

MS.40.4*Acta Cryst.* (2008). A64, C75**Perovskites ABX₃ under pressure: Transition to post-perovskite CaIrO₃ type and other scenarios**

Maxim Avdeev, Sergey Yakovlev

Australian Nuclear Science and Technology Organisation, Bragg Institute, PMB 1, Menai, NSW, 2234, Australia, E-mail: max@ansto.gov.au

Recently we have performed a systematic quantitative analysis of crystal structure distortion for ~1300 ABX₃ perovskites in terms of A- to B-site polyhedra volume ratios VA/VB [1]. The analysis identified a number of compositions close to the boundary of perovskite type stability which we have studied experimentally by in situ high-pressure synchrotron X-ray powder diffraction. Here we will present the results of these experiments for several materials studied under pressure for the first time and will discuss our theoretical and experimental findings focusing on the following aspects of perovskite (pv) and post-perovskite CaIrO₃ (ppv) structure types: (1) interplay between geometry and symmetry in distorted perovskites (is there any intermediate phase between pv and ppv?); (2) topological and geometrical constraints for ABX₃ stoichiometry (what might be the structure of hypothetical structure types denser than ppv?); and (3) the effect of vacancies in ABX₃ and pressure-induced amorphization as an alternative to pv-ppv transition.

[1] M. Avdeev, E. Caspi, S. Yakovlev, *Acta Cryst B* 63 (2007) 363.

Keywords: perovskites, phase transitions and structure, amorphization under pressure

MS.40.5*Acta Cryst.* (2008). A64, C75**Ab-initio crystallography of kaolin minerals: Synthesis, diagenesis and mantle pressures**

Patrick H.J. Mercier, Yvon Le Page

National Research Council Canada, Institute for Chemical Process and Environmental Technology, 1200 Montreal Road, Building M-12, Ottawa, Ontario, K1A 0R6, Canada, E-mail: patrick.mercier@nrc-cnrc.gc.ca

In this abundantly illustrated talk, we deduce ab initio the stable kaolin phases and explain nearly all observations about the kaolin system, starting from just ideal topology of kaolin layers Al₂Si₂O₅(OH)₄ and basic scheme for interlayer H bonds [*Acta Cryst.* B64 (2008)]. Energy independence of non-neighbour layers leads to a complete list of 36 possible lowest-energy polytype models. VASP optimization of ideal cells and coordinates gives total energies. The four known kaolin minerals, including experimental distortions, are among the 36 optimized models created from ideal geometry. Using ab initio energies and cell volumes, we build a 0K enthalpy/pressure graph. We read off this graph that kaolinite and dickite are lowest-energy solutions, whereas nacrite and HP-dickite are lowest-enthalpy solutions at moderate pressure (P). Minor temperature (T) dependence of this novel calculated 0K graph would explain current facts about synthesis and diagenesis of kaolin minerals. Kaolinite is the stable phase at ambient T and P < 1GPa. HP-dickite is the stable phase that forms at P > 2GPa for T > 300K but transforms reversibly to dickite at ambient conditions. Nacrite forms over a narrow stability domain wedged between kaolinite and HP-dickite at T-P combinations not found with normal geothermal gradients. Mineralogical reports about mutual transformation of kaolinite, dickite and nacrite all involve dissolution and recrystallization, a necessity for polytypes with different layer-to-layer rotations. Ab initio compression to 60GPa of 19 polytype models involving no layer-to-layer rotations shows that kaolinite survives up to

~12GPa. Beyond that pressure, novel kaolin polytypes with different H-bonding not possible at ambient conditions become prime candidates for post-kaolinite phases.

Keywords: *ab-initio* calculations, polytypism, mineralogy and crystallography

MS.41.1*Acta Cryst.* (2008). A64, C75**Solving zeolite structures using electron crystallography**Chris J Gilmore¹, Chris J Gilmore¹, Douglas L Dorset², Wei Dong¹

¹University of Glasgow, Chemistry, Joseph Black Building, Glasgow, Scotland, G12 8QQ, UK, ²Advanced Characterization, ExxonMobil Research and Engineering Co., 1545 Route 22 East, Annandale, New Jersey 08801, USA, E-mail: chris@chem.gla.ac.uk

Zeolite structures can be very challenging to solve, particularly in early stages of synthesis and characterisation when the samples are poorly crystallised. The crystallite sizes are often so small that peak broadening makes the powder patterns hard to deconvolute, and often they become nm sized so that only electron diffraction can be used to solve them, and this technique presents its own challenge with problems associated with dynamical scattering, sample bending, multiple scattering, the missing cone problem etc. Recently we have applied techniques that use density building functions and density histogram matching methods coupled with entropy maximisation and likelihood analysis to solve a number of structures ab initio using both electron diffraction data in 2- and 3-dimensions most of which were collected using the precession method.

1. A low resolution structure is generated using low resolution structure factors combined with the origin defining rules of direct methods [2].

2. New reflections are given permuted phase angles and analysed using density building functions [3] or density building functions are used to improve the resolution of the low resolution maps.

3. Phase sets are selected according to density criteria and subjected to entropy maximisation [4].

4. Likelihood and density histograms are used to select the optimal phase set from these.

The method is quick, and largely automatic.

1. Dorset, D.L., Dong, W. & Gilmore, C.J. *Acta Cryst.* (2008). A64, 284-294; 295-302.

2. Rogers, D. (1980) *Theory and Practice of Direct Methods in Crystallography* edited by M.F.C. Ladd & R.A. Palmer pp. 23-92. New York: Plenum Press.

3. Gilmore, C.J., Bricogne, G & Bannister, C. (1990). *Acta Cryst.* A46, 297-308.

4. Bricogne, G & Gilmore, C.J. (1990). *Acta Cryst.* A46, 284-297.

Keywords: electron crystallography, zeolites, precession method

MS.41.2*Acta Cryst.* (2008). A64, C75-76**Prospects for structure solution by electron diffraction of three-dimensional protein crystals**Jan Pieter Abrahams¹, Dilyana Georgieva¹, Linhua Jiang¹, Henny W Zandbergen²

¹Leiden University, Biophysical Structure Chemistry, Institute of Chemistry, Einsteinweg 55, Leiden, South Holland, The Netherlands, 2333 CC, Other country, ²Kavli Institute of Nanoscience Delft, Delft

University, Lorentzweg 1 2628CJ Delft, E-mail : abrahams@chem.leidenuniv.nl

The ultimate limit in resolution of protein crystal structures is determined by beam damage. Since electrons are about three orders of magnitude less damaging to biological materials than X-rays, we intend developing electron crystallography as an alternative to X-ray crystallography. Here, we discuss our progress in this endeavour:

Electron diffraction up to 0.2 nm resolution could be observed from 3D protein nano-crystals (up to 200 nm in size) and up to 0.1 nm for pharmaceutical nano-crystals;

By precessing the electron beam, a substantial fraction of spots could be made to fully pass the Ewald sphere, increasing the number of fully recorded reflections, whilst simultaneously reducing the effect of dynamical scattering;

By computer analysis of the spacings of randomly oriented diffraction patterns, we could determine the unit cells;

In favourable crystal settings, we could index the diffraction patterns; we are making progress in indexing all random diffraction patterns.

We anticipate that these steps will ultimately allow us to integrate the observed, indexed reflections, opening the way to full structure determination by cryo-electron diffraction.

Keywords: electron diffraction, structural biology, nanocrystallography

MS.41.3

Acta Cryst. (2008). A64, C76

Symmetry determinations from electron precession: Comparison and advantages with CBED

Jean-Paul Morniroli

Laboratoire de Metallurgie Physique et Genie des Materiaux, UMR CNRS 8517, USTL and ENSCL, Bat. C6, Cite Scientifique, Villeneuve d'Ascq, Nord, 59655, France, E-mail: Jean-Paul.Morniroli@univ-lille1.fr

The electron precession technique displays some interesting features connected with the crystal symmetry:

The integrated intensities of the diffracted beams present on electron precession patterns can be used to identify the "ideal" symmetry of the pattern, i.e. the symmetry which takes into account both the position and the intensity. It is shown that this "ideal" symmetry is connected with the Laue class;

The precession patterns exhibit a two-beam behaviour especially at large precession angle meaning that multiple diffractions are strongly reduced. This property can be used to identify the kinematical forbidden reflections due to screw axes and glide planes. It can also be used to detect reflections which exhibit weak differences of intensity. These reflections are very useful when dealing with the study of crystal displaying small symmetry departures;

The patterns display a large number of reflections in the Zero-Order Laue Zone (ZOLZ) but also in the High-order Laue Zone (HOLZ) whose observation allows an easy and sure identification of the shifts and periodicity differences of the reflections located in the HOLZ with respect to the ones located in the ZOLZ. These features are connected with the Bravais lattice and with the glide planes, respectively. A few possible space groups can be identified from all these observations. CBED and LACBED are also valuable techniques to deduce the point and space groups but the experiments are more difficult to perform since they require a perfect alignment of the zone axis and an adapted crystal thickness.

Keywords: electron diffraction, forbidden reflections, crystal symmetry

MS.41.4

Acta Cryst. (2008). A64, C76

Quantitative 3D electron diffraction data by precession and electron rotation methods

Sven Hovmöller, Peter Oleynikov, Junliang Sun, Daliang Zhang, Xiaodong Zou

Stockholm University, Structural Chemistry, Svante Arrhenius Väg 14, Stockholm, Stockholm, 106 91, Sweden, E-mail: svenh@struc.su.se

We present a quantitative investigation of data quality using electron precession, compared to standard selected area electron diffraction (SAED), and present the new Electron Rotation Method for collecting 3D electron diffraction data. The SAED pattern of $K_2ONb_{14}O_{35}$ (projection symmetry $4mm$, $a = 27.5\text{\AA}$) (left) in the Figure goes to 1.10 Å resolution ($h = 25$), while the $hk0$ precession pattern (right) goes to 0.76 Å resolution ($h = 36$). The total number of unique reflections is doubled for precession compared to SAED. Precession patterns were obtained with SpinningStar from NanoMEGAS on a JEOL 2000CX TEM with a 16-bit CCD-camera and quantified by ELD from Calidris. Rmerge = 5%. The structure was solved by Sir97, both from SAED and from precession data, and refined with SHELX. Metal atom positions were refined; R-value 19% for precession and 28% for SAED. Niobium atoms were on average within 0.04 Å from those obtained by X-ray diffraction for the isomorphous $Tl_2ONb_{14}O_{35}$. We are trying to localize the oxygen atoms. Reference: Oleynikov, P. Hovmoeller, S. and Zou, X.D. Precession electron diffraction: observed and calculated intensities. Ultramicroscopy 107 (2007), 523-533

Keywords: electron diffraction, precession, quantification

MS.41.5

Acta Cryst. (2008). A64, C76-77

Models for simplified treatment of precession electron diffraction

Wharton Sinkler¹, Christopher S Own², James Ciston³, Laurence D Marks³

¹UOP LLC, Corporate Research, 200 E. Algonquin Rd., Des Plaines, IL, 60017-5017, USA, ²Nion Co., Kirkland WA, USA, ³Northwestern University, Dept. of Materials Science and Engineering, Evanston, IL USA, E-mail: wharton.sinkler@uop.com

Precession electron diffraction (PED) is an experimental approach to reducing the severity of dynamical effects in electron diffraction [1]. In PED, the incident beam is tilted along a cone about the zone axis; intensities from all orientations in the cone are integrated. This reduces the number of simultaneously excited beams as well as averaging over many orientations. It will be shown that PED reduces the complexity of the intensities vs. thickness $\{I(g,t)\}$, in a statistical sense using principal component analysis. Specifically, the number of parameters necessary to describe all variation within the set $\{I(g,t)\}$ for a given zone axis is reduced with respect to a direct zone axis orientation. However, this reduction of complexity does not extend to an ability to accurately describe PED $I(g,t)$'s using accessible parameters such as spatial frequency $|g|$ and structure factor amplitude (as in e.g. kinematical or 2-beam models)[2]. Thus, it is necessary to include at least some details of the interactions among simultaneously excited beams in order to develop anything beyond a fairly crude approximation of PED. This explains the limitations of 2-beam and Blackman models [2,3]. The development of more sophisticated models will be discussed. It will be shown that PED intensities are relatively insensitive to structure factor phases. The phase-insensitivity may provide a basis for close approximation