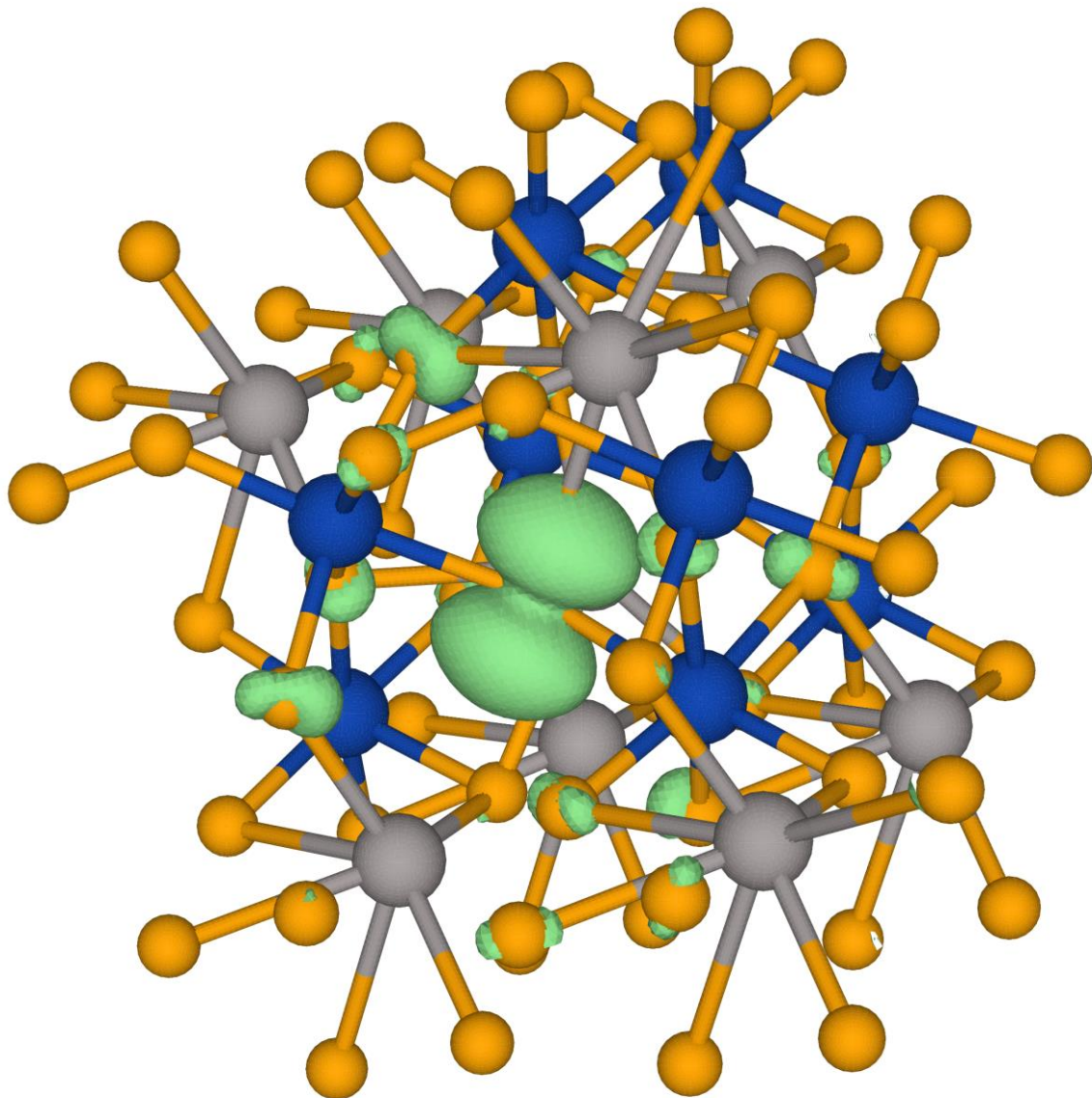


Fermi Level Engineering of Antiferroelectrics and Beyond

International Workshop, 12.3.-16.3.2023, Heidelberg (Germany)



Content

Welcome address	2
Conference venue	3
How to get there	3
Programme and abstracts	4
Session 1, Monday 13.3., 8:30--10:15 (Chair: K. Albe)	5
Session 2, Monday 13.3., 10:45--12.00 (Chair: M. Maglione)	6
Session 3, Monday 13.3., 13:30-15.00 (Chair: T. Granzow)	7
Session 4, Monday 13.3., 15:30-17.00 (Chair: D. Damjanovic)	8
Session 5, Tuesday 14.3., 8:30-10:45 (Chair: P. Erhart)	9
Session 6, Tuesday 14.3., 10:45-12.00 (Chair: B. Malic)	11
Session 7, Tuesday 14.3., 13:30-15:00 (Chair: M. Imlau)	12
Session 8, Wednesday 15.3., 9:00-9:56 (Chair: T. Frömbling)	13
Session 9, Wednesday 15.3., 10:45-12:00 (Chair: W. Donner)	14
Session 10, Wednesday 15.3., 13:30-15:00 (Chair: B. Xu)	15
Session 11, Wednesday 15.3., 15:30-17:00 (Chair: A. Klein)	16
List of attendees	18

Welcome address

Antiferroelectrics are emerging materials for more efficient conversion of electrical energy from renewable sources and for electromobility. Understanding of antiferroelectric properties is still rather limited but required for replacing the currently used Pb-based compositions by less hazardous alternatives. The workshop is aiming at a discussion of the results and understanding achieved in the FLAME project by synthesis, characterization and modelling of Pb-based and Pb-free antiferroelectrics. Together with international experts, the discussions shall particularly address the role of the structure and electronic structure, and the contribution of mobile and immobile electronic and ionic defects on the antiferroelectric behavior. Synergies with the field of ferroelectrics and relaxors shall also be addressed.

We welcome all of you in the city of Heidelberg and look forward to a lively workshop with active scientific discussions!

Andreas Klein



Karsten Albe



Chairs of the Workshop

Conference venue

We are gathering in one of the most beautiful cities of Germany. [Heidelberg Castle and the extensive castle gardens](#) are a magnet for visitors and the city's top attraction. In the city, you will find a large variety of historic buildings, impressive memorials and elaborate fountains, all of which have fascinating tales to tell.

The workshop is held in the [Qube-Hotel Bahnstadt](#), which is in a modern new quarter close to the central train station.

How to get there

Due to its central location, the [Qube Hotel Bahnstadt](#) is excellently connected to the motorway and main station (main station/motorway exit approx. 300m away). The historic old town with its romantic streets and squares can be easily reached by public transport (bus stop approx. 50m from the hotel) in approx. 15 minutes.

If you travel by plane, you can see if you find a direct flight to Mannheim, which is nearer to Heidelberg than Frankfurt am Main. From Mannheim, you can catch a train to Heidelberg train station, which will take about 30 minutes.

Heidelberg is also close to Frankfurt and can be most conveniently reached by train. If you arrive in Frankfurt International Airport, move on to "Fernbahnhof" or "Hauptbahnhof", where you can catch an ICE/IC or regional train towards Mannheim/Heidelberg. At the Heidelberg main station, you are approx. 900 m away from the hotel. Leave the main station on foot via the Europaplatz / Bahnhof Süd exit. From the Hauptbahnhof Süd stop, take line 22/26 in the direction of the Gadamerplatz stop. Get off here and after a few meters you will see the Qube Hotel in Bahnstadt on the left-hand side of the street.

Have a look at the homepage of [Deutsche Bahn](#) for ICE/IC and regional trains.



Programme and abstracts

The program starts on Sunday night with an opening reception and dinner. Talks are scheduled in a way that provides ample of time for discussions. On Tuesday, we will have the conference dinner in a traditional restaurant downtown Heidelberg after we return from a guided tour through Heidelberg castle.

Sunday	Monday	Tuesday	Wednesday	Thursday
	Breakfast			
	<i>S1 (Albe)</i>	<i>S5 (Erhart)</i>	<i>S8 (Frömling)</i>	Departure
08:30	1-1 Klein	5-1 Sinclair	8-1 Maglione	
09:15	1-2 Donner	5-2 Fulanovic	8-2 Huang	
09:45	1-3 Egert	5-3 Villa	8-3 Moxter	
10:15	Coffee+Tea			
	<i>S2 (Maglione)</i>	<i>S6 (Malic)</i>	<i>S9 (Donner)</i>	
10:45	2-1 Iniguez	6-1 Dickey	9-1 Damjanovic	
11:30	2-1 Zhang	6-2 Hui	9-2 Xu	
12:00	Lunch			
	<i>S3 (Granzow)</i>	<i>S7 (Imlau)</i>	<i>S10 (Xu)</i>	
13:30	3-1 Imlau	7-1 Malic	10-1 Genenko	
14:15	3-2 Sanna	7-2 Erdem	10-2 Granzow	
15:00	Coffee+Tea			
	<i>S4 (Damjanovic)</i>	<i>Guided Tour Heidelberg Castle</i>	<i>S11 (Klein)</i>	
15:30	4-1 Erhart		11-1 Schneider	
16:15	4-2 Wiktor (online)		16:00 11-2 Frömling	
17:00	<i>Discussion</i>		<i>Discussion</i>	
18:00	Opening Reception			
19:00	Dinner	Dinner	Banquet	Dinner

1-1 | 8:30

Electronic structure and charge transport in NaNbO₃

Nicole Bein, **Andreas Klein**

Institute of Materials Science, TU Darmstadt, Germany

The electronic structure and charge transport of NaNbO₃ have been studied by X-ray photoelectron spectroscopy, transmission electron microscopy, impedance spectroscopy, and with direct current conductivity measurements in dependence on electric field, temperature, and oxygen partial pressure. The measurements reveal that the fundamental gap is considerably larger than the optically determined energy gap of 3.5 eV [1]. The optically derived band gap is assigned to excitonic transitions involving trapped charge carriers in agreement with theoretical calculations for LiNbO₃ and KNbO₃ [2,3]. AC and DC conductivity indicate that i) DC conductivity is probing only electronic conduction, ii) ionic conductivity is higher than electronic conductivity, and iii) two types of ionic and two types of electronic carriers are involved in electric conduction. By assuming that electronic conductivity is dominated by hopping of electrons, suggested to be localized on Nb, and of holes, suggested to be localized on oxygen, the temperature dependence of electronic transport in air and in nitrogen can be consistently described for undoped and for donor-doped NaNbO₃. The model reveals a fundamental energy gap of 4.5 eV and trapping energies of electrons and holes of 1 and of 0.2 eV, respectively. The model is particularly capable of describing the change of activation energy and of conduction type (n- vs. p-type) at ~300°C.

[1] N Bein et al, Phys. Rev. Mater. 6, 084404 (2022)

[2] W G Schmidt et al., Phys. Rev. B 77, 035106 (2008)

[3] F Schmidt et al., Phys. Rev. Mater. 3, 054401 (2019)

1-2 | 9:15

Electron density studies on sodium niobate

Leif Carstensen, **Wolfgang Donner**

Institute of Materials Science, TU Darmstadt, Germany

Sodium Niobate is one of the prototype antipolar materials. Its room temperature „P phase“ evolves from the cubic parent phase through a series of phonon instabilities. In an effort to understand the electronic origin of those instabilities, we performed studies of the electron density through the analysis of powder diffraction experiments. We interpret our results in terms of the Pseudo Jahn-Teller effect.

Compositional modification, phase stability, and the local structure: Functional oxides probed with NMR spectroscopy

*Sonja Egert**, Pedro Groszewicz, Gerd Buntkowsky

**School of Chemistry, University of St. Andrews, UK*

Institute of Physical Chemistry, TU Darmstadt, Germany

The sensitivity of solid-state NMR spectroscopy to bond lengths, distortion, octahedral tilting, and disorder makes it a powerful technique for the characterization of the local structure. In this work, NMR-active nuclei ^{207}Pb and ^{23}Na are used as local probes to elucidate relationships between the compositional modification, local structure, and phase stability of ferroelectric (FE) and antiferroelectric (AFE) oxides based on the analysis of two-dimensional NMR line shapes. As an example of substitution in lead-containing oxides, the composition-induced phase transition from the AFE to the FE state in modified PbZrO_3 is studied *via* the analysis of the chemical shift interaction, and a local structural model is proposed based thereon. In NaNbO_3 -based oxides, the analysis of NMR parameters in combination with first-principles calculations sheds light on the effects of solid solution formation on bond-length disorder, the distortion of the local environments, and octahedral tilting.

Session 2, Monday 13.3., 10:45--12.00 (Chair: M. Maglione)

Is HfO_2 a soft-mode (anti)ferroelectric?

Jorge Íñiguez

LIST, Department of Physics and Materials Science, University of Luxembourg, Luxembourg

Hafnia (HfO_2) and related compounds (e.g., ZrO_2 , $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$, and doped versions of them) are polymorphic materials that can be prepared in both ferroelectric and antiferroelectric phases. Ferroelectric order in hafnia is generally believed to be improper; the transitions between its various (anti)polar and non-polar polymorphs tend to be strongly discontinuous; phase coexistence is observed in most samples. These observations suggest that the relevant energy landscape of these compounds is very intricate, with multiple local minima separated by high energy barriers, and no trace of the soft-mode phase-transition behavior that is typical of perovskite oxides like ferroelectric BaTiO_3 or antiferroelectric PbZrO_3 . In this talk I will present recent first-principles results [1] that challenge this picture. More precisely, I will show that it is possible to identify a high-symmetry reference phase of HfO_2 from which all the low-lying polymorphs of the compound can be obtained as simple soft-mode instabilities. The proposed reference structure helps explain key experimental observations (e.g. uniaxial ferroelectricity without ferroelasticity, dielectric anomalies typical of soft-mode proper ferroelectrics) while confirming behaviors established by previous theories (e.g., weak tendency for lateral growth of ferroelectric domains). Interestingly, our proposed picture suggests that HfO_2 compounds may in fact be ideal Kittel antiferroelectrics, and even the possibility of a novel antiferroelastic behavior is revealed. We thus introduce a new way to look at hafnia and related compounds, bringing them close to the traditional soft-mode picture and opening a wealth of possibilities for further exploration. *Work done in collaboration with Hugo Aramberri (LIST) and funded by the Luxembourg National Research Fund through project INTER/NWO/20/15079143/TRICOLOR.*

[1] Theoretical approach to ferroelectricity in hafnia and related materials, H. Aramberri and J. Íñiguez (in preparation).

2-2 | 11:30 am

First-principles Investigation of (Anti-)ferroelectric Materials beyond the Harmonic Approximation

Hongbin Zhang

Institute of Materials Science, TU Darmstadt, Germany

As represented by ferroelectric (FE) and antiferroelectric (AFE) materials, displacive structural phase transitions driven by electric fields have a vast spectrum of applications. To improve the current elusive understanding on such structural transitions, it is essential to go beyond the harmonic approximation. In this talk, I will focus on the treatment of anharmonicity combining accurate first-principles calculations and machine learning modelling and elaborate its effects on both the thermodynamic and thermal transport properties. To parameterize the potential energy surfaces into effective Landau Hamiltonians, we implement an active learning approach and apply it to describe the temperature driven phase transitions in BaTiO₃. Moreover, based on compressive sensing lattice dynamics, we demonstrate that the thermal conductivity can be tailored significantly upon FE-AFE phase transitions, and elucidate how imaginary phonon mode can be treated properly. I will also show how homogeneous electric fields can be considered and share a vision on how to perform future atomistic simulations of electric field driven phase transitions.

Session 3, Monday 13.3., 13:30-15.00 (Chair: T. Granzow)

3-1 | 13:30

Correlative nonlinear optical fs-spectroscopy applied to polar oxide crystals: Accessing the interplay of small polaron and self-trapped exciton dynamics

Mirco-Kai Imlau

School of Physics, Osnabrück University, Germany

Self-localized carriers with strong coupling to the lattice significantly influence the optical and electrical properties of polar oxide crystals. Although they allow spectroscopic access due to broad, distinct absorption bands, the experimental study requires the application of time-resolved spectroscopic techniques to access the formation dynamics in the sub-ps time domain and the transport and relaxation kinetics in the microsecond to seconds time domain. Of particular interest is the elucidation of the interaction of different quasi-particles, for example the interaction of small polarons with self-trapped excitons. In this context, nonlinear optical time-resolved spectroscopy methods and their special possibilities for the study of the dynamic properties of self-trapped charge carriers will be presented. Using lithium niobate as an example, it will be shown how the dynamic processes of small polarons and STEs can be experimentally differentiated and how the question of the transformation between the charge carrier types can be answered.

3-2 | 14:15

Spectroscopic signatures of small polarons in LiNbO₃ and LiTaO₃ calculated from first principles

Simone Sanna

Institute for Theoretical Physics, Justus Liebig University Gießen, Germany

Small polarons are quasiparticles that are formed in crystals with large lattice polarizability, when the electron (or hole)-lattice interaction is large enough to overcome the Coulomb repulsion and localize

the carrier at substantially one lattice site. Depending on the particular lattice location (regular site, point defect, defect pair, etc.) polarons of different flavors can be created. Spectroscopic signatures related to polaronic states have been demonstrated in many crystals, as polarons are known to strongly affect the material's linear and nonlinear optical response. This is particularly true in ferroelectric crystals such as LiNbO_3 and LiTaO_3 . Besides a high lattice polarizability, these metal oxides feature a high concentration of intrinsic point defects of potentially polaronic character. Thus, the whole optical response of the isomorph materials LiNbO_3 and LiTaO_3 is generally interpreted within the polaronic picture. As polarons are sensitive to thermal and optical excitations, pressure, electric fields and further factors, it is in principle possible to tune the optical properties of LiNbO_3 and LiTaO_3 by defect engineering, provided the polaronic states are sufficiently well known at the microscopic level.

In this contribution, the actual knowledge of polaronic structures in LiNbO_3 and LiTaO_3 based on first-principles atomistic calculations is summarized. The structural properties of polarons formed on different lattice sites as revealed by density functional theory are discussed and used as basis for the calculation of the electronic structure and spectroscopic signatures within many-body perturbation theory. Calculated and measured absorption bands are compared and interpreted on the basis of electronic transitions involving the polaron-induced defect states within the fundamental band gap. By comparing the defect structures in LiNbO_3 and LiTaO_3 , we evaluate the general assumption that there is little difference between the aforementioned properties of the two ferroelectrics.

Session 4, Monday 13.3., 15:30-17.00 (Chair: D. Damjanovic)

4-1 | 15:30

Dynamical materials: From atomic scale modeling via machine learning to experiments

Paul Erhart

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

The dynamical behavior of materials at the atomic scale, i.e., the motion of individual atoms, is crucial not only for their thermodynamic stability but directly impacts their electronic, optical, and transport properties. Detailed insight into these dynamics is therefore fundamental for understanding and designing materials. By the very nature of the problem the length and time scales involved are extremely short. As a result, atomic scale modeling plays an important role in guiding and interpreting experimental studies and discovering novel phenomena and mechanisms.

Traditional approaches of condensed matter physics are built on perturbation theory and typically assume a regular (crystalline) reference lattice. As the complexity of materials increases, for example, through dimensional engineering as in the case of layered materials or by integrating organic and inorganic components such as in hybrid perovskites, these approaches reach their applicability limit, both due to the explosion of the degrees of freedom and a failure of the underlying assumptions. Here, the combination of atomic scale simulations, correlation function based analysis, and machine learned potentials is emerging as a tool set that can lead to a paradigm shift in how we approach these questions.

In this presentation, I will show some recent work from my group that showcases the approach and illustrates its potential. In the first part I will focus on extremely anisotropic thermal conductors based on large-area van-der-Waals thin films with random interlayer rotations [1]. They can produce among the highest room-temperature thermal anisotropy ratios, which can be used for very efficient thermal management in electronic devices at the nanometer scale. Using a combination of molecular dynamics simulations, neuroevolution potentials [2], and correlation function analysis [3], we are able to quantitatively explain experimental data and reveal a one-dimensional glass-like thermal transport

that is concurrent with a two-dimensional crystalline transport mechanism. We show that this behavior is transferable between chemistries and identify a simple descriptor that allows one to predict the dependence of the through-plane conductivity on the rotation angle.

The second part of the presentation will be concerned with the atomic dynamics in perovskites, a very large class of materials with wide-ranging applications in, for example, actuators, sensors, energy harvesting, and optical devices. I will show recent work concerned with the systematic construction of transferable and accurate models for these materials [4]. The latter enable one to quantitatively analyze the dynamics associated with the phase transitions that are pivotal for the unique properties of perovskites. In particular, one can show that the so-called soft modes associated with these transitions exhibit overdamped behavior already hundreds of Kelvin above the actual transition temperature [5]. This gives rise to a pronounced feature in the vibrational density of states in the zero-frequency limit, which is confirmed by quasi-elastic neutron scattering experiments. These results have implications for our understanding of the local structure in these materials, which is important for the electronic and optical properties.

[1] Kim et al., Nature 597, 660 (2021)

[2] Fan et al., Journal of Chemical Physics 157, 114801 (2022)

[3] Fransson et al., Advanced Theory and Simulations 4, 2000240 (2021)

[4] Fransson et al., arxiv:2301.03497

[5] Fransson et al., arxiv:2211.08197

4-2 | 16:15 am (online)

Charge localization in complex metal oxides: challenges in modeling and effect on material properties polarons in perovskites

Yulia Wiktor

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

Charge localization, either in the form of polaronic self-trapping or associated with defect formation, is a prevalent phenomenon in metal oxides. At the same time, charge localization plays a crucial role in determining the material properties of materials, affecting energy alignments, charge mobility, and recombination. I will first discuss the computational challenges of modeling polarons in complex metal oxides. I will highlight the techniques used to mitigate the self-interaction error in polaronic modeling and the importance of exploring a wide range of polaronic configurations. Using BiVO_4 as a case study, I will demonstrate how polarons can impact the Fermi-level pinning and the oxygen-evolution-reaction.

Session 5, Tuesday 14.3., 8:30-10:45 (Chair: P. Erhart)

5-1 | 8:30

Chemical doping mechanisms in NaNbO_3

Derek C Sinclair

Department of Materials Science and Engineering, University of Sheffield, United Kingdom

NaNbO_3 is a well-known antiferroelectric perovskite that has been extensively studied as the primary phase or in combination with other polar perovskites (eg KNbO_3 , BaTiO_3 , $(\text{Na,Bi})\text{TiO}_3$) for a variety of dielectric/piezoelectric applications. Here we will survey a range of aliovalent A and B site dopants (donors and acceptors) in NaNbO_3 to establish the favoured doping mechanisms and their influence on the dielectric and/or electrical transport properties. For example, A-site donor-doping usually

results in ionic compensation via the creation of A-site vacancies. In the case of Bi-donor doping this creates a substantial solid solution based on the formula $\text{Na}_{1-3x}\text{Bi}_x\text{NbO}_3$ (with $x \leq 0.20$) which undergoes a displacive order/disorder transition between $x \sim 0.1$ and 0.2 which has a dramatic effect on the dielectric properties. In contrast, B-site acceptor doping with the creation of oxygen vacancies produce limited solid solutions. In the case of Ga-acceptor doping based on the formula $\text{NaNb}_{1-x}\text{Ga}_x\text{O}_{3-x}$ the solid solution limit is low ($x \sim 0.05$) and has little effect on permittivity-temperature profile of NaNbO_3 albeit with higher dielectric losses.

5-2 | 9:15

Dielectric permittivity in antiferroelectrics governed by an electric field-induced phase transition

Lovro Fulanovic¹, Mao-Hua Zhang¹, Binxiang Huang¹, Nikola Novak² and Jurij Koruza^{1,3}

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³*Institute for Chemistry and Technology of Materials, Graz University of Technology, Austria*

Antiferroelectrics (AFE) feature unique properties due to their electric field-induced phase transition to the ferroelectric (FE) phase. AFEs are characterized by high dielectric permittivity values, which are temperature- and electric-field-dependent. In contrast to the other dielectric materials, AFE exhibits a sharp increase of permittivity with an increasing electric field when approaching the AFE/FE phase transition [1]. It was suggested that the electric field-induced phase transition is responsible for the peculiar dielectric behavior of antiferroelectrics. However, some lead-free AFEs do not exhibit such a dielectric behavior, although they exhibit a double loop of polarization versus an electric field. Hence, the mechanisms contributing to the peculiar dielectric behavior still need to be understood. Even more, the dielectric behavior of antiferroelectrics is an essential feature for realizing high voltage DC-link or snubber capacitors needed in emerging green technologies.

To elucidate field-dependent permittivity in AFE lead-free AFE, NaNbO_3 and AgNbO_3 are contrasted to the PbZrO_3 -based composition [2,3], focusing on AFE/FE phase transition. A series of comprehensive permittivity measurements were performed under different AC and DC fields and in a broad temperature range. In addition, phase transition properties were complemented with polarization versus field data. The results were compiled in the electric field vs. temperature diagrams, a figure of merit for the field-induced phase transitions.

[1] B. Jaffe, Proc. IRE. 49 (1961)

[2] M.-H. Zhang et al., Acta Mater., (2020), 200, 127-135

[3] L. Fulanovic et al., J. Eur. Ceram. Soc., (2021) 41, 5519-5525

5-3 | 9:45

Impact of doping conditions on the Fermi level in sodium niobate

Lorenzo Villa, Karsten Albe

Institute of Materials Science, Materials Modelling Division, TU Darmstadt, Germany

In recent years extended research has been focusing on improving the properties of capacitors for energy storage applications. In this context, lead-free antiferroelectric materials (AFE) are excellent candidates due to their ability of displaying high energy density, high energy efficiency and low environmental impact. In this class of compounds, NaNbO_3 is amongst the most promising materials, due to the possibility to obtain double P-E loops at room temperature. One of the mostly used methods to obtain narrower antiferroelectric P-E loops is via doping. In fact, it has been shown that the P-E loops

of NaNbO_3 can be improved upon doping with SrSnO_3 .

When impurities are introduced into a system, they will interact with the already present intrinsic defects and can lead to formation of defect dipoles, which will affect the switching behaviour of the electric dipoles and therefore the P-E loops. For these reasons, we have studied both the equilibrium and quenched defect thermodynamics of intrinsic and extrinsic defects, including defect complexes, in the promising Sodium Niobate, using Density Functional Theory. In particular, we have computed the formation energies for all types of vacancies and substitutions, accounting for all possible charge states, in different regions of the stability diagram. Moreover, we have developed an original approach to account for charge state transitions in the defect quenching model, in order to more properly reproduce the experimental conditions.

We show that the binding energies of the defect complexes are negative, indicating their presence in large concentrations. Therefore, they will most likely influence the switching mechanisms and the P-E loops. Moreover, we show that defect quenching considerably shifts the Fermi level, indicating that the Fermi level could be engineered to obtain better AFE properties.

Session 6, Tuesday 14.3., 10:45-12.00 (Chair: B. Malic)

6-1 | 10:45

Local to meso-scale order in non-linear dielectrics characterized by aberration -corrected scanning transmission electron microscopy

Elizabeth C. Dickey

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, USA

The ability to design the composition and microstructure of electronic ceramics for emerging technological applications requires sophisticated characterization techniques that can provide quantitative information about local structure and chemistry. Such structure quantification is particularly important to the fundamental understanding of properties in many important non-linear dielectrics, where chemical heterogeneities associated with dopants or intrinsic lattice defects give rise to local inhomogeneities in charge, strain and polarization. Such local deviations from the global average structure and symmetry are often linked to enhancements in macroscopic dielectric and electromechanical properties. This seminar discusses the use of aberration-corrected scanning transmission electron microscopy (STEM) to quantify short- and medium-range lattice disorder in electronic oxides, including antiferroelectrics, ferroelectrics and relaxor ferroelectrics. The ability to quantify local structure on a sublattice basis and in real space provides unique insight into the polarization of these materials.

6-2 | 11:30

Domain morphology and atomic structure of antiferroelectric perovskites

Hui Ding

Department Structure and Nano- / Micromechanics of Materials, Max-Planck-Institut für Eisenforschung (MPIE), Düsseldorf, Germany

This talk will focus on the domain and atomic structure of antiferroelectric oxides with chief attention to the prototype PbZrO_3 and NaNbO_3 resolved by advanced high-resolution transmission electron microscopy (TEM) techniques. Extended materials include NaNbO_3 -based solid solutions which realized stabilized double hysteresis loops at room temperature. By correlating their microstructure and macroscopic properties, we are able to provide insight into their enhanced energy storage properties. Moreover, the influence of structural defects will be discussed.

Influence of chemical modification on the microstructure and properties of alkali niobite based perovskite ceramics

*Barbara Malič, Brigita Kmet, Andreja Benčan
Jožef Stefan Institute, Ljubljana, Slovenia*

Doping has been one of the standard methods to change the properties of ferroelectric and piezoelectric ceramics. Acceptor and donor doping of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) solid solution have been extensively researched. It was discovered that the defects introduced by foreign ions contributed to modifying the piezoelectric properties. A similar approach was transferred to lead-free piezoelectric ceramics, including alkaline niobate perovskites. The effect of low amounts of dopants in the case of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) could be mainly described as following similar trends as observed in lead-based perovskite ferroelectrics, i.e., change in phase transition temperatures, changes in densification and grain size, and/or domain mobility and related physical properties. Interestingly, introducing a larger amount of strontium dopant into the KNN lattice contributed (more than 2 mol%) to a strong reduction of grain size, poor densification, reduced monoclinic cell distortion and formation of secondary phases, but the solid solubility of strontium in the perovskite lattice was not exceeded up to the studied range of 8 mol% [1]. Solid solutions of KNN with alkaline or alkaline-earth perovskites or, in other words, by compensating valence substitution in both A- and B-sublattices. Typically, such chemical modification resulted in the enhancement of piezoelectric properties, better densification and fine grain size. In the contribution, we discuss selected cases of chemical modification of KNN and its implications on microstructure and physical properties.

[1] Hreščak et al., J. Europ. Ceram. Soc., 2017

Role of defects in nanosized metal oxides for applications in energy storage systems

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Orhanli, Istanbul, Turkey*

Electron paramagnetic resonance (EPR) spectroscopy is a very powerful method due to its enhanced sensitivity to unpaired electrons. In order to understand the defect structure in functional nano-materials we use multi-frequency EPR spectroscopy. In this presentation i) basics of EPR spectroscopy, ii) quantum confinement effects in ferroelectric nano-materials and iii) EPR and Photoluminescence (PL) investigations of intrinsic defect centers in semiconductor zinc oxide (ZnO) nanoparticles will be given. Starting with the introductory information about EPR spectroscopy; doping and nano-size effects will be discussed for the ferroelectric materials such as, PbTiO_3 , BaTiO_3 , PbZrTiO_3 (PZT) etc. In the last part of the talk, surface and core defects and their reactivity under temperature and light will be presented for ZnO semiconductor nano-materials. Defect models will be discussed. Finally, application of such materials as electrode materials and their electrochemical performance test results in the supercapacitor devices will be presented.

Fermi level engineering in doped BaTiO₃ multilayers

Mario Maglione¹, Christopher Castro Chavarría^{1,2}, Sandrine Payan¹, Alla Artemenko¹, and Andreas Klein²

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²Institute of Materials Science, Electronic Structure of Materials, TU Darmstadt, Germany

Mobile charges are able to alter the effective dielectric permittivity in oxides. This was previously shown in a variety of perovskites single crystals and ceramics at high temperatures [1] and at room temperature in CaCu₃Ti₄O₁₂ ceramics [2]. In the case of ferroelectric single crystal KTiOPO₄ used in Non-Linear Optical applications, the mobile charges under interest are K⁺ ions [3]. After an overview of these previous results in bulk materials, the focus of this lecture will be BaTiO₃ based multilayers in the search towards a better understanding of interfacial charges localisation.

As in any semiconductor, the Fermi level of ferroelectric Materials is tuned under heterovalent substitution. We have used Nb, La and Mn as such dopants in BaTiO₃ thin films and multilayers. We first show that in-situ XPS is a very efficient tool for probing the Fermi level position in the bulk of the films and its bending at interfaces. In the case of Nb/La multilayers, a large bending was shown to arise from extended cross-diffusion between the layers and an exceptional overall dielectric permittivity resulted [4]. Such an extrinsic behaviour may be ascribed to space charge accumulation at interfaces on donor levels in the band gap close to the bottom of the conduction band.

On the other hand, Mn acceptor doping is able to restore and intrinsic behaviour of BaTiO₃ films which are usually very sensitive to unwanted oxygen vacancies. Such curing effect of Mn doping has already been used in many instances for BaTiO₃ ceramics or thin films. By following the Fermi level position by in situ XPS and confirming the electron trapping at Mn sites by EPR, we bring microscopic evidence supporting this model [5].

[1] O.Bidault, P.Goux, M.Kchikech, M.Belkaoumi and M.Maglione. Phys Rev B. 1994, 49 (12), 7868-7873

[2] DC Sinclair, TB Adams, FD Morrison, AR West, Appl. Phys. Lett. 80, 2153 (2002); <https://doi.org/10.1063/1.1463211>

[3] M. Maglione, A. Theerthan, V. Rodriguez, A. Peña Carlota Canalias, B. Ménaert and B. Boulanger Optical Materials Express 6, 137 (2016)

[4] C. Castro Chavarría, S. Payan, J.-P. Salvetat, M. Maglione and A. Klein Surfaces 2020, 3, 567–578; doi:10.3390/surfaces3040038

[5] C. Castro Chavarría, S. Payan, A. Artemenko, M. Maglione and A. Klein, *to appear*

X-ray photoelectron spectroscopy analysis of anti-ferroelectric (Pb,La)(Zr,Sn,Ti)O₃

Binxiang Huang, Andreas Klein

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We have studied the interface properties of nominally undoped and of donor (La) doped Pb(Zr,Sn,Ti)O₃ (P(L)ZST) by means of X-ray photoelectron spectroscopy. In order to avoid charging of the highly insulating materials during photoemission, thin conducting electrodes, which are permeable for the

photoelectrons, have been applied to the surface of the materials. The comparison between high work function RuO₂ and low work function Sn-doped In₂O₃ (ITO) electrodes reveals a difference of the Fermi level position at the interface of 1.1 eV. This is similar to the difference in work function of the two electrode materials, indicating the absence of Fermi level pinning. The same behavior is observed for ferroelectric and anti-ferroelectric compositions. We have further studied the interface behavior at elevated temperature with applied electric field across the sample. Undoped PZST exhibits a substantial increase in current with time (resistance degradation). In contrast, the conductivity of donor-doped PLZST, which is almost 3 orders of magnitude lower than that of undoped PZST, decreases with time. Despite the strongly different electrical behavior, both samples develop a metallic Pb component at the interface with increasing voltage stress. These experiments constitute a unique opportunity to study the chemical stability of interfaces of highly insulating materials.

8-3 | 9:45

Application of antiferroelectric materials in high voltage technology

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The possible application of antiferroelectric materials in power engineering is discussed in this contribution. Due to their field-dependent permittivity, antiferroelectric materials could be used as possible fillers in nonlinear field grading of high voltage isolation systems. In order to understand this specific application, the focus will initially be on the fundamentals of field control before turning to the use of antiferroelectric materials as fillers. Here, the function and effects of the filler on the physical properties of the composite will be explained, whereby the aspect of electric field strength in the antiferroelectric particles will be considered in more detail. Subsequently, the results of the characterization of sodium niobate as the first lead-free antiferroelectric are shown. For this purpose, the material was mixed into epoxy resin with different filler concentrations and characterized with different experimental setups for their dielectric properties.

Session 9, Wednesday 15.3., 10:45-12:00 (Chair: W. Donner)

9-1 | 10:45

Defects, polarization and electro-mechanical coupling in oxides

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Point defects play a major role in controlling properties of materials. The most often discussed mechanism in ferroelectrics is interaction of defects with domain walls. The direct contribution of defects to polarization, strain and electro-mechanical coupling has been much less investigated. In this presentation, I will first review indirect effect of defects in oxide ferroelectrics, via domain-defect interactions. This has important practical implication for hard and soft piezoelectrics. Then, apparently direct contribution of defects to the strain, polarization and their coupling will be discussed for recently developed lead-free ferroelectrics and for non-ferroelectric oxides and halides where influence of defects on polarization, strain, electrostriction and piezoelectricity may be more visible in the absence of intrinsic polarization.

9-2 | 11:30

Phase-field modeling and simulation of (Anti-)Ferroelectrics

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Featured by high power density and high cyclic stability, ferroelectric (FE) and antiferroelectric (AFE) perovskites are distinct type of materials for energy storage and conversion particularly in pulse power equipment, miniaturized electronic devices and electronic control system in electric vehicles. The key issue is to increase the energy storage density, which is strongly related to ferroelectric domain structure in the materials and its interaction with defects. In this talk I report our recent progress on phase-field modeling and simulations of antiferroelectrics, followed by example and perspective on how to include Fermi-level energy and defect chemistry into them.

Firstly, I present a high order gradient phase-field model for antiferroelectrics [1]. The model enables simulations of the observed incommensurate modulations of (anti-)ferroelectric polarization configuration, which goes beyond the capability of the established models like the Kittel sublattice model. Simulations on the domain structure and hysteresis will be shown, along with the comparison of the simulated temperature induced FE-AFE phase transition with the related TEM results. At the end, I show that ferroelectric phase-field ferroelectric model can be extended to include the space charge related to defect chemistry and Fermi energy, along with demonstrating simulation results.

[1] Liu and Xu, *Scripta Mat.* 2020, 10.1016/j.scriptamat.2020.04.040

Session 10, Wednesday 15.3., 13:30-15:00 (Chair: B. Xu)

10-1 | 13:30

Stochastic domain formation in ferroelectrics: the role of depolarization fields

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The role of electric depolarization fields and field-mediated correlations in the formation of polarization domains in ferroelectrics and their field-driven switching remains a highly debatable issue. To study this problem, we have developed a new stochastic model of uniaxial ferroelectrics based on the time-dependent Landau-Ginzburg-Devonshire approach where polarization and electric field components are self-consistently treated as Gaussian random variables. A closed system of evolution equations for auto- and cross-correlation functions for all stochastic variables was formulated and solved analytically and numerically.

Evolution of the system starting from various initial quenched disordered states at different temperatures and applied electric fields was investigated. Phase diagram in terms of the average value and dispersion of polarization revealed different possible equilibrium states and available final single-domain and multi-domain states. Time-dependent evolution of the average polarization and dispersion disclosed a bifurcation behavior and the temperature-dependent value of the electric field deciding between the single-domain and multi-domain final states. A significant role of the feedback via depolarization fields was established. Explicit formulas for the time-dependent longitudinal and transverse spatial polarization correlations were derived. The correlation radius of polarization

fluctuations, which can be interpreted as a characteristic domain size, was found analytically and demonstrated a diffusion-like time behavior.

10-2 | 14:15

Solution-deposited (anti-) ferroelectric perovskites: Strain- and defect-engineering of charge transport and optical properties

A. Blazquez-Martinez^{1,2,3}, P. Grysan^{1,3}, S. Girod¹, S. Glinsek^{1,3}, N. Aruchamy^{1,2}, P. Biswas^{2,3}, M. Guennou^{2,3}, T. Granzow^{4,3}

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Investigations of optical and electronic properties of ferroelectric thin films often focus on epitaxially grown materials, as their properties typically outperform those of polycrystalline films. On the other hand, most epitaxial growth methods are quite un-economical compared to deposition methods for polycrystalline films. In this presentation, we look at the electrical and optical properties of perovskite-structured polycrystalline ferroelectric films prepared via a chemical solution deposition (CSD) route by spin coating. The material of choice is bismuth ferrite (BiFeO₃, BFO), the only ‘true’ room-temperature multiferroic single-phase material and therefore a prime candidate for optical and electrical studies. However, the high electrical conductivity of BFO often makes it difficult to achieve fully polarized samples.

Here, we demonstrate that high-quality polycrystalline BFO films with strong (001) out-of-plane texture and properties rivalling those of epitaxial films can be prepared on many different substrates using a seed layer of PbTiO₃. Both dark conductivity and light-induced charge transport strongly depend on doping: while Ti-doping leads to a trapping of oxygen vacancies but does not fundamentally alter the charge transport mechanism, doping with Mn modifies the electronic properties, strongly reducing dark current, but drastically increasing light-induced charge transport at sub-bandgap photon energies. This charge transport is shown to result from a true bulk photovoltaic effect. The photovoltaic response can be further tuned by inducing mechanical stress in the film by different substrate materials. The electrooptic effect at low driving voltages is notably lower than that reported for epitaxial films, but is strongly enhanced for super-coercive electric field amplitudes. The electro-optic properties are compared to those of PbZrO₃ thin films of comparable geometry where the response stems largely from an electric-field-induced antiferroelectric-ferroelectric phase transition. It is found that for a carefully chosen combination of doping, mechanical substrate stress, electrode structure and domain configuration, the polycrystalline BFO films are both excellent subjects for basic scientific studies and have high application potential.

Session 11, Wednesday 15.3., 15:30-17:00 (Chair: A. Klein)

11-1 | 15:30

Strain dependence of antiferroelectricity in NaNbO₃ thin films

Thorsten Schneider, Lambert Alff, Institute of Materials Science, TU Darmstadt

The impact of strain on the phase balance between the antiferroelectric (AFE) and ferroelectric (FE) phase is investigated via growth of epitaxial thin films of NaNbO₃. Structural analysis of films grown under optimized conditions reveals the incorporation of epitaxial strain on various substrates. Reciprocal space maps and transmission electron microscopy confirm an AFE ground state for thin

films subjected to compressive or small tensile strain, while larger tensile strain stabilizes the FE phase, even beyond the relaxation thickness. The electrical characterization indicates a significant increase in saturation polarization for films grown with compressive strain, with the polarization versus electric field behavior resembling a FE hysteresis. For films under tensile strain, a rotation of the polarization towards the in-plane direction is observed. The combination of the polarization increase from compressive strain with the stabilization of the AFE phase via doping shows promise for further enhancing the energy density of AFE materials.

11-2 | 16:00

The effect of controlling the defect chemistry in lead-free ferroelectric ceramics

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$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) based ceramics are excellent lead-free ferroelectrics and relaxor materials. However, the opportunities to modify ferroelectric properties by doping differ from the known lead-based systems. For example, acceptor doping of NBT induces mobile oxygen vacancies, making it one of the best oxygen ion conductors at intermediate temperatures [1]. This behavior is unwanted for the transfer of NBT-ferroelectrics into applications. However, increased frequency-independent piezoelectric activity (Qm) develops. For KNN, it could be rationalized that A-site non-stoichiometry dominates the properties even with intentional doping of the material. Therefore, a detailed understanding of the defect chemistry of NBT, KNN, and their solid solutions is highly important. Otherwise, it is almost impossible to derive and control aging and degradation mechanisms that are certainly different from other well-known ferroelectrics. We developed a model to elucidate the defect chemistry of NBT ceramics [2]. Furthermore, methods to control the ionic conductivity, ferroelectric properties, and microstructure of NBT and KNN will be discussed in this work [3, 4]. This will illustrate the opportunities to alter the properties of NBT and KNN-based material for multiple applications.

[1]. Li, M., et al., *Nature Materials*, 2014. 13(1): p. 31-35.

[2]. Koch, L., et al., *Journal of Materials Chemistry C*, 2017. 5(35): p. 8958-8965.

[3] Steiner, S., et al., *Journal of the American Ceramic Society*, 2019. 102(9): p. 5295-5304.

[4] Xu, Z., et al., *Angewandte Chemie International Edition*, 2022. p. e202216776.

List of attendees

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1. Karsten	Albe	TU Darmstadt, Germany
2. Leif	Carstensen	TU Darmstadt, Germany
3. Mian	Dai	TU Darmstadt, Germany
4. Dragan	Damjanovic	EPFL – Lausanne, Switzerland
5. Elisabeth	Dickey	Carnegie Mellon University, USA
6. Hui	Ding	MPIE – Düsseldorf, Germany
7. Wolfgang	Donner	TU Darmstadt, Germany
8. Sonja	Egert	University of St. Andrews, Scotland
9. Emre	Erdem	Sabanci University, Turkey
10. Paul	Erhart	Chalmers University, Sweden
11. Till	Frömling	TU Darmstadt, Germany
12. Lovro	Fulanovic	TU Darmstadt, Germany
13. Yurij	Genenko	TU Darmstadt, Germany
14. Torsten	Granzow	LIST – University of Luxembourg
15. Pedro	Groszewicz	TU Delft, Netherlands
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17. Binxiang	Huang	TU Darmstadt, Germany
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24. Julian	Moxter	TU Darmstadt, Germany
25. Simone	Sanna	JLU Gießen, Germany
26. Thorsten	Schneider	TU Darmstadt, Germany
27. Derek	Sinclair	University of Sheffield, UK
28. Lorenzo	Villa	TU Darmstadt, Germany
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