

Welcome

Welcome to the fourth edition of the quarterly EMRP Nanostrain project newsletter. Over the next three years this newsletter will provide you with everything you need to know on the latest project developments, as well as interviews with global industry leaders and a summary of upcoming global events and academic conferences on the exciting technological area of nanoscale piezoelectrics.

Project news

Force Field Developments in PZT modelling

Researchers from NPL are collaborating with partners at UCL to develop a robust approach for modelling the properties of large-scale piezoelectric systems. The work, carried out by Oliver Gindele, a joint PhD student at the two institutions, Dr Anna Kimmel (NPL), and Dr Dorothy Duffy (UCL), forms a part of Work Package 4, aimed at providing an insight into the properties of piezoelectric materials through modelling.

Complex insulating perovskite $A(BB')O_3$ and $AA'(BB')O_3$ alloys have exceptional piezoelectric properties, which make them suitable for a range of potential applications. Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) is a technologically important piezoelectric due to its superior electromechanical properties (which have only recently been surpassed by PMN-PT). PZT belongs to a class of disordered solid solution perovskite materials $A(BB')O_3$, where the disorder is caused by the random arrangement of B cations, i.e. Ti and Zr (Figure 1a). Relating the origin of compositional phase transitions and morphotropic phase boundaries (MPBs) to properties of individual atoms is crucial for understanding the way variations in atomic composition affect material properties. Such microscopic understanding is needed for the design of better materials and is most naturally obtained from calculations based on first principles.

Such *ab initio* calculations, based on density-functional theory (DFT) have, over the years, been extensively applied to various ferroelectric materials. They have provided a fundamental insight into the origin of ferroelectricity, as well as the behaviour of domain walls, grain boundaries, and interfacial phenomena.

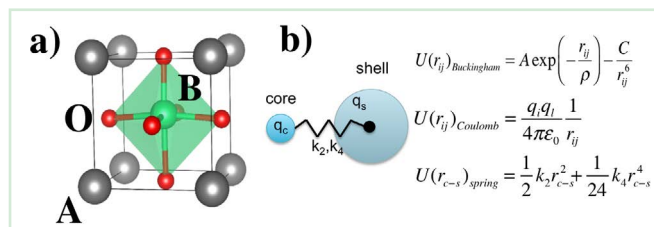


Figure 1

- (a) Structural unit of ABO_3 perovskite.
- (b) Shell model represents ion that consists of two particles, a core and a shell standing for the atomic nucleus and electron shell, respectively. Shell model is parametrised with three types of interactions: long-range $U_{Coulomb}(r_{ij})$, short-range $U_{Buckingham}(r_{ij})$, and core-shell $U_{spring}(r_{c-s})$ spring potentials.

Although the DFT method is a powerful tool, modelling PZT (as well as more general solid solution systems) from a first principles perspective can be challenging as it is only possible to study small system sizes with this method. The quenched disorder in the B-cation arrangement creates a

“statistical gap” between small, density-functional theory (DFT)-accessible super-cells and the real material. The long-range Coulomb interactions of the charged ions in the system enable long-range structural correlations, which are indirectly seen via diffraction experiments, and these display a variety of phase distortions away from the high-symmetry positions which cannot be modelled in small systems. Interatomic force fields, based on the shell model, can be used to bridge the statistical gap as these force fields can be used for atomic simulations of large systems that capture the full disorder of the real materials.

Ferroelectricity originates from the delicate balance between long-range Coulomb and short-range repulsive interactions, and the shell model can explicitly represent both. Moreover, the shell model is capable of describing ionic polarisability by assuming the existence of two hypothetical particles – a core and a shell – which represent the atomic nucleus and electron shell respectively (Figure 1b).

The aim of the project is to use this shell model to develop a robust interatomic force field for PZT that reproduces its phase stability, structural and ferroelectric properties, as well as details of the phase diagram.

To this end, the parameters of the shell model functions were carefully fitted so that the force field (FF) correctly reproduced the fundamental properties of the PbTiO_3 , PbZrO_3 and the lowest energy $P4mm$ ordered phase of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (minimal size approximant at MPB), including phase stability, crystal structures, elastic constants, and effective charges derived from DFT calculations. The optimized FF successfully yields the tetragonal structure of both ordered and disordered phases of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ at $x=0.5$ %.

PZT is a perovskite alloy of PbZrO_3 and PbTiO_3 . The end member of the PZT phase diagram, PbTiO_3 , is a tetragonal ferroelectric, while PbZrO_3 is characterised by an antiferroelectric ground state. Neither PbZrO_3 nor PbTiO_3 are particularly good piezoelectrics, but mixing these materials gives rise to exceptionally high piezoelectric response at about 52/48 ratio of Ti/Zr content (so-called MPB).

The developed FF accurately reproduces the details of the PZT phase diagram in good agreement with experiment. Indeed, the FF fully reproduces the

tetragonal structure of PbTiO_3 in PZT at $x=100$ %. With the decrease of Ti-content ($0.5 < x < 1$) the structure remains tetragonal. Meanwhile, at the other end of the PZT phase diagram ($x=0$ %), the FF also reproduces the antiferroelectric structure of PbZrO_3 (Pbma space group), and supports rhombohedral structure on the zirconium-rich side (Figure 2).

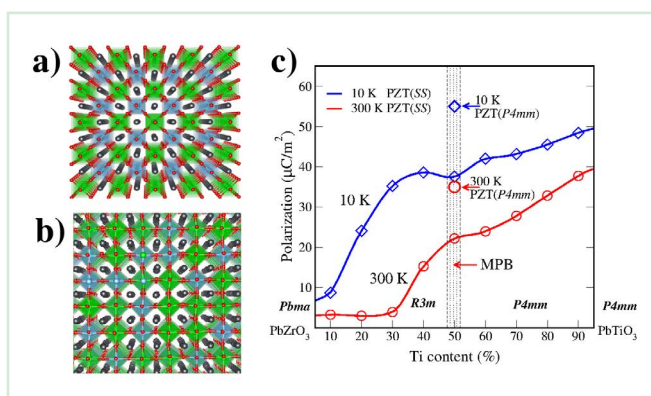


Figure 2

(a) Phase diagram of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ reproduced by shell-model force field. At $x=0$ % antiferroelectric Pbma phase is supported, while at another end ($x=100$ %) $P4mm$ phase of PbTiO_3 is supported. At low Ti-content FF reproduces rhombohedral phase, while at high Ti-content tetragonal phase is prevalent.

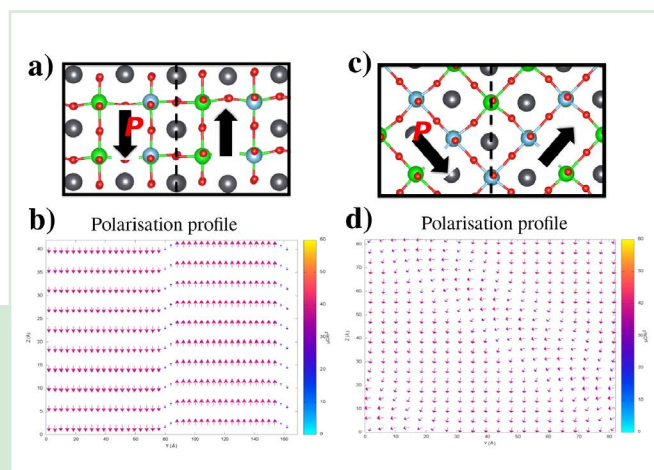
Calculations of the structure and stability of 180° and 90° domain walls (DW) in $P4mm$ phase of PZT produce excellent agreement with properties predicted from ab initio calculations (Figure 3). In particular, the 180° DW energy of $142 \text{ mJ}/\text{m}^2$ was found to be almost three times greater than the 90° DW energy ($45 \text{ mJ}/\text{m}^2$), similar to the ratio found in tetragonal BaTiO_3 and PbTiO_3 . The relatively low energy 90° DW means that this intrinsic two-dimensional defect is more favourable than the 180° DW, consistent with the observation of 90° DWs in experiments. Moreover, our FF predicts very sharp domain walls of about 8 \AA that are also in good agreement with TEM images.

This significant success widely extends the applicable range of atomic-level simulations of ferroelectrics based on the shell model potential. Further molecular dynamics simulations based on our shell model force field will provide the atomic-level insight into the domain wall kinetics in a multi-domain system under external stimuli (such as strain and/or electric field).

Markys Cain, the Nanostrain Project Lead at NPL, said “This NPL-UCL collaboration makes use of both theory and modelling to support our experimental research programme under EMRP Nanostrain. The ability to predict domain wall formation and their dynamics is central to design at the nanoscale level, and such research takes us a long way towards accomplishing this important goal.”

Figure 3

Domain walls in ordered **P4mm** phase of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ $x=0.5$: atomistic (a, c) and local-dipoles plot (b, d) for 180° and 90° domain walls, respectively.



Near-field imaging and nano-FTIR spectroscopy with broadband Synchrotron Radiation

In 2012 a team of researchers at the Physikalisch-Technische Bundesanstalt (PTB) in Germany developed an innovative technique based on the use of ultra-broadband synchrotron radiation^[1] for high-resolution imaging and nano-FTIR spectroscopy. By coupling a scattering-type scanning near-field optical microscope (s-SNOM) with the broad infrared light provided by PTB’s low-energy electron storage ring Metrology Light Source (MLS) they could demonstrate a significantly improved spatial resolution as well as a sensitivity several orders of magnitude greater than conventional far-field methods. Within the framework of EMRP IND54 Nanostrain this near-field technique based utilizing broadband synchrotron radiation (SR) has now been evaluated for characterizing semiconductor materials and thin films.

The researchers from PTB and Freie Universität Berlin, including Peter Hermann, Arne Hoehl, Bernd Kästner, and Burkhard Beckhoff, demonstrated the potential of this technique by performing measurements on a semiconductor-insulator system and proving the material discrimination capability by acquiring near-field IR spectra from thin films.

The IR-SNOM system can be regarded as an atomic force microscope (AFM) operated in tapping mode and an asymmetric Michelson interferometer (Figure 1). The highly brilliant and polarized synchrotron

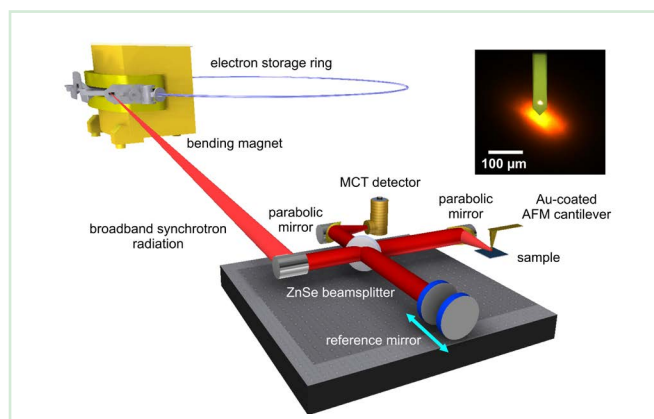


Figure 1

Schematic diagram of the experimental s-SNOM setup using broadband synchrotron radiation in the IR regime from the electron storage ring MLS.

radiation is coupled out from the storage ring at a bending magnet and guided to the experiment by several mirrors. The irradiated metal coated AFM tip acts under optimized conditions as an antenna that confines the incident electric field around the tip apex, thus providing a nanoscale light source for near-field investigations. The backscattered radiation from the sample is analysed by the Michelson interferometer consisting of a reference arm and a second arm containing near-field probe and sample. In order to separate the intensive far-field signal from the relatively weak near-field contribution the signal

recorded by the detector is demodulated at the 2nd, 3rd and 4th-harmonics of the tip oscillation frequency. This provides a signal with strongly decreasing background contribution for higher harmonics ($n > 1$).

For the acquisition of an interferogram the mirror in the reference arm of the Michelson interferometer is translated over a distance of up to 800 μm . The Fourier transformation of the obtained interferogram as a function of the optical beam path difference provides the corresponding nano-FTIR spectrum. The interferograms recorded from bulk 6H-SiC, 30 nm SiO₂, 10 nm TiO₂ (anatase) and 50 nm Si_xN_y and the corresponding nano-FTIR spectra obtained by Fourier transformation are illustrated in Figure 2.

The obtained results were recently published in Optics Express^[2]. As a next step SR-based IR-SNOM and nano-FTIR spectroscopy will be evaluated for characterizing intrinsic strain fields in thin PZT layers.

[1] P. Hermann, A. Hoehl, P. Patoka, F. Huth, E. Rühl, and G. Ulm, Opt. Express 21, 2913-2919 (2013).

[2] P. Hermann, A. Hoehl, G. Ulrich, C. Fleischmann, A. Hermelink, B. Kästner, P. Patoka, A. Hornemann, B. Beckhoff, E. Rühl and G. Ulm, Opt. Express 22, 17948-17958 (2014).

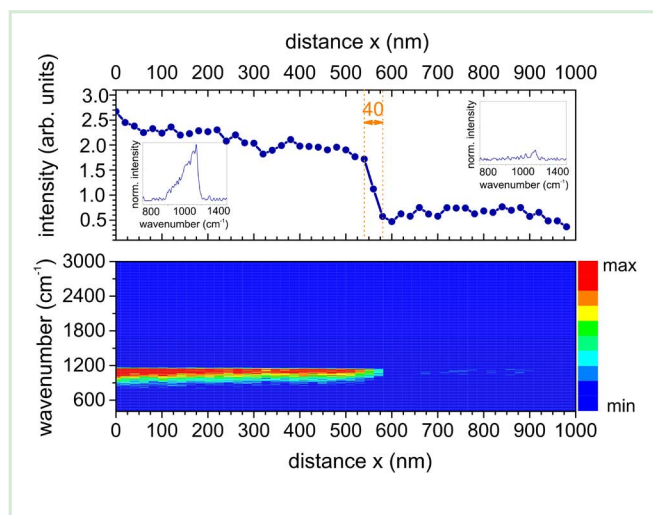


Figure 2

Intensity (a) and spectroscopic nanoimaging (b) using ultra-broadband IR radiation provided by the electron storage ring MLS.

NPL workshop at Piezo2015

The Piezo 2015 conference: Electroceramics for End-users VIII will take place in Maribor, Slovenia from the 25th to the 28th of January 2015. A number of Nanostrain project partners will be presenting at the conference, including a team from NPL on the latest step height measurement results as well as recent work undertaken at ESRF.

The conference will also feature a workshop organised jointly with METCO on best practice for high temperature piezoelectric measurements including resonance and interferometry. Dr. Paul Weaver, who works in the Functional Materials group at NPL and is the co-ordinator of the METCO project, will also lead discussion on developments in high temperature piezoelectric materials from research and industry perspectives.

This free to attend workshop will run from 1000-1600 on January 25th in the hotel Bellevue, situated in the ski-centre Mariborsko Pohorje, at the outskirts of Maribor, the second largest city in Slovenia.

Full details of the conference can be found at www.piezo2015.com.

Nanostrain project partners are encouraged to attend the conference, as it will provide an excellent opportunity to meet fellow researchers from a wide range of backgrounds as well as potentially useful contacts in industry.



Upcoming events

[Nanometa 2015](#)

Seefeld, Austria

January 5-8 2015

[6th NRW Nano-Konferenz](#)

Dortmund, Germany

January 12 2015

[ICNN 2015: International Conference on Nanochemistry and Nanoengineering](#)

Zurich, Switzerland

January 13-14 2015

[Piezo 2015](#)

Maribor, Slovenia

January 25-28 2015

[Nanotech 2015](#)

Tokyo, Japan

January 28-30 2015

[2015Flex](#)

Monterey, USA

February 23-26 2015

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