ICDD Annual Spring Meetings

Eileen Jennings
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Members of the International Centre for Diffraction Data met during the week of 17 March 2014 for the Annual Spring Meetings. Members from 12 countries gathered, along with guests and staff, at ICDD Headquarters in Newtown Square, Pennsylvania. They learned about ICDD's database and product developments, and educational events over the past year, and reconnected with one another. Throughout the week of meetings, members and staff broke into committees, subcommittees, and task groups for smaller, special-interest discussions (Figure 1).

All were in attendance for the Plenary Session, 18 March. The plenary featured four speakers. **Matthew Suchomel** is a staff scientist at Argonne National Laboratory; his topic of discussion was entitled *Synchrotron Scattering Techniques for Solid State Chemistry and Materials Science.* **Scott Speakman** recently began working as Principal Scientist for PANalytical, Inc. Prior to that, he was manager of the X-ray Shared Experimental Facility (SEF) at MIT. Scott's talk was entitled *Supporting Interdisciplinary Research in a User-Oriented Characterization Lab.* **Andrew Payzant** leads the Engineering Materials Group in the Neutron Sciences' Chemical and Materials Engineering Division at Oak Ridge National Laboratory. Andrew's talk was about *The Science and Applications of Neutron Diffraction at the ORNL User Facilities.* And, Tom Blanton, Publication Manager for the International Centre for Diffraction Data, spoke on *X-ray Diffraction Analysis of Polymers – Expanding Materials Characterization Capabilities Using the ICDD Powder Diffraction File*™ (Figure 2).

Following the Plenary Session, members, guests, and staff were invited to our social event, poster session, and reception which took place at the **A**merican Helicopter Museum and Education Center in West Chester, Pennsylvania (Figure 3).

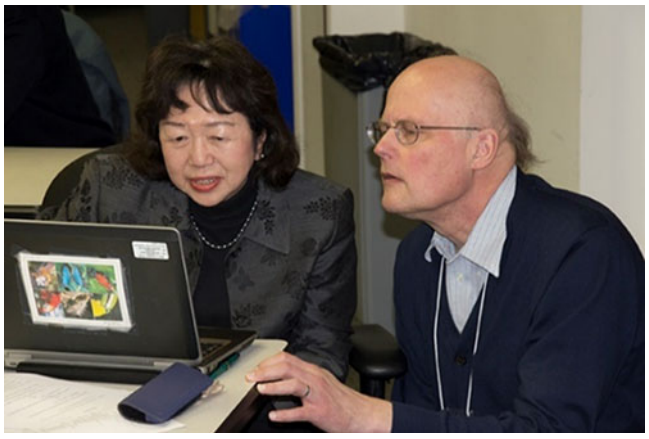


Figure 1. (Color online) W. Wong-Ng & J. Kaduk, networking during meeting week.

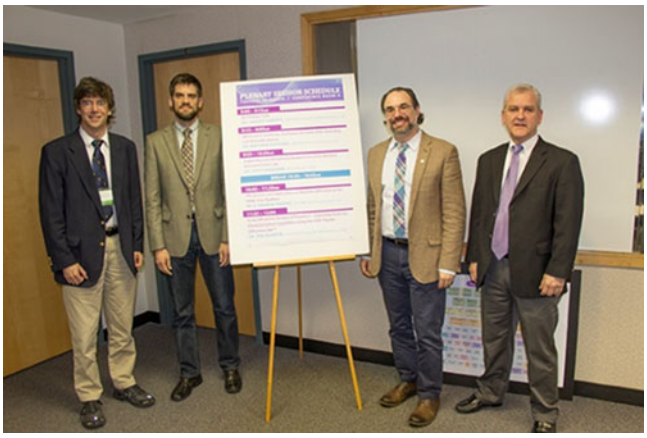


Figure 2. (Color online) Plenary Speakers – A.E. Payzant, M. Suchomel, S. Speakman & T. Blanton.

A total of 26 posters were on display for members and guests to view. Members were asked to vote on their favorite poster, and the posters receiving the most votes were on display at ICDD Headquarters for the remainder of the week. This year, we had one overall winner, and a three-way tie for second place. The poster voted best by ICDD members was *SiC-Based Diluted Magnetic Semiconductor* presented by **Bo Song** of Harbin Institute of Technology, Harbin, People's Republic of China. The second-place winners were: *New Neutron Diffraction Data Capability In The ICDD PDF-4+ 2014 Relational Database* presented by **John Faber** of Faber Consulting, Thornton PA; *Crystal Structures Of Large-Volume Commercial Pharmaceuticals* presented by **James Kaduk**, of Illinois Institute of Technology, Chicago, Illinois; and The Improbable Complete AB-Initio Structure Solution Of Synthetic Dashkovaite $Mg(HCOO)_2.2H_2O$ From Laboratory Cu$K\alpha_1$–$K\alpha_2$ X-ray Powder Diffraction Data presented by **Robert J. Papoular** of IRAMIS/LLB/CEA/CEN-Saclay, Gif-sur-Yvette, France.

The week's events concluded with the Annual Meeting of Members, 20 March. The following awards were presented:

Distinguished Fellow Award:
Certain members who have given long and meritorious service to ICDD, and are currently recognized as Fellows, may be granted the title of Distinguished Fellow. Scott Misture presented the Distinguished Fellow Award to **Evgeny Antipov** of Moscow State University (Figure 4).

Fellow Award:
The designation of Fellow may be given by the ICDD Board of Directors to individuals who have given their time and talents beyond that normally associated with membership. Scott Misture presented ICDD Fellow Awards to: **Graciela**

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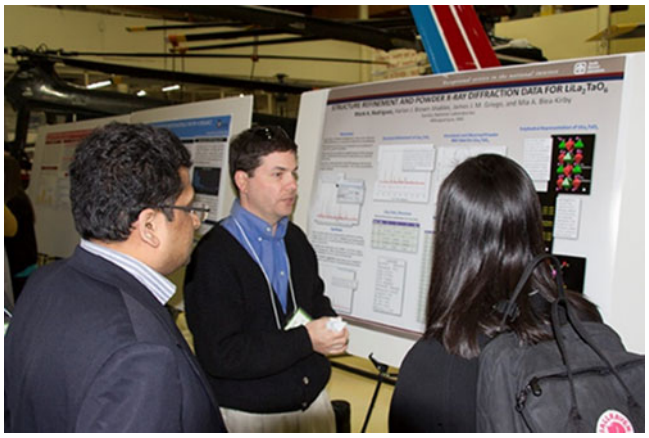


Figure 3. (Color online) M. Rodriguez at Poster Session.



Figure 4. (Color online) E. Antipov accepting the McMurdie Award from S. Misture.

C.D. de Delgado, of University de Los Andes, for serving 2 years as Chair of the Grant-in-Aid Committee; **Robert Papoular**, of IRAMIS/CEA – Saclay, for serving 2 years as Chair of the X-ray Diffraction Methods Subcommittee; **Jordi Rius**, of Institute de Ciencia de Materiales de Barcelona, for serving 2 years as Director-at-Large, and **Bryan Wheaton**, of Corning Incorporated, for serving 2 years as Chair of the Electron Diffraction Subcommittee.

The 2014 McMurdie Award was presented to **Evgeny Antipov** of Moscow State University, in recognition his many significant contributions over the last two decades to the Powder Diffraction File™, in particular, the Ceramics Subfile, and to recognize his role as an ICDD Ambassador to the Eastern European community.

Full details of the ICDD meetings can be found at www.icdd.com/profile/march14.htm.

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

CHOICE OF EXTERNAL STANDARDS FOR AMORPHOUS PHASE QUANTIFICATION

Jeffrey P. Nicolich
W. R. Grace & Co. – Conn., 62 Whittemore Ave, Cambridge, Massachusetts

The external standard method for quantification of amorphous or poorly crystalline phases has gained much attention in recent years as researchers attempt to quantify increasingly complex mixtures which may contain an amorphous component. Examples of this are cementitious mixes, cement hydration reactions and equilibrium catalyst samples from fluid catalytic cracking (FCC) units. The method has several advantages. The sample remains unperturbed, thus sample preparation is simplified and there is no error in mixing or blending an internal standard. Minor phases can be quantified with greater precision as there is no loss of signal due to dilution. Furthermore, reactive systems are not contaminated with potential nucleation sites.

Differences in mass absorption between the sample and the standard are corrected by calculation. It will be demonstrated that the normalized intensity remains constant over a wide range of mass absorption coefficient values.

Not all pure phase materials are suitable as an external standard due to difficult to model differences such as preferred orientation, fluorescence and packing density variations. It is imperative that a standard be qualified before use. Measurements of several phase pure and phase identical compounds obtained from various sources will be presented. The observed variation of intensity (Rietveld scale factor) is similar in magnitude and origin to what has been published on differences of reported I/I_c values in the ICDD powder diffraction databases.

ICDD AND ASM DATABASE SURVEY OF THE THERMOELECTRIC HALFHEUSLER MATERIAL SYSTEMS

Winnie Wong-Ng,[1] and J. Yang[2]
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[2]Materials Science and Engineering Department, University of Washington, 418 Roberts Hall, Seattle, Washington

Phase diagrams and X-ray powder diffraction patterns provide critical information for thermoelectric research. We have conducted a survey of phase diagrams and powder diffraction patterns of thermoelectric systems in the ASM Metal/Alloy database and ICDD Powder Diffraction File (PDF), respectively, for their availability and crystal systems. In this paper, we focus on thermoelectric materials that have the half-Heusler XYZ structure, and related compounds, based on a set of materials selection rules. We found that among 306 potential XYZ compounds that we have surveyed, 234 have powder diffraction patterns in the PDF, but only 28 have phase diagram information. Among the 234 phases with powder patterns, 84 were reported to have Cubic F-43m half-Heusler-type structure, the remainder have hexagonal, orthorhombic, or other structure types. Some XYZ compounds have both cubic and hexagonal phases. This information will provide the basis for future activities for improvement of the databases. These activities include filling the missing gaps in both PDF and phase equilibria databases, as well as adding thermoelectric and pertinent physical properties to the PDF.

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STRUCTURE REFINEMENT AND POWDER X-RAY DIFFRACTION DATA FOR $LiLa_2TAO_6$

Mark A. Rodriguez, Harlan Brown-Shaklee, and James J. M. Griego
Sandia National Laboratories*, Albuquerque, New Mexico

The rare-earth tantalate phase $Li_5La_3Ta_2O_{12}$ is exploitable as a fast ion conductor and a great deal of research has been devoted to the synthesis/processing of this important compound. In our recent synthesis of $Li_5La_3Ta_2O_{12}$ we have observed $LiLa_2TaO_6$ as an impurity phase. This phase is especially prevalent during cases of Li-deficiency during processing, often as a result of Li-volatility. $LiLa_2TaO_6$ has been documented within the PDF database (see PDF entry 00-039-0897). However, the PDF entry currently lacks crystallographic structural information, making quantitative analysis difficult. We have isolated the $LiLa_2TaO_6$ phase via our synthesis routes and have performed Rietveld structure refinement for the purposes of obtaining a full structural identification of this phase including atom positions, site occupancies, and bond lengths/angles. We have employed the isostructural $LiLa_2SbO_6$ phase (PDF entry 04-011-5544) as a starting model for the refinement. We present the final refined structure for $LiLa_2TaO_6$ phase from our powder X-ray data along with tabulated powder X-ray data for identification purposes.

*Sandia is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the United States Department of Energy's National Nuclear Security Administration under contract DEAC04-94AL85000.

BONDING IN GROUP 1 CITRATE SALTS

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Computational (both density-functional and molecular mechanics) studies of >15 new crystal structures and the ten previously reported structures of alkali metal citrates provide insight into why the atoms are where they are. Both atomic charges and Mulliken overlap populations indicate that the metal-citrate bonding is predominantly ionic, with very little covalent character. The covalent character decreases as the cation size increases. Bond valence calculations indicate that most cations are crowded, and that the crowding decreases as the cation size increases. Although most oxygen atoms coordinate to the metals, a few do not, and they tend to be the least-negative oxygens. Trends in the coordination are discussed. Both the citrate hydroxyl groups and water molecules tend to bridge two cations, and the carboxylate coordination is more varied. Molecular mechanics calculations demonstrate that the solid state energy differences are dominated by differences in van der Waals and electrostatic energy contributions. In the Li and Na salts, the citrate anion occurs predominantly in a higher-energy "kinked" conformation, rather than the extended lowest-energy conformation observed in salts of the larger cations. Detailed conformational analysis of the citrate anions (carried out in water rather than vacuum) enables quantification of the conformational energy costs in these solids. Hydrogen bonding is important to the stability of these salts. The Mulliken overlap population in the hydrogen bonds provides a quantitative measure of their strength, and permits identification of long (weak) interactions which are significant in some of these compounds. Some of the hydrogen bonds are very strong. Patterns in both the local environments of the hydrogen bonds and the more-extended features (graph sets) are noted. Polymorphs and sets of isostructural compounds permit more-detailed analysis of the structures and energetics in these compounds. The order of ionization of the three carboxylic acid groups is in general central/terminal/terminal, but there are two exceptions. While we have concentrated on salts containing a single alkali metal cation (and hydrogen), the structures of $NaK_2C_6H_5O_7$ and $NaKHC_6H_5O_7$ provide an exciting window on a larger universe of mixed salts.

CRYSTAL STRUCTURES OF LARGE-VOLUME COMMERCIAL PHARMACEUTICALS

James A. Kaduk,[1] Cyrus E. Crowder,[2] Kai Zhong,[2] Timothy G. Fawcett,[2] Amy A. Sarjeant,[3] and Matthew R. Suchomel[4]
[1]Illinois Institute of Technology, Chicago, Illinois
[2]ICDD, Newtown Square, Pennsylvania
[3]Northwestern University, Evanston, Illinois
[4]APS, Argonne National Laboratory, Argonne, Illinois

The crystal structures of a surprising number of the largest dollar volume commercial pharmaceuticals are unpublished. To provide high-quality reference data for the Powder Diffraction File™ database and to determine the crystal structures, synchrotron powder patterns have been collected on many materials at ambient conditions. The new crystal structures to be discussed include (at least): atomoxetine hydrochloride (Strattera™), dutasteride (Avodart™), fingolimod hydrochloride (Gilenya®), levalbuterol hydrochloride (Xopenex®), paliperidone (Invega), norgestimate (progestin, a component of Ortho Tri-Cyclen®), raltegravir potassium (Isentress™), rivastigmine hydrogen tartrate (Exelon®), sitagliptin dihydrogen phosphate monohydrate (Januvia®), ziprasidone hydrochloride monohydrate (Geodon®), and the beta polymorph of 17áestradiol (which turns out to be a hemihydrate). Density-functional geometry optimizations enable detailed analysis of the bonding in the solid state, particularly the hydrogen bonding. Powder patterns of these materials, as well as nine compounds for which the crystals structures have been reported and ten amorphous pharmaceuticals will be incorporated in the 2014 release of the Powder Diffraction File™.

ICDD PDF-4 PRODUCT DEVELOPMENTS FOR RELEASE 2014

J. Blanton, R. Vithayathil, K. Zhong, J. Faber, and C. Crowder
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The PDF 2014 product line will contain numerous improvements and several added capabilities for release in September. For the phase identification software SIeve/

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SIeve + , ICDD has significantly improved the search algorithms and options available to the user. When selecting phases in a search, the phase's peak intensities are now subtracted from the experiment peak intensities, producing "residual peak intensities" that are used for subsequent phase searches. These phase peak intensities are now automatically scaled as a set, using one of two user-selectable algorithms. Alternatively, the intensity scale for the identified phase can be manually adjusted by the user. Also, based on an identified phase, the user can now perform a 2-θ shift correction, transparency correction, or displacement correction to their experimental data when searching for additional phases. The precision of experimental intensities has been increased from zero decimal places to four decimal places, allowing for more accurate analysis of high intensity data such as that obtained at synchrotrons. Lastly, a dynamic pie chart is now displayed showing the estimated weight percent of accepted phases using I/I_c values.

Also for Release 2014, many developments have been made to improve the support for modulated structures, which are described using more than three-dimensional (3D) space. A Modulation Dimension search has been added, allowing for three additional dimensions to be searched. A Subsystem search has been added, allowing one subsystem (standard) or multiple subsystems (composite structure) to be searched. Additionally, the 3D structure display (Jmol) has been updated to dynamically display modulated structures. New 3D structure options have been added that allow the user to switch the modulation on/off, simulate the modulation by vibrating the 3D structure, and dynamically switch between subsystems.

Lastly, the neutron diffraction capabilities in the PDF-4 software have been dramatically enhanced for entries where ICDD has access to the atomic coordinates. Neutron diffraction specific strong lines, long lines, and I/I_c values can now searched as well as displayed on the PDF card. Also, diffraction patterns simulated using neutron diffraction now use Debye Scherrer geometry (used at virtually all neutron powder diffraction beamlines), along with new user-changeable "packing factor" and "sample can diameter" options. Additionally, SIeve+ has been updated to support phase identification for neutron powder diffraction experimental data using neutron diffraction intensities and I/I_c values. These are just some of the many value-added developments designed to make the ICDD PDF-4 products more functional and powerful for 2014.

SIC-BASED DILUTED MAGNETIC SEMICONDUCTOR

Bo Song
Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150080, China

SiC is an important wide-gap semiconductor with a band gap of 3.26 eV (6H-) at room temperature. Novel SiC-based DMS devices have been developed and gained considerable attention because of their excellent physical properties. For SiC-based diluted magnetic semiconductor, we have several important experimental results as follow:

(1) In ultralow Mn-doped 6H-SiC, it was found that the defects-related effects other than the Mn content play a more important role to determine the magnetic ordering.
(2) We synthesized Al-doped 4H-SiC, and magnetic properties measurement showed a typical glassy ferromagnetic (FM) feature. We propose a possible explanation for the origin of FM order: the coeffect of sp2/sp3 configuration along with the structural defects. Our work has exposed the exciting possibility of doping non-magnetic atoms to control the spin moments in wide-gap semiconductor.
(3) We study the defects and magnetism in 6H-SiC single crystals irradiated by varying doses of neutrons. VSiVC are found to dominate in defects in crystals after irradiations. Our results unambiguously verify that defects can induce magnetism. The localized nature of the defect sp states foster the formation of local moments, whereas the extended tails of the defect wave functions induce the long-range coupling between the moments caused by VSiVC. The results show the possibility of tuning the magnetization of SiC and other wide band gap (WBG) semiconductors through defect engineering.

STRUCTURAL CHARACTERIZATION OF PRAZIQUANTEL: A BROAD SPECTRUM ANTHELMINTIC

Robert Toro,[1] James Kaduk,[2] Miguel Delgado,[1] and Graciela Díaz de Delgado[1]
[1]Laboratorio de Cristalografía-LNDRX, Departamento de Química, Universidad de Los Andes, Mérida, Venezuela
[2]Department of Biological and Chemical Sciences, Illinois Institute of Technology, Chicago, Illinois

Praziquantel, PZQ, (*R*,*S*)-2-(cyclohexylcarbonyl)-1,2,3,6,7,11b-hexahydro-4*H*-pyrazino[2,1-*a*] isoquinolin-4-one, is a low-cost powerful anthelmintic with a broad activity spectrum, used to treat infections caused by several types of parasites in humans and animals. It is included in the Model List of Essential Medicines of The World Health Organization.

A search of the Cambridge Structural Database (CSD) V 5.35 (Allen, 2002) using the molecular diagram of PZQ resulted in several entries. One of them corresponds to the anhydrous racemic mixture (Refcode: TELCEU), one to the *S* isomer hemihydrate (Refcode: SIGBUG) and the other to the *R* isomer hemihydrate (Refcode: SIGBUG01). Additional entries contain the structural information of *co-crystals* and chemically substituted PZQ derivatives. The PDF-4/Organics contains two reports: an unindexed experimental pattern (PDF 00-055-1912) and a powder diffraction pattern (PDF 02-095-5302) calculated from the CSD entry for SIGBUG.

The diffraction pattern recorded at the Advanced Photon Source (ANL) for the raw material, provided by Laboratorios CAM, is different from the patterns contained in the PDF-4/Organics but similar to the pattern calculated using the crystallographic data from TELCEU. The indexing of this pattern was performed using DICVOL06, and produced a triclinic unit cell. The analysis of the data with NBS*AIDS83 led to a cell with ***a***

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= 10.4669(2) Å, b = 15.1401(3) Å, c = 22.9659(5) Å, α = 99.437(2)°, β = 98.496(2)°, γ = 108.333(2)°, and V = 3329.86 (9) Å^3 [M20 = 29.6, F30 = 342.7 (0.0016, 56)].

In an attempt to obtain polymorphic modifications of Praziquantel, crystallization experiments were carried out by slow evaporation using water, ethanol, methanol, 2-propanol, 1,2-ethanediol, and DMSO, among other solvents. After recrystallization of the raw material in a methanol/1,2- ethanediol solution, needles were obtained. A single-crystal structural study reveals that this compound crystallizes in space group P-1 with unit cell parameters a= 10.402(3) Å, b = 14.887(4) Å, c = 22.663(6) Å, α = 99.056(6)°, β = 98.501 (5)°, γ = 108.265(5)°, V = 3217.6(15) Å^3, and Z = 8 in agreement with the crystal data contained in TELCEU. The examination of crystals grown in methanol/ethylenediamine resulted in a cell, also triclinic, but with volume double the value of the cell obtained for the crystal prepared in the methanol/1,2-ethanediol solution. In this contribution, the results of these studies will be presented.

Acknowledgments

The authors thank M. Suchomel (Argonne National Laboratory). Use of the Advanced Photon Source at Argonne National Laboratory was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

EFFECT OF PREFERRED ORIENTATION ON SYNCHROTRON POWDER DIFFRACTION MEASUREMENT

Takashi Ida, Hideto Funahashi, and Hisashi Hibino
Advanced Ceramics Research Center, Nagoya Institute of Technology, Tajimi, Japan

It has been proposed that the effect of preferred orientation about platy or rod-like crystallites in powder specimens on observed diffraction intensities can be modeled by the March–Dollase pole (probability) density profile function[1]. However, it should be noted that the preferred orientation factor about diffraction intensity is equivalent to the pole density profile only in the case of symmetric reflection measurements for rotating flat specimens.

In this study, we have derived mathematical formulas and effective numerical algorithms to evaluate the preferred orientation factors about the March–Dollase model applied to capillary transmission and asymmetric reflection mode measurements, frequently used in synchrotron powder diffractometry, and examined the effect of application of an appropriate model.

A polycrystalline disc sample of NaCl was prepared by uniaxial press and heat treatment. Preferred orientation of {100}-directions normal to a flat face of the disc has been detected by incident angle (Ω) scans of diffraction peak intensities, and modeled as a two-phase mixture of components with preferred and random orientations. The integrated peak intensities of 28 peaks have been extracted from the powder diffraction intensity data measured in asymmetric reflection mode with a fixed incident angle. The R-factors of the diffraction intensities have been estimated at 21.3 and 2.8% for symmetric and asymmetric formulas about preferred orientation, respectively.

1. Dollase, W. A. (**1986**) J. Appl. Cryst. **19**, 267–272.

STREAMLINED PROCESSING FOR POWDER DIFFRACTION AND BIBLIOGRAPHIC MATERIAL

Nicole M. Ernst Boris, and Diane Sagnella
International Centre for Diffraction Data, Newtown Square, Pennsylvania

This poster shows some of the planned bibliographic and *Powder Diffraction* journal workflow updates. Beginning this past year we started receiving alerts every 2 weeks. Moving forward, part of the updated process will be to send these alerts, which come from a variety of databases, directly to our Writes database to contact the corresponding author. The alerts from Chemical Abstracts (CAPlus) will continue to be manually reviewed as they come in to get the best targeted results. We also plan on streamlining Rapid Communications submitted to *Powder Diffraction* for dual publishing consideration in both the journal and Powder Diffraction File (PDF™). This process will allow for both quicker editorial review and published results. Also covered is a brief review of 2013 bibliographic and journal efforts. In just this past year, over 9000 patterns (both experimental and calculated) were entered into our bibliographic (BIBS) database. In addition to the four regular issues of *Powder Diffraction*, two supplements were published. Two more supplements are planned to be published in Powder Diffraction this coming year, including the Australian X-ray Analytical Association proceedings.

NEW NEUTRON DIFFRACTION DATA CAPABILITY IN THE ICDD PDF-4+ 2014 RELATIONAL DATABASE

J. Faber,[1] C. Crowder,[2] J. Blanton,[2] S. Kabekkodu,[2] O. Gourdon,[2,*] T. Blanton,[2] and T. Fawcett[2]
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Neutron powder diffraction is a useful tool because elemental scattering contrast is quite different when compared to X-rays. Elements in the periodic table often have quite different scattering amplitudes (the scattering cross sections are not strictly proportional to atomic number, Z). Unlike the standard laboratory X-ray sources, neutrons are available both at nuclear reactors and pulsed sources. In this paper, we treat the constant wavelength (CW) neutron case. Synchrotron X-rays sources and neutrons have followed parallel development paths and focus on the use of major dedicated user facilities. These facilities are available world-wide. The PDF-4+ 2014 will have ~200 000 entries with atomic coordinates that can be used to

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calculate powder diffraction patterns. To effectively use calculated neutron powder diffraction patterns, we must accurately take into account the wavelength of the incident beam, the energy dependence of the sample absorption cross-section, the precise details of the cylindrical sample geometry (Debye-Scherrer with sample diameter and packing fraction), and the instrumental resolution function. In general, the CW neutron diffraction resolution is broader than for X-rays, and tends to be dominated by the source rather than the sample contributions.

In this study, we have calculated neutron scattering patterns for ~200 000 entries in the PDF-4+ 2014. We will show how these patterns are calculated. In particular for CW experiments, the sample absorption cross-section, the instrumental resolution, and the calculation of I/I_c are energy dependent and follow from the selection of incident neutron energy. We shall show how these quantities are treated. We have implemented search/match methods using Hanawalt, Fink and Long8 methods for phase identification and built dedicated tables in the PDF-4+ 2014 to accommodate these search/match methods. We shall discuss a number of examples where unique scattering contrast offers complementary data when compared with inhouse X-ray sources. Following the development of the PDF-4+ for X-rays, the goal of this project is to build an experimental collection of neutron scattering experimental data sets from the user community and to populate these data in the PDF-4+. This work will be extended to consider time-of-flight data from a pulsed neutron source.

ICDD GRANT-IN-AID PROGRAM

S. Wolkov, S. Kabekkodu, A. Gindhart, S. Gates, and T. Blanton
International Centre for Diffraction Data, Newtown Square, Pennsylvania

One of the ICDD's main objectives is to expand the range of material references by archiving or producing high-quality diffraction patterns. To further this effort, the ICDD supports a well-developed program of grants to researchers around the world to provide high-quality reference diffraction data. Each year the ICDD extends financial support to qualified investigators, in the form of Grants-in-Aid awarded on a competing proposal basis, for the preparation of reference X-ray powder diffraction data.

The duration of a Grant-in-Aid is 12 months with two grant cycles per year. Cycle I begins 1 April and Cycle II begins 1 October.

Benefits offered to grantees are:

- Financial support to aid current research
- Publication of pattern(s) in the Powder Diffraction File (PDF) if accepted by the Editorial
- Department
- Receive calibration standards
- Purchase certain products at reduced prices
- Web-based access to the list of compounds in the ICDD master database – includes
- published patterns as well as patterns still in the editorial process
- First-time grantees receive a complimentary 1-year subscription to *Powder Diffraction.*

To date, 28 000+ data entries have been added to the PDF™ as a result of the ICDD Grant-in-Aid program. In addition, a new targeted grant for pharmaceuticals was initiated in 2013 resulting in 30 new data entries to be published in the PDF in 2014.

INTRODUCTION TO THE MODULATED STRUCTURE SUBFILE IN THE POWDER DIFFRACTION FILE™ DATABASE

Diane E. Sagnella, Olivier Gourdon, Delphine Gout, and Soorya Kabekkodu
International Centre for Diffraction Data, Newtown Square, Pennsylvania

With the evolving capabilities of X-ray diffractometers in terms of X-ray sources, detector sensitivity, and new X-ray optics, peaks previously unseen are becoming more evident. However, trouble arises when these peaks cannot be indexed in three dimensions. Typically a user may fear an impurity has found its way into the sample. Those unidentified peaks may very well be satellite reflections to the main reflections of a *modulated* structure.

Modulated and composite crystals are fascinating and complex structures which violate the traditional idea that a perfect crystal structure must possess a three-dimensional periodicity. Generally considered aperiodic, these structures actually do obey rules of periodicity but their description requires four or more dimensions for this periodicity to become obvious. These modulations are a result of fluctuations in the position or occupation of the atoms that compose the crystal. The relevance of these structures goes beyond that of pure mathematical curiosity as many exhibit interesting ferroelectric, magnetic, superconducting, as well as other properties, which cannot be fully understood by looking solely at the average structure.

Looking to the future the ICDD has continued its effort to create the largest modulated structure database in the world with the addition of 178 new modulated entries to be released in 2014 for a total of 463 to appear in the next release of the PDF4+ 2014 database. This presentation will explain the work that has gone into creating this database and show how the user will benefit.

SUCCESSFUL IMPLEMENTATION OF NEW TARGETED MATERIALS FOR PDF-4/ORGANICS

E. Foster, A. Gindhart, A. Skalski, and M. Hammock
International Centre for Diffraction Data, Newtown Square, Pennsylvania

The ICDD finished its first production cycle for the implementation of new novel powder diffraction patterns, calculated from experimental single crystal structural data, into the PDF-4/Organics 2014 database. These patterns included, but were not limited to, materials that have pharmaceutical and/or bioactive characteristics. The patterns went through the same enhanced quality system that our other PDF™

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products go through. In total, 6854 entries were published, each having a known crystal structure and a calculated pattern. As we enter the next production cycle for the 2015 product, we are optimistic that over 8500 patterns will be added in the September 2015 release. These materials are coming from cutting edge publications and will include papers published as recently as February 2014. The overall coverage of novel materials continues to grow with each year's product and will continue to set a precedent for quality that our customers know and expect.

X-RAY DIFFRACTION CHARACTERIZATION OF POLYLACTIC ACID: PHASE IDENTIFICATION AND POWDER DIFFRACTION FILE™ REFERENCE PATTERN GENERATION

Tom Blanton, and Stacy Gates
International Centre for Diffraction Data, Newtown Square, Pennsylvania

Polylactic acid, PLA [polylactide, poly(2-hydroxypropionic acid)], is a biodegradable polymer finding application in many consumer products. Commercial non-solvent methods to manufacture PLA have evolved, using the fermentation of dextrose from corn to produce lactic acid leading to the production of PLA prepolymer. The low molecular weight oligomers are then converted to lactides that can be L- or D-isomers. Using a tin-organometallic catalyst, ring opening of the stereo lactides occurs resulting in polymerization that takes place in the melt state. Monitoring the amount of D-isomer in the final product is important in controlling PLA crystallinity. Typically when D-isomer levels are greater than 10%, PLA cannot be crystallized.

Commercially important polymer diffraction data continue to be added to the Powder Diffraction File (PDF). This study focused on X-ray diffraction (XRD) characterization of PLA materials and ICDD editorial evaluation of the diffraction data resulting in new entries that will be added to the PDF databases released in 2014. These data entries will be populated with the traditional d-spacing and intensity data along with the PD3 raw data patterns for amorphous and crystalline forms of PLA (Figure 5).

SUBFILE POPULATION IN 2014 PDF™ RELEASES

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The classification of entries into various subfiles is important to enhance the effectiveness of search/match for phase identification using the Powder Diffraction File™ (PDF). The use of subfiles becomes obvious when considering there are over 800 000 entries in the combined PDF-4+ and PDF-4/Organics databases. The identification and assignment of subfiles is accomplished in two ways: (i) manually, by the ICDD's editorial team and task group members, (ii) semi-automatically by a 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 2014 PDF releases.

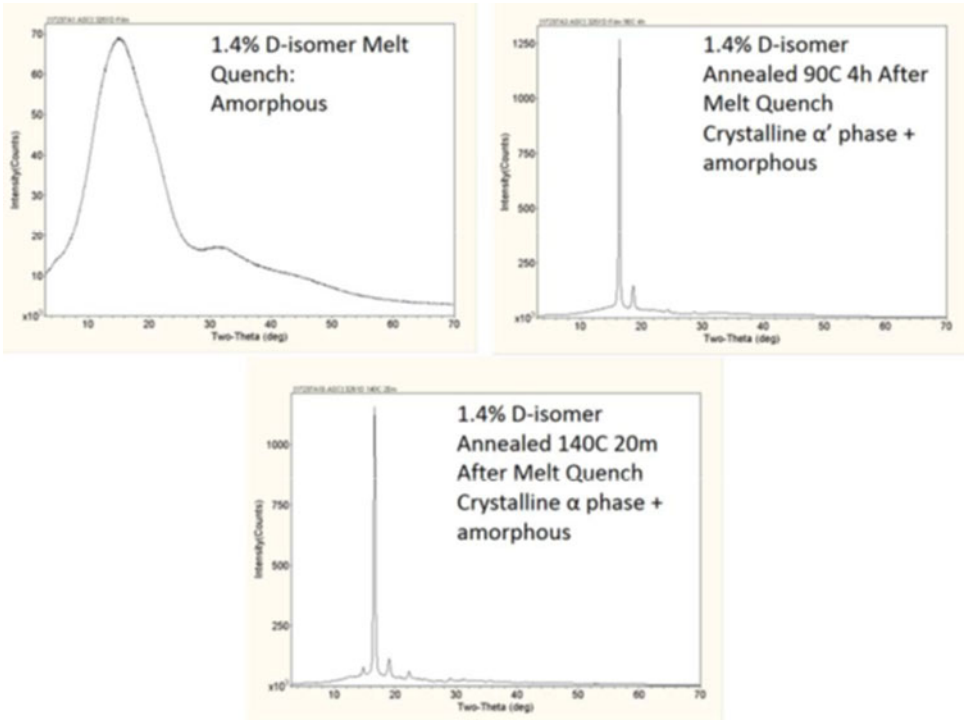


Figure 5. (Color online) PD3 raw data patterns for amorphous and crystalline forms of PLA.

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ENHANCEMENTS TO HISTORICAL ENTRIES IN THE PDF-4/ORGANICS DATABASE

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One of the key features of the Powder Diffraction File™ search/match options is the ability to search by common classes of materials or subfiles, which are vital to the continuing growth of the database. The Editorial team introduced seven new organic subfiles in the PDF-4/Organics 2010 release and since then has implemented the classification of Metal Organic Frameworks. In the PDF-4/Organics 2014 we have abstracted and implemented over 36 000 crystal structures to pre-existing entries, the majority of which are located in those specific subfiles. This integration of atomic coordinates allows the user to access features that are popular in PDF-4+, for instance, 3D visualization and bond angle /distance calculations as well as being able to use the coordinates for Rietveld refinements.

During the evolution of this project, we have found many entries where the patterns were not fully described for their disorder when we received them from Cambridge. Those entries are now being re-abstracted completely and published as part of the new calculated patterns project for the 2015 product. Not only are the patterns being enhanced by the addition of atomic coordinates, but they are also being improved. Some of these patterns currently published and described as "Blank" quality are now going to be replaced with a "Star" quality pattern. The PDF-4/Organics product continues to grow and evolve with each production year to keep up with the standards that the ICDD's customers know and expect.

THE TRADE NAME PROJECT: AN ADVANCEMENT IN PHARMACEUTICAL AND BIOACTIVE SUBFILES

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The Powder Diffraction File™ (PDF) PDF-4/Organics product consists of over 470 000 organic diffraction patterns. Not only do we focus on expanding the number of entries in the PDF-4 database, but we also place emphasis on insuring that the published data are up-to-date and comprehensive. Numerous compounds that exhibited promising bioactive and pharmaceutical properties at their time of discovery have undergone further testing in the scientific arena. Since their time of initial insertion in the PDF-4 product, our knowledge of various compounds has expanded. In response, the "Trade Name Project" was established to review this material and obtain any information that may improve the user's experience. The project's intention is to focus on compounds that are advancing or have already advanced through the stages of drug development. Over the past year, 9800+ bioactive and pharmaceutical entries have been reviewed for trade names. Trade name establishment, as well as other pertinent information such as CAS numbers, additional systematic and common names, and any new bioactivity findings has been recorded and updated. This information benefits the user and allows for more efficient data-mining searches with results that contain more complete and valuable material.

THE EXCIPIENT PROJECT: POPULATING THE EXCIPIENT SUBCLASS AND TARGETING NEW EXCIPIENETS FOR ACQUISITION OF POWDER DIFFRACTION DATA

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Currently, the Powder Diffraction File™ (PDF) contains diffraction data for a host of materials that are classified as excipients. Many of these entries have been defined as such by the US Pharmacopeia. ICDD specifies these USP classified materials in a distinct subclass; excipients (EXP). The excipient subclass is a subordinate group of the pharmaceutical subfile (PHR) because excipients are customarily encountered when performing pharmaceutical diffraction analyses and are commonly the highest concentrated ingredient. Pharmaceuticals often contain one or more of these excipients in various amounts that can add to the complexity of powder diffraction patterns. Often times the presence of excipients can make it difficult for one to identify the API without first identifying the excipients, with the excipient customarily having the dominant contribution in the diffraction pattern. The goal of this project is to: (i) assign appropriate materials currently present in the database to the excipients subclass and, (ii) acquire new excipients from literature, data contributions, or future targeted diffraction experiments.

ICDD – CORRELATING SOCIAL MEDIA POSTS TO WEB TRAFFIC

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The ICDD.COM website strives to meet the information and communication needs of ICDD members, customers, scholars, professionals, grant-in-aid participants, developers, and students. Twenty-one months ago, the ICDD embraced social media networks – creating and nurturing Facebook, Twitter, LinkedIn, and Google+ profiles. Our goal is to engage people who might not seek out information on icdd.com regularly. This presentation will describe ICDD's social media evolution and how social media posts translate to ICDD web traffic.

INCREASING THE COVERAGE OF THE TOP 200 BRAND NAME PHARMACEUTICAL DRUGS IN THE POWDER DIFFRACTION FILE

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After reviewing the top 200 brand name drugs by 2011 US sales[1], we surprisingly found a large number of important pharmaceuticals containing small molecule active pharmaceutical ingredients (APIs) with unpublished structures. In order to increase the coverage of these pharmaceuticals in the Powder Diffraction File (PDF), diffraction patterns of 44 commercial APIs were collected with synchrotron radiation on beamline BM-11 at the Advanced Photon Source, Argonne National Laboratory. At this time, eleven new crystal structures have been solved, and X-ray powder patterns were collected for ten amorphous APIs. Nine additional powder patterns will be published for previously known crystal structures, and the analysis for the last 14 powder patterns is in process. Thirty of these patterns will be incorporated in the 2014 release of the PDF. Our next goal is to extend the database coverage to the top 200 pharmaceutical drugs in 2012 by both US sales and prescriptions[2], from which 30 APIs with unknown structure have been targeted.

1. http://www.pharmacytimes.com/publications/issue/2012/July2012/Top-200-Drugs-of-2011
2. http://www.pharmacytimes.com/publications/issue/2013/July2013/Top-200-Drugs-of-2012

STABILIZATION OF NITRO-AROMATICS

Jeffrey R. Deschamps

For a variety of reasons, including US Federal law and improved safety, it is desirable to have insensitive munitions (IM). Although a variety of methods are available to reduce the sensitivity of munitions only changes to the high explosive (HE) itself result in increased safety during storage, transportation, handling, and deployment. IM are almost always filled with fire resistant, shock resistant insensitive HE such as triaminotrinitrobenzene (TATB). The high cost of TATB has limited its use. In this study, we examine 28 nitro-aromatics, including TATB and three previously unpublished structures, in the solid state in order to identify forces that stabilize the HE. We show that by summing the energies involved in van der Waals forces, hydrogen bonds, and other intermolecular interactions there is a direct relationship between the estimated energy of stabilization and the sensitivity of nitro-aromatic explosives.

THE IMPROBABLE COMPLETE *AB INITIO* STRUCTURE SOLUTION OF SYNTHETIC DASHKOVAITE $MG(HCOO)_2.2H_2O$ FROM LABORATORY CU$K\alpha1$–$K\alpha2$ X-RAY POWDER DIFFRACTION DATA

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Our initial goal was to synthesize an Mg-based MOF compound α-$[Mg_3(O_2CH)_6]$, already obtained, studied and published by Rood, Noll, and Henderson (Inorg. Chem., 2006, **45**, 5521). In spite of measured 1H-NMR spectra gathered on our sample (synthesized at PUCP, Lima) and compliant with the targeted compound, a preliminary X-ray powder diffraction pattern collected with our Bruker D8 Advance X-ray powder diffractometer (UOI, Ioannina) using Cu ($K\alpha_1 + K\alpha_2$) radiation was found incompatible with the above-mentioned published unit cell from Rood *et al.*

Our first dataset was tentatively indexed using both N-TREOR and DICVOL, with high factors of merits F(n) and M(n). It was found to be compatible with the prevalent space group no. 14 [$P21/c$]. A double search based on the unit cell and the expected elements (Mg, C, and O) through the UK CCDC CSD [Cambridge Crystallographic Database] pointed toward a candidate compound $Mg(O_2CH)2.2H_2O$, aka synthetic dashkovaite. The related crystal structure has been known from single-crystal diffraction from the work by Osaki, Nakai, and Watanabe since 1964 (J. Phys. Soc. Japan, **19**, 717). An excellent GSAS-based Rietveld fit was obtained using the atomic positions from this latter work, now making it very likely that the compound synthetized in Lima was indeed synthetic dashkovaite rather than the initially desired MOF material.

In order to prove this beyond doubt, we remeasured our sample down to atomic resolution [$d = 1$ Å; $2\theta max = 101°$] in place of our previous [$d = 1.6$ Å; $2\theta max = 57°$] conditions and then managed to solve the crystal structure *ab initio* using Direct Methods as implemented in EXPO2011 and EXPO2013. Whereas finding the correct structure solution remains a rare and random event with EXPO2011, the latter solution is ALWAYS found in LESS THAN A MINUTE using EXPO2013. We attribute this fact to the improved implementation of the Resolution Bias Modification (RBM) devised by Giacovazzo *et al* (J. Appl. Cryst., 2013, **46**, 1231). The effectiveness of the structure solution process using EXPO2013 will be demonstrated LIVE during our poster presentation.

Acknowledgments

The Authors wish to thank Professor Carmelo Giacovazzo (University of Bari) for kindly providing them with the EXPO 2011 & 2013 packages. They are also hugely indebted to Professor Daniel Louër for key suggestions regarding their experimental setup, and to Burkhard Annighofer (CEA-Saclay) for helping them to implement the latter on the UOI X-ray diffractometer. Lastly, PUCP funding through Proyecto DGI 2013-0016 is gratefully acknowledged.

THE ELUSIVE CASE OF COPPER(II) OXALATE HYDRATE, $CUC_2O_4{\cdot}nH + O$: *AB INITIO* STRUCTURE SOLUTION FROM NEUTRON AND X-RAY POWDER DIFFRACTION STUDIES

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The current understanding of the crystal structure of Cu (II) oxalate, $CuC_2O_4{\cdot}nH_2O$, is based on the now 40-year-old work by H. Fichtner-Schmittler [Cryst. Res. Technol., 1984, **19**, 1225; Mber. Dt. Akad. Wiss. Berlin, 1968, **10**, 581], complemented by EXAFS measurements by Michalowicz & Fourme [Acta Cryst. A, 1981, **37**, C-307]. Owing to the great difficulty of growing single crystals of this material, its crystal structure remains an open problem. As of today, this structure is described as disordered, centrosymmetric and monoclinic $P21/c$. But is it?

In order to shed more light on this issue, a few cc of a Cu (II) oxalate powder sample were synthesized at the University of West Florida and subjected to: (a) neutron diffraction at the CEA-Saclay Orphée reactor [$\lambda = 2.4266$ Å], (b) laboratory X-ray powder diffraction on a Bruker D8 Advance diffractometer [Cu($K\alpha_1 + K\alpha_2$)] at UOI, and (c) synchrotron radiation at the 11-BM beamline of the APS/ANL [$\lambda = 0.413\,732$ Å]. **No single dataset** allowed us to index our diffractograms but using **each single one individually** allowed us to solve the crystal structure of our sample *ab initio* using simulated annealing as implemented in the FOX package of Favre-Nicolin and Cerny [J. Appl. Cryst., 2002, **35**, 734] using the non-centrosymmetric space group *Pn* and the unit cell published by Fichtner–Schmittler in 1984, resulting in an ordered structure, fully compliant with the geometric arrangement described in Figure 3 of the paper.

Specifically, a DFT model for the oxalate ion C_2O4^{2-} was first obtained. Next, rigid and planar Cu–C_2O_4–Cu blocks were introduced at random positions in the unit cell which were optimized using the tempered parallel algorithm in FOX. Lastly, the compatibility of the neutron and the laboratory X-ray data were checked through a joint X–N GSAS-based Rietveld refinement, yielding a final global $R_p = 0.043$.

Our initial reasons for using neutron diffraction were, firstly, to estimate the H_2O content (i.e., the value of n in the title formula) and, secondly, to check for low-temperature antiferromagnetic ordering, which we did not observe down to $T = 1.7$ K. In retrospect, however, while our work may not provide the final structural answer for the case at hand, it does raise the following points: (a) Why choose a disordered centrosymmetric crystal structure when a perfectly ordered acentric one does the job? (b) On the basis of diffraction data alone, should the centric solution be preferred? (c) Would it not be pertinent to deposit some complementary evidence together with the diffraction data (e.g., EXAFS data) to back the claim of a disordered structure?

The authors wish to thank Burkhard Annighofer (CEA-Saclay) for crucial help with preparation of the sample used for neutron diffraction. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the US Department of Energy, under Contract no. DE-AC02-06CH11357.

Acknowledgments

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SYNTHESIS OF MONOCLINIC HYDROXYAPATITE AND STRUCTURAL CHARACTERIZATION BY SYNCHROTRON RADIATION

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Monoclinic hydroxyapatite, with $P21/b$ symmetry was obtained by mechanical milling of a stoichiometric mixture of $CaCO_3$ and $(NH_4)_2HPO_4$ followed by a thermal treatment at 850 °C for 24 h.

The powder diffraction data of the obtained sample and LaB_6 (as reference standard) were measured using the X-ray source located at the Stanford Synchrotron Radiation Laboratory (SSRL). A Si (111)-based detector was used on the powder diffractometer which receive the incident radiation from the beam line 2-1 with 12 keV. The wavelength used was $1.033\,49 \pm 0.000\,07$ Å which was obtained calibrating with the reference standard over a full range of scattering angle 2θ from 5 to 70°.

The X-ray diffractogram obtained shows some characteristic peaks that only could be indexed considering a monoclinic symmetry. That is the case of the monoclinic 031 Bragg reflection, which appears as a single peak at $2\theta \approx 13.9°$. Other reflections that appear as single peak in the hexagonal symmetry show a structure corresponding to a set of overlapping reflections around the Bragg angle for monoclinic symmetry. Overlapping effect at $2\theta \approx 27.8°$, 39.2°, 49.38°, and 49.48° are exhibited around the positions indexed as 131, 420, 414, and 153 in the hexagonal system and the overlapping peaks can be indexed using the cell parameters reported for the monoclinic hydroxyapatite (ICSD 50656). Calcium oxide was identified and refined as secondary phase.

THE BLACK POLYMORPH OF TTF–CA: TTF POLYMORPHISM AND SOLVENT EFFECTS IN MECHANOCHEMICAL AND VAPOR DIGESTION SYNTHESES, CRYSTAL STRUCTURE FROM POWDERS, AND PROPERTIES

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Tetrathiafulvalene–chloranil (TTF–CA) was synthesized by two methods, liquid-assisted grinding (LAG) and vapor digestion (VD), which largely reduce the use of reaction solvents. The effects of the small quantities of LAG solvent and solvent vapors in VD toward the formation of a particular TTF–CA product polymorph were studied from both TTF forms (orange and brown) as reactants. It was concluded that a high-solvent polarity index favors the formation of the ionic black polymorph of TTF–CA vs. the quasi-neutral green form, whereas the crystal structure and crystal habit of the orange TTF polymorph also favor the formation of the black TTF–CA, which occurs using smaller volumes of the polar solvents. The latter effect is likely owing to similarities in the TTF packing motifs, in particular the presence of TTF columns available for reaction in the exposed faces of the orange TTF crystallites.

The crystal structure of the black TTF–CA was determined from synchrotron X-ray powder diffraction and it consists of dimerized $TTF^{+\bullet}$ and $CA^{-\bullet}$ radical ions, in agreement with room temperature magnetic susceptibility measurements indicating the material is diamagnetic. FTIR showed that the compound has a small band gap of ~0.198 eV and it remains ionic at lower temperatures.

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