FM 4: Focus Session: (Anti)ferroic states – Non-conventional states I

chair: Nives Strkalj (University of Zagreb, HR)

This focus session explores recent advances in understanding and control of (anti)ferroic states. Emphasis will be placed on theoretical modelling, advanced characterization techniques, and the engineering of emergent properties for use in nano-electronic devices. The session aims to bridge fundamental research with emerging device-relevant functionalities, bringing together experimental, and theoretical perspectives on ferroic materials.

Time: Monday 15:00–17:45 Location: BEY/0138

Invited Talk FM 4.1 Mon 15:00 BEY/0138

(Anti)Ferroelectric HfZrO2: from non volatile memory to energy storage applications — •Bertrand Vilquin[1], Gregoire Magagnin[2], Jordan Bouaziz[3], Martine Le Berre[1], Sara Gonzalez[2], Ingrid Canero Infante[2], Brice Gautier[1], Kevin Alhada-Lahbabi[1], and Damien Deleruyelle[1] — [1]INSA Lyon, Ecole Centrale de Lyon, CNRS, Universite Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, 69621 Villeurbanne, France — [2]CNRS, INSA Lyon, Ecole Centrale de Lyon, Universite Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, 69621 Villeurbanne, France — [3]Ecole Centrale de Lyon, INSA Lyon, CNRS, Universite Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, 69621 Villeurbanne, France

Fluorite-structured HfZrO2 and ZrO2 thin films are promising for both non-volatile memory and energy storage applications. Antiferroelectric (AFE) capacitors were fabricated by PE-ALD and annealed using BEOL-compatible thermal budgets. All devices exhibit AFE double hysteresis loops, with polarization strongly dependent on film thickness and annealing temperature. Phase-field modeling reveals thickness-driven phase transitions enabling low-voltage, high-polarization operation. These characteristics are relevant for future AFE FET. Energy storage performances of linear dielectric (LD), ferroelectric (FE), and AFE films are compared. While FE films show high energy density but large losses, LDs offer high efficiency with low storage density. AFE ZrO2 provides an optimal balance, reaching up to 84 J/cm3 with 75% efficiency. These results position HfZrO2 as a multifunctional platform bridging memory and energy storage technologies.

FM 4.2 Mon 15:30 BEY/0138

From metal to oxide: Oxygen vacancy evolution in HfO_2 controlled by PLD — •Berk Yildirim[1], Oliver Rehm[1], Philipp Gebauer[1], Marc Neumann[1], Andrei Gloskovskii[3], Christoph Schlueter[3], Lutz Baumgarten[2], Ron Tenne[4], and Martina Müller[1] — [1]FB Physik, U Konstanz — [2]FZ Jülich — [3]DESY, Hamburg — [4]Technion, Haifa, Israel

Hafnium dioxide (HfO_2) has emerged as a ferroelectric material for non-volatile memory applications. The ferroelectric phase is linked to the presence and amount of oxygen vacancies (OVs), but their direct experimental observation is challenging. In this work, a combination of in situ soft X-ray and ex situ hard X-ray photoelectron spectroscopy is used to trace the evolution of OVs. To systematically control the oxidation and OV concentration in HfO_2, 120 nm films are grown from stoichiometric targets by pulsed laser deposition (PLD) without oxygen supply, but varying the $SrTiO_3$ (001) substrate temperature T. With increasing T, the amount of metallic Hf is systematically reduced, while the oxide fraction increases. The evolution of Hf 4f spectral features is evaluated as the indirect signature of the T-dependent OV concentration through the Hf^{3+}/Hf^{4+} spectral weight. In addition, photoluminescence measurements confirm the presence and T-dependent variation of OVs. In situ RHEED, ex situ AFM and XRD validate T-driven changes in morphology and structure, linking Hf oxidation state, vacancy concentration and film properties. These results demonstrate that T-controlled oxidation enables a systematic control of OVs and helps clarify how defects influence the formation of ferroelectric HfO_2.

FM 4.3 Mon 15:45 BEY/0138

Influence of Different Transition-Metal defect Dipoles on Polarization Rotation in $BaTiO_3$ — •Aldo Raeliarijaona[1], Ronald E. Cohen[2], and Anna Grünebohm[1] — [1]Ruhr-Universität, Bochum,Germany — [2]Carnegie Institution for Science, Washington D.C., U.S.A

Ferroelectric materials are an important class of materials for various technological applications such as non-volatile random-access memory mainly due to spontaneous electric polarization. Key ferroelectric property is the switching mechanism induced by an electric field. However, defect dipoles in ferroelectrics can act like a bias field or restoring forces to rotation of the polarization after an electric field has been applied and then removed. Using first-principles molecular dynamics, we compare polarization rotation induced by defect dipoles, in which divalent transition metal dopants on the perovskite B-site couple with neighboring oxygen vacancies, in the archetypical ferroelectric BaTiO3. We compare the effects of Cu^{2+}, Mn^{2+}, and Fe^{2+} dopants. We find that copper is much more efficient at enhancing electromechanical coupling or restoring polarization direction, over manganese or iron. We relate this effect of chemistry to the shape and bonding of the transition metal cations.

FM 4.4 Mon 16:00 BEY/0138

Reentrant relaxor behaviours in Ba(Ti0.85Zr0.15)O3-Bi(Zn2/3Nb1/3)O3 — •Vladimir Shvartsman[1], Eva Kröll[1], Boriana Mihailova[2], Vadzim Haronin[3], Juras Banys[3], and Doru Lupascu[1] — [1]University Duisburg-Essen, Essen, Germany — [2]University of Hamburg, Hamburg, Germany — [3]Vilnius University, Vilnius, Lithuania

Upon decreasing temperature, thermodynamic systems usually transform from a disordered high symmetry phase to a more ordered phase with lower symmetry. However, in some cases an unusual phase sequence is observed, where after this *normal* transition, an ordered system reenters a disordered phase. We observed the reentrant behavior in the relaxor ferroelectrics (1-x)Ba(Ti0.85Zr0.15)O3-xBi(Zn2/3Nb1/3)O3 (x = 0 - 0.15) by analysis of temperature dependences of the dielectric permittivity. Namely, a frequency-independent maximum associated with the ferroelectric phase transition is followed by a frequency-dependent anomaly at lower temperatures, which is typical of relaxors. Raman spectroscopy revealed a competition between polar and antiferrodistortive modes. Softening of the polar mode related to correlated B-cation displacements leads to the ferroelectric phase transition. On the other hand, correlated antiferrodistortive rotations of the oxygen octahedra give rise to nanometer size clusters of antipolary shifted A-site cations distributed within the polar matrix. Slowing down the dynamics of these clusters leads to the low-temperature dielectric anomaly and reentrant relaxor behavior.

FM 4.5 Mon 16:15 BEY/0138

Time-domain thermoreflectance for monitoring thermal conductivity switching in ferroelectric thin film — •Wasim Akram[1], Stefan Dilhaire[2], Thomas Maroutian[3], and Guillaume F. Nataf[1] — [1]GREMAN UMR7347, CNRS, Université de Tours, France — [2]CNRS-LOMA/UMR5798, Université de Bordeaux, France — [3]C2N, CNRS, Université Paris-Saclay, France

Ferroelectric materials that exhibit thermal conductivity switching under external stimuli could serve as promising candidates for thermal conductivity switches [1,2]. To integrate these switches into miniaturized devices, nanoscale ferroelectric films are essential. In this work, we aim to study ferroelectric thin films and propose to manipulate their thermal conductivity by applying an electric field. To monitor the thermal conductivity, we employ time-domain thermoreflectance (TDTR). In TDTR, the sample surface is periodically heated with a far-infrared pump laser through a metallic transducer, and the resulting thermoreflectance response is probed using a delayed probe laser. The probe reflectivity change is directly related to the temperature evolution at the sample surface. The analysis relies on multilayer heat-transfer models that incorporate the substrate, film, and transducer. However, modelling is sensitive to several experimental constraints, including non-uniform interface properties and interfacial thermal resistance. Here, we address these challenges by optimizing both data-acquisition and sample-preparation methods. We use a home-made software based on Thermal Quadrupole model to fit the signal received by the photodetector [3]. Additionally, we propose to apply an electric field to ferroelectric films to modulate their domain structures, with the goal of achieving multiple fold switching of thermal conductivity. This approach could pave the way toward a device-compatible ferroelectric thermal conductivity switch. [1] Ihlefeld et al. Nano Letters 15 (3), 1791-1795 (2015). [2] Nataf et al. Nature Reviews Materials 9, 530 (2024). [3] Dilhaire et al. J. Appl. Phys. 110, 114314 (2011).

Coffee break

FM 4.6 Mon 16:45 BEY/0138

Correlated domain and crystallographic orientation mapping in uniaxial ferroelectric polycrystals by interferometric vector piezoresponse force microscopy — •Ruben Dragland[1], Jan Schultheiss[1], Ivan Ushakov[1], Roger Proksch[2], and Dennis Meier[1,3,4] — [1]NTNU Norwegian University of Science and Technology, Trondheim, Norway — [2]Asylum Research an Oxford Instruments Company, Santa Barbara, USA — [3]University of Duisburg-Essen, Duisburg, Germany — [4]Research Alliance Ruhr, Bochum, Germany

Advances in scanning probe microscopy techniques are expanding the possibilities for nanoscale characterization of functional materials, giving new opportunities for correlated studies of their local properties. Here, we apply a recent extension of piezoresponse force microscopy (PFM) for simultaneous mapping of polarization domains and local crystallographic orientation in a uniaxial ferroelectric. By shifting the laser beam position on the cantilever, direction-dependent piezoresponse signals are acquired analogous to classical vector PFM, but without the need to rotate the sample. Using polycrystals of the uniaxial ferroelectric $ErMnO_3$ as a model system, we demonstrate that the reconstructed piezoresponse vectors correlate one-to-one with the crystallographic orientations of the micrometer-sized grains, carrying grain-orientation and domain-related information. We establish a versatile platform for rapid, multimodal characterization of polycrystalline uniaxial ferroelectrics, enabling automated, high-throughput reconstruction of polarization, and grain orientations with nanoscale precision.

FM 4.7 Mon 17:00 BEY/0138

Optical control of ferroelectric polarization in epitaxial lead titanate thin films — •Valentine Gillioz, Manfred Fiebig, and Morgan Trassin — ETH Zurich, Switzerland

In this work, we use light as an active tool for remotely and dynamically controlling ferroelectricity in epitaxial $PbTiO_3$-based thin films and heterostructures. The exposure to above-bandgap ultraviolet (UV) light enables the manipulation of charge-screening dynamics via the accumulation of photo-induced charge carriers at the bottom electrode/ferroelectric Schottky interface. A transient light-induced enhancement (or suppression) of spontaneous polarization is observed using second-harmonic generation (SHG) in films with a pristine upward (or downward)-oriented polarization. Here, we explore the impact of $PbTiO_3$ growth conditions on the photoresponse of the films in more depth. Importantly, we show a robust and improved cyclability of the optical modulation of the ferroelectric polarization in films grown at low oxygen partial pressure ($\sim 10^{-2}$mbar) pointing to the role of oxygen vacancies in the light-induced polarization change. In addition, we combine our ability to monitor the polarization dynamics during the thin-film growth process using in-situ SHG with the UV light exposure to balance the depolarizing-field contribution and the light-induced polarizing effect in our heterostructures. We report a strong on/off ratio in the optical manipulation of ferroelectric polarization between a fully depolarized state in dark conditions and a polarized state under UV light exposure. Our work, hence, constitutes a critical step towards all-optical control of ferroelectricity in functional thin films.

FM 4.8 Mon 17:15 BEY/0138

Ferroelectricity in organic - inorganic TMCM-BCl3 (B=Mn, Fe, Zn) materials — •Mwanaidi Mauwa Namisi and Anna Grünebohm — Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-University Bochum, Germany

Ferroelectric materials have switchable polarization in external electric field and play a central role in sensors, memory devices and dielectrics. Although oxide ceramics have been the main focus, they have limited chemical flexibility [1]. In contrast, hybrid organic-inorganic perovskites combine multiple degrees of freedom of both inorganic and organic frameworks enhancing structural versatility [2]. Their phase transition mechanisms and origin of ferroelectricity however remain underrepresented in literature. Here, we investigate the class of TMCM-BCl3 (B=Mn, Fe, Zn) hybrids using DFT methods and discuss these open questions. Furthermore, by B site compositional tuning, we explore the structure-property relations and how the choice of transition metal affects polarization, electronic properties and magnetism.

[1] Y-M You et al., Science 357, 6348 (2017). [2] Ghosh et al., Phys. Rev. Lett. 125, 207601, (2020).

FM 4.9 Mon 17:30 BEY/0138

Tuning the Properties of the Organic Supramolecular Ferroelectric BTA by Dipole Engineering — •Sophia Klubertz[1], Florian Behrendt[2], Johannes Brendel[2], and Martijn Kemerink[1] — [1]IMSEAM, Heidelberg University, Germany — [2]Bayreuth University, Germany

Benzene-1,3,5-tricarboxamide (BTA) has become the paramount example of an organic supramolecular ferroelectric. To widen the property space of these compounds, and to gain insight into the underlying structure-property relations, this work examines the impact of a stepwise replacement of BTA's three amide groups by urea groups, as well as of the anchoring point of the dipolar group. We investigate BTA-C6/2 analogues, where one (BUDA), two (BDUA), or three (BTU) amide groups are substituted by urea groups. The compounds were newly synthesized in their C-centered and N-centered versions, regarding the amide connectivity. True ferroelectric behavior was experimentally demonstrated for C- and N-centered BUDA and BDUA through temperature- and time-dependent electrical switching measurements. By investigating remnant polarization values and double structures in the switching currents, we can draw conclusions about the switching behavior of urea groups in comparison to amide groups of either connectivity. Moreover, we find orders-of-magnitude differences in key properties like retention time, which we rationalize through molecular dynamics simulations. Overall, the results show how chemical structure translates into (ferroelectric) properties.