. The chalk cliffs of Rügen are often said to be the island´s famous landmark. Forming an exceptionally beautiful landscape they are more or less lined up along a coastline which extends over several kilometers.

   http://www.ruegen-infoweb.de/english/other-places.htm#Chalk-Cliffs
   http://www.koenigsstuhl.com

TALKS

K 01: Effect of Relaxor-Ferroelectric Transitions on Fatigue of BNT-based Lead-free Piezoceramics

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Piezoelectric devices are a key enabling technology in industrial, manufacturing and automotive industries. Piezoceramics are currently lead-based, causing toxic by-products, especially during manufacture and waste incineration. Consequently, the search for non-toxic piezoceramics which can replace lead-based materials such as $Pb(Zr,Ti)O_3$ (PZT) is one of the major challenges in science and engineering and BNT-based systems show considerable promise as an alternative.

The fatigue behavior of a ferroelectric composition 94BNT-6BT under bipolar and unipolar electrical cycling was investigated as a function of temperature from 25 to >100°C. For both bipolar and unipolar cycling a decrease of polarization, mechanical strain, permittivity ε_{33} and piezoelectric coefficient d_{33} are observed, with most of the degradation occurring within 10^4 cycles. In situ neutron diffraction in the unloaded state revealed a phase transformation and formation of ferroelectric order within 1000 cycles at room temperature but then a disappearance of the ferroelectric order with subsequent cycles, despite the retention of piezoelectric properties. However, as temperature increased observable ferroelectric order disappeared at all levels of cycling.

When the composition is altered to 91BNT-6BT-3KNN, the material demonstrates no observable fatigue at room temperature and is no longer ferroelectric, yet retains a similar piezoelectric coefficient.

The presentation will posit that fatigue behavior in these systems can be explained by an electric field-temperature (E-T) phase relationship with the loci of transitions between phases varying with composition.

[1] H. Simons, J.E. Daniels, J. Glaum, A.J. Struder, J. Jones and M. Hoffman, “Origin of large recoverable strain in 0.94(Bi0.5Na0.5)TiO3-0.06BaTiO3 near the ferroelectric-relaxor transition”, Appl. Phys. Lett. 102, 062902 (2013)
[2] Z. Luo, S. Pojprapai, J. Glaum, M. Hoffman, “Electrical Fatigue-Induced Cracking in Lead Zirconate Titanate Piezoelectric Ceramic and Its Influence Quantitatively Analyzed by Refatigue Method” J. American Ceramic Soc 95 (2012) 2593-2600
[3] H. Simons, J. Glaum, J.E. Daniels, A.J. Studer, A. Liess, J. Rödel and M. Hoffman, “Domain fragmentation during cyclic fatigue in 94%(Bi1/2Na1/2)TiO3-6%BaTiO3”, Journal of Applied Physics 112[4] (2012)
[4] Z. Luo, J. Glaum, T. Granzow, W. Jo, R. Dittmer, M. Hoffman and J. Rodel, "Bipolar and unipolar fatigue of ferroelectric BNT-based lead-free piezoceramics", J. Am. Ceram. Soc., 94 [2] 529-535 (2011)

Notes:

O 01: Developing Lead-Free Piezoceramics

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Electric fatigue for ferroelectrics is of utmost relevance for piezoelectric actuators and sensors. About ten years ago, international research and legislation suggested that there is a credible opportunity to finally abandon lead-based piezoceramics. The SFB responded and today holds the international leading position as an academic institution in this development effort.

Scientific work included material development, methodological advancement, structural characterization, atomistic simulation and in-depth understanding of salient material properties.

In the beginning, BNT-based relaxors with very high strain based on field-assisted reversible phase transition were developed. The accompanying high electric fields were reduced using a novel concept of relaxor-ferroelectric composites and one of core-shell structures. The atomistic structure was elucidated using DFT computation, electron paramagnetic resonance and recently nuclear magnetic resonance. Diffuse scattering and in-situ neutron and synchrotron diffraction and in-situ transmission electron microscopy provided key information. Some of these techniques were performed using single crystals financed through the SFB, while the applied fatigue characterization was enabled through an external industrial partner, who provided multilayer actuators. In the beginning the development was focused on soft piezoceramics, with recent work also including hard doping and aging. Experimental capabilities were greatly enhanced and include now determination of large and small signal ferroelectric and piezoelectric properties from -100°C to +400°C at variable electric field, uniaxial stress and frequency.

For room temperature applications materials based on $(Ba,Ca)(Ti,Zr)O_3$ proved very attractive with strains significantly higher than soft PZT. Again, in-situ TEM and diffraction techniques were crucial to determine the respective roles of intrinsic and extrinsic piezoelectric effects. The quality of the morphotropic phase boundary was particularly quantified using dynamic polarization experiments. With this material, electromechanical characterization and (fracture-) mechanical characterization also are already in the international pole position.

This research focus benefitted vastly from internal SFB collaborations and also created strong international ties. In the near future, transfer into application will be one of the prime interests.

Notes:

T 01: Static and Dynamic Disorder in Ba-doped Bismuth Sodium Titanate

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Bismuth sodium titanate (BNT) is a chemically disordered, lead-free piezoelectric. Doping with barium leads to instabilities that induce structural phase transitions and thereby modify the piezoelectric behavior. We used several x-ray and neutron scattering techniques to determine the influence of Ba-doping on chemical disorder, structural disorder [1] and lattice dynamics. A model will be presented that tries to unify all results in a coherent picture.

[1] John E. Daniels, Wook Jo, Jürgen Rödel, Daniel Rytz, Wolfgang Donner
Applied Physics Letters, 98, (2011), 252904

Notes:

T 02: Lead-free BNT-xBT relaxor ferroelectrics characterized by ^{23}Na NMR

Pedro B. Groszewicz[1], **Hergen Breitzke**[1], **Wook Jo**[2], **Robert Dittmer**[2], **Eva Sapper**[2], **Gerd Buntkowsky**[1] **and Jürgen Rödel**[2]
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Environmental matters stimulate the research on $_{(1-x)}(Bi_{1/2}Na_{1/2})TiO_3 - _{(x)}BaTiO_3$ as a lead-free alternative to piezoelectric ceramics. These solid solutions exhibit very small distortions from the ideal perovskite structure and lack long range coherence, what renders their characterization by diffraction techniques very challenging. In order to assert what structural features are relevant for tuning electric properties, we studied samples with a barium content of $0<x<0.15$ by means of solid state nuclear magnetic resonance of sodium (^{23}Na NMR), a technique sensitive to the local structure.

From our analysis of line position as a function of composition we could identify two chemical shift ranges, which were attributed to the different symmetries observed by diffraction techniques on both sides of the alleged morphotropic phase boundary (MPB) of this system, around 6% barium content. In addition to that, from the ^{23}Na NMR point of view, the investigated materials are disordered at the local structure level. NMR also allowed one to assess the degree of local order/disorder by analyzing line widths of homogeneously broadened lines. To achieve this we employed a two-dimensional NMR experiment (2D-MQMAS), which separates contributions from two different interactions, namely the chemical shift and the quadrupole coupling (electrostatic interaction). The width of the distribution of chemical shift values was constant for most compositions, probably as a consequence of occupancy disorder, but it peaked for compositions 6% and 7%, showing that a wider variety of local symmetries is present for these specific compositions and indicating that the idea of an MPB also contributes to their enhanced piezoelectric properties. We could also correlate the distribution of quadrupolar coupling constants, which are intimately connected to local displacements and therefore polarizations, to the tendency of a composition with given barium content to show either relaxor or a spontaneous ferroelectric behavior, being able to deliver structural evidence for the atypical relaxor-to- ferroelectric crossover observed on permittivity data of compositions in the investigated barium content range.

Furthermore, the quadrupole interaction is also a very sensitive tool for detecting a breaking of cubic symmetry on a local scale, even for partially disordered materials. By comparing shape and relative intensity of quadrupole related NMR spectral features for samples before and after electric poling, we could observe that a cubic and a polar phase coexist for relaxor compositions, a result that supports a model of polar nanoregions (PNRs) embedded in a cubic non-polar matrix for the low temperature state of these lead-free relaxors. Moreover, by field cooling relaxor samples, we observed that the cubic phase disappears when a ferroelectric long range order sets in, together with indication that the local symmetry of the polar phase did not change upon electric poling. These results support a view for which the growth of PNRs to macroscopic ferroelectric domains is aided by electric poling. This electric field induced phase transformation occurs only to the cubic matrix, as its local structure will change, and assume that of nearby PNRs.

Notes:

T 03: Structure-Property Relationships in the Relaxor Ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$

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Abstract Text The necessity of substituting $PbZr_xTi_{(1-x)}O_3$ by lead-free piezoelectric materials in numerous applications, such as sensors, actuators and ultrasonic transducers, has led to a large number of research activities on perovskite solid solutions based on $Na_{1/2}Bi_{1/2}TiO_3$ in recent years.

$Na_{1/2}Bi_{1/2}TiO_3$ (NBT) is a model relaxor ferroelectric with a complex perovskite structure having two different cations on the A-site. Similarly to $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) or $PbSc_{1/2}Nb_{1/2}O_3$ (PSN), both relaxor ingredients are present, i.e. off-centering (Bi^{3+} for NBT and Pb^{2+} for PMN or PSN) and random cation distribution on the mixed cationic site. In addition, like in PMN- or PSN-based solid solutions, NBT-based materials show extraordinarily high strains and are thus promising environmentally friendly alternatives to the lead-containing standard piezoelectric materials.

In addition to the relaxor behavior NBT displays a complex temperature phase sequence. Despite intensive research effort, there are still open questions concerning the existence of chemical order, intermediate phases, lower-symmetry phases, tilt faults etc. [1, 2] The chemical order is of great interest as it might strongly affect the polar displacements and thus the local symmetry and it is believed to be the origin of the so-called polar nanoregions (PNRs) i.e. the key component of relaxors.

In order to get more insights into the complex structural features exhibited by $Na_{1/2}Bi_{1/2}TiO_3$, we combined ab-initio calculations with Landau theory and group theoretical tools in order to investigate the tendency for chemical ordering and its consequences on the local structure and ferroelectric properties.

We present phase stabilities depending on chemical order and hydrostatic pressure and show how different distortion modes evolve under compressive and tensile conditions. We find that the local structure in NBT arises from a delicate balance between octahedral tilting, ferroelectric distortions and chemically induced ionic displacements and is extremely sensitive to the local A-site configuration. Surprisingly, at zero pressure we find a mixed-phase state to be most stable, which consists of a chemically disordered matrix with an R3c-like average structure and {001}-chemically ordered nanoregions possessing Pbnm-like average structure, which in fact are polar with considerable spontaneous polarization comparable to that found for the R3c-like structures. Thus, our results clearly support the existence of nanoscale chemically ordered regions in $Na_{1/2}Bi_{1/2}TiO_3$ and are in good agreement with an earlier experimental report showing characteristic diffuse scattering [3]. Overall, ferroelectic properties and tilt patterns are primarily determined by the local chemical configuration.

[1] G. Trolliard and V. Dorcet, Chemistry of Materials **20** (2008) 5074.
[2] I. Levin, I. M. Reaney, Advanced Functional Materials **22** (2012) 3445.
[3] J. Kreisel, P. Bouvier, B. Dkhil, P. A. Thomas, A. M. Glazer, T. R. Welberry, B. Chaabane, and M. Mezouar, Physical Review B **68** (2003) 014113.

Notes:

T 04: Reversible multi- to single domain transition in $Ba(Zr_{0.2}Ti_{0.8})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$ ferroelectrics under poling conditions

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Due to technological importance in piezoelectric applications, lead based ceramics with perovskite structure, like lead zirconate titanate, have been studied for the last 50 years [1]. Although lead-containing ferroelectrics have excellent dielectric, piezoelectric and mechanical properties, the toxicity of the heavy metal lead [2, 3] is the reason for searching environmentally friendly alternative for these materials [4].

In the present study, the lead-free $Ba(Zr_{0.2}Ti_{0.8})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$ piezoelectric ceramic with x = 0.30, 0.50, 0.52 (abbreviated as BZT-xBCT) under an applied electric-field was investigated in situ using transmission electron microscopy. The BZT-xBCT compositions were synthesized by a conventional solid state reaction route from oxides and carbonates. For all compositions, significant changes in domain structure have been observed under an applied electric field. The single domain state was formed in all studied composition during poling process. This multi- to single domain transformation is found to be reversible since multi-domain configuration reappeared inside the grains upon field removal (Fig. 1). It should be noted that an intermediate nanodomain state has also been observed during electrical poling. For all studied compositions the selected area electron diffraction patterns show neither any reflection splitting nor detectable changes during electrical poling.

Domain wall displacement during poling and the absence of any changes in the selected area electron diffraction patterns indicates high extrinsic contribution to the piezoelectric properties in BZT-xBCT ferroelectrics. The intrinsic effect of the lattice seems to be negligible.

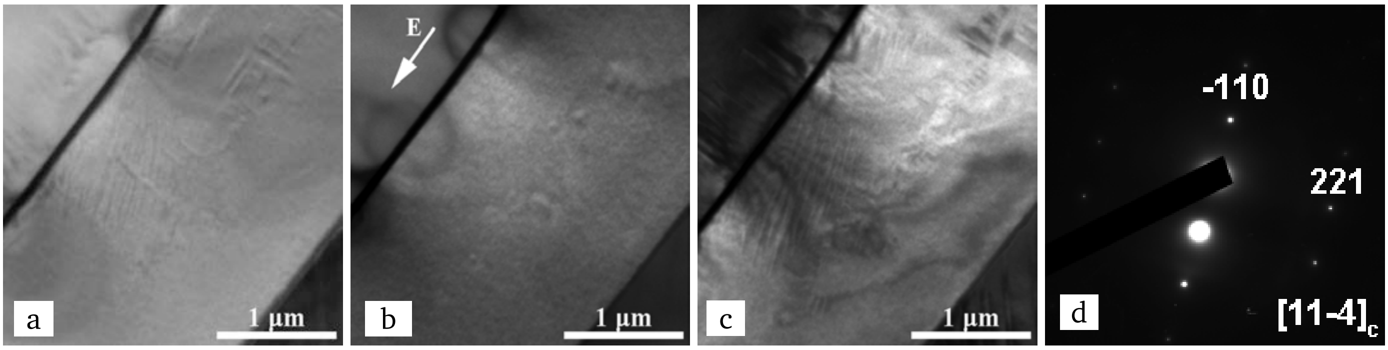

Fig.1: In situ TEM bright field images of the BZT-0.3BCT along the [11-4]c zone axis at
(a) zero field, | (b) 50 kV/cm | (c) zero field after two cycles | (d) The SAED pattern at 50 kV/cm
The direction of the poling field is indicated by the arrow in (b).

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Notes:

I 01: Interplay between lattice, spin, orbital and charge orders in bulk and layered ABO_3 perovskites

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Ferroelectricity in ABO$_3$ perovskites and related compounds has been a topic of intensive research over the last 60 years. Recently, the coupling of the ferroelectric lattice mode with other non-polar modes has attracted an increasing interest [1-5] since it offers promising and still widely unexplored possibilities to couple ferroelectricity with other functional properties and even to produce unusual phenomena. In this context, the trilinear coupling between ferroelectric and oxygen rotational modes [1, 2] in naturally-occuring and artificially-layered perovskites emerged as a practical way to produce unusual dielectric properties [1] or to achieve enhanced magneto-electric coupling [3-5]. Focusing on vanadates and half-doped titanates, we will discuss here how even more interesting phenomena can appear when additional orbital and charge orders enter into play!

Work done in collaboration with J. Varignon, N. Bristowe, D. Fontaine and E. Bousquet and supported by a Francqui Research Professorship, the ARC project TheMoTherm and the FNRS project HiT4FiT.

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Notes:

I 02: Design and Fabrication of all-solid-state rechargeable lithium batteries using ceramic electrolytes

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The replacement of organic liquid electrolytes with inorganic solid electrolytes is a challenge to extend the versatility of rechargeable lithium batteries. The safety and operating temperature of batteries are surely enhanced by the thermal stability of solid electrolyte. However, new insights to form an electrochemical electrolyte/electrode interface are needed since the interface is changed from a conventional liquid/solid contact to a solid/solid contact. In conventional batteries using liquid electrolytes, the electrochemical interface is automatically formed by impregnation of liquid electrolytes to a porous electrode. In contrast, all-solid-state batteries using solid electrolytes suffer from the formation of electrochemical interface since solid electrolytes do not have such fluidity, resulting in a very high internal resistance. One of the most desirable features of solid electrolytes is high mechanical strength, which enables to fabricate various kinds of structures. For example, when the 3D patterned solid electrolyte shown in Figure 1 is applied, a 3D interdigitated electrode configuration can be formed. This configuration increases an electrochemical electrolyte/electrode interface in a unit volume compared with conventional 2D fashions (layer-by-layer electrode configurations), resulting in a smaller internal resistance. Thus, the formation of 3D solid electrolytes is one of keys to develop practical all-solid-state batteries. So far, we have focused on oxide-based solid electrolytes such as Li0.35La0.55TiO3 (LLT) [1-2] and Li7La3Zr2O12 (LLZ) [3] due to high lithium-ion conductivity as well as high mechanical strength, and formed their hole-array structures. In the presentation, the fabrication of those hole-array structures and evaluation of the all-solid-state batteries using the structured solid electrolytes will be reported.

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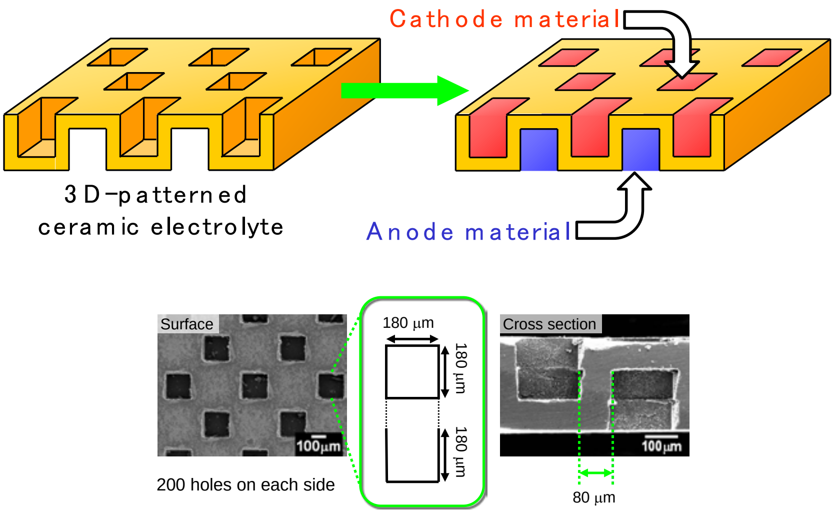

Figure 1: (a) Design of all-solid-state batteries using 3D-pattened ceramic electrolytes, (b) 3D-patterned LLT.

Notes:

T 05: New insights into understanding of irreversible and reversible lithium storage within SiOC and SiCN ceramics

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Within this work we try to find out which structural properties of silicon carbonitride (SiCN) and silicon oxycarbide (SiOC) ceramics determine reversible and irreversible lithium storage capacities, long cycling stability and define major differences in the lithium storage within SiCN and SiOC. The experimental observations are addressed with respect to DFT modelling [1].

For both ceramics we correlate the first cycle lithiation or delithiation capacity and cycling stability with the amount of SiCN/SiOC matrix or free carbon phase, respectively. The first cycle lithiation and delithiation capacities of SiOC materials [2, 3] do not depend on the amount of free carbon, while for SiCN materials the capacity increases with the amount of carbon to reach a certain threshold value at about 50% of carbon phase [4, 5]. The cycling stability of carbon-poor ceramics is however very low for both SiCN and SiOC, while increasing significantly for materials with higher carbon content. For SiOC a clear linear dependence of the insertion capacity on the amount of silicon oxycarbide phase is revealed, while for silicon carbonitride there is no dependence between first cycle insertion capacity and SiCN matrix amount. In contrary to the tendency observed for SiOC, the SiCN lithiation capacity is very low for high (> 70 %) amount of SiCN matrix.

It has been stated that replacing oxygen with nitrogen renders the mixed bond Si-tetrahedra unable to sequester lithium [6]. Lithium is more attracted by oxygen in SiOC network due to more ionic character of Si-O bonds, leading to a high electron density on oxygen. This brings about very high first lithiation capacities, even at low carbon content. With continuing cycling lithium is irreversibly captured within the SiOC network resulting in low cycling stability. If oxygen is replaced by nitrogen, the ceramic network becomes much less attractive for lithium ions due to more covalent character of Si-N bonds and lower electron density on the nitrogen atom. This feature explains why a significant difference in electrochemical behavior of carbon-poor SiCN and SiOC materials is found. For carbon-rich ceramics the free carbon phase starts to play a dominant role causing high cycling stability, but also leading both to high irreversible and reversible capacities.

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Notes:

T 06: In Situ Raman Diagnostics of Intercalation Batteries

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The potential of Raman diagnostics for spatially-resolved and *in situ* diagnostics of lithium-ion batteries is demonstrated. Focus is put on $LiCoO_2$ electrode materials, which were investigated in detail as composites of $LiCoO_2$ with binder (PVdF) and conductive (carbon) additives. Besides the $LiCoO_2$ active mass, Raman spectroscopy allows to detect carbon and PVdF-related bands as well as electrolyte bands [1].

Detailed wavelength-dependent analysis reveals the first observation of a resonance Raman effect for $LiCoO_2$-based materials for green (514 nm, 532 nm) laser excitation. The resonance effect is confirmed by a dependence of the A_{1g} and E_g phonon band intensity ratio on excitation wavelength and the occurrence of an overtone of the A_{1g} band for green excitation. The resulting signal enhancement strongly facilitates the spatially-resolved and *in situ* analysis of $LiCoO_2$ composite electrodes. Spatially resolved analysis, i.e. Raman mapping of $LiCoO_2$ composite electrodes, shows a significant variation of chemical composition across the electrode surface and the presence of individual active mass particles, which are ~10-20 μm in size [2].

Raman spectra recorded under electrochemical conditions are largely invariant regarding the degree of lithium de-/intercalation indicating no significant structural changes on the surface of the active mass particles. To this end, Raman experiments are complementary to X-Ray diffraction experiments. Interestingly, spatially resolved Raman analysis (Raman mapping) of $LiCoO_2$ composite electrodes demonstrates the chemical redistribution during electrochemical cycling. To this end, Fig. 1 shows the results of an *in situ* Raman mapping of a $LiCoO_2$ composite electrode (85% $LiCoO_2$, 10% PVDF, 5% carbon black) before and after four cycles at C/12 rate. Interestingly, our results reveal that the chemical redistribution is correlated with changes in the $LiCoO_2$ phonon band intensities. In particular, within areas small chemical redistribution only small variations in the A_{1g}/E_g intensity ratios before and after cycling are observed, whereas areas of large chemical redistribution show significant changes of A_{1g}/E_g intensity ratios from typically 2.0 (before cycling) to 1.5 (after cycling). This behavior strongly suggests that the chemical redistribution is accompanied by changes in the electronic structure of the active mass particles.

Current mapping experiments focus on changes in the behavior between the first and subsequent cycles to gain insight into the processes occurring during SEI formation. Additional information is expected from the evaluation of the Raman background showing systematic intensity variations during lithium de-/intercalation.

Our results highlight the potential of Raman diagnostics to contribute to the ongoing discussion on the mode of operation and degradation of lithium-ion batteries due to its ability to deliver spatially resolved and *in situ* information.

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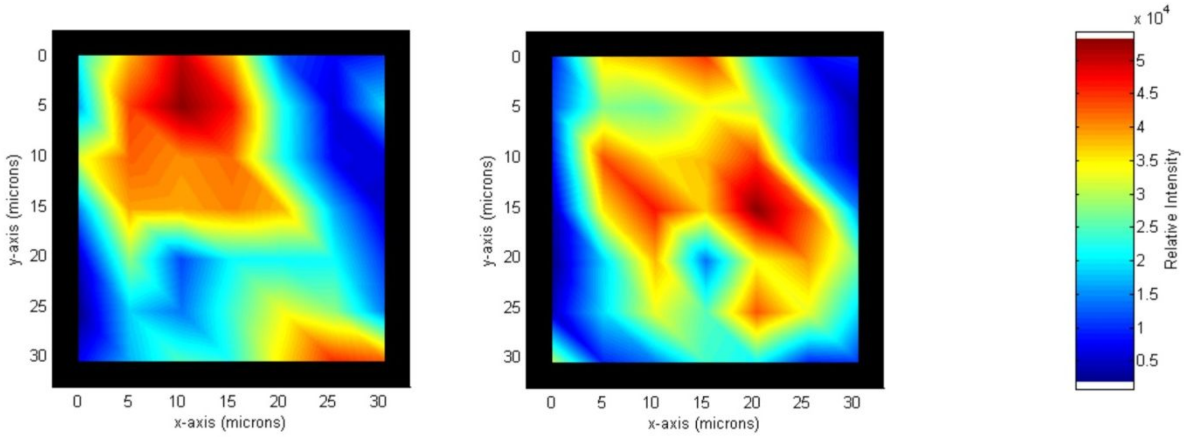

Fig. 1: Raman mapping of a $LiCoO_2$ composite electrode (85% $LiCoO_2$, 10% PVDF, 5% carbon black) before and after four cycles at C/12 rate using 532 nm laser excitation.
The scale refers to $LiCoO_2$. The electrolyte consisted of 1M $LiPF_6$ dissolved in EC/DMC = 1:1.
As counter electrode lithium foil was used.

Notes:

T 07: Surface science investigations of electrode-electrolyte interfaces in Li-ion batteries

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Electrode-electrolyte interfaces play a key role for the performance and degradation of Lithium-ion cells. Li-ion transfer and (parasitic) electron transfer depend on interface properties such as energy level alignment, surface concentration of charge carriers and electric double layer. These interface properties are reflected by the electronic structure of the interface.

We use a surface science approach to investigate interfaces between Li-ion electrode materials and liquid as well as solid electrolytes. The approach consists of the stepwise formation of interfaces by condensation or thin film deposition of electrolyte phase onto a thin film electrode (or vice versa), with intermediate analysis by photoemission. The data allow detection of reaction phases as well evaluation of energy level diagrams.

In this contribution, we report results on different interfaces (e.g. $LiCoO_2$/DEC, $LiCoO_2$/LiPON, LiPON/Li) and discuss them with respect to fundamental aspects of interface formation, such as electrochemical equilibrium and adjustment lithium chemical potential [1, 2]. In the investigations, the $LiCoO_2$ behaves like a p-type semiconductor and exhibits band bending. We find that the interfaces $LiCoO_2$/DEC and $LiCoO_2$/LiPON are non-reactive and governed by Li-ion transfer. On the other hand, the LiPON/Li interface is reactive, depending on LiPON composition. We present energy level diagrams for half- and full cells.

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Notes:

T 08: Structure and Properties of Amorphous LiPON Electrolyte by First-Principles Simulations

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In the framework of thin-film Li-ion batteries, Lithium Phosphorus Oxynitride (LiPON) represents an increasingly popular choice as a solid electrolyte. RF-sputtering of a lithium orthophosphate target in a nitrogen plasma leads to the deposition of amorphous glasses. 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 [1]. In this work we present the results of Density Functional Theory calculations. By combination of an evolutionary algorithm followed by ab-initio simulated annealing, we have been able to generate an amorphous structure with realistic cross-linking. We discuss the computed properties of the solid electrolyte with the aim of unravelling the mechanisms of Li diffusion and defects thermodynamics in the pristine material. We then proceed to tackle the issue of the formation of an interface with a cobalt oxide cathode, which we also characterize with respect to its electronic and structural properties in order to rationalize the migration of Li ions through the interface and the occurrence of potential interphases.

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Electrochem. Solid-State Lett., **14**, 2, (2011), A11

Notes:

I 03: Sodium insertion properties of titanates and related materials as negative electrodes for Na-ion batteries

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Lithium reservoirs are located in politically conflictive areas [1] and demand of new deposits of minerals is rapidly increasing, and alternatives to scarce lithium minerals are urgently needed.

Sodium appears as good alternative to lithium for energy storage systems, owing to its similarity to lithium in many aspects. The inexhaustible estimated resource of this metal, compared to the rather limited deposits of lithium minerals constitutes its main advantage. Thus, sodium-ion batteries are coming back to the focus of researchers, challenging lower cost and sustainability at least for large scale stationary application [2].

In contrast to a wide portfolio of different cathode materials for Na-ion batteries, only few anode materials operating at low voltages have been reported to date. Sodium hexatitanate, $Na_2Ti_6O_{13}$, has been recently evaluated as anode host for sodium ion batteries [3]. In this work we have investigated the sodium insertion properties of several hexatitanates $A_2Ti_6O_{13}$ having different A channel ions. Furthermore, hollandite-type TiO_2 has been investigated as new low voltage Na insertion electrode [4].

Structural evolution during electrochemical sodium insertion and de-insertion has been monitored in depth by using *in situ* synchrotron X-ray diffraction operated in CR2032 coin-type cells. The small volume changes during discharge-charge cycling point to these Ti-based oxides as new long life negative electrode material in sodium-ion batteries.

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Notes:

I 04: Degradations of Dielectric ceramic materials

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Studies on degradation mechanism of dielectric materials are increasing their importance, because the materials, which are typically used in dielectric capacitor applications, have suffered harsh conditions, such as at high temperatures, at high electric fields, and so on. Each layer thickness in the multilayer ceramic capacitors, has become below 1□m. The electric field applied to each dielectric layer has become greater for recent years. On the other hand, high temperature applications of dielectrics have been growing, for example, for automotive electronics applications. In order to provide reliable dielectric materials for the applications under such harsh conditions, we should know how the dielectric materials degrade. Firstly degradation phenomena and degradation mechanisms of dielectric ceramic materials are reviewed, and material designs for highly reliable dielectric ceramic materials are also discussed.

Notes:

T 09: Aging in of Fe-doped (1-x)($Bi_{1/2}Na_{1/2}$)TiO_3-x$BaTiO_3$ piezoelectric ceramics

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Acceptor-doping of ferroelectrics is a key tool for tailoring piezoelectric properties since it lowers dielectric losses and increases the mechanical quality factor. Intrinsically connected to acceptor-doping is aging, defined as the time-dependent change of piezoelectric properties. Thus, the application of acceptor-doped piezoelectrics calls for the quantification of aging effects as well as for a detailed understanding of the underlying mechanism. While aging is well-described in perovskite-structured materials with long-range-order [1-3] information is scarce when it comes to relaxors. In particular, effects in the field-induced ferroelectric state have not been investigated yet.

In this work, the aging behavior of piezoelectric properties was investigated in lead-free (1-x)($Bi_{1/2}Na_{1/2}$)TiO_3-x$BaTiO_3$ doped with 1mol% Fe. The results demonstrate that the relaxor character of the unpoled material effectively prevents macroscopic aging effects, while in the field-induced ferroelectric phase phenomena similar to those found in lead zirconate titanate or barium titanate occur. Most prominent changes during aging are the development of an internal bias field dependent on poling direction and the decrease of switchable polarization. The effects are temperature activated and can be explained in the framework of defect-dipole reorientation. This picture is further supported by EPR spectra indicating the existence of $(\mathrm{Fe}_{\mathrm{Ti}}'\text{-}\mathrm{V}_{\mathrm{O}}^{\bullet\bullet})^{\bullet}$ defect dipoles in the Fe-doped material.

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Notes:

T 10: Fatigue free in epitaxial KNN films

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(K,Na)NbO3 was supposed to be one of the most promising substitutes for toxic Pb-based ferroelectrics because of the comparable properties to PZT system.[1] Therefore, tremendous efforts have been devoted to the environment-friendly KNN-based material during the past decade. Modern devices require function materials with low dimension. In this presentation, we report on epitaxial (1-x)(Na0.49K0.49Li0.02)(Nb0.8Ta0.2)O3-xCaZrO3 [KNN] films grown by pulsed laser deposition on SrTiO3 substrate. The effects of deposition parameters and electrode configurations on their ferroelectric properties were systematically studied. High resolution XRD, Raman scattering and XPS were carried out to characterize the quality of the films. The film made with optimized parameters shows high crystallinity with FWHM at ∼ 0.1o and exhibits large remnant and saturated polarization of 13.2 and 27.9 μC/cm2. More interestingly, it is found that KNN epitaxial films show a high fatigue resistance even with Pt metallic or n-type conductive oxides electrode, which is dramatically different from PZT films,[2] indicating a higher capability of integration in modern micro-electromechanical systems (MEMS).

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Notes:

I 05: In situ TEM Study on the Aging and Fatigue of Piezoelectric Ceramics

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Piezoelectric ceramics, primarily based on $Pb(Zr,Ti)O_3$, are widely used in a variety of engineering technologies. The toxicity of lead in these functional materials has led to intensive worldwide search for lead-free substitutes. These oxides are generally produced in the form of polycrystals. To develop piezoelectricity, as-sintered polycrystalline ceramics have to be poled, where an intensive DC electric field is applied to align the polarization in individual grains through ferroelectric domain switching. During service, these ceramics are subject to different forms of electric fields, most of the time, cyclic fields.

Apparently, the domain structure evolution under electric fields during the initial poling process and in service plays a key role in determining the piezoelectric properties and performance of these materials. The *in situ* TEM technique is very powerful in revealing the dynamic response of ferroelectric domains to applied fields at the nanometer resolution in real time. In this talk, results on several composition systems will be presented. The *in situ* TEM observations made on $(1-x)(Bi_{1/2}Na_{1/2})TiO_3–xBaTiO_3$ ceramics revealed complicated phase transitions during electrical poling [1,2]. The metastable phases in poled ceramics contribute to the piezoelectric effect [3]. In the $0.948(K_{0.5}Na_{0.5})NbO_3–0.052LiSbO_3$ ceramic, it was found that the origin of the excellent piezoelectric performance was due to a tilted monoclinic phase that emerges when poling fields greater than 14 kV/cm were applied [4]. During poling of the $0.5Ba(Ti_{0.8}Zr_{0.2})O_3–0.5(Ba_{0.7}Ca_{0.3})TiO_3$ ceramic, it was observed that the initial multi-domain state transformed to a single domain state at very low fields (2~4 kV/cm), then reappeared at higher poling fields [5].

The *in situ* TEM study on the aging behavior of the high-performance $0.5Ba(Ti_{0.8}Zr_{0.2})O_3–0.5(Ba_{0.7}Ca_{0.3})TiO_3$ ceramic suggested a possible reverse phase transition. During re-poling, the single-domain state could be realized again [6]. In addition, the morphology evolution under bipolar cyclic fields in polycrystalline ceramics of $[(Bi_{1/2}Na_{1/2})_{0.95}Ba_{0.05}]_{0.98}La_{0.02}TiO_3$ and $Pb[(Mg_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ was examined in TEM. Domain fragmentation during cycling was revealed for the first time.

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Notes:

O 02: Aging and fatigue in ferroelectrics: experimental results and current understanding

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The talk presents a wide overview of research on aging and fatigue phenomena in ferroelectrics conducted during the whole SFB period 2003-2014. The first phenomenon describes gradual changes in parameters of materials and devices with time under external equilibrium conditions whereas the second one is characterized by a degradation of the material properties in presence of external electric and/or mechanical load. Both phenomena are related to the composition of a ferroelectric ceramic including the quantity and type of dopants. Three material families are covered in the studies: the most widely used

$Pb[Zr_xTi_{1-x}]O_3$ (PZT) ceramics and most commonly known lead-free materials, namely, bismuth sodium titanates $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) and alkali niobates $(K_yNa_{1-y})NbO_3$ (KNN). While aging is studied in poled and unpoled states the variety of different loading regimes for fatigue includes dc electric field, unipolar, sesquipolar and bipolar cycling and all these differently combined with mechanical loading at different frequencies and temperatures. Also the role of device geometries and electrode materials is investigated. Structural evolution of materials is traced by various methods and tools comprising optical microscopy, XRD, TEM, SEM, EDX, EPR and PFM. Electrical and mechanical properties are studied by dynamic polarization, strain and impedance measurements. Theoretical studies are focused on the two competing concepts of aging: charge migration and defect dipole re-orientation. To this end quantitative models using both phenomenological and first-principle tools are advanced and compared with experimental results. Using DFT approach, formation and switching of defect dipoles and defect kinetics are investigated. On the mesoscopic scale, space charge effects are studied by drift-diffusion equations and phase-field theory in ferroelectrics accounting for their semiconducting features.

Notes:

K 02: Electrical Engineering with nanostructured materials: Examples from Photovoltaic and Thermoelectric

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This talk gives a few examples on our research on application of nanostructured materials in electrical engineering.

The first part of the talk is addressed to the low permittivity of organic materials as a reason for loss mechanism in organic solar cells. A concept is introduced, which allows for reduced Coulomb interaction in organic solar cells and as such for enhanced power conversion efficiencies. First, the basic principle is demonstrated by the enhanced photoconductivity of pentacene on insulating high-k substrates. The electrostatic interaction on a high-k interface is simulated by an analytical model, which demonstrates that even at a distance of 20 nm to the organic/inorganic interface of the nanostructure, the Coulomb interaction in the organic semiconductor can be reduced by more than 15%. The concept is implemented in solar cells using P3HT:PCBM with integrated high-k nanoparticles (strontium titanate). The results are critical discussed with respect to morphological changes of the organic layer induced by the incorporation of nanoparticles.

The second part of the talk is addressed to thermoelectric. After a short introduction, the effect of nanostructures on thermoelectric properties will be demonstrated on nanostructured silicon. The current–activated pressure-assisted densification (CAPAD) process for nanostructured bulk material will be critical analyzed with respect to sample inhomogeneities. Sample stability under higher temperature is analyzed under cyclic stress. While the morphology seems to be stable up to 1000°C, a change of electrical properties above 700°C is assigned to kinetic/dynamic of the dopands. A more system-related consideration will question, how far the common material parameter zT is still a good figure of merit for thermoelectric materials, especially with respect to a cost-efficiency trade-off.

Notes:

O 03: Electrical fatigue of polymer light-emitting diodes based on *poly*(*p*-phenylene vinylene) derivatives: a comprehensive approach

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In this work the current knowledge on the electrical degradation of polymer-based light-emitting diodes is reviewed focusing especially on derivatives of *poly*(*p*-phenylene vinylene) (PPV) [1]. The electrical degradation will thereby be referred to as electrical fatigue. Studied are observed phenomena, mechanisms and material properties changing during continuous device operation at constant current. This review focuses on the effect of chemically induced defects introduced during synthesis and elaborates their influence on transport properties such as charge carrier mobility and device lifetime [2]. Highlighted will be the influence of a halogen defect that leads to a degradation of the electrodes and therewith is mainly responsible for device degradation. In addition, an optical effect will be introduced exhibiting that the absorption of the emitted light by the semiconductor itself is one reason for device degradation [3]. Finally, the influence of the triplet density is investigated indicating that local deposition of energy is also an important factor to contribute to degradation [4]. All experiments were accompanied by theoretical modeling shining light on how the change of injection barriers, charge carrier mobility or trap density influences the current-voltage characteristics of the diodes. Especially interesting is thereby the introduction of image charges in a single carrier model through the Schottky effect [5], which allows to describe barrier lowering and therewith the device performance in a more realistic way. However, due to the complexity of the electrical fatigue modeling of device degradation is still in its infancy.

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Notes:

I 06: Status, Technology and Challenges in OLED Development

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Organic light emitting diodes (OLEDs) have many advantages for future display applications. OLED based displays are self-emitting enabling high contrast ratio as well as high refresh rates. Self-emission also allows for omission of the backlight unit and other component parts used in LC displays, thus reducing the cost. Furthermore OLEDs show an excellent color gamut as well as steadily improved power consumption. New applications such as bendable, flexible, and transparent displays turn OLED into an even more exciting technology. In the past decade, OLED has commercialized successfully and more than 200 Million small size displays (i.e. smartphones) have been sold already. Since 2013 also the first OLED TVs have been launched.

An OLED display consists of multiple materials with specific functionalities. One key factor to ensure OLED's long term technology success is the material development. Some highlights: Improving the spectral properties and the efficiency of the dopant materials, like deep blue, will lead to lower power consumption and a wider color gamut of the display. Improving host and transport materials will enhance the display's lifetime, efficiency, and reduce the driving voltage. Another key success factor is the production technology: While thermal evaporation produced OLEDs show advantages in stack design and are already performance optimized, soluble OLED fabrication has the potential to be a more suitable production technology for large size displays.

An overview of the different technologies and latest material developments will be presented.

Notes:

T 11: Poly(*p*-phenylene vinylene)s – Highlights of 12 years of research within the SFB 595

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The Research on Poly(*p*-phenylene vinylene) (PPV) within the SFB 595 started in 2002. The idea was to investigate defect formation during the manufacturing process of the polymer and the influence of constitutional and morphological defects on the fatigue behavior of resulting organic light emitting diodes (OLEDs). The synthesis of PPV was achieved via the Heck, Suzuki and Gilch methodology. With regard to synthetic procedures many issues had to be faced.

For the Heck and the Suzuki method a main goal was to achieve high molecular weights and to remove all traces of remaining catalyst. Here our investigations lead to a new catalyst system that results in higher molar masses. Unfortunately suppression or control of the formation of critical defects, for e.g. the exomethylene defect, couldn't be observed with the help of this catalyst system [1].

Concerning the Gilch methodology we had to face problems of a totally different nature. At first investigations of the mechanism had to be performed to understand the origin of constitutional defects that might arise during the synthesis. Here we were able to clear up the mechanism of the Gilch reaction [2-9].

Furthermore we were able to pinpoint the most critical defects for OLED applications, the halogen defects. Eventually we were able to reduce the content of those defects in the resulting polymer considerably to improve life time and efficiency in OLEDs [9-11]. Based on this knowledge our latest investigations deal with the influence of lateral substituents on the emission color and fatigue behavior of PPVs in OLEDs. Here we were able to realize PPVs that emit light in almost the whole range of the visible spectrum.

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Notes:

T 12: Self-consistent description of charge-carrier injection at a conductor / organic semiconductor interface: extension to the case of a degenerate semiconductor

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Injection of charge carriers from a conductor to an insulating medium has a crucial impact on the functioning of a wide range of electronic devices based on organic semiconductors (OSCs) such as organic light-emitting diodes, organic field-effect transistors or organic photovoltaic cells. In view of that, the problem of an adequate description of this process is still of great importance. Recently, a self-consistent continuous model of injection in insulating media in terms of carrier densities and mean fields with account for discreteness of the injected charge carriers, based on the matching of the electric displacement and the electrochemical potential at the interfaces, was developed [1]. It was satisfactorily applied to description of a hole transport in an OSC diode at different temperatures accounting for a Gaussian density-of-states (DOS) distribution in the organic layer [2]. Nevertheless, this model has only accounted for the Boltzmann statistics of the charge carriers thereby being restricted to the case of low densities of carriers in an OSC; a condition which can be particularly violated at the injecting electrode.

In the present study we extend the above approach to the case of large densities of injected carriers using the analytical approximation [3] for the density of carriers as function of the Fermi energy defined as the integral over the Gaussian DOS multiplied by the Fermi–Dirac distribution function. We demonstrate the modified voltage-injection barrier chart for the electrode/OSC interface, applicable now for arbitrary values of carrier densities in an OSC, and discuss exemplary current-voltage curves for symmetric and asymmetric OSC diodes.

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Notes:

O 04: Do TCOs contribute to electrical fatigue of organic light emitting diodes?

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The most widely used transparent conducting oxide electrode in organic electronics is indium-tin-oxide (ITO). Despite being a degenerately n-doped semiconductor (high Fermi level), ITO is used to inject holes (low Fermi energy) into the organic conductor in an OLED. This has led to the original proposal that the surface potential, which is the key for hole injection, may change during operation and hence contribute to electrical fatigue.

The surface potentials depend on: (i) the doping of the material and in particular on the defect concentrations; (ii) surface space charge regions; (iii) surface orientation and termination. Research in the SFB has therefore concentrated on the clarification of these issues by systematically studying surface potentials of ITO and other TCO materials using photoelectron spectroscopy (project D3) and by DFT calculations of the thermodynamics and kinetics of defect formation in TCOs (project C1). In addition, charge injection mechanisms have been modelled in project C5. During execution of the project it has furthermore been realized that oxygen exchange is particularly feasible at ITO surfaces. The release of oxygen during device operation has therefore also been considered as a possible source of fatigue, which has consequently been studied both experimentally and theoretically.

The combined experimental/theoretical efforts have led to a comprehensive description of the defect and surface properties of TCOs and particularly of ITO. Neither changes of barrier height for hole injection nor release of oxygen during operation could be identified as a major source of fatigue in OLEDs. This may partially be related to advanced device structures, which use highly conducting charge injection layers like PEDOT-PSS or doped organic molecular layers. However, inhomogeneous charge injection at polycrystalline ITO surfaces may contribute to formation of hot spots and release of oxygen can only be excluded for the dark and field free situation. During operation, however, very high electric fields and illumination may enhance oxygen diffusion significantly.

Notes:

K 03: An overview of the behaviour of layered oxides in lithium and sodium batteries

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Keywords: Intercalation, Battery, Positive Electrode, Layered Material

In the lithium-ion battery story, the lithium layered oxides are at the corner stone of their development. $LiCoO_2$, which was proposed by Goodenough in the beginning of the 80's, is the archetype of the positive electrode material and it is still the most used material for portable devices.

The high price of cobalt has suggested a lot of studies on homologous material and in particular on nickel derivatives like $LiNiO_2$; unfortunately the difficulty to obtain the stoichiometric material and its low thermal stability in the deintercalated state impede its use in practical devices despite its very good electrochemical behaviour.

Then a huge number of researches was devoted to improve $LiNiO_2$ by cationic substitution. In all cases cobalt play an important role for the cyclability while Al and Mn increases significantly the thermal stability in the deintercalated state, leading to the $Li(Ni,Co,Al)O_2$ (NCA) and $Li(Ni,Mn,Co)O_2$ families (NMC).

For the last ten years the Li-rich Li(Li,Ni,Mn,Co) phases focused intense activity thanks to their large capacity (over 200 mAh/g). Nevertheless, the exact mechanism occurring during the cycling is not completely understood.

In all cases, the characterisation of these materials has required very innovative technics. Numerous in situ and in operando characterizations were developed in classical labs and also in large size facilities (neutron and synchrotron). A significant role was also played by *ab initio* calculation, which is now commonly used by numerous laboratories.

For several years the homologous sodium phases, which were discovered in the 80's, are revisited and recently very interesting results were reported. The versatility of the sodium layered oxides structure, which can present several sodium environments, opens new fields in this area. Moreover, the strong sodium-sodium electrostatic repulsions in the interslab space lead to a lot of reversible phase transitions. The topology of the sodium distribution induces specific electron distribution in the transition metal layers, which leads in some case to very original physical properties.

A general overview of all these points will be presented in this conference.

Notes:

O 05: Investigations on fatigue of Li-ion batteries

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Li-ion batteries are the most enhanced energy storage system for mobile applications with respect to both high power and high energy densities. The use of Li-ion batteries in electromobility has attracted even more attention on safety concerns and further increased the demand for a lower cost of the battery system. Both aspects require a fundamental understanding of the processes, which take place inside a battery during operation under very different operation conditions. This includes all possible states of charge and all states of health. A competitive application of Li-ion batteries for the energy storage system in electric vehicles requires a battery life time as long as the expected useful life of the cars. Such ambitious goals require a comprehensive knowledge of all relevant fatigue mechanisms.

This contribution gives an overview about the working principle of a Li-ion battery with a focus on the specific challenges for each component. The main important fatigue mechanisms are compiled, and specific examples are shown how to reveal the underlying processes. Li-ion batteries are devices with an exceptional high degree of complexity. Only a combination of different methods can contribute to reliable life-time models and pave the way for enhanced electrochemical energy storage devices.

Notes:

I 07: High-power, high energy-density lithium ion batteries – impact of atomic-scale processes on electrochemical performance and cyclic aging

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Lithium-ion batteries are promising energy-storage devices for stationary and mobile high-power, high energy-density applications. Strategies to improve the energy density involve the use of high-voltage cathode materials (spinel-type $LiNi_{0.5}Mn_{1.5}O_{4-\square}$) and high-capacity anode materials (metallic Lithium). Two major challenges to overcome are the increase of ionic charge transport in the cathode and the preventing of dendrite growth at the metallic anode for high power densities. Charge transport may be significantly enhanced by tailoring the defect structure of the cathode in terms of aliovalent doping and non-stoichiometry. The dendrite growth in turn may be reduced by additives to the electrolyte.

Dedicated '*in-operando*' experiments have been developed and applied in order to gain insight on atomic-scale processes. In particular, mechanisms of cyclic aging in terms of a reduction and subsequent anti-site diffusion of transition-metal ions have been observed.

Notes:

I 08: Polarons in oxides and halides

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Wide band gap materials are prone to polaron formation, i.e. it is energetically favorable for excess charges to localize by coupling to lattice modes ("self-trapping"). This is in sharp contrast to smaller band gap materials, for which excess charges typically occupy delocalized (band) states. In this contribution I will review theoretical and computational work carried out over the past few years regarding the properties of polarons in both halides and oxides. The former class of materials is of interest in so far as many halides are so-called scintillators, which convert high-energy radiation (keV and above) to low energy (eV range) photons. Thanks to this property they have important applications in medical imaging, high-energy physics, and radiological surveillance. Specifically I will discuss results regarding the behavior of polarons in alkali halides, $LaBr_3$ and SrI_2. In this context I will also allude to methodological advances that were required in order to deal with the complex lattice structure of these systems. The methods are generally applicable and have already been successfully applied to a much broader class of materials. The second part of this contribution will specifically address the application of our methods to the study of polaron formation and dynamics in oxides in the perovskite structure with emphasis on the distinction between bulk and surface. It will be shown that self-trapping in these systems is sensitive to geometric constraints whence polaron formation at surface is greatly enhanced compared to the bulk.

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Notes:

T 13: Transparent Conducting Oxide Electrodes

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Transparent conducting oxides (TCO) are used to electrically contact the active layers in organic light emitting diodes and to transmit light generated in the device to the environment. The most widely used TCO material is Sn-doped In_2O_3 (ITO), which is used as a hole injecting electrode. This contribution reviews the most important results of project D3, in which ITO and related transparent conductors were deposited as films using magnetron sputtering and analyzed with respect to their electronic properties, particularly emphasizing on the aspects of surfaces and interfaces. The measurements have led to a revised understanding of the fundamental energy gap of In_2O_3 [1] and to an understanding of the general dependencies of the work function of transparent conducting oxides on surface orientation, surface termination, and doping [2-4]. The orientation dependence of the work function of In_2O_3 is a natural source for inhomogeneous charge injection [3], which could be the origin for the formation of hot spots.

In the first stage of the project, it was furthermore discovered that oxygen can be released from ITO during contact formation with organic semiconductors [5]. This is a consequence of the weak binding and high mobility of interstitial oxygen in ITO. Following this observation, the oxygen exchange at the surfaces of TCOs was studied in more detail [4,6-8]. For a better understanding of the underlying processes, unique facilities for measurement of Hall-effect and conductivity relaxation have been setup [8]. With such measurements it has been identified that dopant segregation is a key factor in TCO materials, which agrees with extensive studies of carrier concentrations and mobilities accumulated during the project. The latter are expected to significantly enhance the understanding of grain boundary contributions to the electrical conductance in TCO thin films.

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Notes:

T 14: Point defects and surfaces of transparent electrodes studied by electronic structure calculations

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Sn-doped In2O3 (ITO is widely used as transparent electrode material for organic light emitting diodes and organic photovoltaics. Due to the orientation dependent ionization potential, a polycrystalline ITO film will exhibit a laterally varying work function, which results in an inhomogeneous charge injection into organic semiconductors when used as electrode material. Thus, a detailed understanding of the surface structure and thermodynamics is a prerequisite for optimizing the transparent electrode.

In this contribution the thermodynamic stability of several experimentally observed low-index surfaces of bcc indium oxide (In2O3) are investigated by means of density functional theory calculations. The influence of hydrogen, water, n-type dopants (Sn), as well as the in-plane lattice strain are studied and compared to results of STM-studies on single crystalline samples. The computed data are also contrasted with results from photoelectron spectroscopy on magnetron sputtered layers and explain, why the orientation dependence of the work function will become even more pronounced when oxygen plasma treatments are performed. Results are also discussed in the context of our finding on intrinsic point defects in ITO.

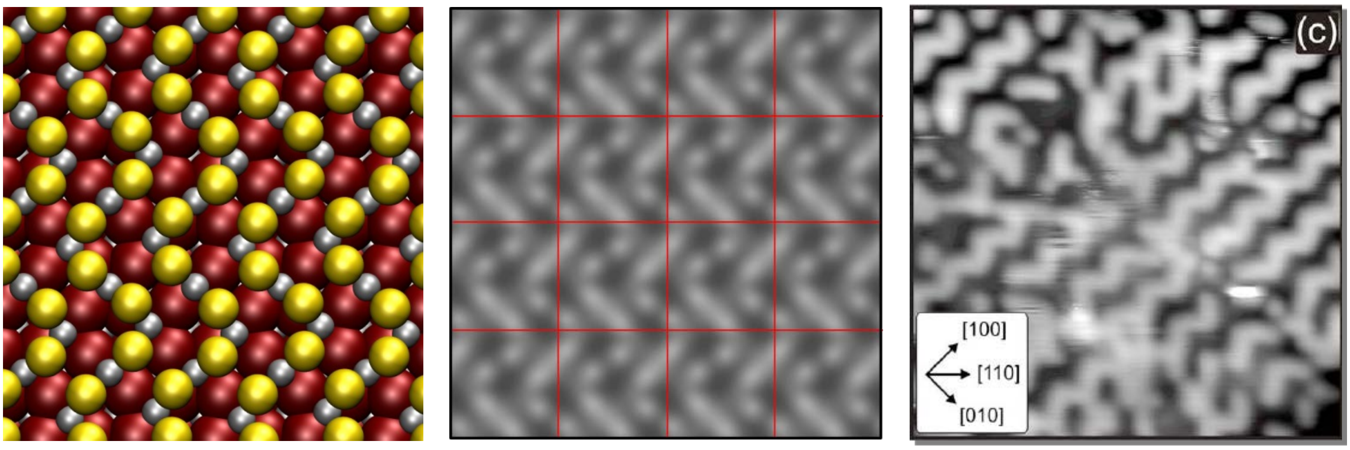

Fig.: Theoretical and experimental STM-image of a (001) surface of ITO.

Notes:

I 09: On the electrical conductivity and point defects in $BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ materials

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Rhombohedral $BiFeO_3$ (BFO) has become the center of research on multiferroics due the high Neél temperature of 370 °C and a Curie temperature of 820-830 °C. $BiFeO_3$ is also an interesting material because of the high crystallographic strain and intrinsic polarization of ~ 100 μCcm^2, which is along the pseudo-cubic (111) direction. A tremendous amount of studies have been performed on singly crystal as well as thin films of $BiFeO_3$ [1], while similar studies of bulk $BiFeO_3$ has been hampered by the severe difficulty to fabricate single phase materials [2] and the problems with dielectric loss and break down due to the high electronic conductivity of $BiFeO_3$ [1].

Tetragonal $Bi_{0.5}K_{0.5}TiO_3$ (BKT) is another interesting material which has received interest as a lead-free alternative to PZT ($PbZr_{1-x}Ti_xO_3$). We have recently investigated solid solutions of BFO and BKT and demonstrated that this material system have potentially interesting properties both in the BKT-rich and BFO-rich regions [2-4]. Doping BFO with BKT (0-30 mole%) reduce the problems with phase purity while keeping the polar rhombohedral space group R3c. The electrical conductivity is reduced by BKT-doping, but more interestingly the electrical conductivity can also be modified by annealing in atmosphere with different partial pressure of oxygen enhancing the electric field induce strain response. The effect of annealing in various atmospheres has also been demonstrated for $BiFeO_3$ [6].

Here, we discuss the nature of the electrical conductivity of $BiFeO_3$-materials with particular attention to the strong dependence of the conductivity with respect to partial pressure of oxygen. We demonstrate by electrical conductivity and Seebech coefficient measurements that the electrical conductivity is p-type in air or oxidizing atmosphere, and we show the onset of n-type conductivity in inert or reducing atmosphere. This opens up for minimization of the electrical conductivity by thermal annealing in controlled partial pressure of oxygen and thereby reduction of the dielectric loss.

The strong influence of the partial pressure of oxygen is rationalized by point defect equilibria involving oxygen vacancies originating from loss of Bi_2O_3 during sintering and variation in the valance state of Fe. Finally, we discuss possible influence of point defects on the large coercive field of pure $BiFeO_3$, coupled with strong domain wall pinning effects [6].

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Notes:

T 15: Phase field simulation of domain structure in ferroelectrics with semiconducting feature

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Ferroelectrics are widely used as actuators, sensors, and memory devices. There is significant effect of semiconductor properties on domain configurations in ferroelectrics, especially for doped materials. A phase field model is formulated and simulations are performed for ferroelectrics with space charges due to donors and electronic charge carriers. The role of donors and electronic charge carriers in the domain structure stabilization is studied in a quantitative way. For ideal insulating ferroelectrics, both kinds of 180 degree domain configurations ("head-to-head" and "tail-to-tail") are not stable due to the bound charges which can generate an electric field [1]. By accounting for semiconducting properties of barium titanate, the appearance of depletion layers near the electrodes is predicted. The stabilization of the head-to-head and tail-to-tail domain structures through the space charge is also demonstrated [2][3].

Further simulations have been performed for the corresponding cases with an initial tail-to-tail configuration and the initial domain wall is tilted. In the case without semiconducting features, the domain wall rotates to the vertical position in equilibrium due to the driving moment. In the cases with semiconducting features, the orientation of the domain wall at the equilibrium state depends on the donor concentration [2].

Since electronic charges accumulate near the head-to-head and tail-to-tail domain walls, they have electric conductivity, which is studied by the phase field modeling.

In this study, two defect systems are investigated: ideal defect system where oxygen vacancies are the only point defects and realistic defect system where doping of manganese gives rise to several kinds of point defects. It is shown that the domain wall conductivity enhanced by electrons or holes depends on domain configuration, type of defects involved, concentration of certain point defects etc. Simulation results are used to explain the controversial experimental results on domain wall conductivity [4][5]. It is also demonstrated that for ideal defect system, the domain wall conductivity decreases or vanishes after some time of diffusion.

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Notes:

T 16: Influence of Lead Oxide Stoichiometry Microstructure and Characteristics of PZT Ceramics and Multilayer Actuators

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The Lead-oxide stoichiometry of Lead-Zirconate-Titanate (PZT) ceramics and multilayer actuators is a critical issue for fabrication and performance. During sintering, the high vapour pressure of PbO and the corresponding volatility of lead oxide require careful design of the sintering setup and choice of the sintering parameters, which both may markedly impact the PbO content in the ceramics and devices.

In order to investigate the effects of lead-oxide stoichiometry, two different experimental approaches were chosen. PZT multilayer actuators were sintered under different PbO partial pressures which had been adjusted by using a powder bed and/or by different crucible configurations. In parallel PZT ceramics with different initial PbO content varying from 2 mol% deficit to 2 mol% PbO excess were prepared.

Structure and microstructure of the materials were characterized by X-ray diffraction and scanning electron microscopy (SEM). Dielectric properties and high field strain behaviour were analyzed with respect to PbO content and grain size. The results are compared to the behaviour of bulk PZT with similar PbO stoichiometries, indicating an excellent correlation between PbO content, structure and high field strain.

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T 17: True Operational Range of Piezoelectric Actuators

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Ferroelectric materials are ideal candidates for high precision, quick response, and high force actuator applications, due to their strong electromechanical coupling. Typical applications are, for example, diesel fuel injection systems, precision positioners, piezohydraulic pumps, and others. In each of these applications, work is performed against an external load with a defined linear or nonlinear stiffness. In order to design, optimize, and match the actuator to its application it is therefore necessary to know the strain behavior under the specific loading regimes. Among the most important figures of merit for materials to be used in actuator applications is the blocking force, defined as the maximum force an actuator can generate in the fully clamped state. However, the commonly used methods to determine the blocking force [1] ignore the nonlinear electrical and mechanical constitutive behavior as well as the path dependence of ferroelectrics, such as, e.g., stress- and temperature-dependence of the electromechanical properties that govern the actuators response [2,3]. Due to these effects the blocking force, as it is currently defined, strongly depends on the loading history and is therefore a path-dependent value. Furthermore, these methods assume a stress-free state, while piezo-actuators are typically pre-loaded with a compressive stress to minimize crack growth. These oversimplifications result in inaccurate prediction of the complex actuator's operational range, which may result in considerable performance decrease, e.g., deviations in impedance matching of the actuator to the system [4].

In order to determine the true operational range of piezoelectric actuators we developed a new experimental procedure that mimics the realistic loading conditions. The sample is mounted in a load frame fitted with a large piezoelectric actuator that acts as a virtual linear spring with an adjustable stiffness, ranging from zero (free displacement) to nearly infinity (blocking force). During testing an electric field is applied to the sample, resulting in an elongation. Through a proportional-integral-derivative (PID) control loop in the measurement program, the voltage applied to the stack actuator is adjusted to ensure a linear displacement-force relationship on the sample. The experimental arrangement also enables the application of different compressive pre-loads and elevated temperatures, allowing for a full characterization of a piezoelectric material under the actual operating conditions. The described experimental procedure was utilized to investigate different bulk piezoelectric samples, such as soft and hard $Pb(Zr,Ti)O_3$, $BaTiO_3$- and $(Bi,Na)TiO_3$-based lead-free compositions, as well as multilayer actuators under various operation conditions. The influence of the compressive pre-load and temperature on the actuation efficiency will be presented and the impedance-matching of realistic spring loads will be discussed with respect to the optimization of actuators performance. In particular, we focused on investigating the selected lead-free compositions, where the observed large strains originate from the electric-field-induced phase transitions and result in strongly nonlinear response. The results are used to directly compare the recently emerging lead-free piezoelectrics to their well-established lead-based counterparts under real loading conditions, with respect to their suitability for actuation applications.

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Notes:

T 18: Interfaces of Ferroelectrics

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The main objective of this work is the understanding of interface properties of ferroelectric materials and their correlation to the fatigue behavior by means of X-ray photoelectron spectroscopy. Such systematic study was missing so far and has been carried out in the framework of sub-project B7. One of the main results is the determination of Schottky barrier heights of $Pb(Zr,Ti)O_3$ with Cu, Ag and Pt as electrode.[1] During the deposition of metals onto PZT defect formation occurs at the interface, which pins the Fermi level and makes the barrier heights independent on metal work function. Such barrier height can be modified by post-deposition treatment in oxidizing or reducing atmosphere.[2] Using conducting oxide, on the other hand, avoids the defect formation and pinning effect, which has been shown by depositing high-work-function RuO_2 and low-work-function Sn-doped In_2O_3 on PZT.[3] The choice of the electrode material has also strong influences on the ferroelectric properties such as spontaneous polarization. $BaTiO_3$ single crystals with Pt, RuO_2 and $(La,Sr)MnO_3$ electrodes show very different remnant Polarization (P_r) and coercive field strength (E_c), which again can be modified by post-deposition treatment.

Energy band alignment at hetero-junctions between ferroelectrics has also been studied. The energy bands of PZT as well as $PbTiO_3$ and $PbZrO_3$ are determined to be ~ 1 eV higher than those of $SrTiO_3$ and $BaTiO_3$,[4] explaining the distinct doping behavior of these two types of ferroelectrics. Lead-free ferroelectrics $BiFeO_3$ and $(Bi,Na)TiO_3$ exhibit even higher energy bands compared to PZT and are therefore more prone to p-type conductivity.[5] The origin of the higher energy bands has been attributed to the lone-pair effect from Pb 6s or Bi 6s orbitals.

Beyond the intrinsic properties,[6] it has been found out that energy band alignment at interfaces is also dependent on ferroelectric polarization. Using $BaTiO_3$ single crystal and RuO_2 as electrode the dependence of Schottky barrier was quantitatively determined for the first time.[7] The result shows that the polarization lowers the barrier height at reversely biased interface and therefore favors electron injection from electrode into ferroelectric material.

Another important aspect to electrical fatigue examined in this sub-project was the electrochemical destabilization of ferroelectrics at interfaces. The composition of PZT thin films grown on different substrates has been investigated. Despite the exactly same deposition conditions, a clear correlation between A-to-B cation ration and Fermi level position was observed. This suggests that the alternating changement of Fermi level position upon polarization switching could lead to severe decomposition in the ferroelectrics, which forms another origin of electrical fatigue.

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I 10: Investigation and Manipulation of Domains on Small Length Scales in Ferroelectric Materials: Limits and Opportunities

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The understanding of nanoscale switching of ferroelectric domains is essential to understand macroscopic material parameters. This knowledge is crucial to develop material systems for various applications, such as actuators or information storage devices. Scanning Probe Microscopy is a well established characterization tool for ferroelectric materials due to years of development and its commercial availability. Here, Piezoresponse Force Microscopy (PFM) is used to image and manipulate ferroelectric domains on the nanoscale. It is used to characterize ferroelectric properties for materials from a wide spectrum, including traditional ferroelectric ceramics and thin films, ultra thin films pushing the limit of ferroelectricity, strained-induced ferroelectrics, and polymers. However, with increasing popularity of the PFM technique and the expansion towards non-traditional ferroelectrics and ionic systems, more and more errors in data interpretation occur due to a simplification of tip-sample interactions.

Here, we will describe the basics of PFM and explain why non-ferroelectric materials can appear ferroelectric due to measurement artifacts. We will focus on how to distinguish between different signal generating mechanisms and how to use this knowledge to study new effects. Once the limits of PFM are understood, we will focus on the unique opportunities this techniques provide to study local ferroelectric behavior. We will discuss the characterization of new order parameters, such as ferroelectric vortex states and unique properties of ferroelectric domain walls as well as bias-induced phase transitions in lead-free materials.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

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T 19: Core-shell domain structure investigation of lead-free incipient piezoceramics by piezoresponse force microscopy

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In the past years, the tendency to develop lead-free piezoceramics to replace $PbZrxTi_{1-}xO_3$ (PZT) for actuator applications has considerably grown due to new regulations regarding hazardous substances (RoHS) imposed by the European Union. Incipient piezoelectrics have been recognized recently as a new class of materials, which exhibit high strains at relatively low electric fields surpassing those of PZT. One of these materials is the $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) system doped with Sr. Systematic studies need to be carried out to understand the physics behind their functionality. TEM analysis of the incipient piezoelectric $0.75(Bi_{1/2}Na_{1/2}TiO_3)$-$0.25(SrTiO_3)$ (BNT-25ST) has clarified that a core-shell domain structure plays an important role for a high electromechanical response.

In this study, we used piezoresponse force microscopy (PFM) to visualize the core-shell domain structure and the tip-induced ferroelectric domains after poling the core-shell region with a DC voltage applied to the tip during scanning. In general, we observed a higher contrast of the lateral PFM signal than the vertical PFM signal. The core-shell configuration of individual grains could be observed. A clear contrast in the core region was observed in the PFM images indicating a ferroelectric polar state whereas the shell region showed a unified signal indicating a nonpolar state. Additionally, we poled a 1 x 1 μm^2 region including the core-shell area by applying a DC voltage of – 10 V and successively imaged this area afterwards. A notable polarization could be induced in the core region, while there was no obvious tip-induced domain in the shell region. This further conformed the ferroelectric state of the core and paraelectric state of the shell. Interestingly, the freshly induced domain in the core region continued growing after poling and merged into the adjacent shell region suggesting that the nucleation of domains at the interface between core and shell facilitates the propagation of the ferroelectric domain of the core region into the shell region.

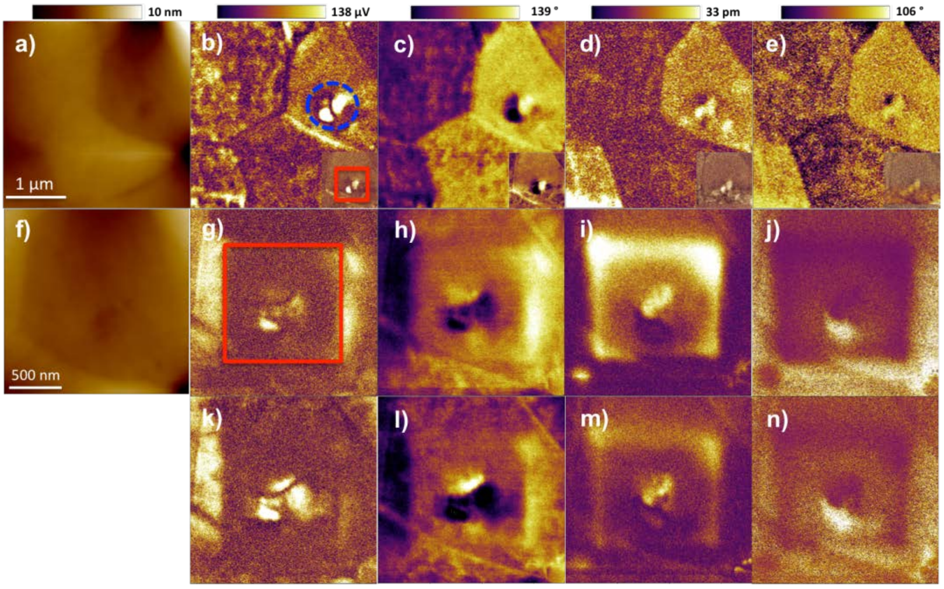

Fig.1: (a,f) Topography, (b,g,k) lateral amplitude, (c,h,l) lateral phase, (d,i,m) vertical amplitude and (e,j,n) vertical phase before (a-e),
8 min after DC poling of BNT-25ST incipient piezoelectric (f-j) and
16 min after poling (k-n).

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T 20: (Co-)doping of lead-free $Bi_{1/2}Na_{1/2}TiO_3$–$Bi_{1/2}K_{1/2}TiO_3$-based piezoceramics

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As of today, the overwhelming majority of the production of piezoelectric sensors and actuators is lead-containing. Lead is a known neurotoxin, hence according to latest EU-regulations lead-based materials are to be replaced by viable alternatives [1]. To address this urgent need, the system $Bi_{1/2}Na_{1/2}TiO_3$–$Bi_{1/2}K_{1/2}TiO_3$ (BNT-BKT) is a promising candidate for certain piezoelectric applications [2, 3]. For various piezoelectric systems, (co-)doping is used to tailor the defect chemistry in order to influence for instance Schottky barriers, defect dipoles or domain walls [4, 5].

In this study, aliovalent (co-)doping of BNT-BKT on the B-site of the perovskite lattice was performed with Mn, Al, Cu, V, Mo and combinations of the respective elements. MPB doping of BNT-BKT, aimed at actuator applications and doping on the rhombohedral side of the MPB, focusing on high power applications was carried out. XRD characterizations were undertaken to investigate phase purity. Small signal measurements as function of temperature (for instance as in Figure 1.) allow for conclusions on the transition from ferroelectric to relaxor behavior, while large signal polarization and strain measurements of doped MPB BNT-BKT consistently revealed polarization loop pinching and a strain increase compared to undoped samples. The piezoelectric constant d_{33} was additionally determined as a function of temperature. For rhombohedral ceramics, P_r and P_{max} could be improved. Furthermore impedance spectroscopy was employed to elucidate the resonance behavior (k_p and Q_m) of the ceramics and in order to study defects and their associations, electron paramagnetic resonance spectroscopy of dopant elements was used to assess their oxidation states.

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POSTER

P 01: Characterization of the $Bi_{1/2}Na_{1/2}TiO_3$-25$SrTiO_3$ lead-free incipient piezoceramic

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The dielectric and electromechanical properties of the $Bi_{1/2}Na_{1/2}TiO_3$ -25 mol % $SrTiO_3$ were studied as a function of temperature and frequency. This material presents a perovskite structure with large strain at 4 kV/mm featured by a d_{33}* of ~600 pm/V at input frequencies ranging from 0.1 up to 100 Hz. The system constitutes a promising lead-free candidate to replace the $Pb(Zr_xTi_{1-x})O_3$ family in stack actuator applications working in the large signal regime. In order to further delimit the operational capabilities of the material, blocking force measurements were also performed as function of temperature.

The high strain of the system is attributed to a reversible electric-field induced phase transition from a mixed relaxor state (i.e., ergodic and non-ergodic coexisting states) to a ferroelectric one. We showed that the phase transition occurs gradually depending on the electric-field magnitude and number of cycles at a given field strength. The induced electric-field phase transition is aided by a core-shell structure as depicted by scanning electron microscopy (SEM) in the back-scattered electron mode and also transmission electron microscopy (TEM). The core features Sr depletion and rhombohedral superlattice reflections (SSR). On the other hand, the shell is rich in Sr and presents mixed rhombohedral and tetragonal SSR. Moreover, by means of in situ high resolution X-ray, Raman, and TEM studies we followed in detail the structural transformation of the core-shell structure as function of temperature. At around 50 °C we observed de-freezing of polar nanoregions as a change in thermal expansion and as an anomaly in Raman shift, consistent with dielectric measurements on poled samples. With further increase in temperature, at around 165 ˚C, we observed the onset of core homogenization (from TEM and Raman) which is concluded at around 250 °C. This results in a fully homogenized microstructure with presence of both tetragonal and rhombohedral SSR in the whole matrix. Above 325 °C SSR almost completely vanish, consistent with reaching a stationary state in Raman and an anomaly in the dielectric properties. These suggest a predominantly cubic structure with no more octahedral rearrangements. Nevertheless, the locally non-cubic lower symmetry structure is still retained, as we do still observe Raman activity above this temperature. During the whole temperature range investigated, X-ray was not able to resolve the non-cubic distortions of the system and only changes in the thermal expansion were detected. This might result from the high amount of Sr giving rise to very small local non-cubic distortions and a presumable coherent interface between core and shell as observed by TEM. Furthermore, in situ electric-field TEM was performed to clarify the core-shell evolution under electric-field and its influence on the electromechanical macroscopic properties previously described.

P 02: Relaxor/Ferroelectric composites for high strain actuator applications

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Bi-based piezoceramics are one of the most promising lead-free alternatives for actuator applications. In this material class, high strains can be generated by a reversible electric-field-induced phase transformation from ergodic relaxor to ferroelectric phase. One of the major drawbacks is the requirement of relatively high electric fields (6 kV/mm) to induce this phase transformation and therefore to obtain the desirable property.

A new approach to overcome this drawback is to fabricate composites, composed of such a high strain ergodic relaxor and small amounts of nonergodic relaxor or ferroelectric material to reduce the field level required to trigger relaxor-to-ferroelectric transition.[1,2,3] In this work, a series of composites with various ratios of nonergodic relaxor BNT-7BT (93 $Bi_{0.5}Na_{0.5}TiO_3$ - 7 $BaTiO_3$) and ergodic relaxor BNT-6BT-xKNN (94-x $Bi_{0.5}Na_{0.5}TiO_3$ - 6 $BaTiO_3$ - x $K_{0.5}Na_{0.5}NbO_3$) with x = 2, 3, 4 and 6 is presented. The influence of different parameters, such as maximum electric field level, frequency, temperature, etc., onto the electromechanical properties is studied. The results suggest that the composite approach provides another degree of freedom in finding a suitable lead-free piezoceramic for actuator applications.

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P 03: Influence of Grain Size on Temperature Dependence of Electric Field Induced Strain in Soft Doped Morphotropic PZT Ceramics

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For a decade high performance fuel injection systems in automobiles are operated by piezoelectric multilayer actuators. The electric field induced strain of soft-doped PZT is used to control the injection valves in these devices, designed for operating temperatures from -40°C to 160°C. The temperature characteristics of the field induced strain are most important parameters for an evaluation of the performance of the PZT materials. From a microscopic point of view, the electric field induced strain is the result of at least three different types of mechanisms: the (indirect) piezoelectric effect, domain switching and phase transitions. “In-situ” X-ray and neutron diffraction taking into account the real structure as observed by TEM are the most advanced methods to identify the structural changes underlying the strain mechanisms.

The focus of the present investigations is on temperature dependent measurements and analysis of field induced strain of morphotropic soft doped PZT ceramics with varying grain size in a temperature range between 20°C and 160°C. In the present state the analysis is correlated to corresponding temperature dependent X-ray diffraction of crushed PZT ceramics, ambient temperature “in-situ” X-ray diffraction results and experience from TEM studies of PZT with similar compositions. For PZT materials not subject to a temperature induced phase transition the field induced strain increases approximately linear with temperature. Although the strain is generally lower for fine grained materials the temperature characteristics of strain are similar to those of corresponding coarse grained ceramics. In coarse grained PZT ceramics which undergo a temperature induced phase transition, a pronounced nonlinear increase in strain with temperature was found. In contrast to that, fine grained materials of the same composition did not show nonlinearity of strain within the temperature range under investigation. The temperature induced phase transition in the fine grained materials seems to be shifted to higher temperatures.

P 04: Temporal phenomena in organic field-effect transistors through Kelvin Probe Force Microscopy

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In the present poster, charging and discharging induced device instabilities of pentacene based organic field-effect transistors (OFETs) are discussed on basis of Kelvin Probe Force Microscopy (KPFM) measurements performed in the vicinity of the charge reversal point [1]. Even for p-type devices, the remnant charging of the transistor channel with electrons in the hole-depletion mode induces a substantial threshold-voltage shift, thus making the device instable. Further, on basis of these measurements, the electric-field and carrier-density dependence of the hole mobility in the sub-threshold regime of pentacene based OFETs can be determined. While the local carrier density and the electric field are obtained from the local surface potential and its gradient respectively, the local current is measured by dynamic KPFM following the charge-carrier front entering the transistor channel from the source and drain contacts. Thus, a KPFM based transient experiment is performed [2]. The obtained hole mobility is compared to a transport model for disordered organic semiconductors comprising its carrier-density and field dependence [3].

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P 05: Carbon-Rich SiOC Ceramic Aerogels as Anode Materials for Rechargeable Lithium-ion Batteries

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In this work we present the synthesis and electrochemical characterization of porous carbon-rich SiOC ceramic aerogels prepared by pyrolysis of preceramic gels synthesised under highly diluted conditions. In a typical preparation a linear Si-polymer, polyhydridomethylsiloxane, PHMS is cross-linked with divinylbenzene in presence of acetone using a platinum catalyst. The obtained wet gels are dried under supercritical conditions using liquid CO_2 and then pyrolysed at 1000 °C in Ar flow. The resulting porous SiOC ceramics are studied in a view of possible application as anode materials in lithium ion batteries for high rate applications. The dried gels have a surface area of 227 m^2 g^{-1} with pore size of 52 nm and the SiOC retains a surface area of around 100 m^2 g^{-1} after pyrolysis at 1000 °C. The tests of lithium insertion/extraction performed under galvanostatic conditions of low currents (18 mA g^{-1}) revealed high capacity of 710 mA h g^{-1} and cycling stability over multiple cycles. During high current tests porous SiOC electrode delivers a reversible capacity in the range of 650 mAhg^{-1} at a charging rate of 360 mA g^{-1} (1C). The enhanced electrochemical performance of porous SiOC materials is attributed to (i) un-usual composite structure in which a free carbon phase is formed in situ within the SiOC matrix (ii) high amount (49 wt %) of disordered free carbon and (iii) thermodynamic stability of the SiOC structure. The highly porous structure reduces the diffusion path of lithium ions and allows for buffering the volume changes during continuous lithium insertion/extraction. Accordingly the materials shows extended cycling stability especially at higher rate of charging/discharging. The significant first cycle irreversibility of about 45%, originates from high surface of the active material and still remains a challenge for the future work

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P 06: Structural evolution and degradation of Si anodes: insights from first-principle calculations

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Due to its high mass-specific capacity for Li storage and abundance, Si is one of most desirable anode materials for future Li-ion batteries. However, rapid capacity fading has so far hindered successful commercialization [1]. Numerous experimental investigations have been conducted since the 1980s in order to improve on the cyclability of Si and, recently, Si nanowires (SiNW) with lifetimes of more than 1000 cycles have been synthesized [2]. Despite these achievements a detailed understanding of degradation mechanisms in Si anodes is still lacking. Atomistic modelling may help in revealing and eventually switching off relevant mechanisms. Here we demonstrate how density functional theory (DFT) calculations can help understanding (i) internal degradation of Si anodes and (ii) anisotropic swelling of SiNWs observed during first-cycle lithiation [3].

Extensive DFT calculations are performed to identify energetically relevant structure models of amorphous lithiated Si (Li_xSi) and to extract formation energies that hint on the phase evolution of Si anodes during cycling [4]. We find the existence of various two-phase regions which are all accompanied by large inhomogeneous volume changes during phase conversion. Such inhomogeneous volume changes may be considered as source of crack formation leading to irreversible losses and thus capacity fading. On this basis, an improved cyclability of amorphous Si results from the absence of a particular two-phase region during lithiation which is present in crystalline Si anodes. Similarly, extended lifetimes achieved using capacity-limited cycling can be understood from the fact that most two-phase regions appear at high Li concentrations and are thus avoided when the capacity is limited.

We also perform calculations of various Si/Li_xSi interface geometries and study the kinetics of Li diffusion across these interfaces. We find that kinetic barriers are largely independent of the orientation of the interface. However, the energetics is not. Among the considered low-index interfaces Si{111}/LixSi interfaces are energetically favoured, Si{110}/LixSi interfaces show high interface energies and Si{100}/LixSi interfaces are situated in between. This hierarchy explains the experimentally observed anisotropy in swelling of SiNWs.

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P 07: Crystal symmetry and domain structure of morphotropic $PbZr_{1-x}Ti_xO_3$-ceramics

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The crystalline structure of $Pb(Zr_{1-x}Ti_x)O_3$ at the morphotropic phase boundary (MPB) at x = 0.46– 0.48 came under debate as a monoclinic structure was proposed based on x-ray powder diffraction (XRPD) [1]. This was controversial as nanodomains were observed in the TEM [2,3] which could produce so called "*adaptive*" reflections of lower symmetry in XRPD [4,5]. For this reason we chose convergent-beam electron diffraction (CBED) which allows diffraction from single domains and is very sensitive to crystal symmetry. Samples with compositions $0.40 < x < 0.55$ were characterized. While for $x \geq 0.47.5$ mainly tetragonal and for $x \leq 0.45$ mainly rhombohedral symmetry was obtained the compositions in between, especially x = 0.46 revealed evidence for monoclinic symmetry [5]. Also coexistence was observed. For x = 0.46 an *in situ* heating experiment endorsed a transition from monoclinic (*C*m) to tetragonal (*P*4mm) symmetry between RT and 300°C in agreement with XRPD [6]. The experimental CBED-patterns agree well with simulations based on structural models retrieved from Rietveld refinement of XRPD results.

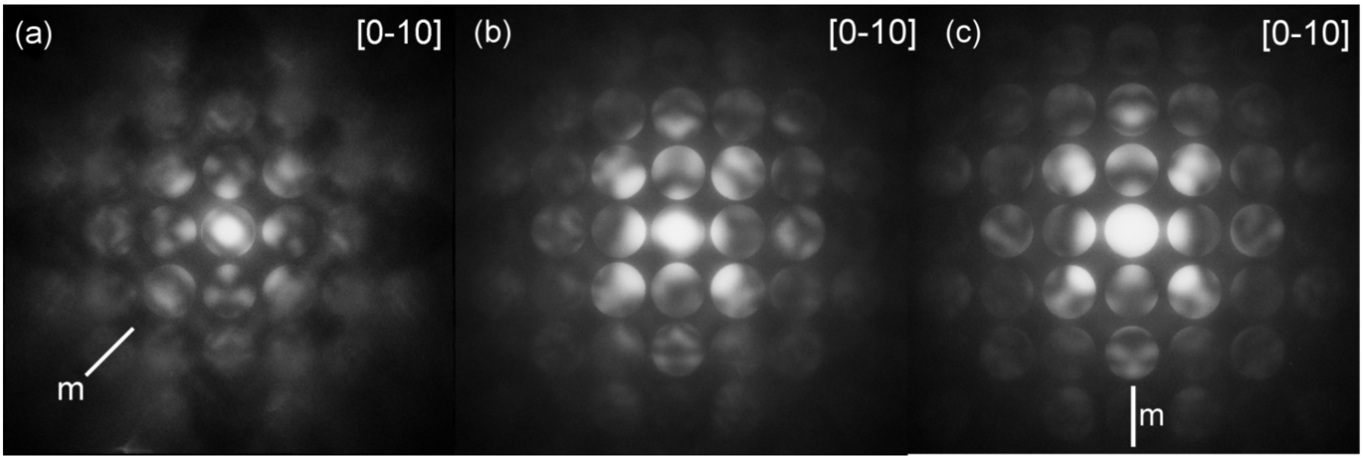

Fig. 1: *CBED-patterns along [0-10] of single domains in* $Pb(Zr_{1-x}Ti_x)O_3$-ceramics with
(a) rhombohedral (-101) mirror plane (x = 0.44)
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P 08: Anisotropy of Ferroelectric Behavior of (1-x)Bi1/2Na1/2TiO3 – xBaTiO3 Single Crystals across the Morphotropic Phase Boundary

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Research in lead-free piezoceramics is focused on solid solutions with end members belonging to the perovskite family with different crystal systems in the hope of finding a morphotropic phase boundary (MPB) with properties favorable to applications. This is despite the fact that the physical reasons for the good piezoelectric properties at the MPB are poorly understood in both classical ferroelectrics and relaxors; in fact, it is even not certain if the concept of an MPB can be extended to non-lead-containing systems. For (1-x) Pb(Mg1/3Nb2/3)O3-xPbTiO3 (PMN-PT) at least, there is some agreement in that the enhancement of the piezoelectric properties at the MPB is connected to the possibility of polarization rotation in rhombohedral systems from the [111]-direction into the [100]-direction. It is unclear whether this approach can be extended to lead-free systems like (1-x)Bi1/2Na1/2TiO3-xBaTiO3 (BNT-BT), as no equivalent research has been done so far.

In this work the electrical properties of BNT-BT single crystals with $x = 0.036$, 0.065 and 0.088 are investigated, covering the rhombohedral to predominantly tetragonal region of the phase diagram and encompassing the MPB, in dependence of the crystal orientation. BNT-BT single crystals were grown by top-seeded solution growth. Dielectric small-signal properties and ferroelectric large-signal hystereses of polarization and strain were measured along the pseudocubic <001>-, <110>- and <111>-direction for all three sample compositions. While the results complied with the current understanding of the crystallographic structure, no enhancement of electromechanical properties based on transient polarization rotation was observed. This clearly sets BNT-BT apart from PMN-PT. An anomaly was observed in the poling behavior of the strain in <001> oriented BNT-BT in the immediate vicinity of the MPB with $x = 0.065$, resulting in a giant small-signal piezoelectric coefficient d33 of 4600 pm/V. This effect is hypothesized to be due to an irreversible phase change from rhombohedral polar nanoregions to tetragonal ferroelectric microdomains.

P 09: Silicon Oxycarbide (SiOC) as Anodes for Li-Ion Batteries: Synthesis and Optimization of Ceramics Prepared from Sol-Gel Precursors

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Polymer Derived Ceramics (PDCs) have been evaluated as potential anode material for lithium ion batteries. Multicomponent silicon oxycarbide (SiOC) ceramics obtained through pyrolysis of various preceramic polymers display a significant lithium storage capacity (500 – 650 mAh/g) [1, 2]. Reversible capacity and stability of the materials strongly depend on the microstructure and the composition of the SiOCs.

Here we present correlation between the electrochemical performance of silicon oxycarbides and their chemical composition and microstructural features. Different SiOC ceramics were prepared by pyrolysis (1000-1300°C, Ar atmosphere) of various polysiloxanes. These preceramic polymers were synthesized using the sol-gel method. Sol-gel synthesis is a powerful tool for tailoring composition and structure of the final ceramic product. Three alkoxysilanes containing different organic group directly attached to the silicon (R-Si, R=phenyl, vinyl, methyl) were used for sol-gel synthesis of polysiloxanes. The precursors ($R\text{-}Si\text{-}(OC_2H_5)_3$) were mixed in different molar ratio in order to investigate the influence of the gels' chemical constitution on the composition and the nano-structure of the final ceramic material. The goal of the synthesis was to achieve optimal composition of the polysiloxanes in order to get carbon-rich silicon oxycarbides. The free carbon phase improves conductivity and provides a main source of lithium storage capacity [3]. However, capacity does not depend linearly with increasing carbon content. Other essential factors influencing reversible capacity are nano-structure and porosity of SiOCs.

Spectroscopic methods were used for investigation of complicated structure of SiOCs. Raman spectra confirm the presence of disordered carbons by the appearance of a well pronounced D band and allow to determine carbon cluster size. ^{29}Si NMR spectra show the presence of mixed bonds tetrahedra such as: $\underline{Si}OC_3$, $\underline{Si}O_2C_2$, $\underline{Si}O_3C$, $\underline{Si}O_4$ in the amorphous SiOC ceramics. The distribution of different mixed bonds tetrahedra depend on the gel's composition and the ratio between organic groups (R-Si) present in the polysiloxanes. Spectroscopic results together with electrochemical studies give an insight in lithium storage mechanism of the silicon oxycarbide materials.

Acknowledgments
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P 10: Isogeometric FE analysis of diffusion induced stresses and phase segregation in Li-ion battery electrode particles

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Li-ion battery has gained great popularity since its first commercialization because of, among others, its high energy density. And with the application of anode materials such as Tin-Oxide, Silicon, etc. the energy density of batteries can be several times larger than it is with graphite anodes. However, as a result of the ion-insertion induced large deformation those anodes experience irreversible mechanical degradation even after limited cyclic charging/discharging processes. Moreover, phase segregation is also observed in electrode materials [1]. This presentation is concerned with the numerical analysis of intercalation induced stresses in Lithium-ion battery electrodes. Thereby a three-dimensional hypo-elastic model coupled with Cahn-Hilliard diffusion is considered.

In the Cahn-Hilliard equation, there is a fourth-order spatial derivative of the concentration. Furthermore, due to a chemo-mechanical coupling, the chemical potential is also a function of deformation gradient, resulting in a coupled term of the third order [2]. To achieve a straightforward numerical treatment of such high-order differential equations, isogeometric concept is applied, in which the basis derived from the geometry is used to approximate the solution fields, allowing for the possibility of higher-order, in our case C^1, continuity.

Previous study applying isogeometric treatment, dealing with small deformation and neglecting the influence of concentration gradient, has been done by P. Stein and B. Xu [3]. This work is supported by the “Excellence Initiative” of the German Federal and State Governments and the Graduate School of Computational Engineering at Technische Universität Darmstadt.

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P 11: *In situ* electric field transmission electron microscopy: Sample preparation & Experiment

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In this study, the preparation of ceramic samples for *in situ* electric-field transmission electron microscopy (TEM) is elucidated. For TEM investigation, thin slices were prepared by a standard procedure of disc cutting, polishing, dimpling and argon ion milling. Sintered samples were ultrasonically cut into discs of 3mm diameter and polished to ∼120 μm thickness. Samples were mechanically dimpled and finally thinned by an argon ion beam until electron transparency.

For electric-field experiments gold or silver electrodes were evaporated on the flat surface of the sample. The evaporation mask is depicted in Fig. 1a. With respect to the electron beam a perpendicular electrode geometry was realized [1]. The nominal electric-field was determined by the voltage applied and the chosen slit width, which ranged between 100- 150 μm. A maximum nominal electric field of 6 kV/mm was attained with this setup. A contacted $Bi_{1/2}Na_{1/2}TiO_3$-0.25$SrTiO_3$ sample is depicted in Fig. 1b. The specimen was glued to the holder using an insulating varnish and contacted with one copper wire. The second electrode was contacted via a conductive epoxy glue.

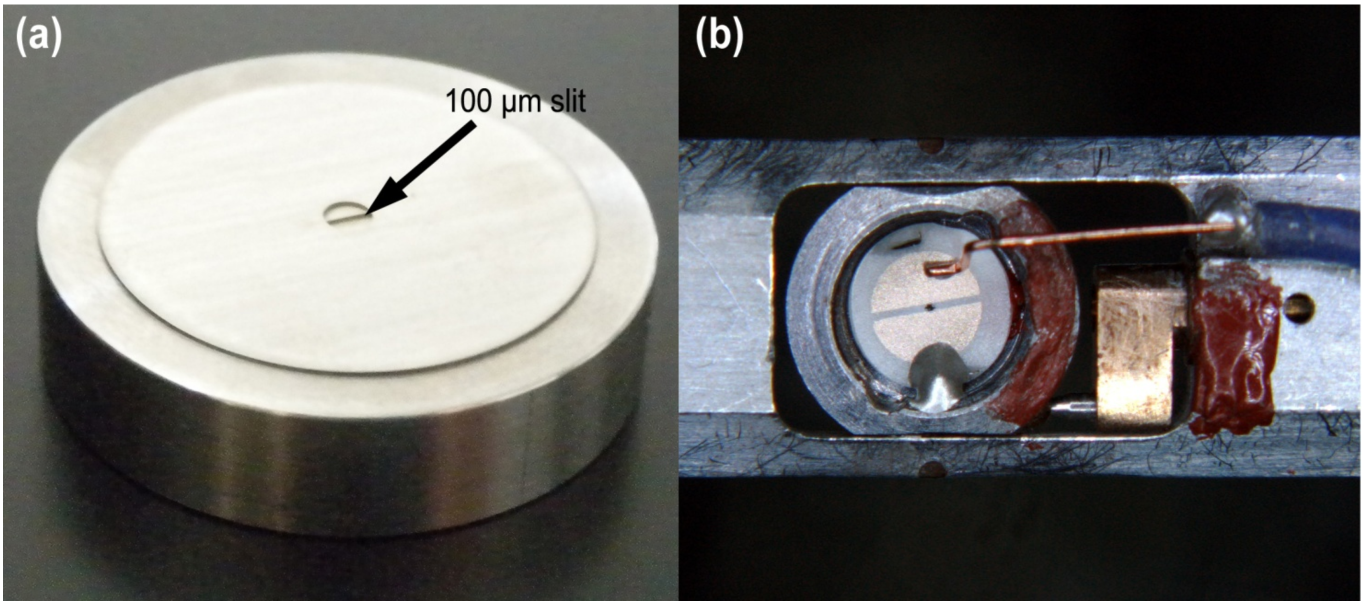

Fig. 1: (a) Evaporation mask with 100 μm slit width.
(b) Tip of the *in situ* TEM holder with contacted specimen.

First *in situ* electric-field experiments on $Bi_{1/2}Na_{1/2}TiO_3$-0.25$SrTiO_3$, which comprise a core-shell structure [2], revealed a change in grain contrast as a function of electric field.

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P 12: A1 Manufacturing of ceramic, textured actuators with high strain

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Subproject A1 advanced the fundamental understanding of various piezoelectric material-systems for actuators and their specific composition dependent material-property relations, additionally revealing prospective applications. A distinct focus lay on the replacement of market-dominant lead-based piezoelectric materials by lead-free alternatives, since lead is a known neurotoxin. The urgent need for alternatives is reflected in several international, *e.g.* EU-regulations, that already existed or entered into force during the project [1].

In the project, giant achievable strains for solid solutions of $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) with $BaTiO_3$ (BT) and/or $K_{0.5}Na_{0.5}NbO_3$ (KNN) [2] as well as other compositional end-members were discovered and thoroughly investigated, especially elucidating dominating strain mechanisms by means of electromechanical characterization as well as temperature dependent high resolution *in-situ* electron microscopic and diffraction methods [3]. High fatigue resistance as well as large blocking stresses, exceeding commercial lead-based materials, could be attributed to BNT as parent material and were explained by the newly introduced concept of incipient piezoceramics [4]. The underlying frequency and temperature dependence of the piezoelectric properties was additionally elaborated, highlighting the potential of BNT-based materials as high temperature dielectrics, for instance possessing a normalized permittivity varying no more than 10% from 43 to 319 °C [5].

Further insight into nanoscale relaxation processes of BNT-based materials and their time dependent behavior was gained *via* piezoelectric force microscopy in combination with neutron diffraction methods [6]. It was not only possible to attribute differences in the relaxation mechanism to the polarity of the applied electric field as well as to the degree of non-ergodicity, correlating with an increase in dynamic polar nanoregions, but also possible to characterize the time-dependence of those regions and the dependence of the mechanism of relaxation on the polarity of the applied electrical field.

The deep fundamental insight gained, enabled general conclusions on BNT-based relaxor materials and will be beneficial in designing high performance lead free piezoelectric materials for actuator applications.

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P 13: A3 Electronic structure as a fingerprint of thermodynamic stability of the layered structure cathode materials and of their chemical compatibility with the electrolytes

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The cathode material plays a key role in the determination of capacity, safety and life cycle of the Li- ion rechargeable batteries (LIB). For the long run performance of a LIB cell, the cathode should satisfy to the following criteria: 1) thermodynamic stability under the preparation conditions [1,2]; 2) thermodynamic stability with respect to the charged state [3] and 3) chemical compatibility with the electrolyte [4]. Thermodynamic properties of a material are defined by its electronic structure. We focus on *in-situ* study of the transition metal (TM) oxide layered cathode materials by using of the electron spectroscopy techniques (XPS, UPS, SXPS, HAXPES; TM *L*-, O *K*-, TM *K*- edges XANES).

Stability of the electronic structure under the preparation conditions is found out by the estimation of stoichiometry of the cathode materials, by the analysis of a) the valence state and spin state of the transition metals and; b) density of the occupied and unoccupied electronic states near the Fermi level. The intrinsic voltage limit of the cathode materials is revealed by the monitoring of the changes of the valence state and spin state of the transition metals, density of the occupied and unoccupied electronic tates near the Fermi level *versus* the charged state of the cathode material. The chemical compatibility of the cathode materials with the electrolytes is found out by the study of the changes of the valence and spin states of the transition metal at the cathode-electrolyte interface, as well as of the chemical composition of the interface. On the examples of the $LiMO_2$ (M=Ni, Co) layered thin film cathode materials, we demonstrate that the Co^{3+} ($t_{2g}^{3}\uparrow t_{2g}^{3}\downarrow e_{g}^{0}$) with low spin (LS) state configuration is more stable than Ni^{3+}($3d^{7}$, $t_{2g}^{3}\uparrow t_{2g}^{3}\downarrow e_{g}^{1}\uparrow$) with LS state ions *against* temperature of the preparation of the film cathode material, whereas the Ni^{3+} ions are reduced to the Ni^{2+} state. On the other hand, thermodynamic stability of $Li^{1+}Co^{3+}O_2$ is limited by the charged state of 4.2 V above which the Co3*d* states ($Co^{3+} \rightarrow Co^{4+}$ redox couple caused by Li-deintercalation) cross the top of O2p bands which is accompanied by a hole transfer to the oxygen site. $LiNiMO_2$ (M=Co, Mn) cathode materials have a tendency for oxygen loss, Li-deficiency and the $Ni^{2+} \leftrightarrow Li^{+}$- cations mixing (the latter takes place during both the preparation of the cathode material and the Li^{+} deintercalation). Therefore, a tender government of the oxygen pressure and the annnealing conditions has to be done for the preparation of $LiNiMO_2$ (M=Co, Mn) with well defined stoichiometry, with proper electronic and crystallographic structures. Electrochemical reversibility of the LIB cells is analysed by using the cyclic voltamogramms. The correlation between the deterioration of a $LiMO_2$ (M=Ni,Co,Mn) battery cells and the electronic and crystallographic structures of the cathode material has been found.

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P 14: A4 Carbon-rich silicon oxycarbide – A promising anode material: Recent findings related to microstructural, electrochemical and electroanalytical characterization

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The electrochemical properties of silicon oxycarbide ceramics (SiOC), in view of application as anode material for Li-ion batteries, were first studied in the middle of the 1990's by Dahn et al. [1,2]. Since that time SiOC compounds with various chemical compositions have been examined and stoichiometries with an exceptionally high content of free carbon were identified as perspective anode materials, with respect to gravimetric capacity, rate capability and cycling behavior [3-6].

Within this work, the comprehensive characterization of carbon-rich SiOC derived from commercially available polyorganosiloxane *RD-684a* (Starfire Systems Inc., USA) is presented. The overview includes the correlation of electrochemical properties with microstructural features in dependence of the ceramization temperature of the Si-based polymer [6]. The dependency of the Li-ion diffusion coefficient on the potential is determined by electroanalytical methods PITT, GITT and EIS and analyzed with respect to the microstructural features of the ceramic [7]. In addition, the benefits of chemical modification of the precursor with $Sn(ac)_2$, in order to enhance the lithium storage properties of SiOC by in-situ precipitation of metallic Sn as additional electrochemically active phase, is highlighted [8]. Finally, our newest results from ex-situ Raman-spectroscopy measurements, which trace and verify the Li-ion uptake within the free carbon phase in the SiOC microstructure, are presented.

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P 15: A5 Poly(*p*-phenylene vinylene) – Highlights within the SFB 595

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In the beginning the main focus of this project was to investigate the defect formation in Poly(*p*-phenylene vinylene)s (PPVs) during the synthesis and the influence of those defects on the fatigue behavior of resulting organic light emitting diodes (OLEDs) [1]. The polymerization method that came in handy here was the Gilch synthesis. In this case the addition of base to a dihalogenated monomer results in polymers of high-molecular weight and good to excellent yields with specific constitutional defects. To clarify the origin of those defects the mechanism of the Gilch polymerization had to be reinvestigated [2-10]

During the further procedure the main focus of this project changed. The new target was to investigate the influence of a variety of lateral substituents attached to the polymers main-chain on emission color and fatigue behavior in OLEDs. Here we were able to realize different PPVs emitting in almost the whole range of the visible spectrum [11].

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P 16: B3 Structural investigations on lead-free $Bi_{1/2}Na_{1/2}TiO_3$-based piezoceramics

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In this study electron, X-ray and neutron diffraction and scattering experiments with emphasis on the binary $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$ (BNT-BT) and ternary $Bi_{1/2}Na_{1/2}TiO_3BaTiO_3$-$K_{1/2}Na_{1/2}NbO_3$ (BNT-BT-KNN) system were performed [1]. Transmission electron microscopy (TEM) and powder X-ray diffraction experiments revealed the presence of a rhombohedral and a tetragonal phase with space group R3c and P4bm, respectively, both on a nanoscale level [2].

Using the technique of selected area electron diffraction combined with dark field imaging, the coexistence of tetragonal nanosized platelets and rhombohedral domains within single grains were verified. A composition dependent study of superlattice reflections in conjunction with microsctructural characteristics showed that the investigated BNT-based specimen have specific properties in common.

Moreover, the evolution of lamellar domains was demonstrated for lead-free $Bi_{1/2}Na_{1/2}TiO_3$-based systems by *in situ* electric-field TEM [3, 4].

Combining the *in situ* TEM results with *in situ* neutron diffraction experiments, an electric-field induced phase transformation was proposed [5], resulting in the giant unipolar and bipolar strain, monitored for specific compositions of the ternary system [6]. *In situ* electric field X-ray diffraction of $Bi_{1/2}Na_{1/2}TiO_3$-$xBaTiO_3$ ($x = 0.06$ and 0.07) revealed a strong, distinct response upon application of an external electric field of 4 kV/mm.

Quasielastic neutron scattering on $Bi_{1/2}Na_{1/2}TiO_3$-$0.04BaTiO_3$ showed pronounced structural relaxation processes related to the oxygen octahedral tilting. The temperature dependences of the corresponding excitation probabilities and relaxation times differ strongly between different tilt systems. Whereas some features are closely related to the dielectric properties of the material, others indicate additional excitation phenomena which were unknown up to now.

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P 17: B4 Correlation between nanostructure and electrochemical performance of Li-rich cathode active ceramics

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Lithium Ion Batteries (LIB) are nowadays the most important type of rechargeable batteries for mobile electronic devices. The growing demand for energy of these devices and introduction of electric powered automobiles require even more powerful batteries. The established LIB technology based on $LiCoO_2$ cathode active material has reached its physical limit and in order to improve energy density of future cells, a new cathode active ceramic needs to be found. Much research is dedicated to Li-rich blends of Li_2MnO_3 and $Li(TM)O_2$ (TM = Ni, Co, Mn) as new cathode material. The composite material offers more than 200 $mAhg^{-1}$ reversible capacity [1]. The nanostructure of these blends is very complex and highly depends on the synthesis conditions [2]. Transmission electron microscopy (TEM) was used to analyze the pristine nanostructure of two samples with the same nominal stoichiometry of $0.5Li_2MnO_3$:$0.5Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ synthesized by a molten salt (MS) and a coprecipitation (CP) route.

The MS sample shows a blending of the two phases close to a solid solution with C2/m ordering on the TM-layer. The CP sample shows a structural and compositional segregation into blocks of Li_2MnO_3-like and solid solution like blocks within one crystallite. The size of the Li_2MnO_3-like blocks is 20-50 nm perpendicular to the layer direction. The size of the solid solution like phase is 80-150 nm. Parallel to the layers the blocks have the dimensions of the particle. The electrochemical performance was measured in coin cells. The coin cell with the CP material shows less initial capacity than the cell with MS material. Upon extended cycling, the charge-discharge profiles of both samples show indications for fatigue in form of capacity and voltage fade. The characteristic changes in the voltage profiles can be assigned to a structural change towards a spinel-like phase. This behavior is more pronounced in the profile of the MS cell. The solid solution like phase of the MS sample is prone to spinel formation upon cycling causing the voltage and capacity fade. The CP cell has less initial capacity because the cycling stability of the Li_2MnO_3 phase is instable. The capacity fade and spinel formation is not as pronounced because the $Li(TM)O_2$ is enriched in the solid solution like blocks inducing a better cyclability. This study reveals the large impact of the nanostructure on electrochemical characteristics especially concerning this material class.

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P 18: B7 Universality of polarization reversal in virgin and fatigued ferroelectrics

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Dispersive polarization response in different classes of ferroics including the widely used lead-zirconate titanate (PZT) ceramics and recent lead-free Cu-stabilized BNT-BT relaxor ferroelectrics was analyzed by the Inhomogeneous Field Mechanism (IFM) model [1]. Obtained results supposed that the global polarization reversal of above materials is predominantly controlled by the statistical characteristics of inner disorder rather than by a specific law of the local polarization switching. Thus, irrelevant to a certain microscopic mechanism behind the local polarization switching the overall polarization response appears to be determined by a statistical distribution of the local electric field values which originates from the intrinsic inhomogeneity of the material and hence is directly related to the degree of the internal disorder. As a result, well disordered ferroelectrics are supposed to display a certain universal feature predicted by IFM approach [2]. Moreover, the IFM model allows direct extraction of the statistical distribution of local field values from experiment. The origin of the effects on the local field and switching time distributions are related to differences in structural and microstructural characteristics of the materials [3]. In addition, comparative studies of polarization switching in virgin and bipolar fatigued PZT and BNT-BT ceramics demonstrate evolution of statistical field distributions with increasing level of fatigue. Appearance of defects such as micro cracks, domain wall pinning centres or dielectric surface layers in the course of fatigue are considered as main factors influencing the local fields and hence the global polarization reversal.

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P 19: B8 In Situ Raman Diagnostics of Intercalation Batteries

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Raman diagnostics is a powerful tool for spatially-resolved and *in situ* diagnostics of lithium-ion batteries as illustrated for $LiCoO_2$ electrode materials, which were investigated in detail as composites of $LiCoO_2$ with binder (PVdF) and conductive (carbon) additives. Besides the $LiCoO_2$ active mass, Raman spectroscopy allows to detect carbon and PVdF-related bands as well as electrolyte bands [1].

Variation of the wavelength of laser excitation reveals a reversal of the intensity of the A_{1g} and E_g phonon bands for all electrode materials studied. For 514 nm excitation, the occurrence of an overtone of the A_{1g} band is observed. To explain the wavelength dependent spectral changes the presence of a resonance Raman effect is proposed. The resulting signal enhancement strongly facilitates the spatially-resolved and *in situ* analysis of $LiCoO_2$ composite electrodes. Spatially resolved analysis, i.e. Raman mapping of $LiCoO_2$ composite electrodes, shows a significant variation of chemical composition across the electrode surface and the presence of individual active mass particles, which are ∼10-20 μm in size [2].

Raman spectra recorded under electrochemical conditions are largely invariant regarding the degree of lithium de-/intercalation indicating no significant structural changes on the surface of the active mass particles. To this end, Raman experiments are complementary to X-Ray diffraction experiments. Spatially resolved *in situ* Raman analysis (Raman mapping) of $LiCoO_2$ composite electrodes demonstrates the chemical redistribution during electrochemical cycling. The relevance of these findings for the degradation of lithium-ion batteries is discussed.

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P 20: B9 Characterization of Structure-Property-Relationships of electrical Functional Materials with Solid State-NMR

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The enhanced electric properties of functional electric materials are believed to be direct consequence of their structure. In order to better understand these structure-property relationships at a local scale, we employed solid-state nuclear magnetic resonance (NMR). This technique is a sensitive probe for the atomic environment because of the very short ranged interactions between nuclei and their close local structure.

Solid state ^{7}Li NMR was applied to investigate anode and cathode materials for Li-ion batteries at different steps during the charging cycle. Structural changes could be observed after $LiCoO_2$ was charged, as the chemical shift of lithium shifted to the low field, an effect attributed to the Knight Shift. After discharging, the ^{7}Li signal returned to the former position, but with broader line width, which indicates a decrease in the degree of local order for this material. Furthermore, a marked increase of the quadrupolar coupling constants of ^{7}Li suggests that the structure of this anode material collapsed after the 37th recycle. Changes in NMR lines of ^{59}Co could also be correlated to the different charging states. In addition, cathode materials based in graphite, hard carbon and ceramics were also investigated. For graphite, ^{13}C and ^{7}Li NMR spectra pointed out the different stages of lithium intercalation. Although the influence of lithium was much smaller for ceramic and hard carbon cathode materials, ^{29}Si NMR lines suggest lithium is located near oxygen anions in Si-O-C ceramics.

Solid state ^{23}Na NMR was employed to investigate lead-free piezoelectric ceramics of composition $_{(100-x)}(Bi_{1/2}Na_{1/2})TiO_3 - _{(x)}BaTiO_3$, with a barium content between $0<x<15$. Spectra indicate that these materials are disordered at the atomic scale. The degree of local disorder and the individual contribution of the chemical shift and quadrupole interactions were characterized by a two-dimensional NMR experiment (2D-MQMAS) as a function of barium content. With this technique, two chemical shift ranges could be identified, which were assigned to the different symmetries present on both sides the alleged morphotropic phase boundary (MPB) for this system, around $x=6$. Moreover, the width of the distribution of chemical shift values peaked for barium contents in this range. These results indicate a wider variety of local symmetries in this compositional range and afford structural evidence for the concept of an MPB at the local scale, a feature that might explain the enhanced electric properties of these specific compositions. Furthermore, we could also correlate the distribution of quadrupolar coupling constants to the relaxor or ferroelectric character of a given composition. This NMR parameter is intimately connected to local displacements and polarizations. These data deliver structural evidence for the atypical relaxor-to-ferroelectric crossover observed on permittivity data of compositions in the investigated barium content range.

At last, we investigated the effect of electric poling on the local structure of these piezoelectric ceramics. By comparing spectral features of quadrupole perturbed ^{23}Na NMR lines of samples before and after electric poling, we revealed the coexistence of cubic and polar phases for relaxor compositions, a result that supports a model of polar nanoregions (PNRs) embedded in a cubic non-polar matrix for the ground state of these lead-free relaxors.

P 21: C1 Ab-initio calculations of the relaxor ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$ and its solid solutions

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$Na_{1/2}Bi_{1/2}TiO_3$ (NBT) and its solid solutions with other lead-free perovskite materials have attracted significant interest for applications in actuators, sensors, and transducers due to their excellent piezoelectric properties. Pure $Na_{1/2}Bi_{1/}$ TiO_3 exhibits a large remanent polarization of $P_r=38$ μC/cm^2 and a relatively high piezoelectric constant $d_{33}=72.9$ pC/N. However, the material is difficult to pole due to the high coercive field of 73 kV/cm and electrical conductivity due to the presence of point defects. These shortcomings can be avoided by alloying $Na_{1/2}Bi_{1/2}TiO_3$ with other perovskites. For several of these systems morphotropic phase boundaries (MPBs) similar to the one found in $PbZr_xTi_{(1-x)}O_3$ (PZT) are reported.

We developed a method based on *ab initio* calculations to predict compositions at morphotropic phase boundaries in lead-free perovskite solid solutions. This method utilizes the concept of flat free energy surfaces and involves the monitoring of pressure-induced phase transitions as a function of composition. As model systems, solid solutions of $Na_{1/2}Bi_{1/2}TiO_3$ with the alkali substituted $Li_{1/2}Bi_{1/2}TiO_3$ and $K_{1/2}Bi_{1/2}TiO_3$ and the alkaline earth substituted $CaTiO_3$ and $BaTiO_3$ are presented. The morphotropic compositions are identified by determining the composition at which the phase transition pressure equals zero.

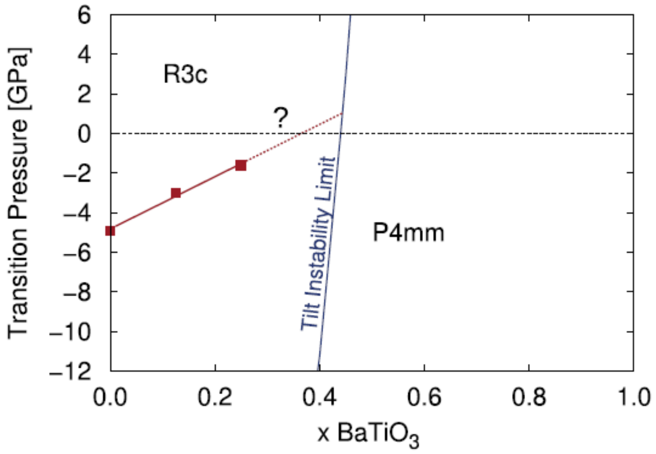

Figure: Phase Diagram of
(1-x) $Na_{1/2}Bi_{1/2}TiO_3$ - x $BaTiO_3$
obtained from ab initio calculations

P 22: C2 First-principles calculations – bonding of benzene on Indiumoxide

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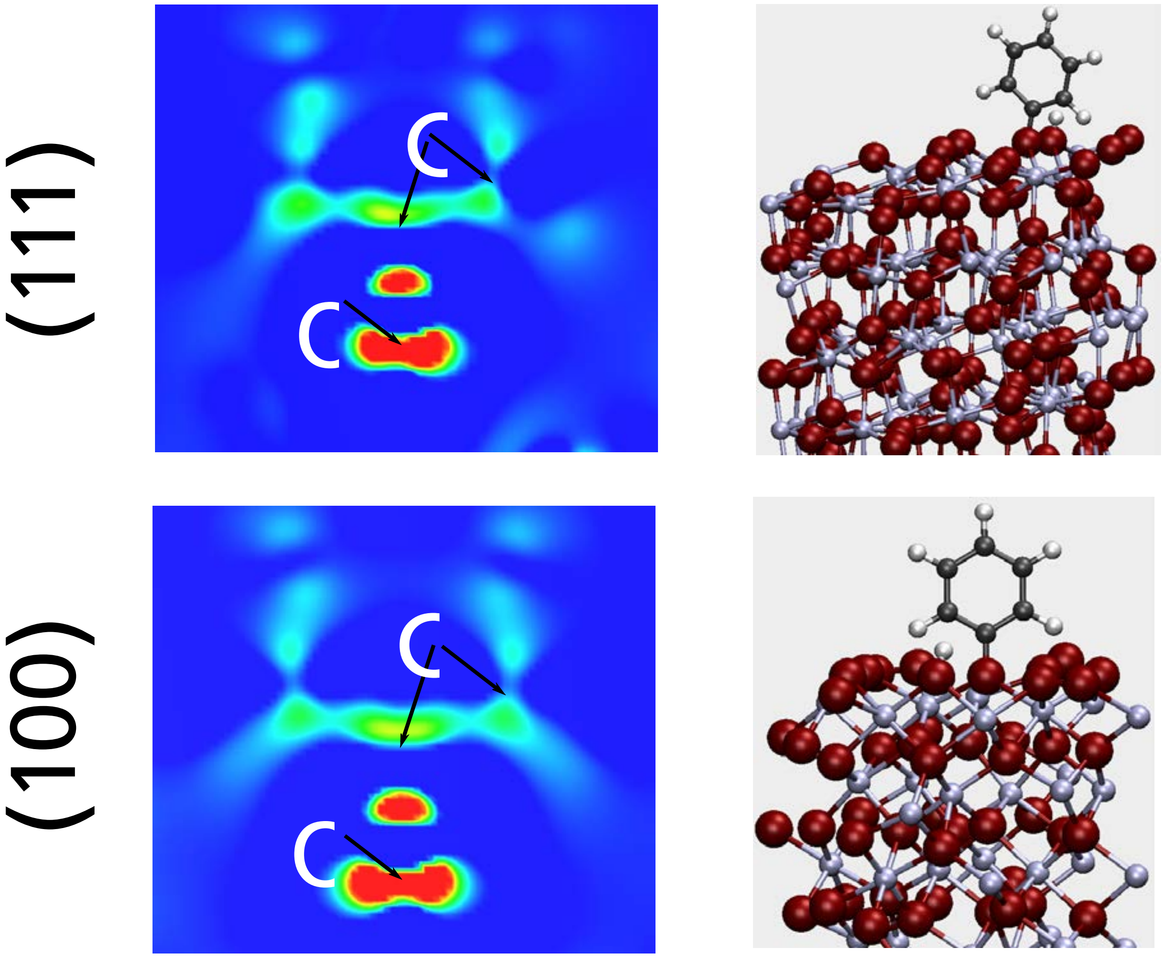
A few years ago the flat panel display market was dominated by Liquid Crystal Displays (LCDs). Recently, new display technology based on the organic light emitting diode (OLED) have emerged. Mobile displays are nowadays already realized by OLEDs. Although the fabrication on larger scales still is a challenge due to the various layers and different fabrication processes used, the advantages of price and power consumption drive the research in this field.

In this contribution we focus on the front-contact of the device which is the interface of the transparent conductive oxide (TCO) and the organic molecule. As the TCO In_2O_3 is used and benzene represents pentacene as the organic molecule. The interaction between the different In_2O_3 surfaces on the one side and the organic thin film on the other side determines the growing of the organic and therefore directly influences the conductivity.

The calculations based on the density functional theory (DFT) were carried out using the Vienna ab initio simulation Package (VASP) with Generalized Gradient Approximations (GGA).



The differential charge density shows a covalent bonding between the C (of benzene) and O (of In_2O_3) on (111)- and (100)- surface.

P 23: C5 Phenomenological modelling of field, charge and polarization distributions in ferroelectrics and organic semiconductors

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The main scientific results of the project C5 obtained during the last funding period (2011-2014) are presented. In particular, we demonstrate application of the self-consistent continuous model of charge-carrier injection in non-generate organic semiconductors (OSCs) accounting for discreteness of the injected carriers, which has been developed previously, to measured current-voltage characteristics of single-layer diodes based on polymer and small molecule organic constituents. Also, using an analytical approximation for the density of injected carriers as function of the Fermi energy, the above approach has been extended to the case of degenerate semiconductors being applicable now for arbitrary values of carrier densities in an OSC.

Semiconductor model was also applied to explain effects of nonlinear screening of depolarization fields, charge compensation and stabilization of domain structures in ferroelectrics. Particularly, it explained the (tunable by doping) conductivity along the domain walls and revealed emergence of an (also tunable by doping) electrostatic potential at surfaces of ferroelectric grains, relevant to the well-known positive temperature coefficient of resistance (PTCR) effect.

Furthermore, the Inhomogeneous Field Mechanism (IFM) statistical model of the polarization switching in polycrystalline ferroelectrics was shown to predict universal scaling properties of switching dynamics in a wide class of disordered ferroelectrics which were confirmed on various materials. Account for the evolution of depolarization fields during the switching in the extended IFM model has disclosed a self-organization of the polarization development providing a coherent reduction of depolarization fields.

P 24: C6 Monte Carlo simulation of phase transition, polarization switching and electrocaloric effects in ferroelectrics with random fields

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For the study of microscopic fundamentals in ferroelectrics (FEs) and relaxor ferroelectrics (RFEs), the lattice based model is utilized to study the phase transition, the polarization switching and ECE. Four different energy terms that significantly influence the material behavior are taken into account, namely the Landau double well potential, dipole-dipole interaction energy, gradient energy and electrostatic energy [1]. In the simulation the Metropolis algorithm is employed to study polarization switching at constant temperature and the influential aspects on the domain size and ECE. After reaching the equilibrium state the ECE is studied within the scope of the Creutz's algorithm with the total energy kept at constant [2].

In order to characterize the role of static random fields in the ferroelectric behavior of RFEs [3], results for the cases with and without random field are compared. In the case without random field, large size domains and sharp phase transition around the critical point are observed. As the gradient energy increases, the transition point becomes higher. During polarization switching domain wall movement is visible, and the remnant polarization is relatively large. The ECE peak appears at the phase transition point. On the contrary, in the case with random field, in the equilibrium state under no external field domain miniaturization and random domain nucleation are observed. The remnant polarization becomes smaller. A broad phase transition appears about the critical point.

These results imply that the random field can be one of the major factors which are responsible for the domain features of RFEs. When the random field magnitude increases, this phenomenon becomes more prominent. Compared with the case without random field, the ECE peak in the case with random fields appears at lower temperature and has a broader ECE range in RFEs, which indicates that RFEs can be an attractive candidate for ECE application.

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P 25: D1 The impact of relaxor properties on aging and fatigue in lead-free (1-*x*)BNT-*x*BT

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The lead-free piezoelectric (1-*x*)BNT-*x*BT (BNT-100*x*BT) is a promising alternative for lead zirconate titanate (PZT), currently the most frequently used material in piezoelectric applications. In contrast to PZT, however, BNT-100*x*BT exhibits pronounced relaxor characteristics, influenced by temperature, electric field, and sample history. Since the electromechanical performance depends strongly on the present relaxor state, the application of lead-free BNT-100*x*BT in actuating devices requires consolidated knowledge about the stability regimes of different relaxor states. Furthermore, also fatigue characteristics [1], [2] and self-heating of multilayer actuators depend on the relaxor character.

To identify stability regions of the nonergodic relaxor state, the ergodic relaxor state and the field-induced ferroelectric state, electric-field temperature (*E-T*) diagrams were established for different BT contents covering compositions across the morphotropic phase boundary. Field-induced transitions were detected with large signal and small signal measurements at temperatures between 25 °C and 200 °C and at a maximum field of 6kV/mm. In compositions with x=0.03, 0.06, and 0.09, the nonergodic state, the ergodic state and the field-induced ferroelectric state are accessible with the aforementioned measurement conditions. Subsequently, aging of the ferroelectric and piezoelectric response was investigated in different relaxor states of iron-doped BNT-100*x*BT. Considerable aging effects of the large signal response, such as the development of an internal bias field, occurred only in the ferroelectric state. The large signal response of the relaxor state was not affected by aging procedures. Since electron paramagnetic resonance spectra indicate the presence of defect complexes in the investigated compositions, the observed aging effects were interpreted in the framework of the defect complex model.

[1] Z. Luo, J. Glaum, T. Granzow, W. Jo, R. Dittmer, M. Hoffman, and J. Rödel, *Bipolar and Unipolar Fatigue of Ferroelectric BNT-Based Lead-Free Piezoceramics,* Journal of the American Ceramic Society, 529-535, (2011)

[2] Z. Luo, T. Granzow, J. Glaum, W. Jo, J. Rödel, and M. Hoffman, *Effect of Ferroelectric Long-Range Order on the Unipolar and Bipolar Electric Fatigue in* $(Bi_{1/2}Na_{1/2})TiO_3$*-Based Lead-Free Piezoceramics,* Journal of the American Ceramic Society, 3927-3933, (2011)

P 26: D3 Hall-effect and conductivity relaxation of doped In_2O_3

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The application of transparent conductive oxides in most electronic devices requires a good knowledge of their electrical properties such as conductivity, but also carrier mobility. In addition, oxygen exchange plays a crucial role for post-deposition treatments and the functionality of devices. In order to elucidate the relation between electrical properties and oxygen equilibration a system for in situ Hall-effect and electrical conductivity measurements of oxide thin films has been set up, giving the opportunity for temperature dependent measurements in controlled atmosphere [1]. The use of the setup is exemplified with differently doped In_2O_3 thin films, which are deposited by magnetron sputtering onto quartz glass substrates. The amount of Sn doping, the oxygen pressure during film deposition and during temperature treatment is varied. The results indicate that oxygen equilibration is not the only factor which affects the electrical properties, but also other slower processes, which are currently mostly ascribed to grain boundary effects. This is also suggested by the oxygen partial pressure dependence of conductivity, which does not show the expected power law dependence with an exponent of -1/6 due to an oxygen vacancy mechanism but considerably smaller exponents. The segregation of Sn to grain boundaries is one possible mechanism contributing to the conductivity relaxation. It is furthermore shown that the electrical conductivity of differently prepared films with identical composition remain different even after heat treatments of several weeks. Samples prepared with oxygen in the sputter gas reproducibly show lower conductivities, which is ascribed to the smaller grain size of the samples. Undoped and Zr-doped In_2O_3 films prepared with oxygen in the sputter gas undergo a strong conductivity minimum during heating to 300°C, which is irreversibly changed after heating to higher temperatures. This behaviour can be ascribed to changes of the concentration of trapped charges at grain boundaries and probably also to grain growth. The measurements are complemented by one-dimensional simulations of electrostatic potential distributions within a grain, in order to quantitatively understand the effect of grain boundaries on electrical properties.

[1] M.V. Hohmann, A. Wachau, and A. Klein, *In situ Hall effect and conductivity measurements of ITO thin films*, Solid State Ionics **262**, 636-639 (2014).

P 27: D4 The harmful influence of triplet excitons on the lifetime of polymer light-emitting diodes

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Due to their processability from solution, polymeric semiconductors offer the possibility to use low cost printing techniques to process organic devices. In this respect polymeric light-emitting diodes (PLEDs) are very attractive devices that have been intensely investigated. However, one of the issues that is still not completely understood is the electric operation-induced degradation that will be referred to as *fatigue*. A lifetime-related factor investigated to a lesser extent until now is the influence of the high density of non-emissive triplet excitons which could be responsible for local heating or act as traps for charge carriers, leading to a degradation of the device.

In this study PLEDs based on an alkoxy-substituted poly(*p*-phenylene vinylene) (PPV) derivative are investigated to understand the influence of triplet excitons on the fatigue. To do so the density of triplets in the PPV film is increased by blending different concentrations of the triplet sensitizer platinum (II) octaethylporphine ketone (PtOEPK) into the PPV matrix. A successful conversion of PPV singlet excitons to triplets has been proven by a decreasing photoluminescence and electro-luminescence of sensitized PPV layers. In PLEDs it is observed that both the t50 and t90 lifetimes are drastically shortened due to electrical stress in the presence of PtOEPK, which indicates that the additional triplets might be harmful to the stability and lifetime of the diodes. To rule out a possible influence of the sole presence of PtOEPK on charge carrier transport, unipolar hole- and electron-only devices with different sensitizer contents were prepared and investigated. In these devices, no fatigue could be observed regardless of the sensitizer concentration, suggesting that the decrease in the lifetimes of the bipolar diodes is indeed caused by the increased triplet population in the diodes with sensitized polymer films and not by the sensitizer additive as such. Furthermore, it could be shown that blending with the sensitizer does not influence the hole mobility of the PPV matrix although an increased temperature of electrically operated devices could be detected indicative for the enhanced non-radiative decay due to the increased triplet density.

P 28: D6 The effect of electric field-induced phase transitions on the blocking force in lead-free ferroelectrics

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Multiple compositions of lead-free ferroelectric materials display exceptional large electromechanical properties that are in certain cases larger than the current state-of-the-art lead containing materials. These findings are very promising for several applications that require large mechanical displacements at reduced input voltages, such as for example nano-positioning or fuel injection systems. Recent investigations relate the enhanced properties to a reversible electric-field-induced transition from an ergodic relaxor to a macroscopic polar ferroelectric state, whereby the instability of the transition enables the re-harnessing of the poling strain with each electric field cycle. The primary aims of this project were therefore to understand the influence of these phase transitions on the operational range and development of the blocking force, compare it to other strain and force developing mechanisms in lead-based and lead-free ferroelectrics, and finally investigate their suitability for actuator applications.

The first part of the project was focused on the methodology and equipment development for the characterization of actuator´s true operational range. To this end a new experimental procedure was developed that mimics the realistic loading conditions. The sample is mounted in a load frame fitted with a large piezoelectric actuator that acts as a virtual linear spring with adjustable stiffness, ranging from zero (free displacement) to nearly infinity (blocking force). During testing the linear displacement-force relationship on the sample is ensured through a proportional-integral-derivative (PID) control loop, which adjusts the voltage applied to the large stack actuator. Furthermore, the experimental setup enables the application of different compressive mechanical pre-loads and temperatures, allowing for a full characterization of a piezoelectric material under the actual operating conditions.

The second part of the project was focused on the investigation of various actuator materials with different mechanisms for strain and force development, such as piezoelectricity, electrostriction, and electric-field-induced phase transitions. The investigated materials included lead-containing ceramics (commercially available soft-type PZT and PLZT), $BaTiO_3$-based lead-free ferroelectrics, $(Bi,Na)TiO_3$-based lead-free ergodic relaxors as well as relaxor/ferroelectric composites. The influence of the different strain mechanisms on the operational range will be compared and discussed with respect to their suitability for actuation applications. In addition, the influence of temperature and pre-load on the operational range of selected materials was investigated.

P 29: T2 Grain Size Effects on the Electromechanical Properties of donor-doped PZT-Ceramics

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Piezoelectric ceramics of the solid solution $PbZr_{1-x}Ti_xO_3$ (PZT) are state of the art materials in sensor applications such as accelerometers and ultrasonic sensors. It is known from literature that these electromechanical properties are grain size dependent.

The current study analysed the grain size effect for different Zr/Ti-ratios and different donor concentrations. Dense ceramics with a grain size between 0.3 – 10.0 μm were obtained by varying the sintering temperature from 875°C to 1250°C. Hereby the Ti content was varied between 45 to 52 mol% with a fixed concentration of 1 mol% La as dopant. In a second step the Ti content was fixed at 47 mol% and the doping content was varied from 1 mol% La to co-doping with 1 mol% La and 0.75 mol% Fe.

While decreasing the grain size of the material a critical size was found, at which the domain structure changes significant from complex 3-D structures to simple lamellar patterns. This is in correlation with a suppression of the distortion of the perovskites lattice below the critical grain size as shown by XRD and Raman experiments. Small and large signal dielectric and piezoelectric properties show changes in non-180° domain switching as well as changes of the intrinsic piezoelectric properties by decreasing the grain size. It is demonstrated that the critical grain size is mostly related to the amount of donor dopant. The ferroelectric behaviour is compared to the ferroelastic properties depending on grain size.

P 30: T3 Investigation of degradation behavior in Li-rich NCM cathode materials with spectroscopic methods

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Layered transition metal oxides that are mainly based on either LiCoO2 or LiNiO2 are still used in portable electronic devices due to their high operating voltage and high specific capacity 140-160 mAh/g. Materials such as the "Li-rich" layered oxides, formed as the composites between Li[Li1/3Mn2/3]O2 (LIR) and LiMO2 (M = Ni, Co, Mn) (NCM) are promising candidates that offer even higher reversible capacities (> 250 mAh/g) and higher safety together with reduced costs [1]. For an economic and efficient operation as cathode materials in electrified vehicles for example, knowledge about mechanisms of degradation in order to optimize these materials for longer life time is mandatory. So far, a gradual decrease of the energy density during electrochemical cycling called 'voltage fade' is a major drawback of this material class. Synchrotron X-Ray diffraction and HRTEM investigations on Li-rich materials (provided by industrial cooperation partner) after long term cycling revealed the formation of ~ 5 nm domains with spinel-like cation ordering within a layered oxide matrix and an overall still coherent ccp oxygen lattice. These micro/nano structural changes are supposed to cause the 'voltage fade' at its final form after long term cycling. Since HRTEM investigations are only available for ex situ states and require work-intensive sample preparation, established 'global' diffraction methods are completed by complementary 'local' spectroscopic methods to follow the evolution of the structural changes during successive degradation on a sub nanometer regime especially at the initial and intermediate stage. First results obtained by EPR and NMR spectroscopic methods (ex situ) on the structural changes related to the degradation processes in Li-rich NCM materials with high commercial potential are discussed with preliminary focus on the empirical correlation with electrochemical degradation.

[1] M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek and S. A. Hackney,
J. Mater. Chem. 17, 3112 (2007)

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