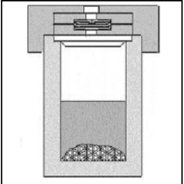
Subcritical solvothermal synthesis of condensed inorganic materials



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The solvothermal method has recently been extended from zeolite synthesis to the formation of *condensed* inorganic solids, which find uses in diverse areas due to properties such as ionic-conductivity, solid-state magnetism, giant magnetoresistance, low thermal expansion and ferroelectricity. This offers specific advantages over the traditional ceramic synthetic routes to inorganic solids and these are highlighted with examples from the recent literature, and the efforts focussed on determining the formation mechanism of solids from the heterogeneous mixtures used in solvothermal procedures are discussed.

1 Introduction: inorganic solids and their synthesis

Solid inorganic materials supply the world with a diversity of useful properties, ranging from electronic properties, such as conductivity, magnetism, and superconductivity, to properties which depend more directly on atomic arrangement, such as porosity, negative thermal expansion, and elasticity.[1] Examples of how these properties are exploited include the latest rechargeable and long-life batteries which rely on transition-metal-containing oxides, the use of magnetic inorganic materials for data storage at the heart of computers, and miniaturised titanate capacitors found in most electronic devices. Furthermore, the fine-chemical industry relies upon solid, inorganic catalysts; for example, the cracking of crude oil, the first step in the production of organic chemicals from fossil fuels, is almost exclusively performed using catalysts based on the microporous aluminium silicate zeolites. These examples illustrate how research into the structures, properties and synthesis of inorganic solids is driven, to a certain extent, by commercial application and their value to the economy. The fundamental physical aspects of their properties, however, also continue to be the focus of much attention by chemists, physicists, and materials scientists from an academic point of view. Because of these reasons, solid-state chemistry continues to be an area of great growth, and with the continued development of new advanced techniques for structural characterisation (such as crystallographic studies of microcrystals, *ab initio* structure determination from powder diffraction data, and new solid-state NMR techniques), huge advances have been made in understanding structure–property relationships of materials. The number of new inorganic materials whose structure is now almost routinely determined continues to increase dramatically year by year. This review will be concerned with one important part of inorganic solid-state chemistry, namely synthesis. This aspect of solid-state chemistry is vital to study, since the development of new synthetic procedures has the great potential to allow the discovery of novel solids, and offers the possibility of controlled synthesis of desired materials with properties tuned for application.

Richard Walton completed his BA degree in Chemistry at the University of Oxford (Worcester College) in 1994 after undergraduate research with Dr Ann Chippindale into the synthesis and structures of new open-framework phosphates which was awarded a University Part II thesis prize. He received his PhD from the University of Reading in 1997 following research with Dr Simon Hibble into the structures of amorphous and poorly-crystalline transition-metal chalcogenides. The same year he returned to Oxford to undertake post-doctoral research in the group of Professor Dermot O'Hare into the development and use of in situ *diffraction methods for following inorganic solid-state reactions, in particular focussing on hydrothermal synthesis. In September 2000 Dr Walton took up his current post as Lecturer in Inorganic Chemistry at the University of Exeter.*

We will be concerned with solids that have extended structures, rather than molecular solids. Molecular solids, of course, exhibit many useful properties, and have been the focus of great attention because of this (for example, a number of families of molecular superconductors are now known). The synthesis of molecular solids relies on crystallisation from a suitable solvent, usually at close to ambient temperature and pressure, and therefore, from the synthesis point of view, little scope for adjusting reaction conditions presents itself. By contrast, extended inorganic solids have been synthesised by a huge variety of methods for a good many years; these range from high temperature 'ceramic methods' to the use of sol–gel precursors, to solvent mediated crystallisations, to reactions performed in molten salts, to topotactic insertion and ion-exchange processes.[1]

Traditionally, a high temperature ceramic approach would be used to form an inorganic solid, whereby solid starting materials containing the desired chemical elements are intimately ground in stoichiometric quantities, and heated at extreme temperature (usually in excess of 1000 °C) for a period of between hours and days. The method is often referred to as 'shake and bake' and the extreme temperature is necessary to enhance interdiffusion of the solid reagents, and so allow chemical reaction to take place. A classic example, and one we will consider in more detail later, is the formation of ferroelectric $BaTiO_3$ from

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$BaCO_3$ and TiO_2 at temperatures in excess of 900 °C. The method is widely applicable (conceivably, solid reagents containing any chemical element can be reacted by this means) and has the advantage in being stoichiometric and so the yield is 100%. Additionally, highly crystalline phases are produced when the extreme temperatures of the ceramic route are employed, which can greatly aid the structural characterisation necessary to understand their properties. These favourable features of the ceramic method of synthesis have been widely exploited over the years to produce materials of increasing complexity; a good example is the synthesis of cuprate superconductors in the 1980s, in which oxides containing up to six different metals, such as $Tl_{1-y}Pb_yY_{1-x}Ca_xSr_2Cu_2O_7$,[1] were prepared from starting materials containing each of the elements required. The ceramic method, however, does present a number of disadvantages: (i) the synthesis protocol is lengthy, often involving periods of heating of days with repeated regrinding necessary to achieve the intimate mixing of reagents, (ii) control of particle size is very difficult to achieve, and in fact often irregularly sized and shaped crystallites are formed, and (iii) since high temperatures and long heating times are used to bring about reactivity, only the most thermodynamically-stable phases crystallise, and there is little scope for kinetic control and isolation of metastable phases, materials which themselves might have desirable physical and chemical properties. New routes to the synthesis of inorganic solids have been developed in an attempt to overcome these shortcomings, and this article will be concerned with recent developments in one of these methods, namely the solvothermal method.

The sol–gel method and the molten-salt method are two methods that have been employed in the synthesis of new solids in the quest for new low-temperature routes to inorganic solids,[2] and it is worth briefly considering these before moving on to discuss solvothermal synthesis. Both synthetic methods provide means to overcome the difficulties in achieving intimate mixing of reagents during solid–solid reactions. The sol–gel method involves two steps. First, soluble metal reagents are mixed in solution, and an amorphous precipitate produced, in which the constituent metals are assumed to be mixed intimately. Second, calcination at high temperature is performed to drive off any by-products and yield the desired crystalline product. The molten-salt method employs a liquid reaction medium, one effect of which is to enhance the rate of diffusion between reagents. Often an alkali metal halide is used as the flux in the molten salt method which will melt in excess of 500 °C, and the sol–gel route uses high temperatures (~1000 °C) to burn off organic components of the gel and to achieve high crystallinity in the product. Although both methods offer conditions milder than those traditionally used, the problems of having little control over particle size and no kinetic control over the material formed produced remain. Table 1 summarises the main synthetic methods available to the solid-state inorganic chemist, with the advantages and disadvantages of each highlighted.

2 The solvothermal method

The historical use of *hydrothermal* synthesis in the production of inorganic solids has been reviewed previously; in particular an excellent article by Rabenau describes the development of the method from the nineteenth century to the mid 1980s.[3] Rabenau defined hydrothermal synthesis as the use of water as a solvent in a sealed reaction container when the temperature is raised above 100 °C. Clearly the definition can be extended further to *solvothermal* chemistry being the use of a sealed reaction vessel and temperature above the boiling point of the solvent used. Under these conditions, autogeneous pressure (*i.e.* self-developing and not externally applied) is developed. The pressure within the sealed reaction container is found to increase dramatically with temperature, but also will depend on other experimental factors, such as the percentage fill of the vessel and any dissolved salts. The use of water as a solvent has been most widely investigated, specifically because of the rôle of hydrothermal processes in geological phenomena occurring in the Earth′s crust. A number of fundamental properties of water are greatly affected by pressure and temperature. For example, the viscosity of water decreases with increasing temperature, and at 500 °C and 10 bar is only 10% of its magnitude under ambient conditions.[3] Even under more mild conditions the viscosity is still lowered, and thus it may be envisaged that the mobility of dissolved ions and molecules is higher under hydrothermal conditions than at ambient pressure and temperature. Similarly, the dielectric constant of water is affected by temperature and pressure, and is considerably reduced above the critical point; this can have major implications on the solubility of solid reagents under reaction conditions.

In terms of practical considerations to consider when hydrothermal synthesis is employed, the most revealing data are those describing the pressure developed inside a sealed reaction vessel as a function of percentage fill of the container and the temperature employed. Fig. 1 shows these data and demonstrates first the dramatic rise in pressure when high percentage fill of reaction vessel is used, and second how the pressure inside the reaction container can be controlled by choice of temperature and/or the volume of solvent used.† Below the critical point of water, and even below 200 °C, a high percentage fill allows access to pressures of hundreds of atmospheres. As an example of how the use of hydrothermal conditions can affect the reactivity of inorganic solids, the solubility of metal oxides under conditions of elevated pressure and temperatures, a topic that has been studied because of its industrial and geological significance, provides useful insight. For example, the solubility of TiO_2 (rutile polymorph) at pH

Table 1 A summary of the characteristics, advantages and disadvantages of some of the common methods used in the preparation of condensed inorganic solids

Method	Typical temperature	Advantages	Disadvantages
Ceramic	800–1500 °C	(1) Stoichiometric (2) Crystalline products	(1) Lengthy cycles of heating and grinding (2) No particle size control (3) Only thermodynamic products are stable
Sol–gel	Step 1: Room temperature Step 2: ~1000 °C	(1) Mixing of reagents (homogeneous product)	(1) Difficult to control particle size (2) Impurities from gel precursor in product
Molten-salt	<1000 °C	(1) Mixing of reagents (2) Single step	(1) No particle size control
Subcritical hydrothermal	100–250 °C	(1) Mixing of reagents (2) Kinetic phases isolated (3) Control of particle size (4) Single step	(1) Difficult to predict outcome of reaction

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† In the references cited, several different units of pressure are used, therefore as a guide for the reader some conversion factors are given. 1 atmosphere = 1.01 bar = 101 000 Pascal = 14.7 psi = 760 mm Hg.

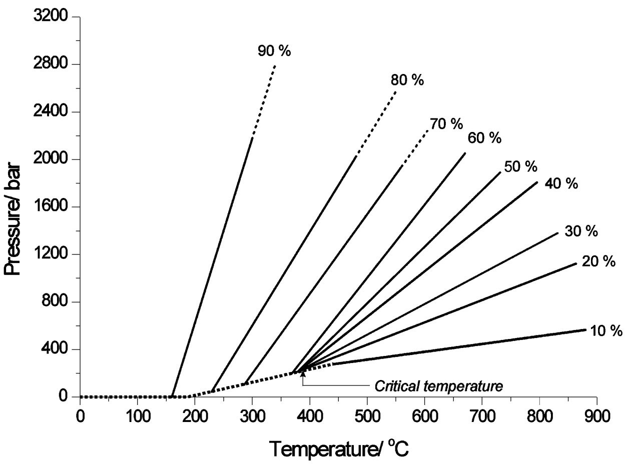

Fig. 1 Pressure as a function of temperature and percentage fill of water in a sealed vessel (after Rabenau[3]).

10.5 was found by Knauss *et al.* to increase by two orders of magnitude on heating from 100 °C to 300 °C under hydrothermal conditions.[4] Such data, although rather limited due to the difficulties in acquiring them, demonstrate how the chemical reactivity of usually insoluble reagents can be hugely modified by application of hydrothermal conditions.

It can be seen that the solvent properties of the water can be vastly changed by use of hydrothermal conditions, and in effect a completely new solvent is found at high temperature and elevated pressure, compared to at room temperature. Other solvent systems have been somewhat less studied, and water still remains the most widely used solvent in solvothermal synthesis; some examples of the uses of organic solvents will be given below. Historically, hydrothermal synthesis utilised temperatures above 300 °C and often took place in the supercritical regime; until the 1980s this was geared largely towards the production of large single crystals of inorganic solids, by the use of the hydrothermal conditions to achieve controlled chemical transport.[3] The vast majority of solvothermal syntheses performed today in the synthesis of inorganic materials utilise subcritical conditions, and I will focus on these much milder reactions conditions (temperature $<$ 250 °C), that are presently being used not only to provide a convenient low temperature route to materials with practical application, but also in the exploratory synthesis of new solids.[5,6] This work has focussed largely on oxide-based materials, but some recent studies have extended the methodology to allow the production of materials such as nitrides.[5]

Subcritical solvothermal synthesis is commonly performed using Teflon™-lined, stainless steel autoclaves, as shown in Fig. 2. The use of an autoclave is necessitated by the pressures developed in the solvothermal reactions, and the inert liner is used to protect the stainless steel outer shell from the corrosive reagents typically used in synthesis (such as strong acids or bases). Such autoclaves can be used at up to 270 °C, and depending on the engineering specification of the steel walls, pressures of ~150 bar can be withheld.

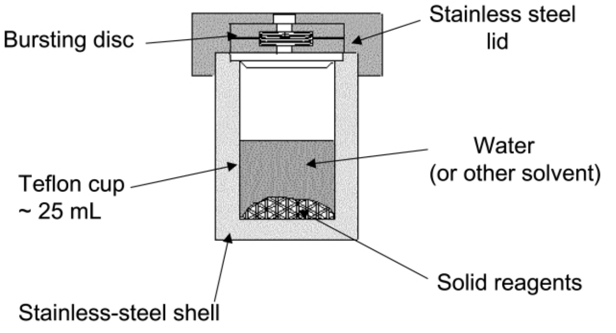

Fig. 2 A schematic of a Teflon™-lined, stainless autoclave typically used in the laboratory to perform subcritical solvothermal synthesis.

The versatility of the solvothermal method has been well demonstrated by the successful synthesis of zeolites and other microporous phases.[7] These solids find widespread application in many areas (including catalysis, ion-exchange and sorption) and hence have been the focus of much attention. In an effort to extend the range of microporous solids away from the silicate zeolites, an incredible range of 'open-framework' solids has been reported in the literature in the past five years; and presently in excess of one hundred new structures types are described each year.[7] These elegant structural architectures have already been much reviewed and the existence of such a range of possible structural types, indicates the versatility of the solvothermal synthesis method. In this current review I will focus on the solvothermal synthesis of *condensed* inorganic solids. The definition condensed is not precise, but in this context is taken to mean materials that do *not* possess the characteristics of zeolites and other open-framework materials, *viz* the presence of pores and channels, the incorporation of 'extra framework', exchangeable cations, and loosely-bound, zeolitic water. Essentially, I will focus on materials that are usually synthesised by ceramic routes, and this will include some layered solids as well as materials with dense structures made up of structural units linked in three dimensions. The review will not be exhaustive; instead I will choose examples that best illustrate the advantages of the use of solvothermal chemistry in solid-state synthesis over other preparative approaches. The authors of references given, and the papers they cite, will provide the reader with many more examples of solvothermal synthesis.

3 Solvothermal synthesis of condensed oxides

3.1 Ferroelectric titanates

Although it well-established that binary transition-metal oxides, such as iron oxides and chromium oxides for use in magnetic recording devices, can readily be synthesised from soluble metal salts or *via* the hydrolysis of metal alkoxides using a hydrothermal reaction,[3] the considerable advantages of the solvothermal method are best demonstrated by considering how mixed metal oxides can be produced, *i.e.* oxides that contain more than one metal. If the ceramic route is used in this case, repeated regrinding and heating are necessary to achieve sample homogeneity. The enhanced interdiffusion of reagents in the solution-mediated hydrothermal reactions, however, allows the rapid, direct crystallisation of a single-phase material. The most well studied example is the ferroelectric material barium titanate, $BaTiO_3$, (whose synthesis I will consider in more detail below). The tetragonal polymorph of $BaTiO_3$ finds widespread application in multilayer capacitors, thermistors, electro-optic devices and dynamic random access memories, and these important commercial uses have driven research into new synthetic routes to its synthesis. The direct hydrothermal crystallisation of $BaTiO_3$ is found to occur at temperatures as low as 80 °C from basic solutions containing a barium salt, and solid TiO_2. For comparison, the solid-state route to the same material requires temperatures of greater than 900 °C. Dutta and co-workers first made extensive studies of this reaction, and showed conclusively that the ferroelectric tetragonal polymorph of $BaTiO_3$ could be prepared from reaction mixtures of $BaCl_2$, NaOH and TiO_2 in water at 200 °C,[8] and others have since developed the method (see for example reference 9). The tetragonal polymorph of $BaTiO_3$ forms on cooling the product through the Curie temperature of 120 °C where the cubic to tetragonal phase transition takes place. Interestingly, in the absence of chloride ions (for example if $Ba(OH)_2$ was used as the Ba^{2+} source), only the cubic $BaTiO_3$ polymorph was produced, and it was suggested that the cubic phase might be stabilised at room temperature by the inclusion of hydroxy groups in the solid. It was also noted that a degree of control of particle size was possible, by varying temperature, time, and choice of starting materials. This dependence of product morphology and even crystal structure upon choice of synthesis conditions illustrates how small changes in reaction conditions can affect the outcome of a hydrothermal reaction. It is now established that barium titanate fine powders (ranging in diameters of 10's of nanometers to microns) can be produced with a narrow particle-size distribution by use of solvothermal conditions; for instance, Pinceloup *et al.* investigated the use of a water–isopropanol mixture as solvent and showed that by varying the composition of the solvent mixture it is possible to adjust the average particle size of the product from 90 to 30 nm, and thus to control surface area of the material produced, Fig. 3.[10]

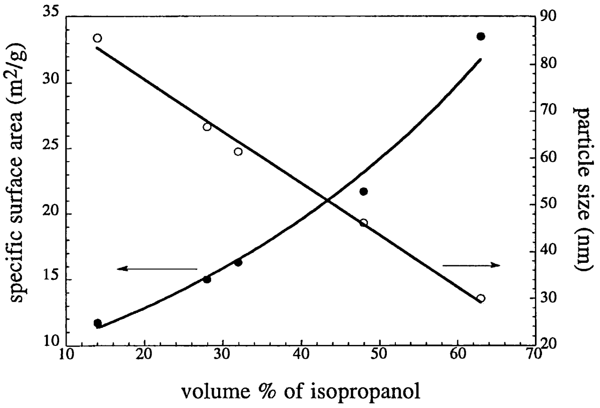

Fig. 3 The dependence of particle size and surface area of barium titanate powders as a function of isopropanol–water mixture used in their solvothermal synthesis. Reproduced from reference 10 with permission of Elsevier Science Limited.

The concept of control of product form has been the focus of much attention for hydrothermal barium titanate synthesis for a number of important practical reasons: fine powders can be easily sintered to produce fine-grained ceramic samples with improved electrical properties, the production of thin (< 5 μm) sheets for multilayer capacitors is possible and the fabrication of miniaturised devices has also been postulated.[11] Additional chemical control of the nature of the products is possible *via* partial substitution of barium or titanium (by Sr or Ca, and Zr or Hf, respectively) and the use of hydrothermal conditions produces highly homogeneous products, which may be attributed to the solvent permitting intimate mixing of the reagents.[11]

Research into ferroelectric titanates is not just focussed on those containing Group 2 metals, and hydrothermal chemistry has also been employed in the synthesis of a number of phases with useful properties. For example, Chen and Jiao have recently described the direct hydrothermal formation of nanosize particles of $Bi_4Ti_3O_{12}$ at 240 °C.[12] Alkali metal bismuth titanates have similar properties and their hydrothermal synthesis was part of an interesting study by Lencka *et al.* into the possibility of predicting the outcome of new hydrothermal reactions.[13] The use of computer modelling, considering the thermodynamics of the equilibria present in multicomponent mixtures of solutions and solids, enabled the calculation of 'stability and yield' diagrams as a function of pH and reagent ratios and concentrations. For example in the synthesis of $Na_{0.5}Bi_{0.5}TiO_3$, a stability plot, such as that shown in Fig. 4, allowed the conditions for the formation of titanate in a pure form, free of unwanted TiO_2 (rutile) and $Bi_4Ti_3O_{12}$ to be determined. Experimental verification of these data illustrated the validity of the method, and demonstrates how computer modelling might have an important rôle in aiding the future development of the 'rational synthesis' of inorganic solids.

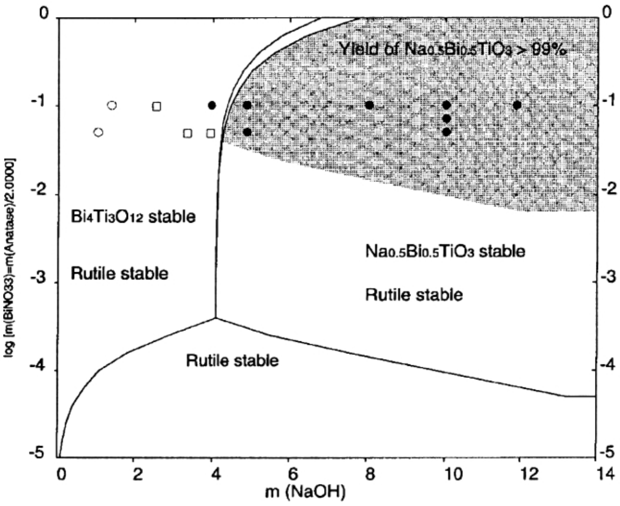

Fig. 4 Stability and yield diagram in the Na–Bi–Ti–H_2O system at 473 K as a function of NaOH concentration, as determined by thermodynamic modelling. The symbols denote the results of experimental syntheses: ● $Na_{0.5}Bi_{0.5}TiO_3$, ☐ $Bi_4Ti_3O_{12}$ + TiO_2 and ○ $Bi_4Ti_3O_{12}$ + TiO_2 + $Na_{0.5}Bi_{0.5}TiO_3$. Reproduced from reference 13 with permission of the American Chemical Society.

3.2 Vanadates

Although the ferroelectric titanates have attracted considerable attention, the successful solvothermal synthesis of other families of mixed-metal, transition-metal containing oxides has been reported in the past few years. The synthesis of some vanadates, of which the V^{IV}-containing materials have exotic magnetic properties, illustrates other important aspects of the solvothermal method. Oka and coworkers have studied the formation of strontium vanadates and lanthanum vanadates using solvothermal conditions.[14,15] In the Sr–V–O system a new phase, SrV_4O_9, was produced by heating mixtures of $SrCl_2$, $NaVO_3$ and $(CH_3)_4NCl$ solutions above 300 °C, Fig. 5. The synthesis is important in two respects: firstly, the material was prepared as single crystals, which considerably eased structure

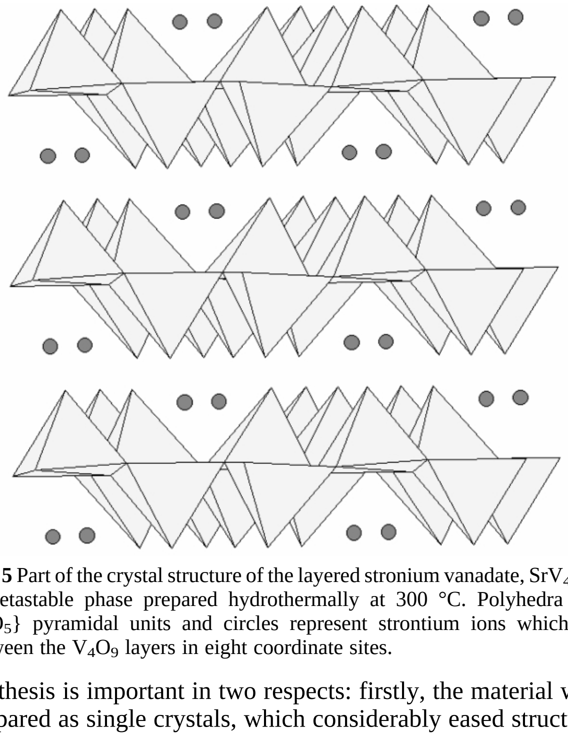

Fig. 5 Part of the crystal structure of the layered stronium vanadate, SrV_4O_9, a metastable phase prepared hydrothermally at 300 °C. Polyhedra are $\{VO_5\}$ pyramidal units and circles represent strontium ions which sit between the V_4O_9 layers in eight coordinate sites.

solution, and secondly, the material is metastable with respect to other strontium vanadates, for example, if $SrVO_3$ and VO_2 are heated in the correct ratio in a sealed tube, then a mixture of SrV_3O_7 and SrV_5O_{11} is produced. The same authors were also able to isolate metastable LaV_3O_7 at temperatures as low as 220 °C, and again single crystals were formed.[15]

3.3 Substituted ceria

In tuning the electronic properties of mixed-metal oxides (to optimise conductivity or magnetic properties for example) a common tactic is the partial substitution of one metal for another of different valence or different ionic radius. An example of this approach was given in the Introduction when the synthesis of the superconducting cuprates was discussed. The synthesis of such phases requires intimate mixing of the reagents containing each individual element, and the ceramic route becomes increasing lengthy as more elements are introduced and further cycles of heating and regrinding are necessary. A second aspect of the substitution of one element by another that must be considered is that structure required might not be stable over the compositional range required: either phase separation might take place or transformation into a solid with completely different atomic arrangement. A good example of such substitution in solid-state chemistry is given by the ternary Fe–Ce–O system, which Li *et al.* studied very recently.[16] By solid-state, ceramic means it was found to be impossible to partially substitute Ce^{4+} in ceria, CeO_2, with Fe^{3+}, and all attempts led to the formation of either binary phases (CeO_2 or Fe_2O_3) or unwanted ternary phases such as $FeCeO_3$ or $FeCe_2O_4$. Using a simple hydrothermal route, however, reaction between alkali cerium nitrate and iron nitrate solutions was achieved at 200 °C, and the products were highly crystalline materials of composition $Ce_{1-x}Fe_xO_2$. By varying the proportion of iron and cerium in the starting mixture, the composition of the product could be controlled precisely, and the maximum Fe^{3+}-substituted ceria was found to be $Ce_{0.85}Fe_{0.15}O_2$ (if $x > 0.15$, then phase separation took place). It should be noted that on incorporation of Fe^{3+} into the fluorite structure of CeO_2, an increase in oxide ion vacancies must be brought about to balance charge. Oxide ion vacancies in metal dioxides with the fluorite structure are responsible for their high solid-state ionic conductivity, and this property finds important uses in solid electrolytes, oxygen sensors, and gives rise to oxygen-storage systems. A number of other workers have also concentrated on the hydrothermal formation of cerium-containing oxides for their properties associated with oxide ion vacancies; for example Greenblatt and co-workers have studied calcium and samarium substitution.[17]

3.4 Lead oxides

A study that is particularly worthy of mention is the hydrothermal synthesis of the bismuth lead oxide $Bi_2Pb_2O_7$ that was recently reported by Feng and coworkers.[18] The solid has the pyrochlore structure, a common structure type among ceramics with the $A_2B_2O_7$ composition, and the family of bismuth oxides have been widely studied for their potential use as solid electrolytes. The ceramic synthesis of lead-containing oxides is extremely difficult to achieve because of the volatility of PbO (even if PbO_2 or lead salts are used as a starting material these decompose into the monoxide) and this means that often inhomogeneous mixtures of solids are produced, and very high pressures (3000 MPa) are necessary to avoid loss of the lead oxides during reaction. Remarkably, the group of Feng showed that highly crystalline $Bi_2Pb_2O_7$ is formed in quantitative yield after heating an alkali aqueous mixture of $Pb(NO_3)_2$ and $NaBiO_3$ in a hydrothermal autoclave at 140 °C for a period of 1 day.[18] This phase had previously only been made at high pressure and is metastable: on subsequent heating of the material in air, collapse of the structure took place resulting in an, as yet, unidentified bismuth lead oxide. Another important feature of the study of Feng, was the demonstration of the effect of choice of reagents on outcome of reaction. For example, $Pb(NO_3)_2$ could only be used as a reagent if $NaBiO_3$ was the bismuth source: if $Bi(NO_3)_3$ was used, then the desired product was not formed. It was suggested that the chemical reaction is a redox process such as:

$$2NaBi^{V}O_3 + 2Pb^{II}(NO_3)_2 + 2OH^- \rightarrow Bi^{III}{}_2Pb_2{}^{IV}O_7 + H_2O + 2Na^+ + 4NO_3^-$$

The formation of $Bi_2Pb_2O_7$ thereby demonstrates how the hydrothermal synthetic route offers the possibility of oxidation state control of constituent elements of a solid product by choice of appropriate starting materials. This is likely to be of great future importance in the formation of transition-metal oxide for which a variety of oxidation states of the metals are possible, and whose electronic properties depend crucially on the balance of oxidation states present in the solid-state. Some recent results by Henry *et al.* confirm this view; these workers investigated the formation of copper substituted bismuth lead oxides *via* hydrothermal chemistry, and were able to isolated two previously unknown solids, $Bi_{2.008}Cu_{0.84}O_4$ and $Bi_2Pb_{0.04}Cu_{0.92}O_4$, both of which contain a mixture of Cu^{2+} and Cu^{3+}.[19] Once again, the choice of starting materials was found to be crucial for synthesis of the desired single-phase product, in particular the oxidation state of the reagents is important in determining the ratio $Cu^{2+}:Cu^{3+}$ in the product.

3.5 Battery materials

The rechargeable lithium batteries which presently find widespread use (for example in the ubiquitous mobile telephone), usually use $LiCoO_2$ as the cathode material. This layered material is able to reversibly undergo intercalation and deintercalation of Li^+. On movement of the lithium ions from the cathode *via* an electrolyte to a graphite anode charging is achieved and the reverse process, discharging, releases energy. Cobalt is an expensive and toxic element, and so replacement cathode materials are at the focus of much research attention.

One successful means of developing new battery materials has been *via* hydrothermal chemistry. The group of Tabuchi has been at the forefront of this research.[20,21] Firstly they demonstrated that the direct hydrothermal synthesis of $LiCoO_2$ from an aqueous Co^{3+} solution in the presence of excess LiOH was possible, using a temperature of 220 °C. Alternatively a Co^{2+} reagent could be used and $NaOH–NaClO_3$ used as an oxidising agent *in situ*. For the formation of iron-doped samples, a mixture of $Fe(NO_3)_3$ and $Co(NO_3)_3$ was utilised, and again hydrothermal reaction performed at 220 °C in LiOH solution. Battery cathode materials with composition $LiCo_{1-x}Fe_xO_2$ ($0 \leq x \leq 0.25$) were successfully prepared by this means. The advantage of the hydrothermal route here is the homogeneity of the products formed; this subsequently allowed a survey of the electrochemical properties of a series of materials with a wide range of precisely-controlled compositions.[21] The authors proposed that the mixed metal species proceed *via* the formation of an amorphous Fe–Co oxide precipitate, Fig. 6.[21]

A number of other potential battery cathode materials have been synthesised using hydrothermal means, for example, ferrates and manganates. The case of $LiMnO_2$ is particularly interesting. The material was first reported in 1996 by the group of Bruce and the material shown to have highly desirable electrochemical characteristics.[22] The synthetic route first used involved two steps: the ceramic synthesis of $NaMnO_2$ from Na_2CO_3 and Mn_2O_3, followed by ion-exchange with a solution of lithium bromide in alcohol. No direct high-temperature

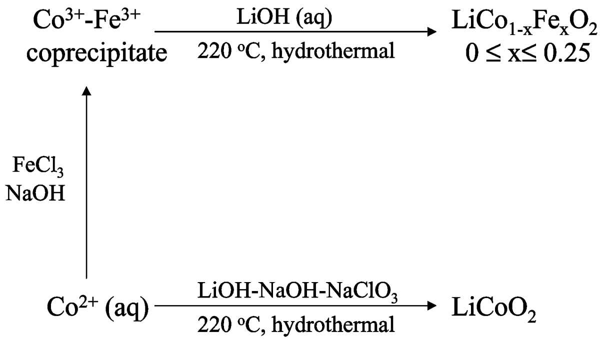

Fig. 6 A scheme for the proposed hydrothermal formation of $LiCoO_2$ and isostructural iron-substituted materials under hydrothermal conditions (after Tabuchi *et al.*[20]).

ceramic route could be found. Hydrothermal chemistry, however, has since allowed the direct one-step preparation of $LiMnO_2$ using mild temperatures (~ 220 °C).[23] Tabucchi *et al.* used a similar methodology to their previous work to achieve this, *i.e.* the reaction of metal salts in a solution of excess LiOH and high pH. The hydrothermal synthesis of layered manganese oxides has now become a focus of great attention, and large number of alkali-metal containing, mixed-metal materials have now been prepared for electrochemical testing; examples include potassium manganese oxides[24] and manganese–vanadium oxides.[25]

4 Solvothermal synthesis of chalcogenides

4.1 General considerations

Metal sulfides, selenides, and tellurides are families of solids that all have diverse properties in the solid-state, and, as with the oxides discussed above, studies of their synthesis and structures is very much application driven. Their use in catalysis (*e.g.* MoS_2 in hydrotreating catalyst) and in semiconducting devices (*e.g.* Zn(S,Se)) are among the most widely-studied uses of the chalcogenides. Synthesis of solid chalcogenides (in this case the chalcogenides are taken to be compounds of elements in Group 16 heavier than oxygen) is often more difficult than the synthesis of oxides; although at room temperature most sulfides and selenides are kinetically stable with respect to the oxide, at the elevated temperatures used in solid-solid reactions, the formation of either SO_2 or SeO_2 is entropically very favourable, and aids the formation of the metal oxide rather than the desired chalcogenide. Thus the solid-state, ceramic formation of sulfides and selenides tends to be performed in sealed containers and under inert atmospheres. Solvothermal approaches for the synthesis of chalcogenides will clearly already use sealed reaction containers, but as with the oxides described above, the use of solvent allows much more control of the nature of the product to be achieved than with traditional solid–solid reactions. In the case of the chalcogenides, a further advantage of solvothermal routes is the low level of oxide impurities in the products.

4.2 Cadmium sulfide

The synthesis of cadmium sulfide, CdS, has recently been the focus of much attention and a solvothermal synthesis route allows the formation of the solid directly from a variety of cadmium salts and thiourea in organic solvents.[26] Yu and coworkers investigated the effect of choice of solvent and reaction conditions on CdS formation at 180 °C and demonstrated a remarkable control of product morphology. When ethylenediamine or ethylenetriamine were used as solvents, particles of CdS with rod-like morphology were produced with widths of 30–90 nm and lengths of up to 900 nm.[26] In contrast, when water, pyridine, or a number of different alcohols were used as solvent, spherical particles with diameters of typically 80–200 nm were produced, the precise size of which depended on the conditions used. The choice of solvent was also found to affect the polymorph of CdS produced: the use of solvents with the lowest dielectric constant (ethanol or THF) led to the formation of pure hexagonal CdS, whereas if solvents such as pyridine or ethylenediamine were used, mixtures of cubic and hexagonal CdS were produced. Yu *et al.* have thus demonstrated the versatility of the solvothermal route to CdS, and although at present the processes taking place within the solvothermal autoclave are not understood, the empirical data relating choice of reagents, conditions and reaction outcome suggest that the method could be used for the preparation of solids of precisely required properties. This is particularly because the electronic properties of semiconductors are highly dependent on the particle size, especially when nanometer-sized particles are studied.

The same workers have more recently extended the solvothermal route to CdS to allow the preparation of ordered macroporous forms of the solid.[27] The importance of such morphologies of CdS lies in their application in photonic band gap technology, a current focus of materials research. By using SiO_2 spherical particles as templates, the solvothermal treatment of a CdS, $CdCl_2$ and thiourea mixture in CS_2 at 160 °C led to the formation of a composite from which the SiO_2 could be removed by HF treatment. This is the first successful demonstration of the formation of ordered macroporous CdS, and the synthetic route employed avoids the problems which plague high temperature routes to sulfides, in particular aerial oxidation.

4.3 Ternary chalcogenides

A good example of a ternary chalcogenide that has been studied by solvothermal means is that of $CdIn_2S_4$, a material that has photoelectric applications. Hu *et al.* have demonstrated that reaction at 180 °C between CdS and $InCl_3{\cdot}4H_2O$ in the presence of thiourea and using water as a solvent allows the formation of $CdIn_2S_4$ in a single step.[28] The distinct advantage of this solvothermal approach over traditional solid–solid reactions is in the control of particle morphology; for cadmium indium sulfide, the particle morphology of the CdS starting material directly affects the morphology of the product. For example ‘nanorods’ with diameter 10–30 nm and length of up to 1000 nm could be formed from rod-like CdS particles, or ‘nanospheres’ from spherical CdS particles.

The use of solvothermal synthesis of chalcogenides is not just limited to sulfides; selenides and tellurides have similar desirable properties and have been successfully synthesised using solvothermal routes. Similar advantages to the systems discussed above are noted, particularly in the advantage of isolating metastable phases not seen at high temperatures. For example, Li *et al.* described the isolation of the phase $Rb_2Hg_3Te_4$ from a mixture of Rb_2Te, Hg_2Cl_2, Te, and $FeCl_2$, using ethylenediamine as a solvent and a temperature of 180° C.[29] In this case, an inert atmosphere within the sealed reaction container was necessary to avoid oxidation of the product . In addition, $FeCl_2$ was found to be vital for the successful synthesis of the desired phase, and it was suggested that it might play the rôle of a reducing agent, since Hg(II) in the starting material must be reduced to Hg(I) to produce the desired product. Li *et al.* give reference to the solvothermal synthesis of a number of other tellurides, and the reader is directed to these for further information.[29]

5 Barium titanate: a model system for understanding hydrothermal crystallisation mechanism of metal oxides?

5.1 The kinetics and mechanism of hydrothermal $BaTiO_3$ growth

In this section I return again to the of barium titanate system and consider the large amount of data relating to the hydrothermal synthesis of this material with a view to understanding how inorganic solids form from heterogeneous mixtures (*i.e.* of solids and fluids) in a solvothermal autoclave. Owing to the commercial value of tetragonal $BaTiO_3$, and the highly favourable control over particle morphology for device fabrication offered by the solvothermal method, the synthesis of this solid has been more widely studied than the other systems mentioned above (in fact as long ago as 1945 a hydrothermal route to $BaTiO_3$ was described in a patent).[30] In recent years, research has focussed not simply on documenting the effect of reaction conditions on the form, purity and crystalline polymorph formed, but also on understanding the chemical processes taking place within the hydrothermal autoclave that lead to the crystallisation of the inorganic solid. This mechanistic insight would be extremely valuable: fine control of the form of the product could be achieved by precise adjustment of the reaction conditions known to affect the nature of the product, and new syntheses developed rationally without lengthy ‘trial and error’ experiments to determine the effect of reaction conditions on the product. Understanding the hydrothermal formation mechanisms of inorganic solids is unfortunately very difficult and this is largely because experimental data are difficult to obtain under real reaction conditions since sealed steel pressure containers are used. Thus not even accurate ‘extent of reaction’ curves have been determined for many solid-forming reactions.

The kinetics and mechanism of hydrothermal barium titanate crystallisation were reviewed in 1996 by Eckert *et al*. who also presented new experimental data obtained by analysing sample quenched from hydrothermal autoclaves after different periods of heating.[30] For the synthesis of $BaTiO_3$ from TiO_2 (usually the anatase polymorph) and barium salts (such as $BaCl_2$ or $Ba(OH)_2$) in alkaline solutions, two distinct reactions mechanisms were put forward, Fig. 7. The first, the ‘*in situ* reaction mechanism’, envisages the complete dissolution of the barium salt followed by a heterogeneous reaction between the dissolved ions and solid TiO_2 particles. The formation of a continuous barium titanate layer on the TiO_2 particles means that at later stages of reaction Ba^{2+} ions must diffuse through this barrier to react with remaining TiO_2. The second, alternative, mechanism is the so called ‘dissolution precipitation mechanism’. This homogeneous mechanism involves the dissolution of *both* Ba- and Ti-containing reagents, followed by crystallisation from solution of $BaTiO_3$. Both models are considered to be extreme types of reaction mechanism, and in reality it is likely that each process might be occurring simultaneously, or at different stages of reaction; for example, dissolution of reagents might occur followed by formation of $BaTiO_3$ from solution on the surface of any undissolved TiO_2. The simple models, nevertheless, provide a starting point for considering how mixed-metal oxides might form from hydrothermal solutions.

The acquisition of experimental data to distinguish the two crystallisation models for hydrothermal barium titanate formation have largely been accumulated by study of samples quenched from the elevated temperatures and pressures present in the hydrothermal autoclave. For example, Kerchner *et al.* examined quenched materials by powder X-ray diffraction, elemental analysis, and transmission electron microscopy.[31] By comparing the amount of barium remaining in solution, and using diffraction to determine the fractional crystallinity of each sample, an extent of crystallisation curve was obtained. It was suggested from these data that two distinct regions of crystal growth are present: one corresponding to dissolution-precipitation and a second stage involving heterogeneous transformation. Additional information on particle morphology from transmission electron microscopy showed that there was no observable particle size growth with time once $BaTiO_3$ had formed, suggesting that nucleation was extremely rapid. In other studies of quenched materials, further qualitative results have been obtained. For example, Pinceloup *et al.* used high-resolution transmission electron microscopy to show that at all stages of reaction, materials isolated were $BaTiO_3$, with no evidence for any Ti-rich particles that might be expected if heterogeneous nucleation were taking place, and furthermore showed that there was no relationship between $BaTiO_3$ particle-size distribution, and the initial TiO_2 particle-size distribution.[10]

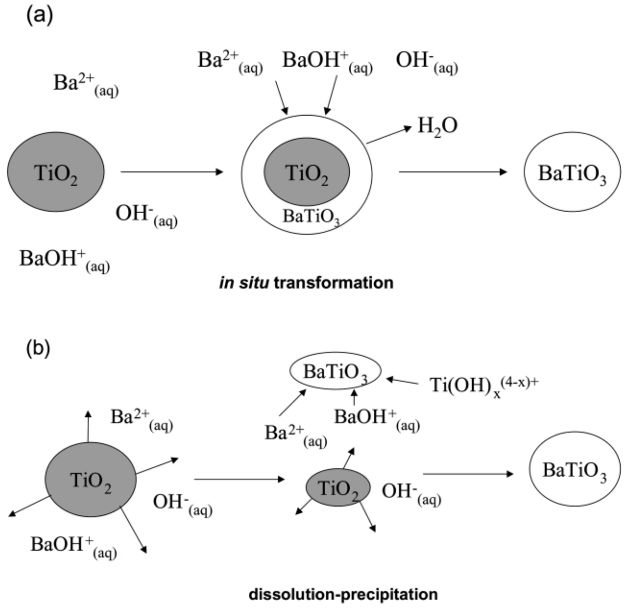

Fig. 7 Schematic of two crystallisation models proposed for the hydrothermal formation of $BaTiO_3$ from Ba salts and TiO_2. (a) The heterogeous *in situ* transformation mechanism, (b) the homogeneous dissolution-precipitation mechanism.

5.2 Time-resolved studies of $BaTiO_3$ formation

There are considerable assumptions made when quenching a sample from elevated temperature and pressure to study extent of reaction: in particular that the solid recovered is the same as that present under reaction conditions, and no changes in the material have taken place on cooling. By developing a means of observing hydrothermal crystallisation *in situ*, however, it is possible to study materials under reaction conditions, and thus to track physical and chemical changes in real time, to obtain extent of reaction curves.[32] Recent work by the author and the group of O′Hare in Oxford has provided new insights into barium titanate formation mechanism by using time-resolved neutron diffraction to follow chemical reactions within a hydrothermal reaction vessel.[33–35] This avoids the problems of the quenching studies, and, since reactions are continually monitored, crystallisation curves can be produced that contain far more points than those determined by a lengthy series of quenching experiments. We have used two of the most recently constructed neutron diffractometers to study hydrothermal barium titanate crystal growth; the GEM diffractometer at ISIS, the UK spallation neutron source, which offers an extremely large detector coverage, and high counting rate, and the D20 diffractometer at the ILL, Grenoble, which has a large position-sensitive detector.[33,34] Fig. 8 shows typical time-resolved diffraction data measured during the formation of $BaTiO_3$ from

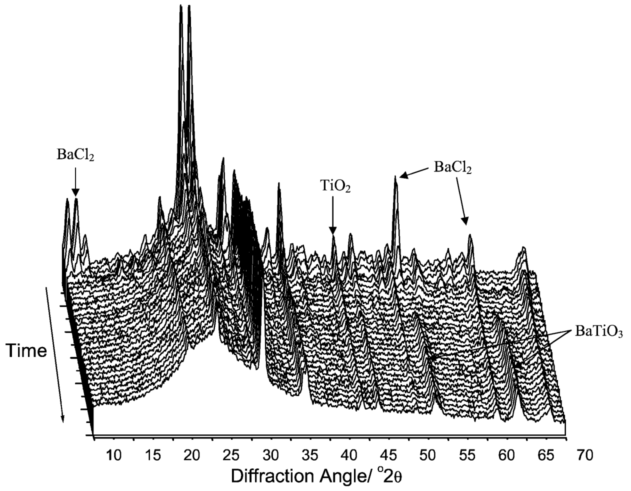

Fig. 8 Time-resolved neutron diffraction data measured during the crystallisation of $BaTiO_3$ from $BaCl_2$ and TiO_2 in an alkaline aqueous solution at 200 °C. Selected peaks of the three crystalline phases present are indicated.

TiO_2 (anatase) and $BaCl_2$ in a NaOD solution (deuterated reagents are used to eliminate the incoherent scattering of protons and reduced background in the data).

These are among the first data available in which the hydrothermal crystallisation of a metal oxide is 'seen' in real time. Integration of characteristic Bragg reflections of the crystalline starting material and product allows quantitative crystallisation curves to be calculated such as those shown on Fig. 9. These data are particularly informative since we can observe directly the decay of a significant amount of TiO_2 before the onset of crystallisation of $BaTiO_3$. This strongly suggests dissolution of TiO_2 is taking place, and thus, at least at the early stages of reaction, a dissolution–crystallisation mechanism predominates. Kinetic analysis of these data was also performed and we were able to successfully model the data by using a nucleation growth model, a model that may be interpreted as resulting from a situation where crystal growth occurs from nucleation sites in a uniform mixture of reactive species formed from the starting materials.[34] This model is consistent with the dissolution–precipitation model for crystal growth, and we have also been able to postulate that the rate of reaction is controlled by the rate of crystal growth at the nucleation sites, and not the rate of formation of the sites.

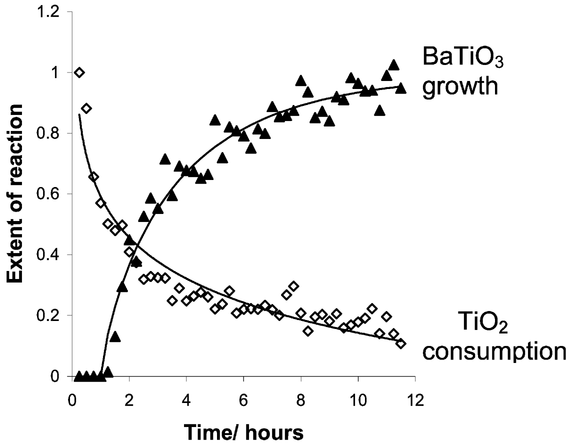

Fig. 9 Crystallisation curves derived from the *in situ* neutron diffraction experiment showing rapid decay of TiO_2, and growth of $BaTiO_3$.

6 Summary and future directions

The solvothermal method has great utility in the synthesis of inorganic materials and as I have demonstrated the method is not just applicable to the well-known microporous, zeotype materials. The advantageous aspects of the solvothermal synthesis route, in particular the formation of homogeneous sample of complex mixed-metal solids, the isolation of metastable phases not seen at high temperature, and the control of crystal form, make the method particularly attractive for future study.

The vast majority of materials discussed has been reported only in the past five years and the rate of publication of new examples of the solvothermal synthesis of new materials continues to increase. There is clearly very much scope for exploratory synthesis in the field described in this article. The use of solvents other than water has been rather limited so far, and this is an obvious direction in which to extend the ideas discussed here. The use of solvothermal chemistry has almost exclusively concentrated on the formation of oxides, and other chalcogenides, and rather less work has so far focussed on the possibility of the formation of nitrides, borides or carbides,[5] families of materials that all are of interest for their particular technological applications. There are literally thousands of possible combinations of metals that could conceivably be combined to formed mixed chalcogenides or pnictides, for example, with the additional choice of solvent, reagents and reaction conditions adding other dimensions to the scope of discovery of new materials. As well as this 'trial and error' approach to synthesis that this last statement suggests, there is considerable research effort taking place into the formation mechanisms of inorganic solids under solvothermal conditions, and the development of new technology for following reactions *in situ* using time-resolved probes to achieve this. The development of *in situ* probes is not only focussed on diffraction methods, that probe changing long-range order with time,[32] but also spectroscopic techniques such as NMR spectroscopy that allow local atomic order to be monitored.[36] Clearly a full description of hydrothermal crystallisation mechanism requires much more information to be gathered, even for a single system like barium titanate for which a variety of starting material and reaction conditions can be employed. The studies that so far have been performed provide the first reliable evidence of the processes taking place within a sealed solvothermal autoclave, and will provide a firm foundation to begin understanding mechanistic detail of the formation of other metal oxides, and then other inorganic solids. An understanding of how materials form will allow new synthesis to be performed with some confidence of the outcome of reaction, and thus solid materials produced with desired properties.

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