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Watching solids crystallise using *in situ* powder diffraction

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The study of the chemical processes that occur during the synthesis of inorganic solids has attracted much recent attention. The ultimate aim of these experiments is the atomic level understanding of reaction mechanisms which lead to the formation of extended inorganic solids, so that rational design of new materials can be achieved. Solid-state syntheses are typically performed under non-ambient temperature and pressures in sealed containers so specialised apparatus must be constructed to allow us to directly probe these reaction mixtures. We review the use of *in situ* powder diffraction to investigate the formation of crystalline solids in real time, and discuss the latest developments in the technology required for these challenging experiments.

1 Introduction

The study of inorganic solid-state chemistry has seen a renaissance in the last 20 years, which has in the most part been brought about by the introduction of new techniques for structural elucidation (CCD cameras for crystallography data collection, and new solid-state NMR techniques, for example), and the investigation of new preparative methods (in particular *chimie douce* methods, such as hydrothermal chemistry and sol–gel techniques).[1,2] An astonishing diversity of novel materials is presently being prepared and characterised, as evidenced by the large numbers of published reports of new inorganic solids. These materials can have technologically valuable properties such microporosity, photophysical properties, electrochemical activity, superconductivity and magnetic behaviour, and thus research in solid-state inorganic chemistry can have significant application focus. A pressing aim of the fundamental research in this area is a quantitative knowledge of the mechanism of nucleation and growth of inorganic solids; this understanding would allow the rational design of new materials for application in the same way that the organic chemist is able to synthesise a complex molecule by use of specific starting materials and reaction conditions. The difficulty in the rational design of new solids is largely due to the lack of mechanistic data currently available, *i.e.* a quantitative understanding at an atomic level of the chemical processes leading to the formation of solids. This is perhaps not too surprising since many materials crystallise from complex heterogeneous mixtures held at elevated pressures or temperatures in sealed, thick-walled reaction vessels.

This article is concerned with recent developments in the use of powder diffraction techniques to follow the course of the synthesis of inorganic solids *in situ* under real reaction conditions. Diffraction clearly is an appropriate technique when following the formation of a crystalline solid and as we will demonstrate, in addition to obtaining qualitative information about the course of a reaction and phase identification at each step, time-resolved diffraction techniques allow quantitative kinetic information to be extracted, since the intensity of a Bragg reflection is directly proportional to the amount of diffracting solid. This information is the first step in being able to postulate reaction mechanisms.

In order to measure powder diffraction data from a reacting mixture of chemicals at non-ambient temperatures (and often pressures) the design and construction of specialised apparatus is required. Powder diffraction patterns of solids under non-ambient temperatures have been recorded since the earliest days of X-ray diffraction,[3] and the construction of furnaces for use in diffraction experiments has been well reviewed.[4] Such high temperature diffraction techniques are now routinely used to investigate the phase transitions and thermal stability of solids, but when the requirement to reproduce real reaction conditions is introduced, for example the use of a solvent or a reactive gas atmosphere, greater constraints are placed upon the experiment. The three most important points to consider when constructing a reaction cell for *in situ* powder diffraction studies are that: (i) the intensity of the radiation used must be high enough to achieve good signal:noise in the diffraction data above diffuse scatter of the amorphous components (solvent for example), (ii) the radiation must be able to penetrate the cell walls and not be obstructed by bulky heating devices or pressure containment, and (iii) the experiment must be optimised to enable rapid data acquisition for kinetic studies. We will limit our discussion to such apparatus, and select examples of experiments that best

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Dermot O'Hare obtained his first degree in Chemistry from the University of Oxford in 1982 and then remained at Oxford for his D.Phil under the supervision of Malcolm Green, where he worked on carbon–hydrogen bond activation using metal atom chemistry. In 1990 he was appointed to a University Lectureship in Inorganic Chemistry and Septcentenary Tutorial Fellowship at Balliol College in 1990. His current interests span a wide range of inorganic chemistry from synthetic molecular organometallic chemistry through to solid state chemistry. He received the RSC's Sir Edward Frankland Fellowship in 1996–97. In 1998, he received the RSC Corday–Morgan Medal and Prize and the Exxon Chemicals European Science and Engineering award.

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illustrate the various *in situ* diffraction techniques currently in use. We begin our article by briefly discussing recent experiments performed using laboratory X-ray diffractometers, before considering experiments performed at synchrotron X-ray sources and at neutron sources.

2 *In situ* diffraction using laboratory X-ray sources

Many modern laboratory diffractometers can be readily modified to enable data to be collected at elevated temperatures, and some of the commercially available environmental chambers can be adapted for the study of the formation of crystalline inorganic solids. Environmental cells for studying the reactions between mixtures of gases and solids or simply solid-solid reactions have been most commonly described. For example Gavra and McMurray constructed a furnace to study gas/solid reactions at temperatures of up to 300 °C and pressures of 50 atm,[5] and used the cell to study the reaction between $EuNi_5$ and H_2 *in situ* at pressure of up to 50 atm, directly observing the formation of crystalline $EuNi_5H_{5.5}$, a material of potential use for hydrogen storage.[6] Samples were contained in 0.3 mm quartz capillaries. A more robust cell has been described by Puxley *et al.*; their apparatus could operate at temperatures of up 1000 °C using a larger amount of solid placed on a flat plate.[7] Data were collected from catalysts under reactive active gas atmospheres, and during the solid-state reaction between SnO_2 and Bi_2O_3. Another good example of the monitoring of a solid-state reaction in the laboratory with powder diffraction is the work of Bondioli *et al.* who studied the formation of the ferroelectric material $BaTiO_3$ from TiO_2 and $BaCO_3$ as a function of temperature up to 1200 °C. They were able to show that $BaTi_2O_4$ is present as a metastable phase at lower temperatures, and proposed a stepwise course of reaction.[8] A recent example of the use of a laboratory diffractometer to follow the formation of an inorganic material form a liquid medium was described by Rathousky *et al.* who followed the precipitation of the mesoporous silica MCM-41.[9] This study was performed at room temperature from a liquid/solid mixture in a *ca.* 0.5 mm^3 container. A small *d*-spacing region of diffraction data was monitored at 130 s intervals, allowing the appearance of the characteristic low-angle diffraction peak of MCM-41 to be monitored in real time.

Lindén *et al.* also studied the formation of mesoporous MCM-41 in the laboratory, using an ingenious tubular reactor in which reagents were mixed and allowed to flow along the apparatus through an X-ray diffraction cell.[10] By varying the length of the tube, or flow rate, samples of material could be studied *in situ* after different periods of reaction. Although meaningful kinetic data would be difficult to determine using this method, the measurement of diffractograms of material under real conditions allows the time-scale of reaction to be judged efficiently, even for reactions taking place on in sort times (less than 3 minutes for MCM-41). Mechanistic insight was possible for the case of the MCM-41 preparation, since under reaction conditions the material was observed to be less condensed than on isolation since on removal of hydration water de-swelling takes place.

These selected examples of the use of laboratory X-ray diffraction to follow chemical reactions illustrate that simple reaction cells can be constructed and mechanistic inferred during the formation of inorganic solids using readily available apparatus. In general, however, even with the best available rotating anode X-ray sources the time resolution is low (data must be collected on time-scales of minutes) and so it is difficult to extract accurate quantitative kinetic information. In addition, the limited range of X-ray energies available from laboratory diffractometers places severe limits of the amount of sample that can be studied and the size of reaction chamber used, because high levels of X-ray absorption greatly affects the quality of data that may be obtained from the sample within the cell. A point to bear in mind is that when scaling reactions down to very small quantities, genuine laboratory reactions conditions may no longer be reproduced. Problems in sampling a representative small portion of a mixture of reagents could arise, especially when mixtures of solids and liquids are studied, giving rise to results that are difficult to reproduce and/or interpret. Nevertheless laboratory diffractometer-based studies play a valuable rôle; they are readily available and provide a straightforward means to begin mechanistic of reactions producing solid materials.

3 *In situ* diffraction using synchrotron X-ray sources

3.1 Monochromatic radiation (angular dispersive diffraction)

Synchrotron-generated X-rays typically have intensity up to 10 orders of magnitude greater than the most brilliant laboratory-generated X-rays, Fig. 1. The high flux of X-rays from a synchrotron allows diffraction experiments to be performed using bulky sample containers since significant attenuation of the incident beam can be tolerated. Another advantage of synchrotron-generated radiation is that X-rays with short wavelengths (and hence high energies) can be utilised; these are less absorbed than higher wavelength X-rays, and so are useful when sample containers are must be penetrated. The experimental geometry of the experiments which use monochromatic synchrotron-generated X-rays are virtually identical to any laboratory diffractometer, but the time taken to record a diffraction pattern, especially when a static position-sensitive detector is used so that all data are accumulated simultaneously, is dramatically shortened; reactions can be followed in milliseconds rather than minutes.

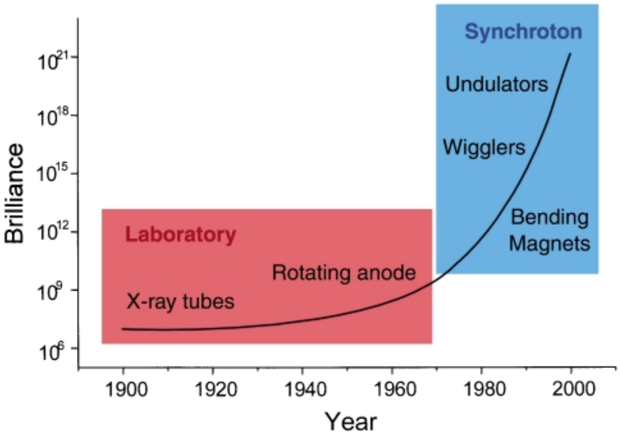

Fig. 1 A schematic of the historical development of available brilliance of X-rays from different sources. Brilliance is defined as number of photons per second per square millimetre per square milliradain per 0.1% bandwidth).

As with the experiments already discussed, much work using synchrotron X-rays has concentrated on the reactions between solids and gases, or solid-solid reactions. Good examples of such experiments are those by Larsen and co-workers who designed a cell to enable self-propagating high-temperature syntheses to be followed in time intervals as short as 10 ms.[11,12] Blocks of solid reagents (*ca.* 0.01 cm^3) are electrically ignited by a tungsten coil and the solid combustion reactions generate temperatures of up to 4000 K; diffraction data are measured by two fixed-angle detectors, each positioned to monitor an area of interest in the diffractogram. The technique has been used to

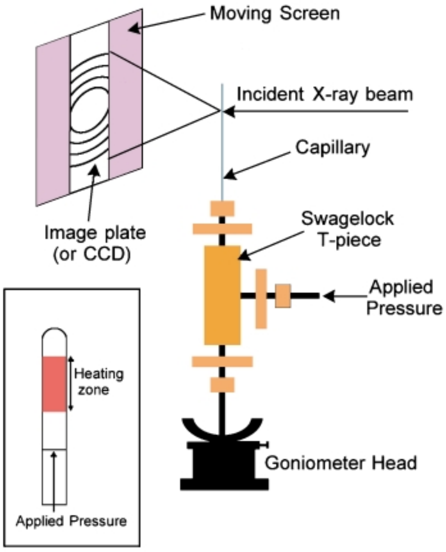

Fig. 2 A schematic of the apparatus developed by Norby and coworkers for time-resolved diffraction studies of hydrothermal crystallisations. The inset shows an enlargement of the capillary.

study syntheses of the carbide TaC.[13] and the ferroelectric $BaTiO_3$.[14] In the former case, the course of reaction was followed at 50 ms intervals and the material was observed to form *via* Ta_2C from Ta and C, with a total reaction time of only 50 s. This is a dramatic illustration of the power of synchrotron techniques for *in situ* studies of chemical reactions.

Norby *et al.* have developed in the last five years a synchrotron X-ray diffraction cell for study the hydrothermal crystallisation of inorganic materials.[15] This apparatus, Fig. 2, uses a quartz capillary as a sample container, pressure is applied externally to balance the pressure generated during a reaction and a 5 mm part of the tube heated by a hot air flow (up to 250 °C when pressures of 45 atm may be produced). Rapid data collection is made possible by use of a novel translating image plate detector. High resolution angular dispersive data are extracted by scanning the image plate after each experiment. Integration of the image plate data typically gives time resolution of 1–2 minutes.[16] Norby and his collaborators have used the apparatus to great effect in the study of the crystallisation of metal-substituted aluminium phosphates,[17–20] materials with useful catalytic properties. Fig. 3 shows typical diffraction data measured using the technique; in this case the crystallisation of CoAPO-5, a microporous cobalt aluminium phosphate from an amorphous gel.[19] As well as direct observation of the time-scale of reaction, these measurements allowed the determination of quantitative kinetic data by monitoring the area of a Bragg reflections with time and such data analysis has enabled rate constants to be determined, and kinetic models for these crystallisations to be proposed.[18,20] The same hydrothermal apparatus has also been used to follow the crystallisation of aluminosilicate zeolites[21,22] and a microporous manganese germanium sulfide.[23] Gross *et al.* used a similar cell to investigate the stability of silica/surfactant nanocomposites, precursors to mesoporous silicas when heated under hydrothermal conditions at 180 °C.[24]

The hydrothermal capillary apparatus has very recently been developed further to allow reactions under more extreme conditions to be studied. By using high energy X-rays ($\approx$35 keV, $\lambda \approx 0.32$ Å) generated at the European Synchrotron Radiation Facility, France and at Brookhaven National Laboratory, USA, Norby *et al.* showed that it is possible to penetrate a steel capillary.[25] Time-resolved diffraction data were measured at 350 °C, 200 atm during the transformation of a zeolite into a dense aluminosilicate. The *in situ* diffraction patterns obtained were of sufficient quality to allow structural information to be extracted by using the Reitveld method; such detailed structural characterisation of materials under reaction conditions is vital for understanding their properties.

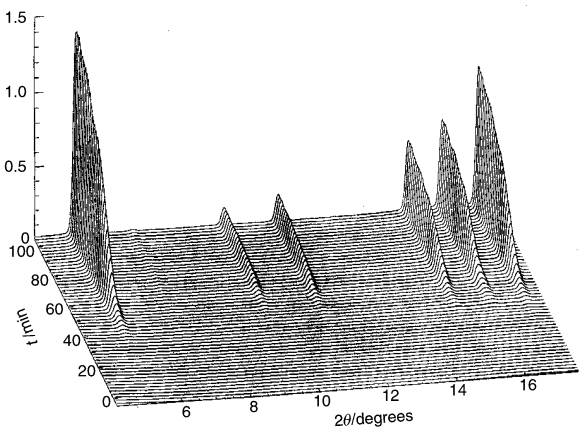

Fig. 3 Time-resolved diffraction patterns measured during the crystallisation of CoAPO-5, a microporous cobalt aluminophosphate from an amorphous gel by Norby and Hanson. Data were recorded at 200 °C in 1 min intervals. Figure reproduced with permission from ref. 19.

3.2 Polychromatic radiation (energy-dispersive diffraction)

Synchrotron-generated X-rays are produced with high intensity over a wide energy range (typically 10 to 120 keV). This unique feature obviously offers the possibility of selection of a specific X-ray wavelength for any given diffraction experiment, but also the opportunity to perform powder diffraction experiments in the energy dispersive mode, utilising all the incident X-ray flux in a single experiment. In the energy-dispersive X-ray diffraction (EDXRD) experiment the intensity spectrum of scattered X-rays from the sample is measured by a fixed-angle solid-state photon counting and energy discriminating detector, and each Bragg reflection is characterised by an energy which is dependent on the angle of the detector.[26] Since no monochromation is employed and only minimal collimation of the incident X-ray beam is used, the flux incident on the sample is high (*ca.* 10^{10} photons s^{-1}) and of sufficient intensity and energy to probe large volume samples in thick-walled reaction vessels. The geometry is particularly suitable for the use of environmental cells, since the fixed-angle detector means that only small windows are necessary for the passage of X-rays through the apparatus so devices with heaters or bulky pressure containment can easily be constructed.[27] The EDXRD method is widely used for the study of the pressure induced phase-transitions of inorganic solids where very confined cells are used,[28] but because data acquisition can be performed in times of the order of seconds the technique is also very useful for kinetic studies. One particular merit of the EDXRD technique is that reactions cells can be 'laboratory-sized', identical in design to apparatus used in preparative chemistry, so that more realistic, bulk reaction conditions are mimicked; this is in contrast to the techniques discussed in section 2.1, which use scaled-down reaction cells to minimise absorption.

Barnes and coworkers have pioneered the use of EDXRD for the study of chemical reactions, and have followed the reactions involved in the hydration of calcium silicate cements on time-scales down to 0.3 s per diffraction pattern.[29–31] These workers also first described the use of EDXRD methods to follow hydrothermal crystallisations. They designed a reaction cell made from the high performance polymer PEEK, that allowed use at temperatures up to 100 °C. They were able to monitor the crystallisation of sodalite, a dense aluminosilicate zeolite, from the layered material kaolinite and determined crystallisation curves describing extent of reaction as a function of time.[32] The hydrothermal formation of the large pore aluminophosphate VPI-5 was also studied by these workers using the EDXRD method.[33] The operating temperature of this early cell was limited by its design and the performance characteristics of the PEEK cell material. We have subsequently described the construction of a large-volume hydrothermal reaction cell from which EDXRD data may be collected at up to 250 °C, more typical of the temperatures used in hydrothermal synthesis.[34] This reaction cell is virtually identical in design and construction to the 23 mL Parr hydrothermal autoclaves widely used in many research laboratories, but the steel walls of the cell are thinned to 0.3 mm to minimise absorption of X-rays, Fig. 4 The Oxford/Daresbury hydrothermal cell has been used on Station 16.4 of the Daresbury SRS, the UK synchrotron radiation source, to study the crystallisation of a wide range of inorganic materials by several groups. The cell has been much used for studying the formation of microporous solids; our group has studied the formation of porous layered tin sulfides,[35] open-framework gallium fluorophosphates,[36–38] and zeolites,[39,40] and Thomas and coworkers have used the cell to study the formation of transition-metal substituted aluminophosphates.[41–43] One important observation we have made during the study of the crystallisation of gallium fluorophosphates is that under certain reaction conditions previously unknown intermediate crystalline phases are observed to form before the onset of the crystallisation of the expected microporous phase, Fig. 5. For the case of the microporous phase ULM-3, a transient crystalline intermediate is only stable under hydrothermal conditions; if the reaction cell is allowed to cool when the intermediate is present, transformation into another, as yet unidentified, phase takes place.[38] This is a dramatic illustration of the need to study reactions under real conditions, and of how quenching experiments are not always a reliable method of determining the species present at reaction conditions. In this particular case it has subsequently lead us to discover some new related metastable gallium fluorophosphates.[44,45]

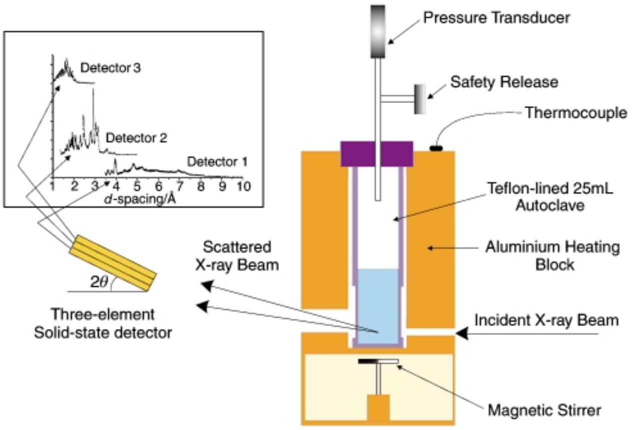

Fig. 4 A schematic of the Oxford/Daresbury hydrothermal autoclave used for energy-dispersive X-ray diffraction studies, developed by us for use on Station 16.4 of the UK synchrotron source at Daresbury Laboratory.

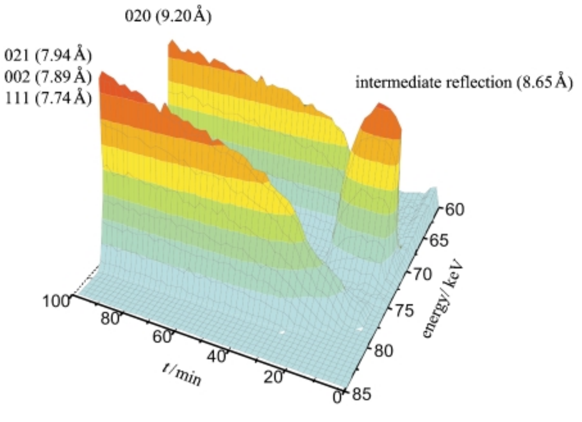

Fig. 5 A small part of energy-dispersive X-ray diffraction data (30 s intervals) measured *in situ* during the crystallisation of the open-framework gallium fluorophosphate ULM-3 from an amorphous phosphate gel at 180 °C. The use of P_2O_5 as a reagent results in the formation of a previously unknown crystalline intermediate phase before the onset of crystallisation of the product.

In addition to the direct observation of crystallisation on a short time-scale, the *in situ* EDXRD method has allowed much new information about the kinetics of the crystallisation of microporous solids to be determined. By determination of changing Bragg peak areas, it is possible to extract quantitative kinetic information, since the intensity of a Bragg reflection is directly proportional to the amount of diffracting solid.[46] Fig. 6, for example, shows crystallisation curves we have recently obtained from a study of the hydrothermal formation of sodium zeolite A, one of the most widely used microporous materials in many industries.[40] The unusual two-step crystallisation curve has never been reported previously, and was only revealed by continuous monitoring of the reaction with high time resolution (30 s per diffraction pattern). The effect is highly dependent on reaction conditions and is believed to arise from dissolution of an amorphous precursor gel controlling the rate of reaction. Such an observation sheds new light on zeolite crystallisation, and these measurements using EDXRD on short time scales will provide new data for computer modelling studies, and ultimately mechanistic information. A recent development in the use of *in situ* EDXRD is the installation of a three element solid-state photon counting, energy discriminating detector on Station 16.4 of the SRS;[47,48] this allows three *d*-spacing regions of the powder diffraction pattern to be measured simultaneously and permits unambiguous phase identification, which has been particularly useful in the study of microporous materials.[49]

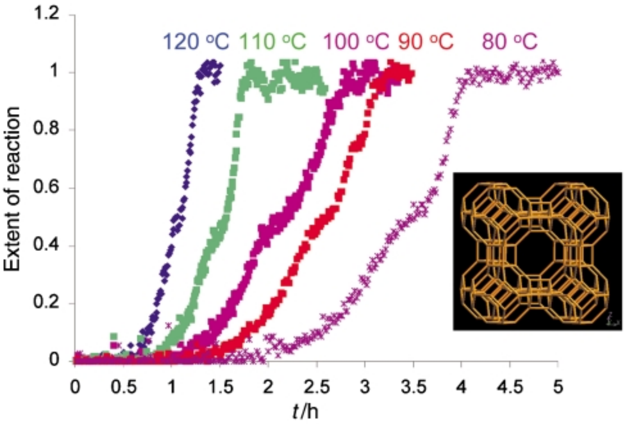

Fig. 6 Crystallisation curves for sodium aluminosilicate zeolite A (inset) determined using the *in situ* EDXRD technique. Diffraction patterns were collected every 30 s while an amorphous aluminosilcate gel was heated in the autoclave.

As well as the studying the formation of microporous materials, the Oxford/Daresbury hydrothermal autoclave has been used by other groups to monitor the formation of inorganic solids. Cahill *et al.* studied the formation of iron sulfides using the cell, and were able to establish a pathway of progressive sulfidation of FeS to FeS_2.[50] Shaw *et al.* recently studied the hydrothermal formation of calcium silicate minerals; this study was performed at the Advanced Photon Source, USA, which offers *ca.* 10 times greater X-ray flux than the SRS, enabling reactions to be performed in cells with thicker walls, and consequently at temperatures of up to 330 °C.[51]

EDXRD has been used by our group in Oxford to study the formation and behaviour of a wide range of other inorganic solids. Time-resolved EDXRD studies of intercalation reactions of layered solids have been very important in understanding their mechanism, and this area has recently been reviewed.[52,53] We have also investigated the kinetics and mechanism of formation mesoporous silicas and the different growth mechanism for MCM-41 *versus* the mesoporous silicate FSM-16, which is derived from kanemite,[54] and of the crystallisation of gibbsite,[55] an important material in aluminium manufacture. The *in situ* EDXRD method is clearly easily extended to following reactions under conditions more extreme conditions than the hydrothermal reactions discussed above, with simple modification of furnace design. We have very recently described the construction of a furnace that operates at 1000 °C and from which EDXRD data can be measured.[56] We have studied the formation of some dense metal oxides at *ca.* 800 °C, both by a traditional ceramic methods using the carbonates of the constituent metals, and by a molten-salt method in liquid alkali-metal halide fluxes. We were able to follow the decay of starting materials, and subsequent growth of the layered perovskite $RbCa_2Nb_3O_{10}$ and show the enhancement of crystallisation rate in the alkali-metal flux.[56] Parkin *et al*. have recently begun a study of self-propagating high-temperature reactions (SHS) using EDXRD on Station 16.4 at the SRS. To study these reactions they have pushed the data collection intervals down to just 100 ms.[57] They also studied the effects of a magnetic field on these reactions using EDXRD.

In summary we anticipate that further advances in apparatus design are likely to follow shortly, and allow reactions over a wide spectrum of temperatures and pressures to be followed by EDXRD.

4 *In situ* diffraction using neutron sources

The complementarity of neutron diffraction and X-ray diffraction for the structural characterisation of materials is well known, in particular the use of neutron diffraction to locate light atoms in the presence of heavy atoms, especially hydrogen atoms, and in the determination of the spin arrangement of magnetically ordered materials.[58] In the context of performing *in situ* diffraction studies, neutron diffraction offers distinct advantages over many of the X-ray diffraction experiments. For example, many materials have very low neutron absorption cross-sections which means that reaction vessels can be constructed which give rise to low backgrounds in diffraction data. Processes involving light atoms, such as reactions involving water can be followed. In additon, use of time-of-flight neutron diffraction with fixed-angle detectors would simplify apparatus construction. One disadvantage of neutron diffraction is the much lower flux available from currently available neutron sources at present compared to synchrotron X-ray sources; this means that at present the time resolution of time-resolved neutron diffraction experiments is relatively poor (of the order of minutes rather than sub-second), but recent development in the area shows the great promise of the method.

Pannetier is well known for his many time-resolved neutron diffraction studies of chemical reactions;[59] he and his coworkers have concentrated on fairly simple systems, such as hydration reactions,[60] and the reactions of solids with gases.[61] Christensen and coworkers performed an extensive study of the reactions between silicates and water under moderate temperatures (up to *ca.* 120 °C) using *in situ* neutron diffraction and were able to measure diffraction data in periods as short as 5 minutes.[62–66] The same workers also performed the first *in situ* neutron diffraction study of a hydrothermal crystallisation, in this case the formation of iron(III) oxides from amorphous iron hydroxides at 120 °C.[67] They were able to measure crystallisation curves and efficiently monitor the effect of experimental parameters on reaction rate. When performing neutron diffraction studies, it is usual to use deuterated reagents to minimise the large incoherent scattering of protons, however the use of protonated reagents can reveal additional information. For example Tuttillas *et al.* studied the calcination of zirconium hydroxide, used to prepare zirconia, with *in situ* powder neutron diffraction at the Institut Laue Langevin (ILL). They were able to detect a massive decrease in background when dehydration was complete (and all protons were lost from the reagents) allowing one step of the reaction to be pinpointed.[68]

Polak *et al.* described the design of an autoclave to allow the acquisition of neutron diffraction data during the hydrothermal crystallisation of tobermorite, a calcium silicate used in cements, and of some zeolites.[69] The cell could operate at temperatures of up to 250 °C, and external pressure was applied. One draw-back of this cell design was the dominance of the Bragg reflections due to the sample containment (aluminium with a Teflon liner) in the measured diffraction data; this could severely limit the amount of structural information available. Our recent work, in collaboration with colleagues at ISIS, the UK neutron spallation source, on the use of neutron diffraction to follow hydrothermal crystallisations has resulted in the design and construction of a novel null-scattering environmental cell from which time-resolved diffraction data can be measured at temperatures of up to 250 °C and pressures of 20 atm.[70] The cell (Fig. 7) is constructed from a Ti-Zr alloy whose component metals are mixed in such a ratio as to cancel their negative (Ti 67.7 atom %, $b = -3.44$ fm) and positive (Zr 32.3 atom%, $b = 7.16$ fm) neutron scattering lengths. The cell is protected from corrosive reagents by a thin internal layer of gold metal, thus the cell is invisible to neutrons and can contain reactive mixtures of solids and liquids. We have commissioned the Oxford/Isis hydrothermal cell on the medium-resolution high-flux diffractometer POLARIS initially and most recently have tested it on GEM, a new neutron diffractometer with a large array of detectors which allows rapid data collection.[71] Our first experiments have addressed the hydrothermal formation of barium titanate, an important ferroelectric material used in the electroceramics industry.[72] The industry requires the crystallisation of the phase pure tetragonal polymorph. The presence of the highly X-ray absorbing barium ions in the sample mixture meant that it was impossible to study this system even using synchrotron X-ray diffraction. However, using *in situ* neutron diffraction we were able to observe directly the dissolution of both the crystalline starting materials, TiO_2

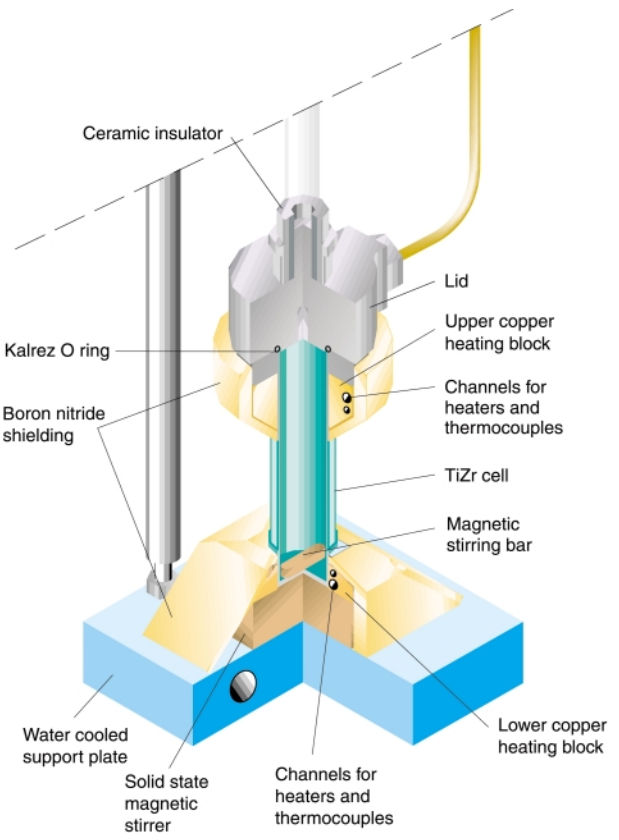

Fig. 7 Schematic of the Oxford/ISIS hydrothermal reaction cell for *in situ* neutron powder diffraction measurements.

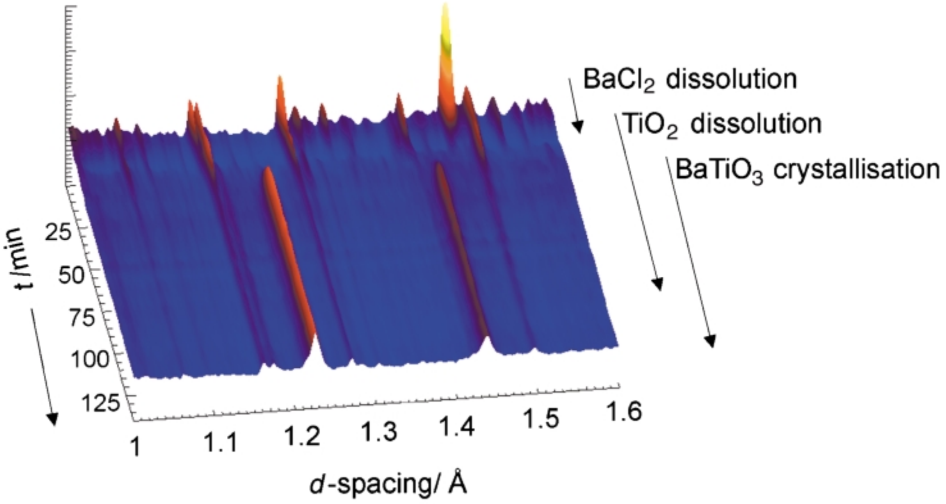

Fig. 8 *In situ* neutron diffraction data measured during the formation of the ferroelectric barium titanate from $BaCl_2$ and TiO_2 in NaOD solution at 200 °C. Data were collected at 5 min intervals using the GEM diffractometer at ISIS.

and $Ba(OD)_2{\cdot}8D_2O$, before the onset of crystallisation of $BaTiO_3$. This allowed us to conclude that a dissolution–precipitation mechanism predominates, rather than a heterogeneous transformation mechanism. Fig. 8 shows *in situ* neutron diffraction data measured using GEM where data were collected in 5 min intervals. As well as the new mechanistic insights, we were able to measure high resolution diffraction data that are suitable for Reitveld profile analysis, Fig. 9. This is a step forward in *the in situ* study of hydrothermal reactions, and shows the potential use of neutron diffraction in real time structural determination of crystalline solids under laboratory reaction conditions. We have most recently used the Oxford/ISIS hydrothermal cell to study the formation of some aluminosilicate zeolites, the archetypal materials synthesised hydrothermally. We have followed the crystallisation of sodium zeolite A and monitored its collapse into the dense phase hydroxosodalite.[73]

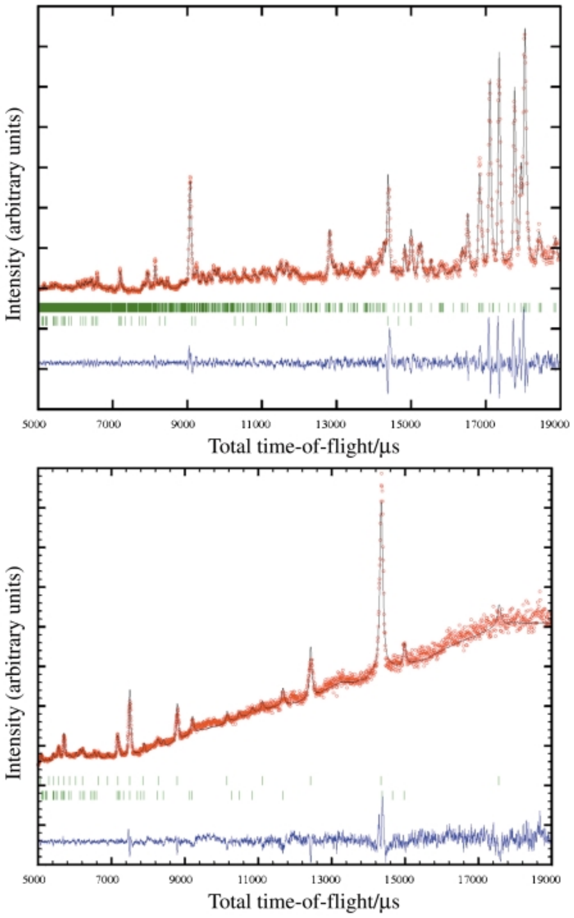

Fig. 9 Neutron diffraction data measured *in situ* during the hydrothermal formation of $BaTiO_3$ from $Ba(OD)_2.8D_2O$ and TiO_2 (a) after 15 min, and (B) after 12 h.

Other recent highlights in the use of powder neutron diffraction to monitor the formation of inorganic solids include following the crystallisation of superconductors from melt-cast precursors,[74] and a study of the reaction between Nd/Fe/V alloys and nitrogen at 800 °C.[75] In the latter study data were collected in around 5 min intervals, and were of sufficient quality to perform Reitveld refinement, and allowed structural determination *in situ*. This study was performed using the recently constructed D20 diffractometer at the ILL, which offers a combination of high neutron flux and high count rate by a novel large surface area position-sensitive detector.[76] Undoubtedly this instrument will lead to many more kinetic studies of solid-state reactions in the coming years.

5 *In situ* powder diffraction combined with spectroscopic probes

The *in situ* diffraction techniques described above yield information about the growth and decay of crystalline ordered materials during the course of a chemical reaction. As the above discussion demonstrates, these methods allow the course of reactions to be observed in real time, including the detection of crystalline intermediate phases, and kinetic information can be determined. Bragg diffraction, however, does not probe any amorphous phases present. For instance no information about the changing local atomic structure of the gel-precursor to zeolites in a hydrothermal crystallisation is obtained. In order to achieve the monitoring of both long-range crystallographic order and short-range atomic order, several ingenious experiments have been designed, combining *in situ* diffraction with spectroscopic methods. The most powerful of these methods is the use of combined X-ray absorption fine structure spectroscopy and X-ray diffraction (XAFS/XRD). This was first described by Couves *et al.* in 1991,[77] and has since been used to monitor various reactions involving solids such as solid-state transformations,[78–80] polymerisations,[81] thermal decompositions,[82,83] and widely used for monitoring catalytic processes under operating conditions.[84,85] High-intensity synchrotron generated X-rays are required for such studies.

Fig. 10 shows the arrangement of a typical XAFS/XRD experiment. This set-up was used by Sankar *et al*. to follow the formation of a microporous cobalt aluminophosphate from an amorphous gel.[86] XRD data were measured for 220 s, followed

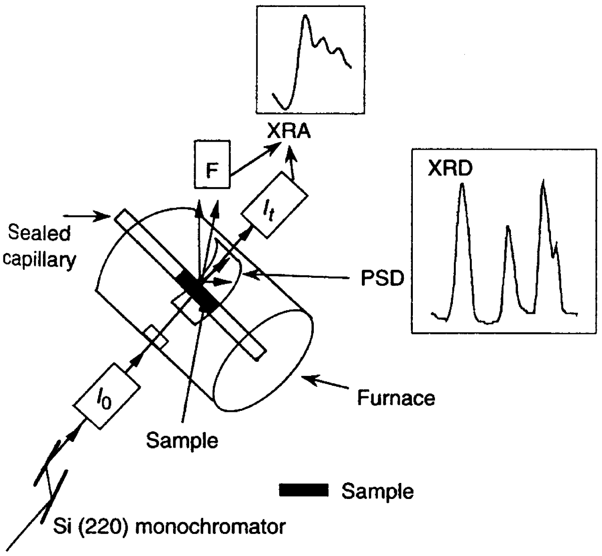

Fig. 10 A schematic of the XAFS/XRD experiment used to follow the crystallisation of a cobalt aluminophosphate. Figure reproduced with permission from ref. 86.

by XAFS data at the cobalt K-edge for the same time (alternation between the two measurements is necessary as the XRD data are acquired with a constant wavelength whilst the XAFS data require a scan over a wavelength range). Changes in the local environment of cobalt were monitored, and related to the changes in long range order apparent in the diffraction pattern, Fig. 11. It was thus shown that the coordination of cobalt changes from octahedral to tetrahedral in the gel immediately prior to crystallisation. The same apparatus was also used to follow the formation of a bismuth molybdate catalyst from a precursor gel,[87] and of small particles of cadmium oxide from a hydroxy gel.[88] In both cases monitoring changes in local atomic environment and relating them to crystallographic order allowed new insights into the reaction mechanism.

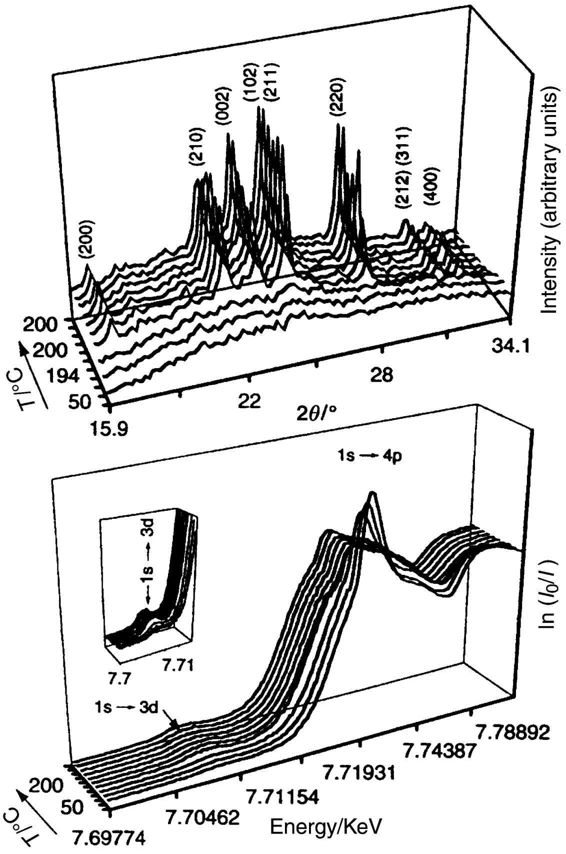

Fig. 11 XRD (top) and Co K-edge EXAFS (bottom) recorded during the crystallisation of CoALPO-5 at 180 °C from an amorphous gel. Figure reproduced with permission from ref. 86.

6 Conclusions and outlook

The measurement of powder diffraction data during the synthesis of many inorganic materials requires the design and construction of specialised apparatus, but in the last five years much progress has been made. The experiments we have surveyed here represent in most cases the first attempts to determine kinetic and mechanistic information about reactions involving the formation of solids from heterogeneous media. The reactivity and structures of solids under non-ambient conditions have been probed directly for the first time. As is apparent from our review, the most impressive advances have been made in the area of hydrothermal chemistry, with several groups developing apparatus that are now widely used on a routine basis to follow directly the crystallisation of a range of porous materials with useful properties. This undoubtedly reflects the fact that hydrothermal chemistry has found to be an incredibly fertile method for the synthesis of new inorganic solids, and is currently used to prepare a diversity of materials from new zeolitic solids[89] to metastable metal oxides.[90] Given the success in using powder diffraction to follow hydrothermal crystallisations, extension of the methodology to other preparative methods is likely to follow shortly; systems such as alkali-metal–chalcogenide fluxes[91] and solvothermal synthesis in alcohols or amines[92] which are currently the focus of attention in synthetic solid-state chemistry.

With the now almost routine measurements of the course of solid-state reactions, a large amount of kinetic data has been accumulated, as well as much qualitative information about the course of reaction and identification of intermediates. Analysis of these data is one of the first steps in proposing reaction mechanisms, but clearly much more work is required in this new field before the rational design of new materials is possible. Computer modelling will undoubtedly have an important rôle in understanding the data obtained by the techniques we have reviewed, and is an area which is developing rapidly; for example the early stages of the formation of zeolite has been modelled in some detail recently and the energetics of these solution-mediated reactions calculated,[93] and the prediction of the structures of new solids using computer-modelling techniques is currently the focus of much attention.[94,95]

In this article we have emphasised how recent progress in the use of *in situ* powder diffraction methods has been intimately linked to developments at synchrotron and neutron sources. The availability of high intensity synchrotron-generated X-rays over a wide energy range and the design of new neutron diffractometers to enable rapid data collection has instigated many of the experiments we have described. As well as the continued use of the experiments already in use, new developments are likely to enable other new experiments to be designed and realised. In many parts of the world new synchrotron and neutron sources are being constructed, including a third-generation synchrotron source in the UK to replace the SRS, and a new spallation neutron source at Oak Ridge USA. These will offer increasingly higher fluxes of radiation and the possibility of rapid data collection; features vital for the future development of *in situ* powder diffraction methods.

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