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Fatigue mechanisms on the atomic scale in high performance Lead Zirconate Titanate (PZT)

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In materials science studies focus on the structure of matter and its applications. The investigation of the correlation between macroscopic properties and structural characteristics is crucial for the development of high performance materials. With *in situ* X-ray diffraction we were able to give an atomic scale description of the macroscopic physical properties of commercial ferroelectric material, lead zirconate titanate (PZT) [1].

These materials are intensively used for technological applications (sensors and actuators, MEMS systems and high frequency devices). One of the factors limiting the applicability of PZT, as well as other ferroelectric materials, is the phenomenon of ferroelectric fatigue. This is mostly manifested by a decrease in the polarization amplitude observed in the ferroelectric polarization hysteresis loop and a change in the temporal response after prolonged bipolar electric field cycling.

In this contribution we present a structural characterization of the fatigue mechanisms on the atomic scale. A specially developed sample environment for *in situ* X-ray diffraction with applied electric fields allowed us to study the effect of fatigue on the poling response. The decrease of polarization amplitude could be related to a change in phase composition. The change in switching kinetics could be attributed to an alteration of the field induced structural response dependent on the cycling frequency. The analysis of the disorder of lead and a microstructural characterization provided detailed structural information.

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Phase transitions in modulated fresnoite phases for piezoelectric applications

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Materials with the fresnoite $A_2TiM_2O_8$ (A = Ba, Sr; M = Si, Ge) structure type are amongst several possible alternatives currently being investigated to replace PZT and other lead-based piezoelectric materials because of their potential to exhibit excellent piezoelectric response coefficients [1, 2]. Critically important to developing new materials with optimised physical properties, which are comparable to or better than those of the current lead-based piezoelectrics, is a good understanding of the underlying structural chemistry of these materials.

We have carefully investigated the composition range of $Ba_{2-2x}Sr_{2x}TiSi_2O_8$ ($x = 0.0 – 1.0$), with particular emphasis on temperature dependent phase transitions that might impact on practical applications. Variable temperature synchrotron powder X-ray and electron diffraction data, e.g., from $Sr_2TiSi_2O_8$ have provided previously unreported evidence of unusual phase behaviour between 125 - 1273 K. Electron diffraction data have confirmed that two incommensurately modulated $Sr_2TiSi_2O_8$ phases, with tetragonal and orthorhombic symmetry, coexist at room temperature, although the phase appears metrically tetragonal from X-ray powder diffraction data. Observed changes of the position of the satellite reflections in $Sr_2TiSi_2O_8$ electron diffraction patterns at elevated temperatures suggests that a symmetry-lowering transition occurs on heating, whereby the tetragonal *P*4*bm* phase transforms into the orthorhombic *Cmm*2 phase at approximately 480 K. This is confirmed for the bulk phase from X-ray diffraction data.

Our investigation was extended to include substitutions both on the fresnoite *A*-site (Ba/Sr) as well as the *M*-site (Si/Ge). Similar behaviour as above has been observed in the closely related $Sr_2TiGe_{0.1}Si_{1.9}O_8$ compound. However, the two phase region for the first order transition from the tetragonal *P*4*bm* to the orthorhombic *Cmm*2 phase is unusually wide, demonstrating the extremely similar energies of formation for the two phases. A combination of variable temperature electron diffraction, synchrotron X-ray powder diffraction, neutron diffraction and resonant ultrasound spectroscopy have been used to further determine the interesting and unusual phase behaviour in this family of compounds.

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Magnetism in defect-induced SIC single crystals

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SiC is considered to be one of the most important semiconductors with great applications for high temperature, high frequency, high power and optoelectronic devices due to its wide band-gap, high thermal conductivity, high breakdown voltage, and so on. Over the past years, the SiC based diluted magnetic semiconductors (DMSs) have attracted much attention as promising material for spintronics. Many efforts have been devoted to investigate SiC DMSs prepared by *3d* transition metals doping. Limited solubility of 3d metals in wide band-gap (WBG) semiconductors, however, often leads to the precipitation of second phases, thwarting the attempts to get the unambiguous experimental results and leaving the origin of magnetism an open question [1], [2]. Recently, there has been increasing evidence that traditional magnetic elements are not the sole source in inducing intrinsic magnetism. RT FMs were observed in highly oriented pyrolytic graphite (HOPG) [3], [5], in Al doped SiC [6], and in Li doped ZnO [7]. Inspired by all these results defect-induced magnetism was observed in neutron irradiated *6H*-SiC single crystals recently [8].

Here, magnetism is further investigated in defect-induced SiC single crystals. Neutron irradiation and heavy doping of non-magnetic elements: B, Al and N were employed to induce defects in *4H*-SiC and *6H*-SiC. It is found that magnetism was observed in undoped, B doped and Al doped *6H*-SiC single crystals after neutron irradiation and in heavy B and Al doped ones. However, although neutron irradiation and heavy doping induced masses of defects in N doped

SiC single crystals, no magnetic signal was detected. We demonstrated that the intentionally created defects are responsible for the observed magnetism and deduced that carriers play an important role in defect-induced magnetism. Our results confirm the existence of defect-induced magnetism further and point out the necessary of tuning carrier to control the magnetism, providing some clues for tuning the magnetism of WBG semiconductors by defect engineering.

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The first rare-earth borophosphates

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In search for new compounds with new crystal structures and properties the exploration of the systems MO_x-B_2O_3-P_2O_5-(H_2O) (MO_x = metal oxide) has been shown to be extremely successful [1]. Numerous compounds have been already synthesized with an amazing structural variety originating from the unique arrangement of isolated tetrahedra (BO_4 and PO_4) and trigonal planar units (BO_3) and/or the condensation between them by the formation of complex borophosphate anions. The synthesis conditions have been mainly optimized for early main-group and 3*d* transition elements up to now. Our recent synthetic efforts are focused on rare-earth elements, especially those with unpaired *f* electrons.

In the course of experiments on rare-earth elements (*RE*) the first hydrated borate phosphates with the general formula $K_3RE[OB(OH)_2]_2[HOPO_3]_2$ (*RE* = Y, Yb, Lu, space group: R-3) were obtained [2]. Isolated REO_6 octahedra are interconnected by PO_4 tetrahedra resulting in layers, which can be regarded as structural derivatives of the mineral Glaserite (Aphthitalite) [3], [4], $K_3Na(SO_4)_2$. Between two of these layers potassium ions and two layers of $OB(OH)_2$ units are intercalated.

Using a reactive flux synthesis method we succeeded in the preparation of a series of isostructural rare-earth borophosphates (space group *Pa*-3, *a* = 13.6508(9) Å (Y) – 13.5490(7) Å (Lu)). The centers of isolated REO_6 octahedra form rhombic dodecahedra, which fill the space by sharing common faces. In each of these rhombic dodecahedral voids potassium ions and two tetrameric BP_3O_{13} units are located. The borophosphate units are linked by a yet not fully characterized atom group. From the point of view of charge balancing the chemical formula the missing unit – named X – has to bear one positive charge. The residual electron density distribution between two neighboring BP_3O_{13} is characterized by a corrugated circle of 12 maxima (*d* = 3.6 Å) with a toroidal arrangement in the center. By taking into account the oxygen corners of the neighboring BO_4 tetrahedra, it can be assumed that the two oligomers are interconnected either by 1) a BO^+ - group (resulting in a BO_3 unit), 2) a $B(OH)_2^+$ - group (resulting in a $O_2B(OH)_2$ – tetrahedron), and 3) a PO_2^+ - unit (resulting in a PO_4 – tetrahedron). With this in mind and supporting information of thermal analyses, NMR, and chemical analyses, the chemical composition of the RE borophosphate is best described by $K_6RE[BP_3O_{13}(X^{1+})\,O_{13}P_3B]$, with X^{1+} = BO, $B(OH)_2$, and /or PO_2, at the moment.

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An eu coordination polymer consolidated by 2,2'-biquinoline-4,4'-dicarboxylate

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Eu(III) chloride was allowed to reaction to sodium 2,2'-biquinoline-4,4'-dicarboxylate ($bqdc^{2-}$) lead to an Eu coordination polymer (**1**). X-ray analysis reveal that **1** crystallizes in triclinic, P-1 space group, a = 11.122(1), b = 11.938(1), c = 14.184(2) Å, α = 74.869(2), β = 76.480(2), γ = 73.859(2) °, V = 1719.8(4) Å^3. **1** consists of an asymmetric unit of $\{[Eu_2(bqdc)_3(H_2O)_2(DMF)_2]\cdot 0.5DMF\cdot H_2O\}$, in which two of Eu atoms are equivalence, each is nine-coordinated with seven O atoms from five caboxly groups of bridging bqdc anions, and two O atoms from a DMF and a water molecules (Fig 1. a), forming a distorted monocapped square antiprism polyhedron, the distance between two neighboring Eu atoms is 4.108 Å. The metal ion is bridged by two types of $bqdc^{2-}$ anions to form a layer. The hydrogen bonds between the $bqdc^{2-}$ ligands and the lattice H_2O molecules connect the neighboring layers together into a 3D network (Fig 1. b). The stack of the layers results in channels along the *c* axis between neighboring layers.

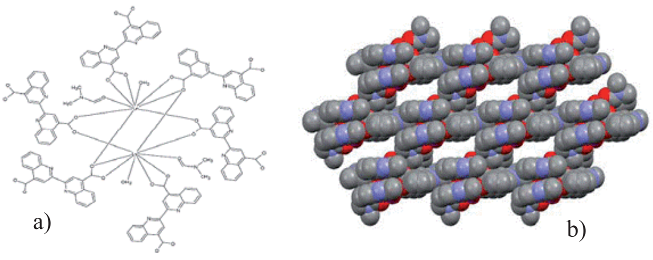

Figure 1. a). The coordination environment of Eu atom; b). Packing diagram of **1** viewed along the *c* axis showing channels. H atoms and the terminal and lattice DMF and H_2O molecules are omitted for clarity. Color scheme: Eu atoms, pink; C atoms, grey; O atoms, red; N atoms, blue.