

ICDD Annual Spring Meetings

Tess Kozul
ICDD, Newtown Square, PA

Members of the International Centre for Diffraction Data met during the week of 14 March 2011 for the Annual Spring Meetings. Members from 11 countries gathered, along with staff and guests, at ICDD headquarters, Newtown Square, PA, to learn about ICDD's educational events, database, and product developments over the past year, and to reconnect with one another. Throughout the week, various committees, subcommittees, and task groups met for special-interest discussions. For the first time ever, the ICDD offered a live, online broadcast of the Technical Committee Meeting and the Annual Meeting, which took place on Thursday, 17 March. The talks from these meetings will be available online for rebroadcasting at a future date.

Many were in attendance for the plenary session, which was held on Tuesday, 15 March. This year's plenary featured five international speakers: Dr. Cyrus Crowder and Dr. Soorya Kabekkodu, International Centre for Diffraction Data, gave a joint talk entitled, *Implementation of Modulated and Composite Structures in the Powder Diffraction File*; Dr. Valeri Petkov, Central Michigan University, spoke on *Structural Characterization of Non-Crystalline Materials by Non-Traditional X-ray Diffraction*; Dr. Rosanna Rizzi, Istituto di Cristallografia-Bari, Italy, gave a talk entitled, *From X-ray Powder Diffraction Pattern to Structure Solution through New Algorithms, Strategies and Tips: The EXPO Program*; and Professor Dr. Leonid Dubrovinsky, University of Bayreuth, Bayerisches Geoinstitut, Germany, gave a talk titled, *Look at the Earth's Interior with X-rays through a Diamond Window* (Figure 1).

After the plenary session, members, staff, and guests traveled to historic Philadelphia for an enlightening afternoon at the National Constitution Center. The Constitution Center is an independent, non-partisan non-profit organization dedicated to increasing awareness about the U.S. Constitution. Guests enjoyed a film and live-acted show, "Freedom Rising," which explains how the Constitution came into existence and its relevance today. The trip to the Constitution Center also included a special exhibit entitled, *Spies, Traitors*

and *Saboteurs: Fear and Freedom in America*. The exhibit, originally displayed in the International Spy Museum, illustrates the challenge of securing the United States without compromising the civil liberties upon which it was founded.

The day concluded with a poster session, in which 22 posters were on display, and reception in the Gold Ballroom at the Concordville Inn (Figure 2). This year marks the 70th anniversary of the ICDD, and to celebrate, a champagne toast was given by Dr. Tim Fawcett, Executive Director. The evening gave ICDD members and staff the opportunity to display their research and discuss with one another their studies and findings.

The week's end brought to conclusion another successful and productive Annual Spring Meeting for all who were in attendance.

At the Annual Meeting, held on Thursday 17 March, the following awards were announced:

This year, the Board of Directors recognized Brian O'Connor, Emeritus Professor of Applied Physics, Curtin University, Australia, as the 2011 *Distinguished Fellow*. This award is given to a member who has given long and meritorious service to the ICDD. Brian has been a member of ICDD since 1983, and held several positions including: a member of the Board of Directors, Vice-Chairman, and Regional Co-chair for the Indian Ocean Rim. Brian has also made significant contributions in the development of modern X-ray and neutron diffraction analysis, including applications of Rietveld crystallographic metrology for material characterization and development of advanced ceramic materials from Western Australian minerals.

The ICDD was pleased to award two ICDD *Fellows*: Lawrence Bernstein, Terrametrix, CA and Richard Bostwick, SPEX SamplePrep, NJ. Larry first became involved with the



Figure 1. (Color online) (Left to Right) L. Dubrovinsky, V. Petkov, C. Crowder, R. Rizzi, S. Kabekkodu.



Figure 2. (Color online) V. Peterson, E. Antipov, and C. Segre engage in discussion during the poster session and reception.

ICDD as an editor in 1992 and in 1997 became a member. Larry was named Consulting Editor for Minerals in 1992 and has been with the Minerals Task Group since then. He is dedicated to his work with the Minerals Task Group and the Minerals Subcommittee. Richard serves as an active member of the ICDD Education Programs, specifically the Specimen Preparation Workshop within the X-ray Fluorescence Clinic and the 3-day Specimen Preparation Workshop. Richard has taught Specimen Preparation for over 30 years, spanning the original SUNY classes, ICDD clinics, and Denver X-ray Conference.

Full details of the ICDD meetings can be found at www.icdd.com.

Below please find the abstracts submitted for the Plenary and Poster session. Further information about each abstract can be obtained by contacting the author whose name is underlined.

Abstracts from the Plenary Session

IMPLEMENTATION OF MODULATED AND COMPOSITE STRUCTURES IN THE POWDER DIFFRACTION FILE

Dr. Cyrus Crowder and Dr. Soorya Kabekkodu, International Centre for Diffraction Data, Newtown Square, PA

The lattice periodicity is considered essential for the characterization and comprehension of a crystal structure. A couple of decades ago, mineral calverite was found and baffled crystallographers since it did not obey the law of rational indices. These types of structures cannot be indexed using conventional three integer indices. Further analysis on such structures revealed that they deviate from the regular structures by having perturbations in their atomic position, occupation, and/or thermal motion. These fluctuations can be described as a modulation wave, leading to the name modulated structures. The symmetry of the crystal structure can be described in the (3+d) superspace using superspace group. In recent years, several of these types of structures attracted various scientists on account of their interesting physical properties. The number of modulated structures being published is increasing steadily, indicating the need for a database to house them and describe them properly. The Powder Diffraction File is responding to this necessity of the scientific community by incorporating modulated structures starting with Release 2011. This talk will emphasize (1) the data validation procedure implemented to evaluate modulated and composite structures before adding them to the database and (2) the software being designed to access and describe the modulated cells of these entries. The talk will include a brief description of the editorial database changes required to house modulated structures as well as an illustration of the modulated structure retrieval and display capabilities being built into the accompanying access software.

STRUCTURAL CHARACTERIZATION OF NON-CRYSTALLINE MATERIALS BY NON-TRADITIONAL X-RAY DIFFRACTION

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Atoms in crystalline materials sit on the vertices of extended, 3D periodic lattices and, hence, produce X-ray diffraction (XRD) patterns rich in sharp Bragg peaks. The peaks form a unique fingerprint of the respective crystal and so can be used to discern its atomic-scale structure. Atoms in a large variety of materials, including nanosized particles, drugs, polymers, composites, and glasses, do not sit on the vertices of extended three-dimensional lattices and, hence, produce very diffuse XRD patterns that are difficult to analyze in an unambiguous way. This renders the structural characterization of such non-crystalline materials by traditional (Bragg) XRD virtually impossible. The problem has its solution in applying a non-traditional experimental approach involving higher-energy XRD coupled to atomic pair distribution function analysis. In the talk, the basics of this approach will be introduced and its great potential for non-crystalline phase identification and structure determination illustrated with examples from recent studies.

FROM X-RAY POWDER DIFFRACTION PATTERN TO STRUCTURE SOLUTION THROUGH NEW ALGORITHMS, STRATEGIES AND TIPS: THE EXPO PROGRAM

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In the last 20 years, the interest in obtaining *ab initio* crystal structure solutions by powder diffraction data has increased considerably. Great efforts in the experimental and theoretical fields have been made to overcome the typical problems of peak overlapping, background, and preferred orientation. The high quality of data, obtained by modern diffractometers and, particularly, synchrotrons, combined with new and powerful computing procedures, has made possible the solution of crystal structures of size and complexity forbidden by old techniques.

The following steps are necessary to perform a crystal structure solution from powder data: (a) unit cell identification, (b) space group determination, (c) extraction of the structure factor amplitudes from the experimental diffraction pattern, (d) crystal structure solution via direct methods (DMs) and/or hybrid/direct space approaches, and (e) crystal structure refinement via the Rietveld method.

Many programs are available today for crystal structure determination from powder diffraction data, each covering one or more of the principal steps in which the crystal structure solution process may be traditionally divided. The EXPO program has contributed greatly to this process through the implementation of new and powerful algorithms aimed at making *ab initio* crystal structure solution from powder diffraction data easier and straightforward, especially in the case of low resolution data and/or organic compounds. The package EXPO now includes new routines concerning the following: (1) *Indexing*. A new indexing procedure exists, optimized for the triclinic system with a new global figure of merit for recognizing the correct unit cell. The procedure is also able to automatically estimate the most probable extinction group. (2) *Space group determination*. The statistical

analysis of estimated integrated intensities is used in performing the full pattern decomposition according to the Laue group. (3) A new criterion for ranking the most plausible set of phases provided by DM. (4) *Crystal structure determination*. In EXPO, a recent theory aimed at reducing the effects of the limited resolution in the electron density maps has been introduced. (5) *Direct space techniques*. Simulated annealing and the hybrid approach.

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LOOK AT EARTH'S INTERIOR WITH X-RAYS THROUGH A DIAMOND WINDOW

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The major goal in geosciences is to understand (and predict) how Earth works. That requires a detailed knowledge of how the mineral phases, which make up Earth, behave under high-pressure and high temperature conditions relevant to deep Earth's interior. The diamond anvil cell (DAC) technique is the most successful method of pressure generation capable of working in the multimegabar pressure range. Laser heating techniques in DACs cover a wide P-T field: $P > 200$ GPa, $T = 1300$ – 5000 K. A sample preparation for laser-heating experiments is relatively easy and there is practically no risk for the diamonds due to heating. However, there are still a number of problems related to high-temperature experiments in DACs. So far, all existing DAC laser-heating systems are stationary; they are linked either to certain equipment or a beam-line and do not allow rotation of a cell during heating with respect to the incident X-ray beam. Studies of crystal structures require mobility of the laser-heating system. We have developed a portable laser heating system for DACs, suitable for the powder and single crystal diffraction experiments, and applied it to studying a number of geophysically important materials at extreme conditions.

Much attention has been focused on investigations of the silicate perovskite and magnesium-iron oxide phases (magnesiowustites), which make up the major part of Earth's interior. Possible phase transformations in these geomaterials have significant implications for Earth's mantle behavior. Although the importance of Fe and Al as minor components of the silicate perovskite phase has been well documented in the past decades, the few studies using methods sensitive to these elements (e.g., X-ray emission spectroscopy and nuclear forward scattering) were not sufficiently systematic and/or sensitive to recognize any significant changes in the pressure range below 100 GPa. The majority of measurements on perovskites have been made on *pure* MgSiO_3 using almost exclusively X-ray powder diffraction. We studied silicate perovskites ($\text{Mg}_{0.88}\text{Fe}_{0.12}\text{SiO}_3$ and $(\text{Mg}_{0.9}\text{Fe}_{0.1}) \times (\text{Si}_{0.975}\text{Al}_{0.025})\text{O}_3$) and a series of magnesiowustites by means of the high resolution X-ray single crystal and powder diffraction in laser-heated diamond anvil cells, Mossbauer spectroscopy, and nuclear forward scattering at pressure up to 120 GPa and temperature above 2000 K. The effects of changes in iron electronic state on the structure of mantle

minerals and their influence on understanding the structure and properties of Earth's lower mantle will be discussed.

Abstracts from the Poster Session:

STRUCTURAL TRANSFORMATION OF $\text{Li}_2\text{CoPO}_4\text{F}$ UPON Li-deintercalation

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Compounds containing two types of anions (fluoride and polyatomic oxyanions) show perspectives as high-voltage cathode materials for Li batteries because a higher ionicity of the M–F bond (as compared to the M–O one) is expected to enhance the potential of the corresponding $\text{M}^n/\text{M}^{n+1}$ redox couple. At the same time, appearance of the monovalent fluoride anion can expand the free unit cell volume available for lithium ion migration thus promoting its faster mobility.

Electrochemical performance and structural properties of the high-voltage cathode material $\text{Li}_2\text{CoPO}_4\text{F}$ have been investigated in the 3.0–5.1 V potential range. These results clearly demonstrated that this phase showed reversible Li-intercalation. The most remarkable feature is the irreversible structure transformation, occurring upon Li-extraction at potentials > 4.8 V, with subsequent Li-extraction/insertion taking place within the “modified” framework. The structural transformation involves mutual rotations of (CoO_4F_2) octahedra and (PO_4) tetrahedra accompanied by the unit cell expansion ($> 3.5\%$) with significant enlargement of tunnels where Li cations are located. This transformation is expected to enhance Li-mobility in the modified framework. This finding is in contrast to the volume contraction (about 7%) observed in the LiCoPO_4 phase for the complete lithium removal. It was shown that the Li-extraction from the modified framework occurs in a solid-solution manner and exhibits almost linear dependence of capacity vs voltage up to 5.1 V with stabilized discharge capacity at around 80 mA Hg^{-1} . The slope of the capacity-voltage dependence derived from the potentiostatic step measurements suggests the complete extraction of one mole of lithium from $\text{Li}_2\text{CoPO}_4\text{F}$ at potentials ~ 5.5 V. The electrochemical behavior of the $\text{Li}_2\text{CoPO}_4\text{F}$ phase is quite different from that reported for LiCoPO_4 where complete Li-extraction is accompanied by two plateaus and occurs in much narrow potential range (4.8–5.0 V). The electrochemical performance of the $\text{Li}_2\text{CoPO}_4\text{F}$ material is expected to be improved by optimization of interfacial reactivity and careful choice of electrolyte with high anodic limit. Future investigations of $\text{Li}_2\text{CoPO}_4\text{F}$ including complete electrochemical characterization will help to make decisive conclusions about perspectives of this material on the practical application in rechargeable lithium-ion batteries.

III-NITRIDE OPTOELECTRONIC DEVICES: GAP-ENGINEERING FROM ULTRAVIOLET TOWARDS TERAHERTZ

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III-nitrides (AlGaInN) offer a wide direct bandgap that can be flexibly tuned over the complete spectral range from deep ultraviolet (~ 6.2 eV) to near-infrared (~ 0.7 eV). Two key spectral regimes [ultraviolet (UV) and visible] have drawn most of the attention historically. However recently, higher control over material and interface quality and growth engineering has enabled the use of intersubband transitions to access a new spectral regime: **Terahertz** (THz).

Terahertz wavelengths penetrate through nonconductors (fabrics, wood, and plastic) enabling a more efficient way of performing security checks (for example, at airports) with terahertz emission. Being a non-ionizing radiation, terahertz radiation is environment friendly enabling a safer analysis environment than conventional X-ray based techniques. Due to deep penetration depth through body and tissue selectivity, terahertz waves are employed in medicine for cancer cell detection as well as for bone analysis. Despite these promising applications, located in-between electronic and photonic wavelengths, terahertz waves are difficult to generate. Thanks to the large longitudinal optical phonon energy (90 meV), III-nitrides is a promising candidate for room temperature (RT) operation of terahertz quantum cascade lasers (QCLs). Realization of a terahertz QCL requires precise control over material and interfaces that are necessary to form the intersubband levels and allow injection via tunneling between levels.

Recently, we have demonstrated III-nitride AlN/GaN and AlGaIn/GaN SLs with near-infrared ($\lambda \sim 1.0\text{--}1.5$ μm) and mid-infrared ($\lambda \sim 4.5\text{--}5.3$ μm) intersubband (ISB) transitions. After demonstrating precise control over intersubband levels, the injector part of the QCLs—the quantum tunneling—become of our focus. First demonstrations of negative differential resistance (NDR) in AlN/GaN resonant tunneling diodes (RTDs) grown by MOCVD employed tunneling regions grown on lateral epitaxial overgrowth (LEO) GaN/sapphire. However, the dislocation densities were still observed to limit the device performance, and these devices suffered from poor reliability—similar to their molecular beam epitaxy-grown counterparts. With the recent commercial availability of lattice-matched freestanding (FS) GaN substrates, polarization-free-engineered AlGaIn/GaN active layers were realized on non-polar M-plane freestanding substrates that have enabled reliable and reproducible room temperature negative differential resistance in resonant tunneling diodes proving for the first time (irrespective of growth technique) that reliable and reproducible quantum tunneling is possible in III-nitrides.

In conclusion, thanks to continuing developments in material growth and design, our recent experimental demonstrations provide strong motivation towards the eventual realization of RT THz QCLs based on III-nitrides.

A MAGICAL MYSTERY TOUR: CRANFIELD FORENSIC INSTITUTE'S X-RAY DIFFRACTION LABORATORIES

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Cranfield Forensic Institute (CFI) currently operates through several specialties including forensic science, forensic archaeology and anthropology, forensic engineering, ballistics and firearms, security technology and also solar cell

technology development and bio-mineralogy. CFI offers a suite of highly successful Masters Degrees through its Forensic MSc Programme. CFI's X-ray Diffraction Laboratories provide research, educational and commercial support for CFI activities. An introduction to the XRD Laboratories is presented.

The study of biological minerals is a strong research focus of the XRD laboratories, particularly the analysis of bone mineral, uroliths, and breast cancer calcifications. Research into bone mineral composition and structure is of value to forensic science, archaeology, and biomedical science. Recent research has included the investigation of variation in bone mineral between different animal species, the relationship between bone mineral and bone collagen upon heating, and the use of XRD as a tool for triaging bone samples prior to DNA analysis. The progression of breast cancer is being studied using SAXS and FT-IR and with highly predictive results.

An analytical service is provided for veterinary practitioners through semiquantitative phase identification of uroliths from a range of domestic pets. Over the last 7 years, the laboratories have run over 10 000 urolith samples. Another commercial service provided by the XRD Laboratories is the analysis of synthetic hydroxyapatite coatings for a manufacturer of endoprosthetics, such as replacement hip joints.

Research is also being carried out to develop fast data acquisition methods for security screening using Focal Construct Technology and the XRD Laboratories have taken part in the UK Supergen Project through materials discovery for photovoltaics. In partnership with auction houses, the XRD laboratories have been involved in testing the authenticity of works of art and heritage artifacts.

X-RAY ANALYSIS OF NATURAL RESINS FOR THEIR USE IN DENTISTRY

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From the X to VI centuries B.C., the use of natural resins such as copal, in dental incrustations of precious stones in dental apatite were commonly practiced in ancient Mexico. According to several authors,^{1–3} pyrite, hematite, jadeite, and turquoise were typically used for this purpose. The technique probably consisted in practicing a cavity on the tooth surface (of anterior teeth) by mean of a drill-like tool and perhaps powdered quartz with water as an abrasive. The stone was then fixed by using an adhesive such as copal² or calcium phosphate-based cement.³ At present, dental inlays (silver-based alloys) can stretch as far as 20 years. Comparatively, the Swedish scientist S. Linné pointed out his surprise saying that “The calcium phosphate cement used for incrustations has performed its goal during 1500 years!”⁴ In spite of the fact that does not make a real adherence, alloy inlays are frequently used today because of their cheapness and longest permanence in mouth in good conditions in comparison with ceramic-based inlays. In case of ceramic inlays (i.e., metal

free porcelain) an interface between tooth and inlay is created by using phosphoric acid, adhesives and, for instance, dual cement. Both surfaces are joined together by a UV-polymerized thin hybrid layer (i.e., polymethylmethacrylate). Ceramic metal free (crown-and-bridge, inlay, and onlay) is very aesthetic material but is not very resistant to rupture and it's very expensive. Also when you use it without an appropriate base like a glass ionomer or other cement, it is possible to damage the vitality of the teeth because of changes in the temperature. In a previous work,⁵ we have reported the presence of a crystalline phase in a copal resin from a Texcoco market; in this work, we report that this crystalline phase is α -amyrin, which was also identified to be present in a sample of copal from the archaeological site of *Templo Mayor* located in Mexico City.

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X-RAY DIFFRACTION CHARACTERIZATION OF INK JET PIGMENTS

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Minor changes in processing can lead to different crystalline forms of inkjet pigments/inks, due to changes in packing of molecules in crystals. Different crystalline forms (polymorphs) of pigments have different physical properties, for example, color. X-ray diffraction (XRD) is uniquely qualified to detect polymorphism. In addition, X-ray diffraction can assess crystallinity and crystallite size in materials. Examples of XRD characterization in support of research, development, and commercialization of pigments used in inkjet printers are presented.

25TH ANNIVERSARY OF THE POWDER DIFFRACTION JOURNAL

Nicole M. Ernst Boris, Carly Bray, International Centre for Diffraction Data, Newtown Square, PA

This year is the 25th anniversary of the *Powder Diffraction* Journal. To mark this special occasion, our Graphic Designer, Carly Bray, has designed a new cover that vividly displays the journal's purpose. Many thanks go to Carly for her beautiful work. Also this year, we debut a new website:<http://powderdiffractionjournal.com>. This reconfiguration, completed and housed by the American Institute of Physics (AIP), is on their C3 platform. On the new platform,

you can easily search volume and page number, keyword, or digital object identifier (DOI) number with the new search tab. You can also perform an advanced search, updated from the previous platform to be more user friendly. Browsing the journal is easier and the pages are modernized. If you are interested in keeping up with our technical reports, editorials, or other types of articles, you can do so with a RSS feed. Within the HTML display of an article, you can "mark," or select, an area of text and find other places within the journal on the same topic. From the abstract view page, the reader can set up email alerts, share content, and utilize the many tools available, such as Download Citation, Email Abstract, Add to MyScitation, Reprints (if you are the author, you can order reprints using this option), Blog This Article, access a Print Friendly view, and Research Toolkit. The research toolkit offers the reader the ability to use tools such as Mozilla Laboratories ubiquity (an experiment into connecting the Web with language), zotero (manages citations, links, files), OCLC OpenURL Referrer (for librarians), and Hyperwords (creates personal searches). Also very helpful, recent browsing history can now be viewed, allowing you to see the list of articles you have been looking at as you browse the journal. We at *Powder Diffraction* hope you will peruse the website and enjoy its new features.

SUBFILE POPULATION IN 2011 PDF® RELEASES

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The classification of entries into various important subfiles is vital in enhancing the effectiveness of search/match using the Powder Diffraction File™ keeping in view the huge number of yearly additions to the database. The identification and assignment of subfiles is done in two ways: (i) manually, by the ICDD's editorial team and task group members and (ii) semi-automatically by query-based assignment that compares entries with matching chemistry and similar crystallographic parameters (with a user-defined tolerance factor). New subfile entries are reviewed by various editors and task group members for consistency. This poster is a report on the subfile population in the upcoming 2011 releases.

A ROCK SALT SYMMETRY RELATED STRUCTURE IN A LITHIUM MAGNESIUM ZIRCONIUM OXIDE

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In the family of complex oxides that have rock salt structure, various cation-ordering sequences are possible with phases containing more than one cation. The structure of the resulting phases shows group-subgroup relations between the space groups of the involved phases. For instance, in the high temperature polymorph of LiFeO_2 with NaCl structure type (S.G. *Fm 3m*, No. 225), the Li^+ and Fe^{3+} ions are disordered over the Na sites;¹ while in the low temperature α - LiFeO_2 , the arrangement of these ions are ordered (S.G. $I4_1/amd$, No. 141).² For the case of the $\text{Li}_2\text{MgZrO}_4$ with

α -LiFeO₂ structure type, the Mg²⁺ and Zr⁴⁺ ions are disordered over the Fe³⁺ sites.³ All these phases are related to symmetry between the space group *Fm 3m* and its subgroup *I4₁/amd*.

In this presentation, we suggest a structural model for the new phase with chemical formula Li₆MgZr₃O₁₀, applying the theory of group-subgroup relations with the knowledge that its unit cell could be indexed considering the new structure as supercell of Li₂MgZrO₄.

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PARTICLE STATISTICS IN PHI- AND OMEGA-SCAN METHODS

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Recently, we have found that the effect of particle statistics in powder diffractometry can quantitatively be evaluated by statistical analysis of diffraction intensity data recorded by stepwise in-plane (ϕ)-rotation of flat-specimens in powder x-ray diffractometry. The method can be applied to evaluation of crystallite size in the order of several-micrometers with a laboratory Bragg–Brentano diffractometer. The effect of particle statistics for stationary specimen can be evaluated by the method, if it is not much smaller than that of counting statistics.

However, it is still difficult to evaluate the effect of particle statistics for flat specimens continuously rotating about ϕ -axis, even though the effect can be related to the statistical properties of incident-angle (ω)-scan intensity data. In this study, ϕ - and ω -scan diffraction intensity profile data collected at a synchrotron powder diffraction beamline, KEK-PF BL-4B2, are compared. It is shown that the effective number of diffracting crystallites can be evaluated from the ω -scan as well as ϕ -scan data.

Errors caused by particle statistics and improvements in quality of diffraction intensity data by a ϕ -spinner will also be discussed.

AN IMPROVED STRUCTURE MODEL OF α -AMYLOSE, (C₆H₁₀O₅)₃(H₂O)₂

J. A. Kaduk, Illinois Institute of Technology, Chicago, IL

Based on recent single crystal microdiffraction results of Popov *et al.*, the structure of α -amylose has been completed by adding hydrogen positions from a density functional geometry optimization. Amylose (the linear form of starch) crystallizes in the monoclinic space group B112, with *a*

a = 21.273(17), *b* = 11.893(13), *c* = 10.633(17), ν = 123.618(32)°, and *V* = 2240.3(47) Å³. According to convention, the polymer chains run along the *c*-axis, leading to the unconventional space group setting.

The structure consists of intertwined sixfold left-handed parallel double helices, tightly packed parallel to one another. Each double helix is centered on a twofold axis. There is an extensive network of inter-strand and inter-double-helix hydrogen bonds. There are hints of intra-chain C-H...O hydrogen bonds, but no intramolecular O-H...O hydrogen bonds.

The improved structure model leads to good Rietveld fits of the powder patterns of corn starch and ground dry corn. The model should yield improved quantitative analyses of samples which contain starch.

CRYSTAL STRUCTURE OF MONOCLINIC

Sr_{2.4}Ca_{0.6}Al₂O₆

J. A. Kaduk, Illinois Institute of Technology, W. Wong-Ng, NIST, and J. T. Golab, INEOS Technologies

Although the Portland cement related phases Sr_xCa_{3-x}Al₂O₆ have been reported to crystallize in the cubic space group *P* α 3 for the whole solid solution range, a monoclinic form of Sr_{2.4}Ca_{0.6}Al₂O₆ was prepared at 1300 °C. Indexing the powder pattern was challenging; the strong split peaks could be indexing on a small orthorhombic cell, and the supercell tools in the old program NBS*LATTICE were used to identify a 32 \times monoclinic supercell which accounted for all of the peaks. The space group was identified as *P*2₁/*c* by examining possible distortions of the *P* α 3 structure using ISODISTORT. Sr_{2.4}Ca_{0.6}Al₂O₆ crystallizes in *P*2₁/*c*, with *a* = 15.7244(8), *b* = 15.7361(2), *c* = 15.7265(8) Å, β = 90.6235(11)°, and *V* = 3891.13(28) Å³. The lowering of the symmetry results in the presence of two independent six-rings of corner-sharing AlO₄ tetrahedra; 1 six-ring is more distorted than the other. The Sr/Ca are mostly ordered; at only one of the 20 alkaline earth sites is the occupation ~50/50. The Ca are not clustered in the unit cell. Symmetry mode analysis shows that the distortion from the cubic structure is complex, but concentrated in oxygen displacements in a few modes. The as-prepared sample contains some amorphous material, which hydrates to Sr₃Al₂(OH)₁₂ on storage. Even in a combined synchrotron/laboratory Rietveld refinement (with extensive use of bonded and non-bonded distance restraints) it was difficult to obtain a precise structure. The final coordinates were determined by a density functional geometry optimization using the fixed experimental unit cell.

ICDD 2011 PRODUCT DEVELOPMENTS: DDVIEW+ and SIEVE+

J. Blanton, D. Crane, J. Torbet, C. Crowder, F. Needham, and T. Fawcett, International Centre for Diffraction Data, Newtown Square, PA

DDVIEW+ is ICDD's powerful data mining and viewing XRD software. It has the ability to search through the entire ICDD PDF-4+ database using numerous permutations of XRD criteria. Once the desired search patterns are obtained, DDVIEW+ can view extensive XRD information including

diffraction, physical, crystal, and bibliographic data. In addition, these patterns have advanced tools such as simulated X-ray diffraction profiles, electron diffraction patterns, 2D ring patterns, and 3D structures. The power of DDVIEW+ can be greatly extended through the use of SIEVE+, ICDD's search-index software plug-in. Using highly optimized algorithms, SIEVE+ can rapidly match the d-spacing lines of the user's experimental data to fit patterns in the PDF-4+ database.

To enhance the value of DDVIEW+ and SIEVE+, ICDD has incorporated many new developments for the 2011 product release. Three new searches have been added: A new Periodic Table search (where search element is Yes, No, or Maybe), a Structural Formula search, and a Property Sheet search. We have upgraded the 3D structure viewer to use JMOL, a fast and powerful open-source viewer. The processing of experimental data for importing into SIEVE+ has also been streamlined with a new wizard. A much improved similarity index, called the R-index, is now an option for experimental data comparison. Additionally, SIEVE+ now allows the user to view a simulation of multiple phases as a single, summed plot. This will also be the first release to contain 54 modulated structures, which are structures that are described using more than just three-dimensional space. These are just some of the value-added developments designed to make both DDVIEW+ and SIEVE+ more functional and powerful for 2011.

ICDD.COML WHO ARE OUR "VISITORS"

M. Kottenhahn, International Centre for Diffraction Data, Newtown Square, PA

ICDD.COM strives to meet the information and communication needs of ICDD members, customers, scholars, professionals, grant-in-aid participants, developers, and students. Any information we can gather on the purposes and characteristics of our site visitors will help us to tailor our website to meet their needs.

This poster will answer some questions regarding the activity of the ICDD website:

- Who is the "typical visitor"? (From what country are they visiting? How do they arrive at the site? When do they visit?)
- What are the most popular pages, documents, and downloads?
- What search engines and websites are driving traffic to icdd.com?

SMECTITE CLAYS AS A QUASI-TEMPLATE FOR PLATINUM ELECTRODEPOSITION

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Smectite clays suspended in platinum deposition solution allow to alter the specific surface area of electrodeposited Pt on gold and to enhance Pt specific activity toward methanol oxidation under steady-state conditions. The templating effects of three different clays (bentonite, montmorillonite, and laponite) are compared. The most pronounced

effect is found for bentonite, the clay bearing the highest specific charge of aluminosilicate platelets. STM, SEM, EDX and XRD characterization discovers the clay effect on size distributions of Pt crystals. The estimates of electrochemically active true surface area are considered in terms of partial coalescence of Pt crystals. The degree of coalescence appears to be lower for templated deposits as compared to conventional electrodeposited platinum.

STRUCTURE AND PHOTOACTIVITY OF EXFOLIATED LAYERED OXIDES

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Structure analysis using neutron diffraction and pair distribution function analysis were used to probe the local structures of Aurivillius oxides of the form $\text{Bi}_2\text{A}_2\text{M}_3\text{O}_{12}$ with $\text{A} = \text{Na, Ca, Sr, Ba, Nd, Pr, and La}$ and $\text{M} = \text{Ti or Nb}$. The results clearly demonstrate that the TiO_6 and/or NbO_6 octahedra are substantially tilted and distorted in a predictable fashion as a function of the size of the A-site cation. Chemical exfoliation to form $\text{H}_2\text{A}_2\text{M}_3\text{O}_{10}$ dramatically increases the surface area and photodecomposition rate for methylene blue. Quantum mechanical band structure calculations show that the density of states at the bottom of the conduction band is dominated by the outer Ti/Nb ions of the three-layer perovskite block. We demonstrate that the photoactivity of the layered oxides rivals that of high surface area P25 TiO_2 .

PDF-4/ORGANICS 2011 DATABASE HIGHLIGHTS AND ITS APPLICATION

F. Needham, C. E. Crowder, and T. G. Fawcett, International Centre for Diffraction Data, Newtown Square, PA

PDF-4/Organics 2011 is the largest organic x-ray powder diffraction (XRPD) database in the world. It consists of 436 901 XRPD phases with 6370 pharmaceutical entries, 4209 forensics materials, 1302 polymers, and 13 145 bioactive substances. The pharmaceutical entries include 1916 excipients. The Organic database is also populated with a number of major life science materials listed below:

Materials	No. of entries
Amino acids, peptides, and their complexes	9378
Carbohydrates	5156
Porphyryns, corrins, and their complexes	4248
Terpenes	3635
Alkaloids	2128
Nucleotides and nucleosides	1842
Steroids	1597

With such large quantity of different phases for organic compounds, PDF-4/Organics 2011 is very useful for characterization of solid state materials. It is also useful for the polymorph screenings. The vast amount of crystallographic information, such as atomic coordinates, cell parameters, cell volumes, cell densities, space groups, unit cell atom numbers, and unit cell formula units, provides instantaneous identification capability for polymorphs.

Through many ICDD internal/external editors' efforts, the extensively edited data provide very high quality data valuable to the users. These high quality data are not only good for data mining purposes but also valuable for a variety of scientific studies. The SIEVE+ accepts multi-phase raw data file. It has many data processing options, such as background subtraction, profile smoothing, powder diffraction peak finding, zero-shift correction, alpha2 stripping, and peak-removal operations. In addition to the graphics, a list of numerical peak display is also provided during data processing session. This allows users to have fine control on the search/match process. A number of search/match methods, including modified Fink/Hanawalt methods and eight strongest/largest d-spacings are used. Here I would like to present some examples of the PDF-4/Organics 2011 database applications.

A WINNING PAIR TO STUDY SOLID PHARMACEUTICALS: THE 11-BM SYNCHROTRON BEAMLINE AT THE APS AND THE EXPO 2009 SOFTWARE

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³Faculté de Pharmacie, Université François Rabelais, Tours, France

The on-going development of sophisticated high-resolution synchrotron X-ray powder diffraction beamlines, in combination with advancement in analysis software, makes it possible to solve structures for more and more complex pharmaceutical crystalline materials *ab initio*. Increased complexity may arise from greater number of degrees of freedom of the molecular moieties or from the reduced symmetry of the crystal. The 11-BM synchrotron powder diffraction beamline at the Argonne Advanced Photon Source, put into operation in 2007, provides the high throughput and the high resolution required to investigate weakly scattering drugs, while minimizing the overlap of Bragg peaks in the measured powder patterns in order to allow for the indexing of low-symmetry unit cells. The subsequent data analysis using the *single* software package EXPO 2009: (i) *indexes* the patterns, (ii) *ranks* suitable crystal symmetries (i.e., *space groups*), and (iii) *solves* the structure using *simulated annealing* for flexible molecular models of linked rigid groups.

The power of 11-BM and EXPO2009 in combination is readily demonstrated on example pertaining to two important powdered pharmaceuticals: (1) the chemotherapy agent Tegafur C₈H₉FN₂O₃ (β -form) and (2) the local anesthetic tetracaine hydrochloride (TCHC C₁₅H₂₅O₂N₂⁺, C⁻). Monoclinic β -Tegafur was initially solved from single-crystal data by Nakai *et al.* and reported in 1986 in the Chem. Pharm. Bull. The structure of triclinic TCHC was first published in 2002 by Nowell *et al.* in the New J. Chem. The synchrotron powder data set was then indexed with DICVOL (Boultif and Louër, 1991) and subsequently solved with DASH (David and Shankland, 2001).

A third and final example relates to the propensity for polymorphism of pharmaceutical drugs. A key feature of the 11-BM beamline is its low-/high-temperature *in situ* capability. In a recent study on the modifications of TCHC, two

distinct patterns were obtained at room temperature from the same initial powdered sample. Polymorphism or blunder? This issue was eventually resolved by slowly varying temperature at 11-BM and watching one pattern gradually transform into the other. Both were indeed successfully indexed by the N-TREOR09 option of the EXPO2009 package.

Use of EXPO2009 from Professor C. Giacovazzo (IC-CNR, Bari) is gratefully acknowledged. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

USING NEUTRONS TO STUDY LITHIUM-ION BATTERIES

Vanessa K. Peterson and Neeraj Sharma, The Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia

Neutron diffraction is being used increasingly in the study of Li-ion batteries, due to its distinct advantages over other techniques of analysis for these materials including high sensitivity toward Li and large penetration depth for bulk analysis. This poster will showcase our results from both *in situ* and *ex situ* neutron diffraction studies of crystalline electrode materials in Li-ion batteries using Echidna, the high-resolution neutron powder diffractometer, and Wombat, the high-intensity neutron powder diffractometer, both at the OPAL reactor facility at ANSTO. In particular, the developments in the construction of electrochemical cells that resemble their real life counterparts but are suited to *in situ* neutron diffraction studies using Wombat, taking advantage of its area-detector allowing for real-time data acquisition. Notable *in situ* neutron diffraction results on commercially available Li-ion batteries, e.g., time-dependent structural evolution of electrode materials correlated with the state-of-charge of the battery will be presented, along with our progress in establishing a facility at the Bragg Institute where electrochemists can bring novel electrodes with good electrochemical properties, and undertake *in situ* or *ex situ* neutron diffraction experiments to determine structural processes at different stages of the electrochemical cycle.

The culmination of this work is aimed at providing a real-time understanding of critical structural processes occurring at the electrodes, from which further research can be tailored or developed. The results presented are intended to highlight the insight one can achieve by marrying neutron diffraction with electrochemistry.

HIGH-RESOLUTION SYNCHROTRON POWDER DIFFRACTION SIMPLIFIED: BEAMLINE 11-BM AT THE APS

Matthew R. Suchomel, Advanced Photon Source, Argonne National Laboratory, Argonne IL

As the newest dedicated powder diffraction beamline at the Advanced Photon Source (APS), 11-BM uses a single-crystal analyzer detection system to obtain the highest resolution available in North America. Its unique mail-in service, operating since 2009, provides users with convenient and rapid access to truly world-class quality data for routine analyses. This is a free service for nonproprietary users and

presents users with a simple web-based interface for requesting sample mounting kits and downloading data. The diffractometer is also available for on-site experiments requiring more specialized measurements. The poster will highlight recent efforts to further expand the potential of this instrument, by uniting the advantages of *in situ* studies and the powerful capabilities of high-resolution powder diffraction.

NEW CLASS OF CATHODE MATERIALS FOR LI ION BATTERIES: $\text{Li}_2\text{MP}_2\text{O}_7$ (M=Fe, Mn, Mg)

Shailesh Upreti, Hui Zhou, Natasha A. Chernova, and M. Stanley Whittingham, Chemistry and Materials, SUNY Binghamton, Binghamton, NY 13902-6000

Olivine structured phosphates, like LiMPO_4 (M=Fe, V, Mg, and Mn), etc., have been greatly explored and are being used in a number of applications now a days. Nonetheless, they still fall short of desired capacity >200 Ah/kg, the demand for next generation PHEV and EV. Such capacities can be achieved in phosphate compounds by making redox reaction exceed one electron per transition metal center. Recently, we published new members of $\text{Li}_2\text{MP}_2\text{O}_7$ family, which has a 3D framework built up of MO_5 trigonal bipyramid sharing edge with MnO_6 octahedra that are interconnected through P_2O_7 groups. Interestingly, two lithium ions located in the tunnels allow accessing two electrons per redox center, changing metal oxidation state from 2+ to 4+. This indeed, motivated us to look into the structure-electrochemistry relationship in detail.

In our preliminary work, metals such as Mn, Fe and Mg have been used to synthesize the target material by a variety of methods. We have shown that lithium can be reversibly intercalated into the phases $\text{Li}_2\text{Fe}_y\text{Mn}_{1-y}\text{P}_2\text{O}_7$ for $0 \leq y \leq 1$ and $\text{Li}_2\text{Fe}_{0.9}\text{Mg}_{0.1}\text{P}_2\text{O}_7$. The pure iron phase has been formed for the first time, and its structure was determined using various characterization techniques including high resolution synchrotron X-ray diffraction. We observed that the Fe containing phase has much better performance than the Mn phase. In our recent finding, we found that either magnesium substitution or particle size reduction to nanoscale (~ 100 nm) significantly improves the capacity and helps achieving the target capacity of >200 mAh/g in the initial charging step. Detailed nature of these compounds in terms of structural diversity and corresponding electrochemistry will be presented in the poster. Magnetic properties and a set of *in situ/ex situ* X-ray diffraction, as a function of Li insertion/extraction, will also be discussed. This work is supported by the U.S. Department of Energy, Office of FreedomCAR and Fuel Partnership through the BATT program at Lawrence Berkeley National Laboratory.

ALUMINUM TITANATE COMPOSITES FOR DIESEL PARTICULATE FILTER APPLICATIONS

Bryan Wheaton, Corning Inc., Corning, NY

In our preliminary work, metals such as Mn, Fe and Mg have been used to synthesize the target material by a variety of methods. We have shown that lithium can be reversibly intercalated into the phases $\text{Li}_2\text{Fe}_y\text{Mn}_{1-y}\text{P}_2\text{O}_7$ for $0 \leq y \leq 1$ and $\text{Li}_2\text{Fe}_{0.9}\text{Mg}_{0.1}\text{P}_2\text{O}_7$. The pure iron phase has been formed for the first time, and its structure was determined using vari-

ous characterization techniques including high resolution synchrotron X-ray diffraction. We observed that the Fe containing phase has much better performance than the Mn phase. In our recent finding, we found that either magnesium substitution or particle size reduction to nanoscale (~ 100 nm) significantly improves the capacity and helps achieving the target capacity of >200 mAh/g in the initial charging step. Detailed nature of these compounds in terms of structural diversity and corresponding electrochemistry will be presented in the poster. Magnetic properties and a set of *in situ/ex situ* X-ray diffraction, as a function of Li insertion/extraction, will also be discussed. This work is supported by the U.S. Department of Energy, Office of FreedomCAR and Fuel Partnership through the BATT program at Lawrence Berkeley National Laboratory.

Porous composites of aluminum titanate and mixed strontium/calcium feldspar are used as a material in diesel particulate filter applications. These materials exhibit low thermal expansion, high thermal shock resistance, high heat capacity, high chemical resistance to ash, and are able to be formed into porous materials with porosity $>50\%$ allowing for efficient filtering of particulate matter without creating an undesirable high backpressure. The growth of aluminum titanate from simple oxide starting materials is constrained by a number of thermodynamic, kinetic, crystallographic, and morphological factors. Reaction-templated growth of aluminum titanate is explored in the present work, where during its high temperature formation aluminum titanate conserves the template morphology and develops texture. X-ray diffraction and electron backscatter diffraction were employed to investigate the impact of template shape and crystallographic orientation in single crystalline and polycrystalline reacting mixtures on the material microstructure and its crystallographic texture.

HYDROGENATION PROPERTIES SUB-FILES FOR ICDD DATABASE

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Search for alternative energy sources constantly attracts the attention of researchers to the elemental hydrogen with its high weight energy content and ecologically safe oxidation reaction, in which the only output product is water. Development of new hydrogen energy concepts requires solution of many fundamental and technological problems, including power generation, hydrogen production, its storage, and transport. In the last case, the use of complex and metal hydrides are very promising. Besides, the electrode materials for Ni-MH batteries, getters, catalysts, and other applications are realized with the use of hydride materials.

Amount of absorbed hydrogen is not sufficient characteristics for estimation of possibility to apply the material under certain conditions. Dependence of absorbed hydrogen amount on temperature and pressure, length of the absorption plateau, and conditions of formation-decomposition of solid solutions and hydrides, are reflected by hydrogen absorption-desorption isotherms. Based on these dependencies the principal thermodynamic characteristics of the process (ΔH and ΔS) can be determined. Charge-discharge curves of metal

hydride materials in electrolyte can be considered as electrochemical analog of absorption-desorption isotherms. Based on these dependencies, it would be possible to theoretically estimate important characteristics of electrode material in power sources, determine pressure of hydrogen absorption by getter materials, determine pressure range for hydrogen storage units, etc.

Based on the existing literature and our own data on the topic, we have already created 60 files representing different classes of hydride materials. Among them are hydrides of

metals and intermetallic compounds, ionic and complex, low- and high-temperature hydrides, etc. The files contain information on composition, structure, preparation, description of experiment and absorption-desorption isotherms. Files can be supplemented by thermodynamic characteristics if available in the source papers. For widely studied materials data provided by different authors are compared. The poster presentation will provide examples of files for different types of hydrides.