

Beyond classical applications of powder diffraction

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Received 3rd March 2004

First published as an Advance Article on the web 14th September 2004

This article provides a short *tutorial review* of how laboratory powder diffraction methods can be used to establish a variety of “non-traditional” pieces of information about solid state materials—information beyond simple phase identification or structure determination at a specific temperature. The examples show how unique insights into synthetic pathways, reaction mechanisms, reaction kinetics, polymorphism, phase transitions and physical properties can be obtained for a variety of different types of materials.

1 Introduction

In this article we will aim to provide a brief overview of some of the “non-classical” chemical and structural information that can be obtained from powder diffraction studies—that is information beyond simple phase identification, cell determination or the determination of a single set of refined atomic coordinates. We hope to show that by performing diffraction experiments as a function of time, temperature, pressure or changing chemical environment a remarkable amount of information about the structure, properties and chemical reactivity of a material can be obtained. Such *in situ* experiments can be performed in a variety of ways using X-ray and neutron diffraction methods and by employing monochromatic or energy dispersive diffraction techniques. Whilst experiments using the high intensity radiation sources available at central synchrotron and neutron facilities are extremely powerful, we choose to focus in this article on experiments that are possible using the conventional facilities available in many chemistry departments. Readers are referred elsewhere for excellent reviews of what is possible at central facilities.^{1,2}

After a brief introduction to powder diffraction, a review of the information obtainable by the technique and some comments on instrumentation, we will describe recent experiments

to follow the mechanisms/structural changes during solid state reactions; to study phase transitions and their kinetics; to prepare or trap unstable materials; and in which subtle information from cell parameters or peak shapes can be used to give valuable chemical insights. We chose to break examples down into broad scientific categories; these categories have, of course, rather fuzzy boundaries but allow comparison of applications of *in situ* diffraction from different scientific areas. The examples chosen are not intended to be comprehensive of what is a wide body of scientific literature, but will hopefully give a flavour of what is possible by *in situ* diffraction methods and inspire others to initiate similar studies in their own areas of interest.

2 Introduction to powder diffraction

In a single crystal diffraction experiment one typically illuminates a suitably mounted crystal of a sample with a monochromatic beam of X-rays or neutrons with a wavelength comparable to the interatomic separations in the material. For conventional laboratory experiments one most often uses the radiation produced by a sealed tube with a Cu (producing $\lambda = 1.54 \text{ \AA}$ X-rays) or Mo ($\lambda = 0.71 \text{ \AA}$) anode. X-rays are diffracted in certain discrete directions in space and collected

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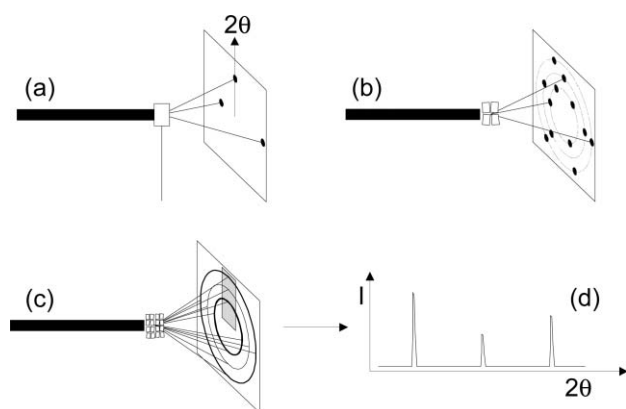


Fig. 1 (a) Diffraction from an oriented single crystal, (b) from a collection of four crystals at different orientations with respect to the incident beam and (c) from a polycrystalline material. One dimensional powder patterns (d) can be obtained by scanning a detector across the cones of diffracted intensity.

by either a point detector or, more commonly nowadays, some form of area detector (Fig. 1). From the directions in which X-rays are diffracted it is possible to determine the size and shape of the unit cell of the material in question. From the intensities of reflections one can, once a suitable solution to the phase problem has been found, determine the identity and positions of atoms in the unit cell, giving what is considered by many the “definitive” proof of a sample’s chemical identity. In a powder diffraction experiment, however, a large (ideally infinite) number of individual crystallites are presented to the incident X-rays and the individual beams of intensity become cones; on the detector individual (hkl) spots become “smeared out” into rings of intensity. In a powder diffraction experiment the 3D information of a single crystal measurement is therefore compressed onto one dimension and one is left with a simple observation of diffracted intensity against diffraction angle (conventionally 2θ) from which to deduce structural information (Fig. 1).

Despite the inherent loss of information relative to a single crystal experiment, the information content of a powder diffraction pattern, if suitably and critically analysed, can be remarkably high. Peak positions are again determined by the size and shape of the unit cell of the material(s) present (*via* the Bragg equation $n\lambda = 2d_{hkl}\sin\theta$). If one knows the unit cell one can predict where reflections might be observed; conversely if one can measure observed reflection positions of a pure sample sufficiently accurately one can determine its unit cell parameters. Peak intensities are again determined by the atomic positions within the unit cell, though one must also account for accidental overlap in 2θ of different (hkl) reflections and any possible preferred orientation of crystallites within the sample. For a multiphase sample one sees one set of reflections due to each phase present, which leads to the classical use of powder methods for qualitative or quantitative phase analysis.

If one has a suitable approximate structural model for a material under investigation it is also possible to derive structural information similar to that obtained from single crystal methods *via* the technique of Rietveld refinement.^{3,4} In this method a mathematical description for the dependence of peak widths, background and certain instrumental parameters with diffraction angle is adopted and a trial diffraction pattern calculated from the approximate structural model and compared to that obtained experimentally. By using non-linear least squares methods one can then adjust the structural model and other relevant parameters to obtain the best fit between experimental and calculated patterns. Using this method, materials of remarkable structural complexity can be studied, with recent work even tackling simple proteins.⁵ By

performing multiphase Rietveld refinement (employing a structural model and weight fractions for each phase present) as a function of time one can obtain quantitative information about the relative amounts of different phases present in an evolving mixture. By mixing a sample with a known quantity of a well understood crystalline phase it is also possible to gain information on amorphous content (amorphous or non-crystalline materials generally give rise to a slowly oscillating contribution to the overall background of a powder pattern). Although traditionally one has required a reasonable starting model to allow Rietveld refinement, it is also possible to determine the structures of both molecular and extended solids directly from powder diffraction data. Despite huge advances in this area in recent years this remains a challenging and complex task and is reviewed elsewhere.^{6–8}

Finally, it is also possible to infer important microstructural information from the width and shape of reflections in a powder diffraction pattern. In the simplest approximation the size of crystallites gives rise to a peak broadening of the form $\text{fwhm} = (K \times \lambda)/(\text{size} \times \cos\theta)$, where K is a shape factor (often 0.9), fwhm the peak full width at half maximum, and λ the wavelength. Sample strain adds a broadening term dependent on $\tan\theta$. Using more sophisticated or “fundamental parameters” approaches, detailed study of the (hkl) dependence of peak widths can be used to yield significant insight into the microstructure of a material under study.⁹

For a more detailed description of the methodology and uses of powder diffraction the reader is referred elsewhere.^{10,11}

3 Experimental considerations for *in situ* experiments

In any powder diffraction experiment one would ideally like to maximise both the count rate and the resolution (in terms of obtaining narrow widths of individual reflections) of the data. In nearly all *in situ* or time/temperature/pressure/*etc.*-resolved experiments one is forced to trade off one of these quantities against the other: the optics required for high resolution measurements inherently reducing the flux of useful photons reaching the detector. There is no doubt that to obtain the highest X-ray flux one would ideally perform experiments at a synchrotron source where useful fluxes are several orders of magnitude higher than from a laboratory source. The highly penetrating high energy X-ray photons available in either monochromatic or energy dispersive modes at synchrotrons, or the low absorption of neutrons at central facilities, can also help penetrate sample environments that would not be useable with a laboratory source. For these reasons reactions involving high pressures or other forms of complex sample containment will largely remain the realm of central facilities.

There are, however, many important studies that can be performed in the home laboratory, and the flexibility of access can in itself allow experiments that simply would not be scheduled at central facilities. Most of the examples described in this review have been performed on a sealed tube laboratory powder diffractometer in Bragg–Brentano or “flat plate reflection” mode. In this set-up a divergent beam of X-rays from a sealed tube line source is refocused following diffraction by the sample. To obtain the highest resolution measurements one would typically employ a Ge(111) incident beam monochromator (which would normally have $\sim 25\%$ reflectivity implying that $\sim 75\%$ of the X-rays are “wasted”) to produce $K\alpha_1$ radiation, narrow divergence/anti-scatter slits, Soller slits to reduce axial divergence and a narrow receiving slit in front of a point detector. Typical data collection times for such a set up might be hours or days. Significant intensity gains, though at the cost of increasing intrinsic peak widths, can be gained by relaxing each of the optical components, by replacing the

monochromator with a multilayered mirror or removing it altogether, and by introducing a position sensitive detector (PSD). With modern equipment data collections of minutes are possible allowing “real time” studies of many evolving systems; using the latest generations of linear or curved PSD’s, by using a rotating anode source, or by employing clever experimental protocols, measurement times of seconds become achievable. In some cases it may be preferable to record samples mounted either in glass/amorphous silica capillaries or mounted on low absorption films in transmission mode. This can reduce preferred orientation effects or allow the use of more complex diffraction cells.

There is a range of apparatus available commercially for non-ambient studies on commercial diffractometers in various geometries. Furnaces capable of environmentally heating samples to ~ 1500 K and Pt strip heaters capable of operating to ~ 2300 K under non-ambient atmospheres are available from manufacturers such as Anton Paar; as are cryofurnaces which operate from ~ 100 to ~ 700 K. Many designs have been described in the literature. For low temperature measurements in our laboratory we use a pHenIX cryostat, which is a closed cycle refrigerator based system capable of operating from ~ 11 K to ~ 300 K and optimised for Bragg–Brentano studies. In capillary mode it is relatively straightforward to employ one of the commercial designs of cold/hot open flow gas systems to cool/warm samples between ~ 35 and ~ 500 K. For more unusual experiments, such as those involving electrochemical measurements, bespoke apparatus may be required. The main consideration when designing such apparatus is that a suitable X-ray transparent window (made of *e.g.* a thin polymer film, carbon fibre or Be) must be included. Care should be taken when using cells with Be windows.

For non-ambient *in situ* diffraction studies powder methods can often be more powerful than single crystal experiments for several reasons. Sample environment apparatus is often easier to design; powder diffraction measurements are typically quicker than single crystal experiments (minutes as opposed to hours); many crystals of interesting materials can crack or pulverise under non-ambient conditions rendering single crystal experiments impossible; many materials are technologically only produced/processed in powder form; finally, for studying chemical reactions powder methods offer the clear advantage that one can simultaneously study the structural evolution of all the phases in the system.

4 Following chemical reactions

One of the most important applications of *in situ* diffraction methods in a synthetic laboratory is the insight such measurements can give into the progress of reactions in the solid state—information similar to that a solution chemist might obtain from NMR/GCMS measurements during experiments.

A typical example of the power of *in situ* studies is in the synthesis of cubic ZrMo_2O_8 , a material that is of interest as it shows “negative thermal expansion” (NTE) and undergoes continuous, isotropic and reversible contraction as it is warmed from 2 to 500 K with a coefficient of thermal expansion of $-5 \times 10^{-6} \text{ K}^{-1}$ —comparable in magnitude to the positive expansion of many “normal” materials. The synthesis of this material is complicated by the fact that the cubic form is only metastable so that conventional solid state syntheses form either trigonal $\alpha\text{-ZrMo}_2\text{O}_8$ or the more dense monoclinic β form. If, however, one takes a hydrated precursor phase $\text{ZrMo}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ it is possible to convert this phase to the cubic material by careful heat treatment.¹² The temperature/time window in which the cubic material can be formed is extremely narrow and optimising such a synthesis by traditional *ex situ* methods is a slow process. In this particular case,

ex situ methods are also hampered by the fact that many of the crystalline phases encountered during syntheses have Bragg peaks which accidentally overlap in the powder pattern, making the composition of a given mixed phase sample very hard to assess from simple visual examination of the powder pattern. Fig. 2, however, shows the results of an *in situ* study where the precursor material is heated continuously in a lab diffractometer from 300 to 950 K over a 24 h period.¹³

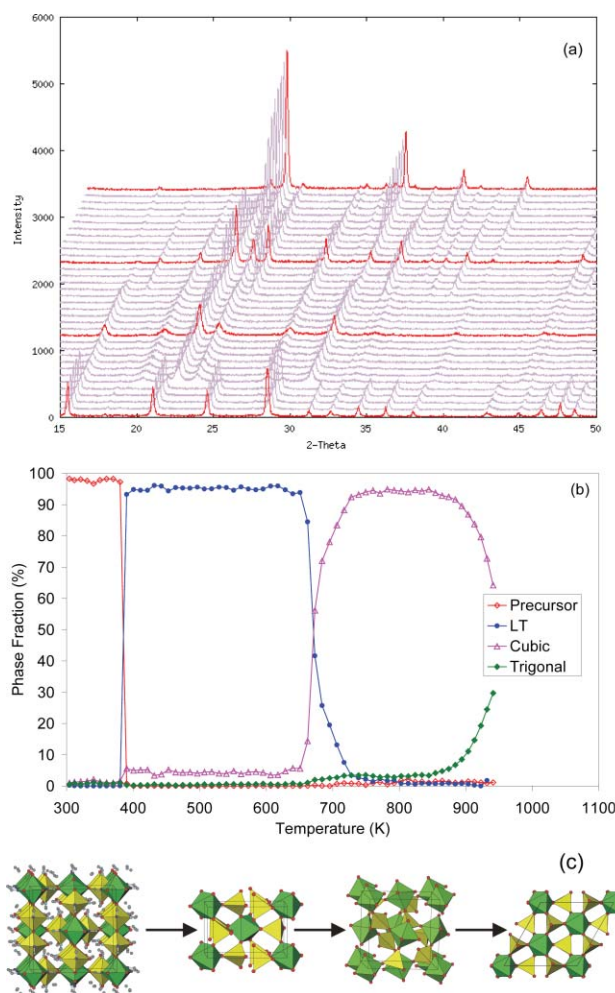


Fig. 2 (a) Selected powder diffraction data recorded on warming a sample of $\text{ZrMo}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ from room temperature to 950 K. Patterns range from low to high temperature up the plot and have (in this and other figures in this review) been offset in 2θ and I for presentation. Patterns containing maximum proportions of the 4 evolving phases ($\text{ZrMo}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ —303 K, LT- ZrMo_2O_8 —543 K, cubic ZrMo_2O_8 —763 K and trigonal ZrMo_2O_8 —953 K) are highlighted, (b) shows results of quantitative Rietveld refinement of each data set recorded and shows how the proportions of individual phases vary during synthesis, (c) shows polyhedral views of the structures of the various phases (Zr green, Mo yellow).

This experiment allowed the identification and structure solution of a new polymorph of ZrMo_2O_8 , the so called “LT” form, stable only between ~ 400 and 600 K. The solution of the structure of this new polymorph allows each of the diffraction patterns of Fig. 2a to be analysed by multiphase Rietveld refinement to determine quantitatively the phases present as a function of temperature. By including a known quantity of a crystalline internal standard it is possible to show that all of the transformations involve crystalline phases (no amorphous products are formed) and to calibrate the temperatures of the transitions. Fig. 2b shows the results of such a Rietveld analysis (the refinements can be readily automated so that the 80

Rietveld refinements contributing to the figure can be performed in minutes!) and shows immediately that the optimal synthesis temperature for cubic ZrMo_2O_8 is around 750 K. At lower temperatures incomplete reaction occurs; at higher temperatures the trigonal phase begins to form. The data shown apply to a specific heating rate. As with any kinetically controlled synthesis there is an additional time dimension to the plot, which can also be readily explored by these methods. The evolution of the structures of the various materials in this reaction pathway also allows one to propose topotactic pathways between several of the phases and make mechanistic inferences to understand why this particular synthetic route yields the desired form of ZrMo_2O_8 .

A second example of the use of *in situ* diffraction methods is recent work following the synthesis of CaTiO_3 , an important dielectric material.¹⁴ The objective was to investigate the difference in the rate of CaTiO_3 formation, product purity and the microstructural characteristics of materials obtained from calcined mixtures of CaCO_3 and TiO_2 with and without prior mechanical activation. Variable temperature X-ray powder diffraction data were collected and analysed by multiphase Rietveld refinement. Without mechanical activation, the sample at room temperature consisted of CaCO_3 and TiO_2 , and a small amount of CaTiO_3 presumably formed during short calcination. CaCO_3 decomposition began at 600 °C and was completed at 800 °C, when CaTiO_3 formation ensued. The final product at 1100 °C contained about 10% unreacted material (Fig. 3).

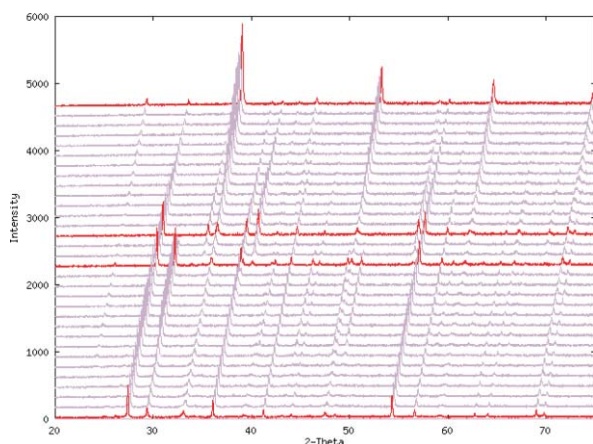


Fig. 3 Powder diffraction data recorded on heating the non-activated mixture of CaCO_3 and TiO_2 . Data at increasing temperatures have been offset vertically. Phase analysis shows that all CaCO_3 decomposes to CaO between 600 and 800 °C and the formation of CaTiO_3 ensues. Highlighted patterns represent the starting mixture (30 °C), start and end of CaCO_3 decomposition (600 and 800 °C) and the final product (1100 °C).

The mechanically activated mixture already contained about 75% CaTiO_3 at room temperature and, once all CaCO_3 had decomposed, CaTiO_3 formation proceeded faster than in the non-activated sample, resulting in a pure, single phase product at 920 °C. Microstructure analysis from diffraction data indicated that the mechanically activated sample yielded a product with smaller crystallite size, and this was confirmed by SEM measurements.

There is considerable current interest in controlling the properties of materials at the nanoscale and *in situ* powder methods can provide information on this length scale *via* the widths of Bragg reflections. In a recent study, Louer *et al.* investigated the formation of nanocrystalline In_2O_3 by the thermal decomposition of the precursor phase indium oxalate decahydrate, $\text{In}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.¹⁵ On heating under an air

flow, it was shown that this phase undergoes a two-step loss of four water molecules to form $\text{In}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, which dehydrates completely by 120 °C to form an amorphous anhydrous phase. Above 250 °C the formation of nanocrystalline In_2O_3 was observed. As the annealing temperature was increased, analysis of the 2θ dependence of reflection widths allowed the evolution of the mean crystallite diameter from ~30 to ~90 nm and a simultaneous reduction in crystallite strain to be followed directly. *Ex situ* SEM measurements on selected quenched samples confirmed the diffraction results, showing the efficacy of powder diffraction analysis when preparing materials with controlled size in the nanometer range.

Linden *et al.* have applied *in situ* powder diffraction to more “exotic” chemical reactions, showing that even reactions occurring extremely rapidly in solution can be studied using laboratory instrumentation.¹⁶ In a paper investigating the formation of the technologically important mesoporous silicate MCM-41, they describe an ingenious experimental set up in which pumped solutions of reagents are mixed and allowed to react as they pass along a variable length of 4 mm polypropylene tubing before flowing between the polymer windows of a purpose-built X-ray cell. Powder diffraction patterns can then be recorded in transmission mode and, due to the continuous flow of reagents/products, long (40 minute) data collections can be performed on reagents which are only allowed to react for extremely short periods. Such an approach considerably extends the time range of what is generally thought of as a “slow” experimental technique. They were able to show that under their conditions hexagonal MCM-41 forms in under 3 minutes and that no intermediate phases could be detected. These methods offer a fascinating alternative to the synchrotron-based high energy methods used by others to study related problems.^{1,2}

5 Topotactic dehydration and desolvation reactions

There are also a large number of areas where the hydration/solvation properties of materials are of crucial importance. Examples range from mineralogy; pharmaceutical materials, where different solvates can have very different clinical (and patent!) properties; catalyst preparation; and materials with important sorption properties such as zeolites, zeotypes, mesoporous materials and organic–inorganic frameworks. In this section we highlight several applications of *in situ* studies to the examination of topotactic desolvation reactions—that is reactions where the structure of the product phase has a clear relationship to the structure of the starting material. *In situ* powder diffraction studies can be ideally suited to studying such systems.

In situ powder methods have been used to follow the dehydration of the layered double hydroxide hydrocalumite ($[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$ —Friedel’s salt), a member of a family with a range of potentially important catalytic and ion exchange properties.¹⁷ These studies have shown that on heating several distinct processes occur: from 80 to 280 °C loss of water occurs to form a new metastable form of the material in which a new Ca–Cl bond is formed, presumably to compensate for the loss of a water molecule originally bound to Ca (see Fig. 4), this material will undergo rapid rehydration at room temperature; from 280–450 °C dehydroxylation occurs with an amorphous phase forming at around 400 °C; at higher temperatures loss of the anion occurs and a mixture of CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is formed. Interestingly, reaction of the amorphous phase obtained at 400 °C with aqueous KCl leads to reformation of the original hydrocalumite. This reconstruction process can be used to form a variety of novel intercalation compounds.

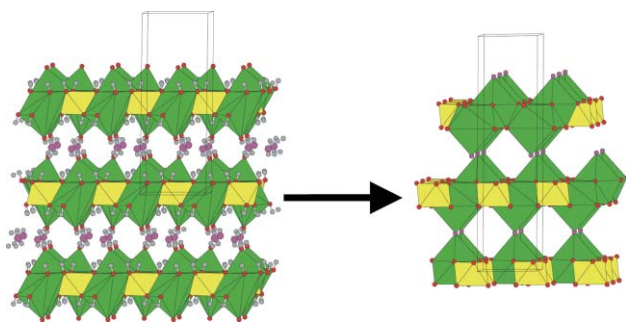


Fig. 4 Structures of hydrocalumite before and after dehydration. AlO_6 octahedra are shown in yellow and CaX_7 ($\text{X} = \text{OH}$, O or Cl) polyhedra in green. On heating the Ca coordination site occupied by water becomes replaced by a Cl^- ion which bridges the layers.

Similar studies can be performed on metal–organic framework materials which have a range of potential applications. For example, Kepert *et al.* have shown how a porous molecular framework composed of hexaaquacobalt(II) cations and redox-active tetra(carboxyl)tetrathiafulvalene (TC-TTF) anions with included water molecules can undergo a remarkable dehydration reaction in which solvent molecules are reversibly lost on controlled heating and the material changes from $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]\text{H}_2(\text{TC-TTF})\cdot 2\text{H}_2\text{O}$ (form **A**) to $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]\text{H}_2(\text{TC-TTF})$ (form **B**), Fig. 5; heating to higher temperatures leads to more drastic structural changes.¹⁸

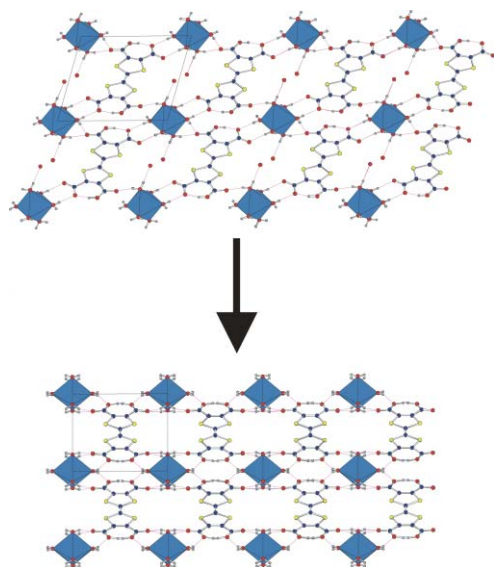


Fig. 5 Views of the hydrated and dehydrated hydrogen bonded frameworks of **A** and **B** (see text). CoO_6 octahedra are shown in blue, S (yellow), C (blue) and O (red) spheres. Hydrogen bonds are shown in pink. Disordered cavity water molecules in **A** are omitted for clarity.

Remarkably this process can occur as a single crystal to single crystal transition allowing the structure of the desolvated form to be solved. *In situ* powder diffraction studies, in which a sample was mounted in an open ended glass capillary and diffraction data collected over a period of 5 days were used to study the reverse re-hydration reaction. Experiments showed that the dehydrated form **B** undergoes a gradual volume increase to a maximally hydrated form (**B'**) before transforming *via* a minimally hydrated form **A'** before proceeding to fully hydrated **A**. These processes appear to occur without significant broadening of diffraction peaks suggesting no significant build up of sample strain and no reduction in

crystallite size—both observations consistent with the ability of this material to undergo single crystal to single crystal dehydration. *Ex situ* powder studies have also shown that **B** will take up small molecules such as methanol whereas larger species such as ethanol, carbon disulfide and acetonitrile are excluded. The remarkable flexibility of this particular framework and its ability to undergo crystalline to crystalline transitions without induced strains causing fracturing has been attributed to the multitude of independent weak hydrogen bonding and non-bonding interactions present.

In related work Cussen *et al.* have described a remarkable solid state phase transition in the metal–organic framework material $\text{Ni}_2(4,4'\text{-bipyridine})_3(\text{NO}_3)_4$ which contains two disordered methanol molecules (**C**) as synthesised that are readily lost on standing in air.¹⁹ The desolvated material has again been shown to be crystalline and stable to 215 °C by powder diffraction and will readily take up ethanol. Synthesis in ethanol produces a structurally distinct framework material $(\text{Ni}_2(4,4'\text{-bipyridine})_3(\text{NO}_3)_4\cdot 2\text{C}_2\text{H}_5\text{OH})$, (**D**). **D** can again be desolvated in a crystalline to crystalline transition. When desolvated **D** is exposed to methanol vapour it transforms over a time scale of ~ 1 day to **C**. The significant insight provided by powder diffraction again comes from following the widths of reflections during the reaction. *In situ* studies have shown that these remain unchanged throughout the transformation, suggesting that it must occur by a propagating front of **D** moving through crystallites; a mechanism for the severe framework changes that occur has been proposed. The mechanism of guest sorption in these framework materials has thus been shown to be distinct from that in framework materials such as zeolites, and that structural rearrangements during guest uptake are of crucial importance. Powder methods provided key information to give this insight.

Peak width information has also been important in the study of the reversible dehydration reactions of the ferrimagnetic layered cobalt hydroxide pillared with *trans*-1,4-cyclohexanedicarboxylate (chdc) reported by Kurmoo *et al.*²⁰ Here *in situ* powder diffraction experiments were performed either as a function of temperature or under a dynamic vacuum, and they show clear evidence that the as prepared material $\text{Co}_5(\text{OH})_8(\text{chdc})\cdot 4\text{H}_2\text{O}$ with an interlayer spacing of 14.5 Å undergoes dehydration initially to $\text{Co}_5(\text{OH})_8(\text{chdc})\cdot 2\text{H}_2\text{O}$ (13.9 Å) before forming $\text{Co}_5(\text{OH})_8(\text{chdc})$ (13.3 Å). There are marked and essentially reversible changes in reflection peak width observed as this process occurs which the authors interpret as being caused by a decrease in the correlation length of the interlayer spacing on dehydration.

Niel *et al.* have described interesting property changes on dehydration of the Hoffmann-like coordination polymers $[\text{Fe}(\text{pyrimidine})(\text{H}_2\text{O})\{\text{M}(\text{CN})_2\}_2]\cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ag}, \text{Au}$).²¹ *In situ* powder diffraction studies have shown that both materials undergo reversible loss of H_2O either under dynamic vacuum or on heating. Both framework water and water bound to Fe are lost and, in the case of the Au compound, powder data have allowed the structure of the dehydrated form to be determined. On dehydration, the Fe coordination site vacated by water is taken up by a previously uncoordinated N of a pyrimidine ligand from an adjacent part of the framework, changing the material's topology. This insight could only be achieved by powder diffraction since single crystals were found to shatter on dehydration. Interestingly, the hydrated compound shows a high spin to low spin transition of 50% of the Fe sites and an associated colour change on cooling to 160 K whereas the dehydrated material shows no such transition. The structural insight from powder diffraction data allows this potentially useful multi-property behaviour to be rationalised.

6 Investigating unstable polymorphs

There are many cases where *in situ* powder diffraction methods have been used to identify new polymorphs of materials that are unstable under normal conditions. Polymorphism is the ability of a substance to crystallize in different forms in the solid state, and it is of great importance since different polymorphs of the same chemical compound can have very different physical properties. For pharmaceutical molecules, the presence or absence of therapeutic activity can sometimes be completely determined by the crystalline form present. The relative stabilities of different polymorphs are governed by a complex interplay of thermodynamic and kinetic factors, and *in situ* diffraction studies can be crucial in unravelling often puzzling and apparently irreconcilable bodies of information from *ex situ* measurements.

One intriguing system from the world of metal oxide chemistry is BiPb_2VO_6 which displays a series of polymorphs between room temperature and its melting point of 780°C .^{22,23} There are two stable polymorphs: room temperature α - BiPb_2VO_6 which is non-centrosymmetric, polar and SHG (second harmonic generation) active; and high temperature δ - BiPb_2VO_6 . *In situ* variable temperature powder diffraction studies have shown that, depending on the heating rate, the α form can transform to the δ form in 3 different ways (see Fig. 6a).

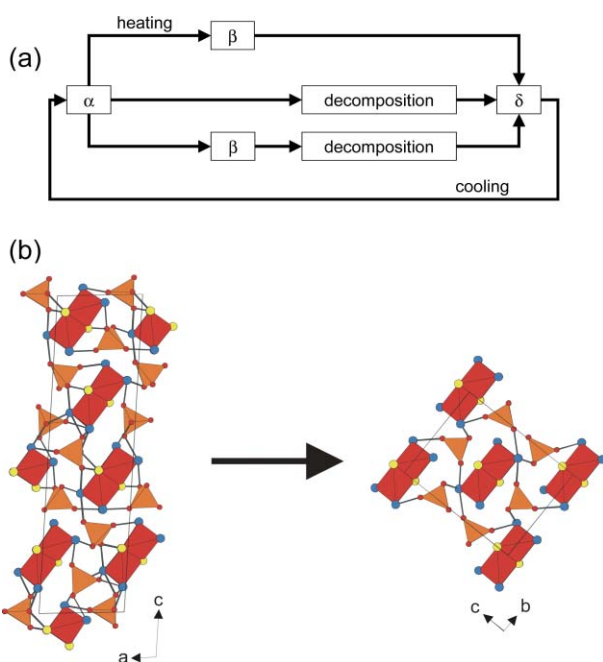


Fig. 6 (a) Polymorphism map of BiPb_2VO_6 , (b) the structural relationship between α - BiPb_2VO_6 and the dynamically disordered δ - BiPb_2VO_6 . VO_4 tetrahedra shown in brown; OM_4 tetrahedra (M = Bi, yellow; M = Pb, blue) shown in red.

The transformation can occur *via* the formation of metastable β - BiPb_2VO_6 at around 415°C , which either converts directly to δ at 475°C or undergoes decomposition followed by δ formation at 630°C . Under different heating conditions α decomposes at about 530°C and δ forms at 630°C . The cooling process always seems to occur *via* the direct transition from α to δ at 450°C . Only *in situ* powder measurements allowed this complex series of phase changes to be resolved. In addition, powder methods allowed the structures of both the α and δ forms to be solved *ab initio*, and revealed the structural relationship between the two phases (see Fig. 6b).

A similar story from the opposite end of the chemical spectrum involves $[\text{S},\text{S}]2,2'$ -(ethylenediimino)-di-1-butanol

dihydrochloride, a pharmaceutical molecule therapeutically active against mycobacterium tuberculosis. The compound was first prepared in the 1960's, but only two polymorphic forms identified. Recently, *in situ* powder diffraction studies have helped reveal the identity of two new polymorphs (forms III and IV).²⁴ Again formation of the various polymorphs depends critically on the thermal history of the samples, and the polymorphism map could only be determined by *in situ* methods (Fig. 7).

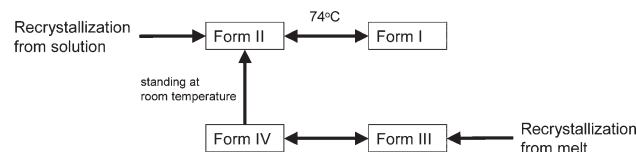


Fig. 7 Polymorphism map of $[\text{S},\text{S}]2,2'$ -(ethylenediimino)-di-1-butanol dihydrochloride.

Diffraction methods, in contrast to the complementary techniques of solid state NMR, hot stage microscopy and thermal analysis used in the study, give one the ability to solve the structures of the new polymorphs and provide full 3D structural information on the transitions.

7 Phase transitions

In situ powder diffraction methods can be used to follow phase transitions in a variety of materials. In other sections we describe a number of examples related to preparing specific polymorphs of materials and following the kinetics of atomic motion in the solid state. Here we concentrate on phase transitions involving more subtle structural changes, which are important in a variety of different areas of materials science.

In the magnetic recording industry there is currently significant interest in Fe_{1-x}Pt alloys. For the 1 : 1 alloy there are two important phases: a high temperature face centred cubic (fcc) disordered material and a low temperature face centred tetragonal (fct) ordered phase (the so-called L_{10} phase). The fct phase has high magnetocrystalline anisotropy making it an attractive candidate (particularly in nanoparticle form) for high-density magnetic storage devices. The fcc to fct ordering phase transition is accompanied by the growth of superstructure reflections in the powder pattern and Osaka *et al.*²⁵ have described how high temperature *in situ* powder diffraction studies can help map out the phase diagram of this system. They have monitored the various order-disorder transitions for different sample stoichiometries by heating ordered phases through the phase transition and also by quenching high temperature disordered phases to specific temperatures to monitor the rate of sample aging. The phase diagram they propose by such techniques differs significantly from that derived by less direct methods.

Displacive phase transitions are a common feature of many framework materials. Classic examples include the low to high temperature phase transitions in quartz and cristobalite in which subtle changes in bond angles between SiO_4 tetrahedra occur on heating. In cristobalite the low temperature Si-O-Si bond angle of $\sim 146^\circ$ becomes, at least on average, 180° at high temperature. Variable temperature laboratory powder diffraction experiments are well suited to studying such transitions. A recent example is the observation of a new high temperature form of trigonal ZrMo_2O_8 .²⁶ As shown in Fig. 8, the cell volume of this material shows a marked discontinuity at 487K . Careful analysis of the high temperature data reveal that this is caused by a symmetry reduction in the material from $P\bar{3}1c$ to a $P\bar{3}m1$ cell with $1/6^{\text{th}}$ of the volume. The structure of the high temperature form has been solved and the mechanism by which

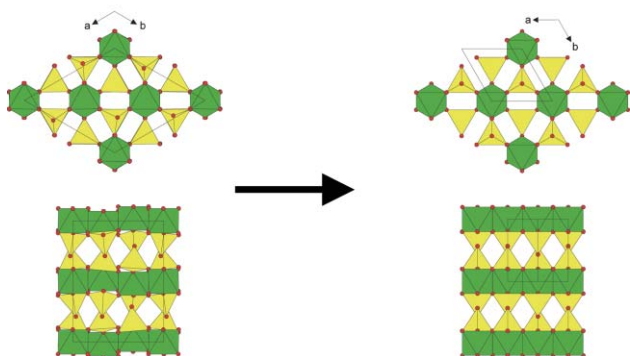
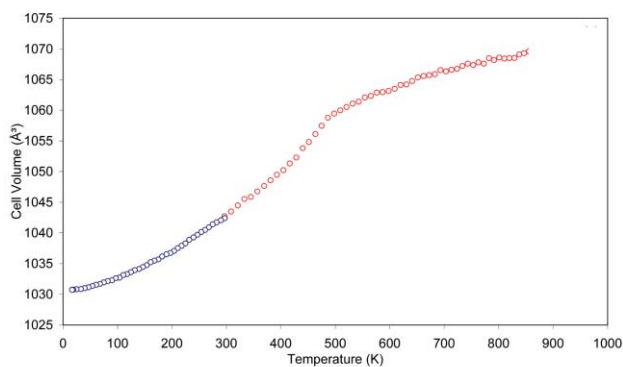


Fig. 8 The temperature dependence of the unit cell volume of trigonal ZrMo_2O_8 shows clear evidence for a phase transition at 487 K. This is caused by the subtle reorientation of ZrO_6 octahedra (green) and MoO_4 tetrahedra (yellow).

the low temperature structure “unfolds” towards the high temperature form described.

Structural phase transitions are also common in molecular materials. One area with much recent activity is in the field of spin crossover materials, which are of interest due to their potential applications in information storage, molecular switches and display devices. In a recent paper, Money *et al.* have demonstrated the use of laboratory *in situ* powder diffraction to look at bis(2,6-dipyrazol-1-ylpyrazine)iron(II) perchlorate.²⁷ Room temperature powder diffraction data were used to solve the structure of the material using simulated annealing methods. Variable temperature data collected on cooling the material revealed a significant volume change ($\sim 20 \text{ \AA}^3$) per formula unit at around 200 K, consistent with the temperature at which magnetic measurements show a fall in susceptibility. The volume reduction is consistent with the reduction in Fe–N bond lengths expected at the high to low spin transition. Examination of diffraction data below the phase transition revealed a doubling of the cell volume showing that in this particular case the magnetic transition is accompanied by a crystallographic phase transition. Interestingly, at temperatures close to the phase transition diffraction data revealed a mixture of high and low spin phases, again consistent with magnetic measurements (see Fig. 9).

8 Solid state kinetic studies

In situ diffraction experiments as a function of time and temperature can also be used to gain information on the kinetics of solid state reactions—information that is hard to obtain by other methods. In our laboratory we have been interested in the AM_2O_8 family of materials which, in addition to their negative thermal expansion properties mentioned above, undergo a phase transition in which oxygen atoms become dynamically disordered in the material at temperatures down to 200 K.²⁸ This is a remarkably low temperature for

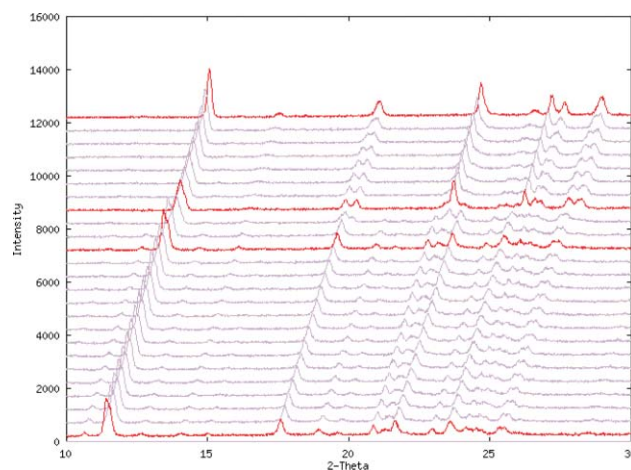


Fig. 9 Powder diffraction data recorded on cooling a sample of bis(2,6-dipyrazol-1-ylpyrazine)iron(II) perchlorate from 300 K (top highlighted pattern) to 16 K (bottom pattern). Marked structural changes including a unit cell doubling can be seen from the two highlighted patterns recorded above and below the phase transition. An intermediate two-phase region has also been identified.

oxygen dynamics in an oxide material. In the case of ZrWMoO_8 the material has dynamically disordered oxygens at room temperature and its average crystallographic structure has the space group $Pa\bar{3}$.

If one quench-cools the material it is possible to “freeze in” the high temperature disordered structure at low temperature. Provided sufficient thermal energy is available the material will, however, gradually transform to the thermodynamically stable ordered form from which has the space group $P2_13$ and subtly different peak intensities in its powder diffraction pattern. The evolution of the diffraction patterns can therefore be followed as a function of time at different temperatures to obtain information on the kinetics of this process. In one series of experiments we recorded 892 diffraction data patterns on this system on samples quenched to a variety of temperatures between 200 and 250 K. Kinetic information could be extracted from the resulting data sets in a number of ways (Fig. 10). Perhaps the most straightforward analysis was to monitor the changes in integrated intensities of certain Bragg reflections absent in disordered ZrWMoO_8 but present in the ordered material. Alternatively, since the process involves a change in unit cell parameters, kinetic information can be derived essentially from the positions of reflections. Finally, it is possible to perform a Rietveld refinement with each data set to monitor evolving fractional occupancies of certain crystallographic sites in the material. By these various methods it was possible to estimate an activation energy for the O migration of 34 kJ mol^{-1} .

Importantly, by performing full Rietveld analysis, one can correlate kinetics with structural changes at the unit cell level (*via* fractional coordinates and occupancies). Additionally, there is valuable information available from the widths of certain reflections as a function of temperature/time which provides complementary information on the microstructure (at the 20–100 nm level) of the material.

9 Information from unit cell parameters

There are many cases where significant information on a chemical change can be obtained from the variation in unit cell parameters (derived from the peak positions) in a powder diffraction experiment. Examples already described include the dehydration reactions of hydrocalumite and several of the framework metal–organic materials, and the use of cell

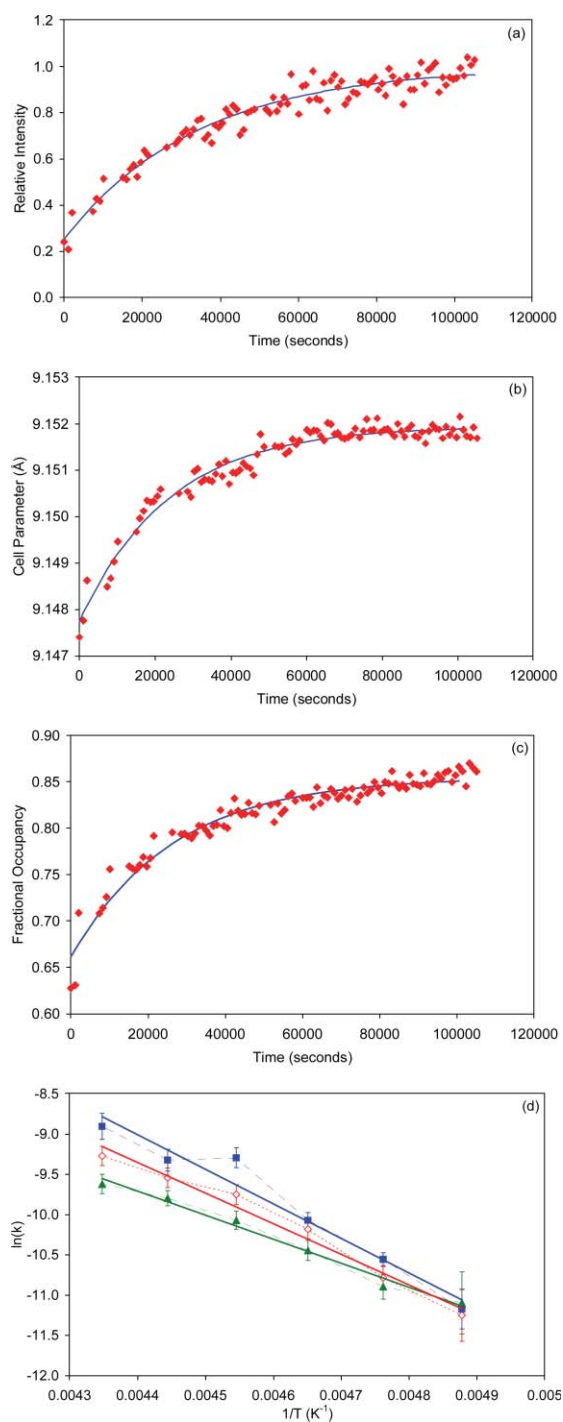


Fig. 10 Kinetic information can be extracted from laboratory powder diffraction data in a number of ways. In a study on oxygen migration in ZrW_2Mo_8 kinetic information on the migration process was derived from (a) changes in intensities of individual peaks in the powder diffraction pattern, (b) changes in unit cell parameters derived from peak positions and (c) by following site occupancies as a function of time derived by Rietveld refinement. Each method gives information on subtly different aspects of the kinetics of the process from which activation energies can be derived from Arrhenius plots (d) (green – intensities; blue – cell parameters; red – fractional occupancy).

parameter information to follow the kinetics of the order–disorder phase transition in ZrW_2Mo_8 shown in Fig. 10b.

In the case of ZrW_2O_8 and ZrMo_2O_8 , cell parameters have been used to extract more subtle information. These examples actually used cell parameters derived from neutron diffraction experiments, though similar data could be obtained by X-ray methods. One of the major contributions to thermal expansion/contraction in solids is, of course, the population of

vibrational modes (phonons) of different energy as a function of temperature. This is expressed formally in the Gruneisen relationship as:

$$\alpha = \frac{\gamma C_V K}{V} \quad (1)$$

where V is the volume of the material, C_V the specific heat at constant volume, K the isothermal compressibility and γ , the Gruneisen parameter, is a measure of whether an individual mode tends to cause lattice expansion (γ positive) or contraction (γ negative). By assuming a model for the heat capacity (e.g. Einstein/Debye models) one can fit high precision cell parameter data as a function of temperature and obtain information on the energy scale of the modes contributing to expansion *via* the Einstein/Debye temperatures required to fit the data (Fig. 11a). In the case of ZrW_2O_8 , where high

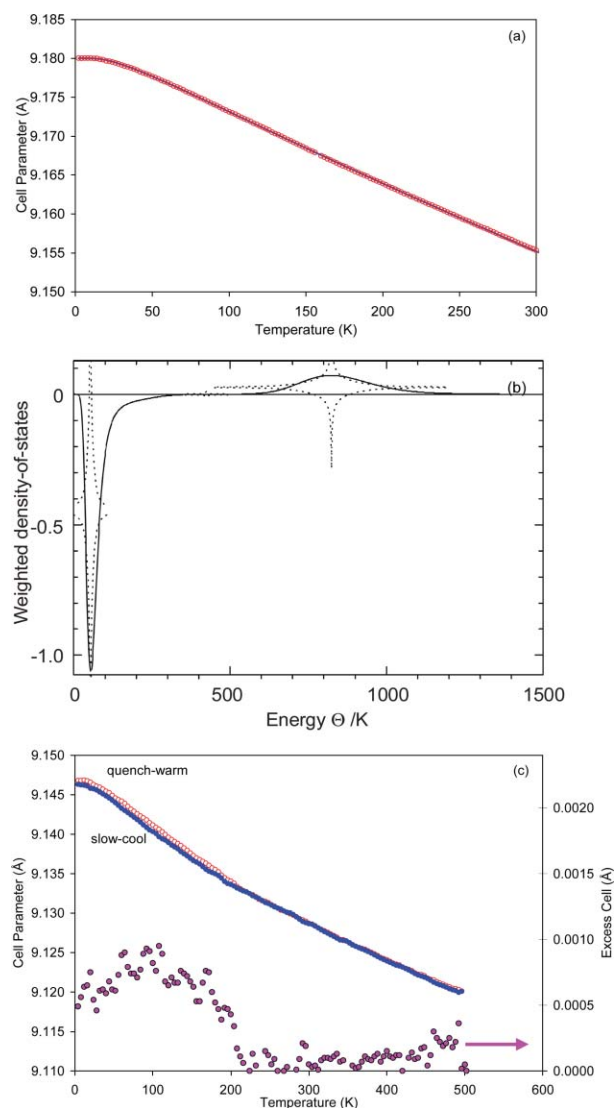


Fig. 11 (a) By assuming a simple model of the heat capacity of a material, the temperature dependence of its unit cell can be fitted using eqn. (1). Data shown here are for the cubic NTE material ZrW_2O_8 . (b) Using maximum entropy methods the energy of vibrations responsible for negative thermal expansion in ZrW_2O_8 can be extracted directly from the temperature dependence of the cell parameter. In ZrW_2O_8 there are low energy modes (~ 5 meV, 55 K) which have a negative Gruneisen parameter and tend to cause contraction and higher energy modes (73 meV, 850 K) which lead to expansion. (c) The temperature dependence of the unit cell parameter of ZrMo_2O_8 on warming a sample quenched from high temperature followed by slow cooling. A clear discrepancy in cell parameters and thermal expansion is seen around 200 K suggesting the onset of dynamic oxygen disorder at this temperature.

precision cell parameter data have been measured from 2–520 K, this approach was taken one stage further and the Grüneisen-parameter-weighted-phonon-density-of-states was extracted directly from the temperature dependence of the cell parameter using maximum entropy techniques (Fig. 11b).²⁹ This gives directly the energy of the modes important for controlling thermal expansion/contraction. Information similar to that from spectroscopic methods is thus available directly from powder diffraction data.

Early variable temperature diffraction data on ZrMo₂O₈ showed no evidence for a phase transition involving order to dynamic disorder of oxygens in the material in contrast to both ZrW₂MoO₈ and ZrW₂O₈.¹² However by collecting powder diffraction patterns at a series of closely spaced temperatures on a sample quenched from high to low temperature, during slow heating and then slow cooling one sees subtle changes in thermal expansion behaviour.³⁰ The inference from this observation is that in this material there is a transition from statically to dynamically disordered oxygens at around 200K—a similar though subtly different transition to that in the related phases. Such a transition is, of course, extremely hard to observe from diffraction data as the intensities of Bragg peaks undergo essentially no change between the different disordered forms of the material. The transition is, however, revealed directly from *in situ* parametric studies in subtle changes in cell parameter magnitudes and, *via* their first derivative, in the temperature dependence of the linear thermal expansion of the material.

Changes in unit cell parameters can also be used to obtain significant insight into the properties and performance of the cathode materials used in rechargeable batteries. By placing a Be window in the stainless steel disks usually used to fabricate the “coin-cells” used for electrochemical characterisation, it is possible to monitor changes in the diffraction pattern of the cathode that accompany the charge/discharge process. For example such methods have been used to follow reactions of Cr doped LiMnO₂. Here changes in cell parameter variation on multiple charge/discharge cycles have been related to irreversible structural changes in the material.³¹

Conclusions

In conclusion, we hope that this article has demonstrated the wealth of information that can be derived by performing diffraction experiments in the home laboratory as a function of an additional variable (time, temperature, chemical reaction, *etc.*). Significant new insight can be obtained into the protocols/mechanisms of syntheses, on forming new metastable materials, and on both structural and microstructural changes. The examples cited are only a selection of a range of elegant work in the literature but will, we hope, whet the reader's appetite to apply similar methodologies to their own areas of scientific endeavour.

Acknowledgements

We would like to acknowledge financial support from the EPSRC and the University of Durham that has allowed some

of the experiments described to be performed. We would also like to acknowledge co-workers who have been involved with some of these experiments and have influenced our thinking on *in situ* methods over the years.

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