

MS.03.4*Acta Cryst.* (2008). A64, C19**Closing the gap between single crystal and powder diffraction**Henning O Sorensen¹, Soren Schmidt¹, Jonathan Wright², Per Christian Hansen³, Henning F Poulsen¹¹Riso National Laboratory for Sustainable Energy, Technical University of Denmark, Materials Research Department, Frederiksborgvej 399, P.O. 49, Roskilde, Roskilde, 4000, Denmark, ²ESRF, 6, Rue Jules Horowitz, B.P. 220, 38043 Grenoble CEDEX, France, ³Department of Informatics and Mathematical Modelling, Technical University of Denmark, Building 321, DK-2800 Lyngby, Denmark, E-mail: henning.sorensen@risoe.dk

One of the major challenges in single crystal structure determination is to obtain crystals of suitable quality and size. If no suitable crystallization conditions one often turns to powder diffraction. Powder diffraction is unfortunately limited in the molecular complexity (unit cell size), which can be solved *ab initio* and the accuracy of the refined molecular parameters. To fill the gap between single-crystal and powder diffraction, we have been developing an alternative method. The method is based on employing hard and highly focussed X-rays illuminating a polycrystalline sample with grain sizes down to 1-10 microns. From this polycrystal X-ray data set reflections are sorted into sets each associated with a certain grain in the sample [1,2]. Hence, one obtains a series of single crystal data sets. One of the difficulties apart from determining the unit cell parameters and the grain orientations is to extract integrated intensities as the spot overlap grows with the number of grains in the X-ray beam. We have adapted a new approach for extraction of the intensity of the overlapped reflections as well as integration of weak reflection by fitting the intensity using an intensity profile. The approach is to reconstruct the orientation distribution function (ODF) on a grid using the strong non-overlapped reflections and from this the profile any reflection can be calculated. The algorithms for reconstructing the ODF and calculation of the reflection profiles are presented together with results obtained.

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Keywords: data analysis, computer algorithm development, data collection on non-routine samples

MS.03.5*Acta Cryst.* (2008). A64, C19**Advances in methods and algorithms in EXPO2008**Carmelo Giacobazzo, Angela Altomare, Gaetano Campi, Corrado Cuocci, Anna Grazia Moliterni, Rosanna Rizzi
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The program EXPO2008 is able to face all the steps necessary for crystal structure solution from powder data: a) diffraction pattern indexing; b) space group determinations; c) phasing process; d) crystal structure refinement by least squares- Rietveld refinement. Recent advances in the program concern:

- the indexing. The program N-Treor (1) has been updated to perform a more exhaustive search of the correct unit cell;
- the space group determination. This step has been improved by integrating probabilistic techniques (2) with a more (automatic) careful analysis of the diffraction pattern;
- the phasing process. For organic structures Direct Methods usually leads to electron density maps which do not provide useful molecular

fragments. That is partly due to the inaccuracy of the diffraction magnitudes caused by the peak overlapping, and partly to the limited data resolution. A recent mathematical approach (3) showed how to minimize the resolution effects in any electron density map. The approach has been implemented into an EXPO2008 routine which combines it with an automatic least squares procedure and proved to be able to solve organic structures *ab initio* with data resolution up to 1.53Å. A further tool available for the EXPO2008 users is a simulated annealing procedure which allows the crystal structure solution when the geometry of the fragments which constitute the molecule is *a priori* known.

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Keywords: structure determination, computing, powder crystallography

MS.04.1*Acta Cryst.* (2008). A64, C19**Supercritical hydrothermal synthesis of organic inorganic hybrid nanoparticles**

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We propose a new method to synthesize organic-inorganic hybrid nanoparticles at supercritical hydrothermal conditions. By introducing organic legands (aminoacids, carboxylic acids, amines, alcohols, aldehydes etc.) into supercritical hydrothermal synthesis atmosphere, organic-inorganic hybrid nanocrystals are synthesized. This is due to the homogeneous phase formation for the organic substance and metal salt aqueous solutions at supercritical conditions. Particle size is in the range from 2.5 nm to 10 nm, and particle size dispersion is extremely narrow. Crystal shape can be controlled to be sphere, nano-cube, nano-ribbon etc. By selecting a proper modifier, particles can be dispersed perfectly in organic solvents or in aqueous solutions. By drying the colloidal solution, self-assembly structure of nanocrystals can be obtained. This implies a variety of applications of the nanoparticles including nanohybrid polymers, nano-ink, nano-paints, and bio-imaging probe.

Keywords: supercritical fluids, nanoparticles, hydrides

MS.04.2*Acta Cryst.* (2008). A64, C19-20**Acidic ammonothermal growth of bulk GaN crystals**

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The crystal growth of hexagonal GaN (h-GaN) is currently a hot topic in spite of high demand for free-standing, lattice-matched wafers for the GaN device technology [1]. Among the other GaN growth techniques, the ammonothermal growth of GaN is very promising for future mass-production and basically is derived from the successful

hydrothermal growth of trigonal SiO₂ and hexagonal ZnO. We are employing a solution of supercritical ammonia and acidic mineralizer at T = 450-550°C and p = 90-150 MPa to improve the solubility of GaN [2]. The temperature effects of the ammonium halogenides NH₄X (X = Cl, Br, I) as mineralizer on the phase stability of GaN synthesized under supercritical ammonothermal conditions is discussed [3]. The tendency to form cubic GaN (c-GaN) increases from X = Cl to I. Decreasing the temperature supports the formation of c-GaN. Single-phase h-GaN can be grown from X = Cl, Br at 550 °C. The solubility of h-GaN is shown in detail. The use of h-GaN substrate has a phase-stabilizing effect and lowers the temperature range for overgrown ammonothermal h-GaN crystal. High-quality nucleation is detrimental to the growth of GaN. Recent results from luminescence on ammonothermal GaN reveal comparable optical quality to high-quality GaN fabricated by currently-standard hydride vapor phase epitaxy (HVPE). The use of GaN fabricated by the acidic ammonothermal growth as substrate material for the successive growth of GaN device structure is shown.

References

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Keywords: gallium nitride, semiconductive A3B5 compounds, solution crystallization

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Vapor-phase hydrothermal preparation of titanate fibers and nanotubes

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Most of hydrothermal syntheses have been performed for many years in solution phases at high temperatures and high pressures. A hydrothermal system in an autoclave, however, is ordinarily comprised of a vapor phase and a solution phase as well as hydrothermal products. In the present study, we focused our research on synthesis and morphology control of fibers and nanotube arrays of titanate compounds in the vapor phases under hydrothermal conditions. In the first place, it was found that some of those crystalline phases which are unstable in the solution phases can be synthesized exclusively in the vapor phases and that some crystalline phases grown in the vapor phases assume morphologies different from those obtainable in the solution phases. K₂Ti₆O₁₃ and H₂Ti₃O₇ fibers with unprecedentedly high aspect ratios (> 100) were successfully obtained so far in the vapor phases of KOH and NaOH aqueous solutions, respectively. Secondly, vapor-phase hydrothermal treatment was found to be very effective to convert amorphous TiO₂ nanotube into highly crystalline anatase phase. Vertically oriented TiO₂ nanotube-arrayed thin films were fabricated first by potentiostatic anodization of titanium metal plates at 10-20 V in 0.3-0.5% HF aqueous solutions at room temperature. With an increase in the applied voltage from 10 to 20 V, the inner diameter of the nanotube increased from 30 to 70 nm and the wall thickness increased from 12 to 17 nm. The nanotube could be grown up to ca. 600 nm in length. All the as-prepared TiO₂ nanotubes were confirmed to be amorphous. However, the amorphous TiO₂ nanotubes were confirmed to be converted into anatase phase in hydrothermal vapor water at 150-200 degree C.

Keywords: hydrothermal method, titanates, nanostructures

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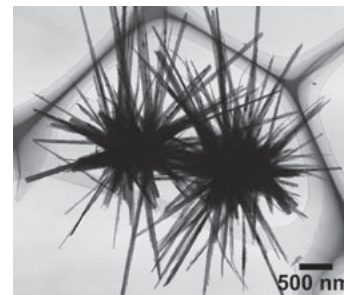
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Selective synthesis of nano-crystalline TiO₂ polymorphs from new water-soluble titanium complexes

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Currently, solution synthesis of titanium containing oxides has to rely on flammable organic solvents or highly acidic and toxic precursors because all soluble titanium compounds are easily hydrolysable in water. We developed variety of stable titanium complexes, which can be used as environmentally benign precursors for solution based synthesis of titanium containing materials. In these new compounds natural and inexpensive hydroxy-carboxylic acids such as citric, lactic or glycolic acid act as ligands to form stable species. Such compounds are stable against hydrolysis and use of water as a solvent makes them attractive for hydrothermal synthesis of nanocrystalline TiO₂. Anatase, rutile, TiO₂(B) and brookite were prepared in a very selective and reproducible way. A simple hydrothermal process was developed for synthesis of TiO₂(B) and brookite as single phase nano-crystals for the first time and their photo-catalytic properties were studied. The choice of synthesis conditions allowed controlling the direction of crystal growth. Thus, nanowhiskers of rutile were prepared as urchin-like structures (in the Figure below) with extremely high photocatalytic activities.



Keywords: titanium water-soluble complexes, selective hydrothermal synthesis, titanium oxide nanocrystals

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Simple processing of functional ZnO from solution - route towards designed nano-hybridmaterials

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ZnO shows potential as semiconducting scintillator and exploitation of the very fast, sub-nanosecond excitonic emission of ZnO for superfast scintillators was recently discussed in the literature (1). However, efficient collection of emission from bulky scintillation elements is limited. Manipulation of the excitonic emission by shifting the excitonic band to lower energies could be a way to overcome that limitation. We are employing two different techniques