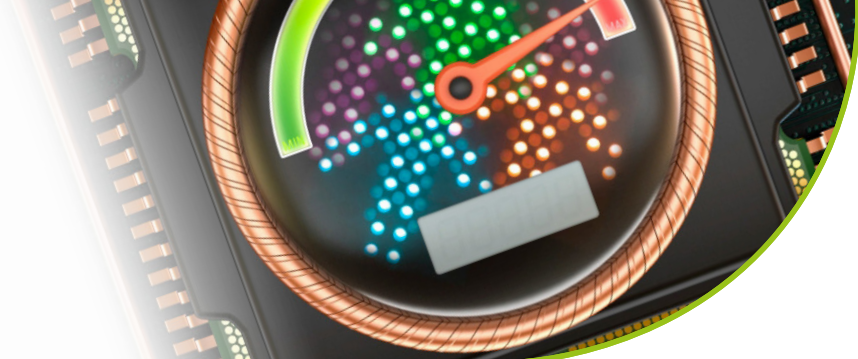




**Nanostrain**

Providing highly accurate measurement of strain in nanoscale systems to drive innovation



e-newsletter • Issue 6 • Spring/Summer 2015

# Welcome

Welcome to the sixth edition of the quarterly EMRP Nanostrain project newsletter. Over the remaining months of the project, this newsletter will continue to provide you with everything you need to know on the latest 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

The mid-term review for the Nanostrain project went very well, with a positive outcome from the assessors and reviewers.

Carlo Vecchini will lead Nanostrain into the final year of the project as the new coordinator.

For any information: [carlo.vecchini@npl.co.uk](mailto:carlo.vecchini@npl.co.uk)

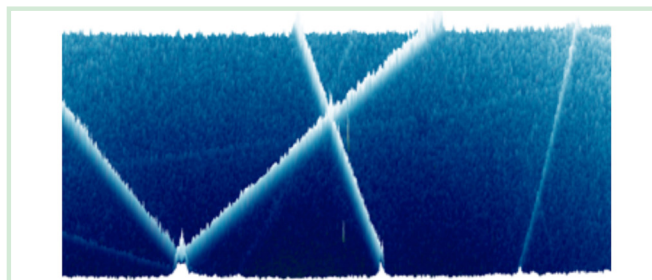
### Ferroelectric domain engineered strain investigated using Diffuse Multiple Scattering

G. Nisbet<sup>a</sup>, C. Vecchini<sup>b</sup>, M. Stewart<sup>b</sup>, F. Fabrizi<sup>a</sup>, T. Hase<sup>c,d</sup>, P. Thompson<sup>c,e</sup>, D. Wermile<sup>c,e</sup>, M. Cain<sup>b</sup>

A century on from Rutherford's experiment marking the discovery of the nucleus and the birth of scattering techniques, a new diffraction process has now been observed. Our team has been attempting to exploit this newly-observed phenomenon to study in situ, ferroelectric materials; in particular PMN-PT single crystals. The process, which is referred to as Diffuse Multiple Scattering or DMS [1], has become apparent only recently thanks to the immense flux of third-generation synchrotron sources and the considerable dynamic range of modern area detectors. While sharing characteristics of Kikuchi, Kossel and pseudo-Kossel lines, the source of the observed lines shown in *Figure 1*, is different. The DMS signal arises from a disruption in the long-range order of the crystal such as structural defects or crystal-surface truncation. This means the incident beam does not need to be tuned to the characteristic

energy of the elements within the crystal. This opens up the possibility of tuning the energy to force multiple line intersections unique to a given set of lattice parameters which significantly reduces the impact of geometrical errors in the experimental setup. They also have advantages over Kikuchi lines because they can be measured in normal atmosphere and in the presence of electric and magnetic fields, providing a powerful technique to investigate ferroelectric materials, with their complex domain and defect structures.

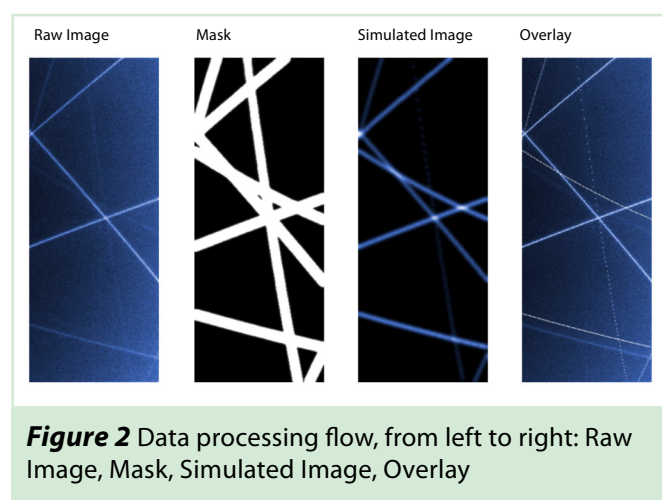
The image below shows the DMS lines, as acquired by an X-ray area detector (Pilatus 100K detector on the I16 Beamline at Diamond Light Source Ltd.). DMS is almost identical to normal multiple scattering in terms of its geometry. However, the Ewald construction is extended beyond the integer case to allow for an extended source within the crystal.



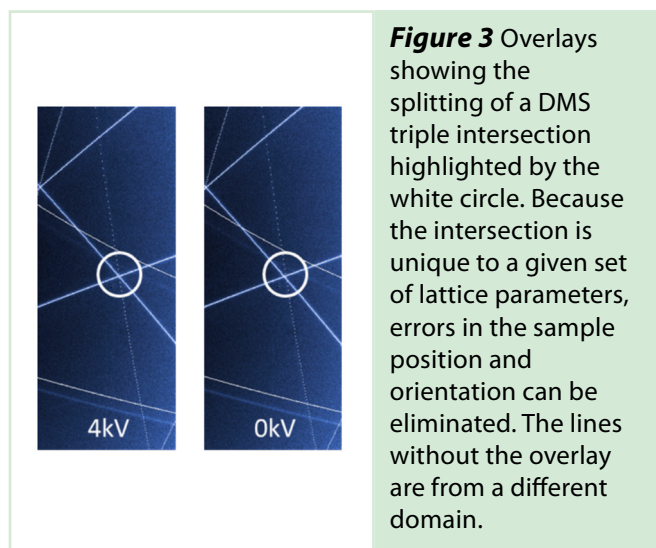
**Figure 1** DMS lines acquired using a Pilatus 100K X-ray area detector on the I16 Materials and Magnetism Beamline at Diamond Light Source, UK.

arising from the diffuse scatter of a nearby Bragg peak, or truncation rod. This is analogous to having a range of incident angles providing a continuous set of reciprocal space origins. Calculating the azimuthal angles at which the crystal reciprocal lattice vectors intercept the Ewald sphere for each of these origins results in lines sweeping across the sphere's surface. Ignoring polarization, this is geometrically equivalent to defining an internal spherical wave and not moving the sample.

The experiment was undertaken at an energy of 7.3039 keV with the incident polarization lying in the main scattering plane. The images were collected as a function of applied electric field at an  $hkl$  of [0.0, 2.084, 2.3906] with an exposure time of 30s. Analysis of the data was done in several steps.



First the images were passed through a Gaussian high pass filter to remove the sloping background. A simulated image of the DMS lines projected on to a virtual detector matching the orientation of the Pilatus detector was then produced to provide a mask to further minimize the contribution of the background. Finally, the resulting images were passed to a fitting routine for optimization against simulated DMS lines using a genetic algorithm followed by the Nelder-Mead gradient descent method. The DMS lines are easily indexable making it easy to vastly reduce the reflection list. This dramatically reduces calculation time allowing the calculated lines to be passed to a cross-correlation routine for optimization of the lattice parameters.



The DMS technique enables real time studies of the structural modifications induced by an electric field in ferroic materials. As the sample does not need to be moved, the data does not need to be corrected for systematic errors and yields results comparable to high resolution diffraction. The static experimental geometry enables a wide range of external stimuli to be applied and opens up high frequency studies using time-delay techniques.

[1] A. G. A. Nisbet *et al.*, *Acta Cryst.* (2015). A71, 20-25

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# Modelling

Anna Kimmel is one of the Nanostrain project researchers based at the National Physical Laboratory in London. Along with Professor Dorothy Duffy from University College London, she supervises two joint UCL/NPL PhD students, Jacob Chapman and Oliver Gindele, who are also active Nanostrain partners.

Over the past few months, Anna and her team have been invited to contribute to numerous prestigious scientific conferences in their field of research, including:

- **Fundamental Physics Ferroelectrics (Knoxville, US), January 2015**

Held every year since 1990, the workshop brings together a diverse set of researchers to help foster the multi-institutional collaborations necessary for comprehensive studies of ferroelectric phenomena.

Anna Kimmel gave an invited talk on the *defects in ferroelectrics and at oxide/ferroelectric interfaces*, illustrating the material-dependence of symmetry-conforming properties of defects using a comparative ab initio study of oxygen vacancies in tetragonal phases of BaTiO<sub>3</sub>, KNbO<sub>3</sub> and low energy P4mm phase of solid solution Pb(Zr<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> (PZT).

- **Study Matter at Extreme Conditions, SMEC-2015 (Miami, US)**

The focus of this meeting is to promote interdisciplinary research in the fields of geophysics, solid state physics, high pressure physics and chemistry and materials science.

Anna Kimmel's presentation was on the subject of *new low energy modulating phase of KNbO<sub>3</sub>: effects of uniaxial and hydrostatic pressure*, in which she showed the capability of structure search method coupled to density functional theory methods in order to probe the energy landscape of KNbO<sub>3</sub> in the perovskite region.

- **Piezo2015 (Maribor, Slovenia), January 2015**

Piezo 2015 presented the latest piezoelectric and multifunctional materials, technologies and devices research and development and brought together the international community within the field for discussion and networking.

In addition to Anna Kimmel's talk on *properties of Pt/Pb(Zr<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub> interfaces*, which discussed a remarkable asymmetry of interfacial properties in terms of the local chemical and electrostatic environment, the team also presented two posters.

Firstly, Gindele, Duffy and Kimmel's poster focused on *developing the semi-empirical force field for Pb(ZrTi)O<sub>3</sub> and its application for the description of mechanism of domain walls motion*, showing how the derived

force field was used to study the mechanism of domain walls motion and their dynamics in bulk PZT, leading to the discovery that rotational degrees of freedom of ZrO<sub>6</sub> octahedra are activated during the propagation of domain walls and play an important role in the reduction of elastic energy.

Secondly, Chapman, Duffy and Kimmel's poster on the *Development of a Shell Model Force-field for BaTiO<sub>3</sub> and its Application for Domain Walls and Surfaces* led to a force-field which incorporates ferroelectric properties such as polarization in good agreement with DFT results, switching properties, energy of domain walls in tetragonal phase of BTO. They also described the effects of different terminations on BTO(001) and BTO(100) revealing an intrinsic dead-layer intruding ~2 nm from the surface, which for nano-devices below a critical size will suppress the ferroelectrically active response to external electric fields.

- **ISIF/ISAF2015 (Singapore), May 2015**

The joint ISAF-ISIF-PFM 2015 conference addresses the science and technological developments related to a broad range of functional materials, covering ferroics, pyroelectrics, piezoelectrics, dielectrics, nanocarbons, and their integration to enable new multifunctional devices.

Oliver Gindele and Jacob Chapman received a travel grant from the conference organisers, to present their posters: *The effect of strain on domain wall dynamics in Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> and Defect induced lattice relaxation and stabilisation in ferroelectric materials*.

- **EMF2015 (Porto, Portugal) July 2015**

This conference encompasses fundamental studies of ferroelectric materials and related materials, tackling their applications in a wide range of advanced technologies, and exploring the frontiers at the very boundaries of this field.

Jacob Chapman is scheduled to deliver a talk on the subject of *Nanoscale Domain Morphology and Dynamics in PbTiO<sub>3</sub> Strained Ultrathin Films*, showing the dependence of domain morphology on temperature using metrics including polarisation and local strain. Meanwhile, Oliver Gindele is due to present a poster on *The effect of B-cation clustering on the ferroelectric and piezoelectric response of Pb(Zr,Ti)O<sub>3</sub>: molecular dynamics studies*, presenting the effects of Ti/Zr clustering on PZT compounds using recently developed force field and specific metrics related to cation clustering.



# Nanostrain workshop at APS Meeting in May

## Developing synchrotron sample environments to study next generation field-driven device physics.

Workshop Organized jointly by Philip Ryan (APS), Markys Cain (NPL), Paul Thompson (XMaS)

In May the Advanced Photon Source (APS), XMaS and the National Physical Laboratory joined forces to gather a remarkable array of talent together for a workshop couched under the APS annual user meeting to discuss the future of *in situ, in operando* sample environments that will be needed for the next generation of synchrotron X-ray experiments. The goal was to focus on field driven capabilities, both electric and magnetic, within the controlled variables of large temperature and pressure ranges, employing medium energy X-ray diffraction and spectroscopy for both scientific and technological endeavors.

Speakers included global leaders in their field as well as young energetic junior faculty members with interests stretching from concept device technologies (including the piezo-resistor, an important part of IBMs'Greenfield' ideas for the future) to expected measurement capabilities needed to understand the principles of fundamental quantum behaviors. We heard from both material scientists and applied physicists on the fundamentals of emerging and rapidly improving piezo-materials and their manipulation to improve applicable characteristics. Several speakers from the condensed matter community (which represent a large component of our collective user base) discussed intricate studies on the physics arising from the coupling of multiple order parameters. Such studies are key to generating not only the carefully engineered samples themselves, but also the *in situ* field application necessary to pump and probe the physical response and learn how these parameters interrelate on a microscopic level. All of which will help us both better understand physical behaviors and generate control parameters with which we describe future technological trajectories.

"Getting an intimate understanding of the needs of our community is crucial when we consider the requirements guiding the next generation of measurement capabilities. We already have a good sense for the future X-ray source characteristics,

particularly the MBA (multi-bend achromat) lattice design with smaller, more coherent beams, but we need to couple the source to the user so that we maximise our collective impact on science", said Paul Thompson (XMaS), one of the conference co-organisers. An important component of this workshop was the EU-funded Nanostrain project which "brings many cutting edge techniques to bear upon the difficult task of understanding and ultimately controlling piezo-driven device control", said Markys Cain, another co-organiser and principal investigator of the Nanostrain project, "and X-rays need to play a vital part of the ensemble-suite focused on reaching industrial performance, scale and reproducibility."

"This workshop gave us serious food for thought regarding what we, in the synchrotron community need to consider when proposing designs for the next generation of experiments", said Philip Ryan (APS), the workshop's third co-organiser, "and we need to consider how to balance the desire for environmental extremes, like milli-Kelvin temperatures and very high magnetic fields, with usability, sample-beam positioning, coherence, dynamics, and correlating macroscopic characteristics with microscopic information." The workshop concluded that the vast synchrotron user community has many very exciting ideas that will require a confluence of intricate engineering and careful consideration of the needs of the community to deliver on its promise to remain the most important large-scale scientific facilitator in the field.

A full list of speakers can be found [here](#)



# Big Interview:

## Henrik Ræder and Frode Tyholdt (SINTEF)

**Henrik Ræder (Senior Business Developer) and Frode Tyholdt (Senior Scientist) work at SINTEF in Norway. Over the last 60 years, SINTEF has created value and innovation through knowledge generation and development of technological solutions that are brought into practical use. Today, SINTEF is a broadly based, multidisciplinary research institute with international top-level expertise in technology, medicine and the social sciences.**

Henrik works in SINTEF Materials and Chemistry (M&C), a contract-based institute offering high levels of expertise in the fields of materials technology, advanced materials and nanotechnology, applied chemistry and biotechnology. This role sees him work closely with global players in the oil and gas, green energy and process industry sectors.

Frode is in SINTEF ICT, a research division in SINTEF, located both in Trondheim and Oslo with around 300 employees. SINTEF ICT carries out research in Information and Communication Technology for industry and the public sector. It works closely with the Norwegian University of Science and Technology and the University of Oslo.

### **What are the objectives of SINTEF?**

SINTEF is an independent technological research and development institute for industry and the public with 2,100 employees. It operates through a foundation and is the biggest independent research institute in the Scandinavian countries. It is similar in ways to the Fraunhofer Institutes in Germany, VTT in Finland and TNO in the Netherlands. A difference between SINTEF and other continental European institutes is that SINTEF has very little basic funding, amounting to only 7% of the total share. The rest



**Henrik Ræder –**  
*Senior Business Developer  
at SINTEF*



**Frode Tyholdt –**  
*Senior Scientist  
at SINTEF*

[of SINTEF's funding] comes from contracts in competition with other institutes. As a result SINTEF is very market orientated, and focuses on eight areas: Materials & Chemistry, ICT, Energy, Building & Infrastructure, Marine, Petroleum, Fisheries & Aquaculture and Technology & Society.

### **What is SINTEF's background in piezoelectrics?**

ICT and M&C have collaborated for approximately 10 years on piezoelectric materials. M&C work with ceramics, basically oxides, and a decade ago we were very interested in piezoelectric materials so we joined up with ICT as they had a predefined process with design guidelines and fabrication procedures for silicon-based microsystems. We soon discovered a need for piezoelectric materials in microsystems because it creates the link between the mechanical movement and the electrical signal, which we thought was very interesting.

The next step was to collaborate with some European partners to develop thin film piezoelectric materials. This has now been in development for many years and is now being implemented in SINTEF ICT. The ambition for SINTEF is to become a major player in Europe on Thin Film Piezoelectric materials. We see the potential application areas as extremely wide, encompassing anything with electronic components from mobile phones to ultrasonic devices in healthcare. Our strength is in developing new concepts where you use piezoelectric technology. It is really an enabling technology, allowing the actuation of different parts.

### **Can you give examples of recent projects?**

We have a large focus on micro optics in SINTEF ICT, which is right now our major focus when it comes to devices. This is used in different applications

areas, for example in recycling systems there are optical laser scanners for recycling systems. Another company is developing a laser-based communications link, which can quickly upload a lot of new movies for a plane's entertainment system, whilst the aircraft is grounded between flights. We are also working with partners in biological sensors and micro-pumps for drug delivery or sampling – which again has many potential applications.

### **What would you like to see the Nanostrain project achieve?**

The most relevant aspect to SINTEF, I believe, is that Nanostrain will develop all its traceable measurements and characterisations under the industrially relevant conditions of high stress electric fields and then make the results available to manufacturers and designers. This is interest to SINTEF and will help the exploitation of piezoelectric technology and the development of new processes and devices for our customers.

### **Finally, is there anything else from SINTEF you would like to add?**

SINTEF's has a unique place in the value chain when it comes to instruments. We are focused on development, even though we have production in our lab, for example we make radiation detectors for medical applications and optical physics and so on – with CERN being a major customer. A lot of our focus is on traceability and quality throughout our work, and we are very flexible compared to a MEMS foundry that only focuses on production. SINTEF is well fitted to develop new processes and new devices for our customers. If it is a low volume product we can help with production before they need to scale up and transfer to a external lab. Ultimately, our strength is in our flexibility as to do development in a fabrication lab is really a hassle!



# Upcoming events

**IEEE Nano 2015:**  
**International Conference on Nanotechnology**  
Rome, Italy  
July 27-30

**ICANM 2015:**  
**International Conference & Exhibition  
on Advanced & Nano Materials**  
Ottawa, Canada  
August 10-12

**ICBNN 2015:**  
**International Conference on Biomedical  
Nanoscience and Nanotechnology**  
Zurich, Switzerland  
July 29-30

**ICNNAM 2015:**  
**International Conference on Nanoscience,  
Nanotechnology and Advanced Materials**  
Venice, Italy  
August 13-14

**ICNT 2015:**  
**International Conference on Nanoscience  
and Technology**  
Barcelona, Spain  
August 17-18

**International Conference on Commercializing Micro  
and Nanotechnology (COMS 2015)**  
Krakow, Poland  
September 13-16

**NANOSMAT**  
Manchester, UK  
September 13-16

**International Conference on Nanomaterials:  
Applications and Properties**  
Lviv, Ukraine  
September 16-23

**Nanoforum**  
Milan, Italy  
September 29-2 October



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