

of the PSCM is to streamline neutron and synchrotron based Soft Matter Research to address 21st century challenges in nanomaterials, biotechnology, environmental and energy sciences. New laboratories equipped for sample preparation and characterization will be hosted in the new Science Building to be soon implemented on-site. This structure should permit to bridge the gap between the ESRF and ILL facilities and the European industry in many issues which require SAS measurements.

**Keywords:** SAXS, SANS, industry

## MS.04.3

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### SAXS in support of industrial research at DuPont

J D Londono,<sup>a</sup> J Meth,<sup>a</sup> B A Wood,<sup>a</sup> P M Cotts,<sup>a</sup> G. Beaucage,<sup>b</sup> S J Weigand,<sup>c</sup> <sup>a</sup>*DuPont Central Research and Development, Wilmington, Delaware (USA)*. <sup>b</sup>*Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio (USA)*. <sup>c</sup>*DND-CAT, Northwestern University, Argonne National Laboratory, Illinois (USA)*.

DuPont offers a wide range of innovative products and services for markets including agriculture, nutrition, electronics, communications, safety and protection, home and construction, transportation and apparel. The SAXS group within the Corporate Center for Analytical Sciences provides support to R&D and businesses throughout DuPont, now in approximately 90 countries. The SAXS technique is unique for the characterization of particle size and agglomeration/flocculation at the nanoscale, providing statistically meaningful information; this technique is particularly powerful when coupled to a synchrotron. Two examples are provided.

The realization of the full potential for polymeric nanocomposites to manifest their entitled property improvements relies, for some properties, on the ability to achieve maximum particle-matrix interfacial area. Well-dispersed nanocomposites incorporating colloidal silica as the filler can be realized in both polystyrene and poly(methylmethacrylate) matrices by exploiting the charge stabilized nature of silica in nonaqueous solvents which act as Lewis bases. We demonstrate that dispersions of colloidal silica in dimethylformamide are charge stabilized, regardless of organosilyl surface functionalization. When formulated with polymer solutions, the charge stabilized structure is maintained during drying until the charged double layer collapses. Although particles are free to diffuse and cluster after this neutralization, increased matrix viscosity retards the kinetics. We demonstrate how high molecular weight polymers freeze the structure of the silica to produce well-dispersed composites. The glass transition temperatures of these composites do not vary, even at loadings up to 50 v%.

An in-situ Study of the pyrolytic synthesis of titania nanoparticles was used to understand the particle growth dynamics in a flame reactor. Particle size (SAXS), chemical speciation (XAS), crystal phase identification (WAXS) were measured as a function of height above the burner to follow the chemical conversion from TiCl<sub>4</sub> to TiO<sub>2</sub> and associated nanoparticle growth and agglomeration dynamics. Much of the observed behavior could be tied to separate hydrolysis and condensation reactions occurring in different lateral and horizontal regions of the flame governed by water concentration and temperature. Crystallization kinetics paralleled the kinetics of particle growth indicating that in some cases single grain particles may form directly from the vapor phase. Due to the lateral distribution of water vapor in the flame and the lateral temperature gradient, hydrolysis and titania conversion had a maximum away from the flame axis, while condensation and nucleation occurred primarily at axial positions. This study

demonstrated that synchrotron SAXS can be used to study pyrolytic synthesis reactions of industrial interest.

**Keywords:** industrial, synchrotron, SAXS

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### SAXS and SANS for industrial materials-by-design

Andrew Allen *Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland (USA)*. E-mail: Andrew.Allen@nist.gov

Over several decades, absolute-calibrated small-angle X-ray and neutron scattering (SAXS and SANS) studies of material microstructures, measured over extended length scales, have helped overcome technological barriers impeding advanced materials development for industrial applications. While much work has focused on applications of soft materials (new polymers, biological systems, etc.), SAXS and SANS also make significant contributions in the development of new high-performance “hard” materials of industrial relevance:

Advanced thermal barrier coating (TBC) development has allowed more efficient gas turbine performance to be achieved for jet propulsion and electricity generation. However, the thermomechanical properties of these coating materials depend critically on their highly anisotropic component void morphologies. SAXS and SANS studies have succeeded in distinguishing and quantifying the different components, and have elucidated many of the processing–structure–property relationships for improved materials design [1].

Solid oxide fuel cells (SOFCs) promise major improvements in energy efficiency, clean energy supply and fuel conversion. The small X-ray beams available for SAXS and ultra-small-angle X-ray scattering (USAXS) measurements at 3rd generation synchrotron sources, together with the X-ray energy tunability, enable the microstructure gradients and the state of the electrochemical interfaces close to the electrode–electrolyte boundaries to be interrogated. Anomalous USAXS studies have quantified degradation during SOFC service life such as arises from the presence of sulfur in the fuel [2].

Despite more than a century of research, fundamental aspects of cement hydration, particularly the nature of the nanoscale calcium-silicate-hydrate (CSH) reaction product, remain elusive. For the cement industry, this situation presents a challenge to the development of new cements with advanced curing properties, or for achieving reduced CO<sub>2</sub> emissions in cement manufacture. Carefully calibrated SANS contrast variation measurements have determined the composition and density of the CSH solid phase from first principles. The atomic packing density within CSH is higher than in related mineral analogs – with repercussions both for cement shrinkage and for new cement design [3].

The global coal industry seeks new sorbent materials to select and remove CO<sub>2</sub> from the flue gas streams of coal-fired electrical power plants. Various classes of metal organic frameworks and similar materials exhibit promising sorption properties, but the structure–dynamics–property relationships are complex. SAXS and SANS studies provide a key role in correlating the structural changes measured by small-angle-diffraction both with the observed sorption performance and with the powder morphology or particle surface area [4].

Using these examples the potential of future SAXS and SANS development will be highlighted in the context of new industrial materials design.

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### In Situ SAXS studies of Jarosite formation

Helen E. A. Brand,<sup>a,b</sup> Nicola V. Y. Scarlett,<sup>a</sup> Ian E. Grey,<sup>a</sup> Robert Knott, Nigel Kirby,<sup>c</sup> <sup>a</sup>*CSIRO Process Science and Engineering, Clayton South, Vic. (Australia)*. <sup>b</sup>*Bragg Institute, ANSTO, Menai, NSW (Australia)*. <sup>c</sup>*Australian Synchrotron Clayton South, Vic. (Australia)*. E-mail: helen.brand@csiro.au

Jarosite group minerals,  $\text{AFe}_3(\text{SO}_4)_2(\text{OH})_6$ , (where A is typically  $\text{K}^+$ ,  $\text{Na}^+$  or  $\text{H}_3\text{O}^+$ ), and related minerals are of great importance to a range of mineral processing and research applications. They are used in the removal of iron species from smelting processes, they occur in metal bioleaching systems, bacterial conditioning in flotation circuits and they are present in acid mine drainage environments. Recently there has been a renewed interest in jarosite minerals with their detection on Mars and the realisation that they are likely an indicator of liquid water on the Martian surface and may hold clues as to the environmental history of the planet. Jarosites are also of considerable theoretical interest as model compounds for spin frustration in kagomé-Heisenberg antiferromagnetic materials.

Knowledge of the conditions of formation of these minerals is critical to the optimisation of these industrial processes and understanding of their potential environmental impacts. To this end we are engaged in a program to study the nucleation and crystallisation of these minerals.

Small Angle X-ray scattering (SAXS) gives us an insight into the size, shape and rate of growth of jarosite through nucleation. Modelling of these early-stage particles suggests they have an elliptical disc form and that the system undergoes one nucleation phase, followed by growth, with possible coalescing of the particles suggested by the late-stage development of correlations at high  $q$ .

**Keywords:** jarosite, SAXS, in situ synthesis

## MS.05.1

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### New tools for the analysis of in-situ XRPD data: symmetry mode analysis, parametric rietveld refinement and MEM

Robert Dinnebier, *Max-Planck Institute for Solid State Research, Stuttgart (Germany)*. E-mail: r.dinnebier@fkf.mpg.de

Due to recent upgrades of synchrotron-sources and the parallel development of new position sensitive detectors it is now possible to collect a vast amount of powder diffraction patterns *in situ* in dependence on external variables with a time resolution in the second or even sub-second regime thus allowing to track many structural and microstructural changes. In order to evaluate this mass of data sophisticated algorithms and suitable software must be available.

Under the simple assumption that structural changes within a crystalline phase vary continuously upon external variables like temperature or pressure, it is possible to parameterize these changes by suitable functions. In this so-called surface or parametric refinement, all powder patterns are refined simultaneously, drastically reducing the number of parameters, thus leading to higher stability of the refinements and more accurate results. Generally, polynomials of low order proved

to be quite successful, in particular for data sets recorded at high pressure. On the contrary, in a consecutive Rietveld refinement, all refinable parameters are refined independently for all powder patterns, requiring high resolution and good counting statistics of the individual powder patterns, in order to avoid strong correlations and outliers.

Under certain premises, so called symmetry (also called distortion) modes can be parameterized<sup>1</sup> instead of using individual atomic coordinates. Modern user friendly computer programs based on group theory like ISODISPLACE<sup>2</sup> or AMPLIMODES<sup>3</sup> are readily available. In case of displacive phase transitions, the application of this techniques allows for the direct determination of physical quantities like order parameters, spontaneous lattice strains, etc.<sup>4</sup> Alternatively, certain types of framework structures where the application of external variables results in polyhedral tilts but not distortions, allow for further parameter reduction by parameterizing internal degrees of freedom of rigid bodies in z-matrix notation. Several comparative case studies will be presented.

Recently we developed a semi-automated computer program Powder3DParametric<sup>5</sup> to ease the process of creating input files for sequential and parametric Rietveld refinement using the general least squares program Topas (Bruker AXS GmbH).

As a complementary approach to Rietveld analysis, in particular if static or dynamic disorder is present, the method of maximum entropy has been successfully applied to series of *in-situ* powder diffraction patterns. It will be demonstrated that the combination of structure factor amplitudes from pattern decomposition methods and phases from charge flipping enables an estimate of the “true” nature of the disorder in dependence on temperature without any strong bias from Rietveld refinement.

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**Keywords:** MEM, symmetry modes, parametric rietveld refinement

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### A high energy view of structure in negative thermal expansion materials

Angus P. Wilkinson,<sup>a</sup> Cody R. Morelock,<sup>a</sup> Benjamin K. Greve,<sup>a</sup> Leighanne C. Gallington,<sup>a</sup> Andrew C. Jupe,<sup>a</sup> Karena W. Chapman,<sup>b</sup> Peter J. Chupas,<sup>b</sup> <sup>a</sup>*School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, (USA)*. <sup>b</sup>*Advanced Photon Source, Argonne National Laboratory, Argonne, IL, (USA)*. E-mail: aw42@mail.gatech.edu

High energy x-rays, when paired with appropriate sample environments, can be used to study a variety of interesting phenomena under non-ambient conditions. They simultaneously give good penetration, providing flexibility in sample cell design, and access to the high  $Q$  scattering data that is typically needed for local structure (Pair Distribution Function) studies. Some of the possibilities for non-ambient studies using high energy x-rays will be illustrated using our work on the evolution of average and local structure when various “ $\text{ReO}_3$  type”  $\text{M}(\text{O}/\text{F})_3$  phases, displaying thermal expansion ranging from strongly positive to strongly negative, are subjected to changes in temperature and pressure. Our low pressure measurements ( $< 300$