FEATURE ARTICLE

Chemical synthesis of ceramic materials

David Segal

AEA Technology, F7 Culham, Abingdon, Oxfordshire, UK OX14 3DB

A range of increasingly important chemical syntheses for ceramic materials are described. These syntheses are coprecipitation, molten salts, sol–gel processes, hydrothermal techniques, liquid-phase and gas-phase reactions, polymer pyrolysis, the Pechini and citrate gel methods, aerosols and emulsions. Common themes relating the syntheses are outlined and their advantages over conventional solid-state reactions are described. The scope for further chemical studies on ceramic synthesis is discussed.

Introduction

Worldwide studies on ceramics, polymers and metals during this century have resulted in the establishment of materials science as a scientific discipline. A feature of these studies, particularly for ceramics, is their interdisciplinary nature and at the present time chemistry is making an increasingly important contribution[1] to the research, development and manufacture of ceramic materials. Chemistry has two major roles when applied to ceramics. The first is the synthesis of novel materials, usually in the form of powders. For example, the discovery in 1986 of high-temperature superconductors such as $YBa_2Cu_3O_{7-x}$ highlighted the role of chemical synthesis in the preparation of novel ceramics. However, successful exploitation of ceramics requires not only methods for their synthesis but also techniques for their fabrication into useful shapes, *e.g.*, coatings, fibres, monolithic ceramics and powders with a controlled particle size for a wide variety of applications. These applications include controlled-porosity coatings for ceramic membranes, coatings on window glass for selective transmission and reflection of solar radiation, optical fibres and fibres for lightweight thermal insulation, ceramic honeycombs for use in automotive catalytic converters and unaggregated powders for high-strength structural ceramic components.

The second chemical role is in the development of fabrication techniques for ceramic shapes, for example coatings, monoliths and fibres. Synthesis and fabrication fall within the subject area of ceramic processing that occupies an interface between conventional studies in chemistry and materials science. Processing is presently an important feature of ceramic studies in universities and industrial environments while chemical methods for ceramic synthesis are under intense and increasing investigation. This is because, compared to conventional ceramic powder processing[2] using solid-state reactions between powder reactants, these methods have the potential to yield ceramics with tailored properties and with performance advantages over conventional materials. In this article the conventional method for the preparation of ceramic powders is first described together with the advantages and disadvantages of the technique. The materials requirements for improved ceramics are then outlined. A selection of chemical routes for the synthesis of ceramic materials in the form of powders, coatings, fibres and monoliths are then described together with examples of the syntheses. The chemical principles involved are highlighted along with areas where a greater chemical understanding is required in order to exploit fully the application of chemistry to the processing of ceramic materials.

Conventional synthesis of ceramic powders

The conventional synthesis[2] for multicomponent ceramic powders is solid-state reaction between oxide and/or carbonate precursors. Thus for barium titanate, $BaCO_3$ and TiO_2 powders are mixed, milled and calcined. Repeated cycles of milling and calcination are carried out to achieve the solid-state reaction. Relatively high temperatures are required for solid-state reactions, typically around 1200 °C because of limited diffusion during calcination, and this can result in decomposition of the ceramic product. For example the phosphor host material[3] $GdAl_2B_4O_{10.5}$ is unstable above 1050 °C and conventional synthesis using oxide powders yielded $<5\%$ of the product phase at 1000 °C and only 15–30% at the same temperature after pelletising the oxide reactants. Other disadvantages of the method are the formation of undesirable phases such as $BaTi_2O_5$ during the preparation of $BaTiO_3$, large grain sizes (detrimental for high-strength ceramic components) due to firing at high temperature and poor chemical homogeneity particularly when dopant oxides are introduced in small amounts during the synthesis of electroceramics. In addition, particle size reduction by milling can introduce chemical impurities into the ceramic product. Carefully controlled addition of dopants is important in ceramic synthesis. For example, in the preparation[4] of $BaTiO_3$-based Y5V and Z5U dielectric compositions for use as multilayer ceramic capacitors, additives include $CaZrO_3$ and $CaSnO_3$ to reduce the Curie point from 130 °C to around 10 °C, $MgZrO_3$ and $CaTiO_3$ to smooth out the temperature variation of capacitance as well as modifiers such as CeO_2 and Nb_2O_5 as grain-growth inhibitors. However, the advantages of solid-state reactions are the ready availability of oxide precursors and the low cost for powder production on the industrial scale. These reactions are also convenient for laboratory-scale preparations.

For non-oxide powders, conventional syntheses include the direct reaction of a metal with a gas, *e.g.*, TiN is produced[5] by nitridation of Ti metal in N_2 at 1500 °C. Carbothermal reduction is also a conventional preparation route[5,6] for non-oxides. Thus TiB_2 is prepared by the carbothermal reduction of a mixture of TiO_2 and B_2O_3 at 1000 °C or by reduction[6] of TiO_2 with boron carbide and carbon at 2000 °C, while industrial SiC powder is made[7] in the Acheson process by carbothermal reduction of silica at temperatures higher than 1800 °C. The main disadvantage of conventional syntheses for these refractory non-oxides is the requirement for extensive grinding for particle size reduction, for example to around 0.5–1.0 µm for TiN, that introduces chemical impurities into the powders. Precipitation from solution is also a conventional preparation for one-component oxides. In the Bayer process[8] for manufacture of α-Al_2O_3, bauxite is hydrothermally dissolved in sodium hydroxide to form sodium aluminate solution. An aggregated gibbsite (α-$Al_2O_3{\cdot}3H_2O$) powder is produced by seeding the solution with gibbsite crystals and it is converted to α-Al_2O_3 at around 1500 °C although this temperature can be lowered by the use of fluorine compounds as mineralisers that also modify the shape of α-Al_2O_3 crystals.

Conventional syntheses produce powders which are not particularly suited for the fabrication of coatings and fibres. Chemical routes are attracting attention for ceramic synthesis because some of them allow direct fabrication of coatings, fibres and monoliths without powder intermediates. These routes have the potential to achieve improved chemical homogeneity on the molecular scale which is very important for electroceramics whose electrical functions are determined by the addition of small amounts of dopant oxides. For structural ceramics, improved mechanical properties such as strength can be obtained by removal of powder aggregates and chemical syntheses allow preparation of unaggregated powders. In addition, when chemical routes are used diffusion distances are reduced on calcination compared to conventional preparations owing to mixing of components on the colloidal or molecular level that favours lower crystallisation temperatures for multicomponent ceramics. These potential advantages for improving the performance of ceramic components have given rise to the increased application of chemistry, through ceramic processing, for the development of ceramic materials.

Coprecipitation

The aim in coprecipitation is to prepare multicomponent ceramic oxides through formation of intermediate precipitates, usually hydrous oxides or oxalates, so that an intimate mixture of components is formed during precipitation, and chemical homogeneity is maintained on calcination. This method has been applied to $BaTiO_3$ powder with a view to fabrication of improved multilayer capacitors. Thus a barium titanyl oxalate precipitate was produced[9] on addition of oxalic acid to a mixed barium and titanyl chloride solution under controlled conditions of pH, temperature and reactant concentration.

$$BaCl_2 + TiOCl_2 + 2H_2C_2O_4 + 4H_2O \rightarrow BaTiO(C_2O_4)_2 \cdot 4H_2O + 4HCl \quad (1)$$

Dopants such as lanthanides were introduced by coprecipitation and the precipitate was calcined up to 700 °C after collection by filtration, washing and drying to produce a $BaTiO_3$ powder after milling of 0.4–1.0 µm. In coprecipitation careful control of solution conditions is required to precipitate all cations and thus maintain chemical homogeneity on the molecular scale. Other examples of powders made by coprecipitation are $LiNi_xCo_{1-x}O_2$ with $0<x<1$ for evaluation[10] as cathode materials in rechargeable lithium-based batteries and nanocrystalline[11] yttria-stabilised zirconia (particle size <100 nm) suitable for compaction and sintering to a nanostructured ceramic where the grain size is less than 100 nm. This fine-grained ceramic with potential improved mechanical properties due to the increased percentage of atoms in the grain boundary region cannot be obtained by conventional synthesis owing to the high reaction temperature. The method is also used for the manufacture of high-performance ceramic powders; thus unaggregated Y_2O_3-stabilised ZrO_2 (Tosoh Corporation) with a particle size of around 0.1 µm is produced by coprecipitation of hydroxides from mixed yttrium and zirconyl chloride solutions after which the hydroxide precipitate is dried, calcined and milled. Washing and drying procedures (*e.g.* water-washing, solvent-washing, azeotropic distillation) that are used for coprecipitated hydroxides can have a drastic effect on the mechanical properties of a sintered powder as they affect the degree of powder aggregation and need to be considered when developing a coprecipitation route to a ceramic powder. Another precipitation technique, not as widely reported as coprecipitation, involves the use of molten salts.

Table 1 Melting points for alkali metal nitrates and eutectic mixtures[12]

metal nitrate	melting point/°C
$LiNO_3$	255
$NaNO_3$	307
KNO_3	334
50 mol% $NaNO_3$–50 mol% KNO_3	220
43 mol% $LiNO_3$–57 mol% KNO_3	132

Reactions in molten salts

The term molten salt refers[12] to the liquid state of compounds which melt to give liquids displaying a degree of ionic properties. Alkali metal nitrates have relatively low melting points (Table 1) whereas even lower melting points are obtained in their eutectic mixtures. A molten salt can behave as a solvent or as a reactant. Thus in a nitrate melt acid–base reactions can occur according to the Lux–Flood formalism[13] whereby an acid is an oxide ion acceptor and a base is an oxide ion donor; nitrate ions are bases in this formalism. Nitrite melts are more basic than nitrate melts whereas addition of Lux–Flood bases such as Na_2O_2, Na_2O and NaOH to a nitrate melt increases its basicity. The starting materials for reactions in molten salts are inorganic compounds, in particular sulfates and chlorides, that are blended with the alkali metal nitrates or nitrites as a powder mixture before heating to the reaction temperature. Thus when $Zr(SO_4)_2$ is used, the Zr^{4+} ions formed on dissolution of the zirconium salt in the melt behave as acids according to the Lux–Flood formalism.

Early studies on the synthesis of ZrO_2 investigated[14] the reaction of molten $Zr(SO_4)_2$ in a $LiNO_3$–KNO_3 eutectic and ZrO_2 powder was produced for reaction temperatures up to 430 °C. For more basic melts made by additions of Na_2O_2, Na_2O and NaOH, the conversion to ZrO_2 occurred at lower temperatures but favoured formation of alkaline zirconates, although the powder characteristics were not determined. In later work[15,16] $Zr(SO_4)_2$ was reacted in a nitrite eutectic of 65 mol% $NaNO_2$–35 mol% KNO_2 (melting point 220 °C) in a one-stage reaction at 270 °C according to the stoichiometric equation

$$Zr(SO_4)_2 + 6NO_2^- \rightarrow ZrO_2 + 2SO_4^{2-} + 2NO_3^- + 4NO \quad (2)$$

Tetragonal ZrO_2 (t-ZrO_2) was obtained at 450 °C with a mixture of amorphous and poorly crystalline ZrO_2 at 300 °C which crystallised to t-ZrO_2 at 500 °C; ZrO_2 had a crystallite size of 5 nm and specific surface area greater than 150 $m^2\ g^{-1}$. Reaction of $Zr(OCl)_2$ with a $NaNO_3$–KNO_3 eutectic at 250 °C yielded[17] amorphous ZrO_2 which crystallised to tetragonal ZrO_2 on calcination, although the conversion temperature for the tetragonal phase decreased as the reaction temperature increased and it was produced directly at 450 °C. For 3 mol% Y_2O_3–ZrO_2 the reaction[18] was carried out at 450 °C between $Zr(OCl)_2$ and YCl_3 in a $NaNO_3$–KNO_3 eutectic. The reaction product, t-ZrO_2 powder, which had specific surface areas around 110 $m^2\ g^{-1}$ and a crystallite size of 6–10 nm, could be pressed and sintered at 1500 °C to 98.5% of the theoretical density, although the extent of powder aggregation was sensitive to washing and drying procedures. Alumina–zirconia solid solutions have also been produced[19] in powder form from $Zr(OCl)_2$ and $AlCl_3$ in a $NaNO_3$–KNO_3 eutectic, and reactions in molten salts have not been restricted to zirconia-based systems. In a recent study[20] cubic $Ba_{0.75}Sr_{0.25}TiO_2$ was prepared by the addition of a $BaCO_3$–$SrCO_3$–TiO_2 mixture to a eutectic melt of 49 mol% NaOH–51 mol% KOH at 300 °C for 12 h. For this reaction the eutectic was a solvent in which the reaction kinetics were considerably faster than in the conventional solid-state reaction.

Reactions in molten salts can be considered to fall within the general class of reactions in non-aqueous liquids and have not been widely applied for ceramic powder preparation even though the reactants are readily available. The nucleation, growth and aggregation of ceramic powders during preparation is of fundamental importance to the usefulness of the powders and is an area of continuing debate within activities in ceramic processing. If unaggregated powders can be obtained in melts for a wide range of compositions then molten salt chemistry could, in the future, offer an attractive route for synthesis of ceramic powders.

Sol–gel processing of colloids

Colloid science is important for the successful application of chemistry to ceramic synthesis. This is because powder preparation involves nucleation and growth of particles to a size often less than 1 μm and thus the powders are colloidal systems.[21] In addition powders are often handled in the form of colloidal dispersions and this is illustrated by the synthesis method known as sol–gel processing of colloids. A sol–gel preparation can be divided[7] into five stages. The starting material, for example a metal salt, is converted in a chemical process to a dispersible oxide, which forms a colloidal dispersion (sol) on addition to dilute acid or H_2O. Removal of H_2O and/or anions from the sol produces a stiff gel in the form of spheres, fibres, fragments or coatings and this transition is usually reversible. Calcination of the gel in air yields an oxide product after decomposition of the salts. For example, ceria sols have been made[7] by first adding $NH_3(aq)$–H_2O_2 to cerium(III) nitrate solution. After careful washing of the Ce^{IV} hydrate to remove entrained electrolyte the precipitate was peptised with HNO_3 to sols with a particle size of around 8 nm. While peptisation involves breaking up coarse precipitates, deanionisation of metal salt solutions involves growing molecular species to colloidal units in the form of polynuclear ions. For example, treatment[22] of chromium(III) nitrate solution with a long-chain primary amine removes hydrolytic HNO_3 from the aqueous solution with the resultant formation of polymeric colloidal species. Flame-hydrolysed powders[23] such as SiO_2 also form sols on dispersion in water. An example of a sol is shown in Fig. 1. It is useful to note that many of the chemical techniques attracting attention for ceramic synthesis are not new and often date back many years. Thus sol–gel processing of colloids was first exploited in the late 1950s for fabrication of ThO_2–UO_2 ceramics for use[7] as spherical fuel powders in high-temperature thermal nuclear reactors. For preparation of multicomponent oxides, sols are blended together before gelation and a component unavailable in sol form can be introduced as an electrolyte solution or oxide powder. Spherical sol–gel powders can be made by the following processes.

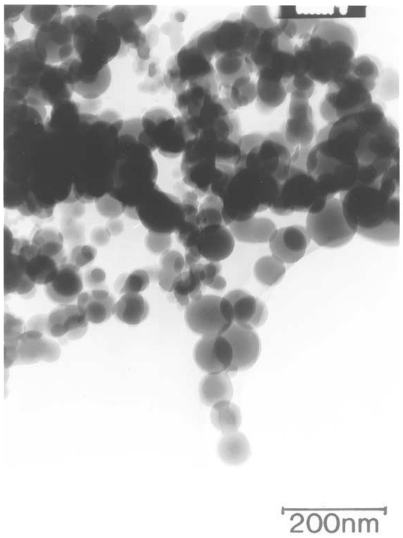

Fig. 1 Transmission electron micrograph of a silica sol

(1) Dispersing a sol to an emulsion in an immiscible organic solvent capable of extracting H_2O from the sol, for example 2-ethylhexanol. Gelation occurs during the dehydration process and this approach was used for thoria-based nuclear fuels.

(2) External gelation in which a sol is dispersed to an emulsion in a water-immiscible solvent and gelation is effected by addition of a long-chain amine or $NH_3(g)$ to the solvent.

(3) Internal gelation in which an ammonia donor such as hexamethylenetetramine or urea is added to the sol before emulsification and gelation occurs by release of $NH_3(g)$ on warming solvent.

Spray-drying[24] sols also produces spherical powders. Examples[1,7] of sol–gel powders are electrically conducting ceramics such as $Ni_{0.3}Zn_{0.7}Fe_2O_4$ and 3% SnO_2–In_2O_3, plasma-spray Cr_2O_3–ZrO_2 powders around 10 μm diameter and catalyst supports. Advantages of this sol–gel technique are good chemical homogeneity due to mixing components at the colloidal level and lower reaction temperatures; thus high-density ThO_2–UO_2 spheres were obtained at 1150 °C, considerably lower than for the conventional powder mixing method (*ca.* 1700 °C). In addition, because it involves handling liquid feeds, small amounts of dopants can be readily introduced while lower crystallisation temperatures enable preparation of phases that are unstable at high temperature.

The versatility of sol–gel processing is illustrated by its use for fabrication of ceramic shapes other than powders. Thus thin oxide coatings around 1 μm can be prepared[7] on substrates by first applying a sol by spinning or dip-coating after which the liquid layer is dried to a gel coating that is calcined to oxide. As an example,[25] silica coatings for improved oxidation resistance of stainless-steel wire mesh were prepared by dip-coating. Although the technique is low cost and simple to carry out, cracking and loss of adhesion can occur on drying. Fibres can be drawn[26,27] from sols with controlled rheological properties and calcined to oxide. Whereas aluminosilicate fibres are conventionally prepared from a melt which limits the Al_2O_3 content to around 65 mass% owing to the melt viscosity, the use of sol–gel yields a much wider range of compositions such as 95% Al_2O_3–5% SiO_2 and a range of polycrystalline ceramic fibres are manufactured[27] from sol–gel materials. Preparation of sol–gel fibres is an example of powderless processing that avoids the synthesis of a ceramic powder with a well defined particle size and its subsequent consolidation into a shape. Powderless processing is an attractive method for fabrication of ceramic monoliths as it can produce near-net size and shape components in a few processing steps. For example, SiO_2 sols in combination with potassium silicate and a hydrolytic agent such as formamide were cast[28,29] directly to monolithic silica gels with a controlled pore size in the range 100–300 nm. After leaching out K^+ ions, the gels were dried by using microwaves and sintered to silica monoliths. A key feature of the synthesis was that large pore sizes reduced the capillary forces on drying the gel, thus preventing cracks in the ceramic. Powderless processing also includes freeze casting.[30] For example, SiO_2 sols were cast into a mould, frozen in liquid nitrogen and the mould was then removed. After thawing, the intact gel was calcined to a near-net size and shape component. An important aspect of these fabrication processes is colloidal processing[31] in which the tendency of sol particles to flocculate and coagulate with the resultant effect on porosity is controlled, but a greater understanding of changes in sol structure taking place during fabrication is required to fully utilise these powderless processing techniques for a wide range of oxide ceramics.

The hydrolysis of cations[32–34] and inorganic polymerisation in aqueous solution are of fundamental importance to wet chemical methods of synthesis such as sol–gel in which sols are formed from cations that can undergo hydrolysis. Monovalent hydrolysis products whose formation[1] is represented by the equation

$$[\mathrm{M(H_2O)}_n]^{z+} \rightarrow [\mathrm{M(OH)}_p(\mathrm{H_2O})_{n-p}]^{(z-p)+} + p\mathrm{H}^+ \tag{3}$$

where n is the number of bound water molecules, p is the number of protons removed from the cation on hydrolysis and z is the valency of the cation M, can condense to polyvalent or polynuclear ions which can be colloidal, for example, $[AlO_4Al_{12}(OH)_{25}(H_2O)_{11}]^{6+}$; polynuclear ions contain OH bridges, M—OH—M (olation) or oxygen bridges, M—O—M (oxolation) and are precursors for particle growth. A quantitative approach for predicting the products of cation hydrolysis as a function of the experimental conditions, known as the partial charge model,[33,34] has been developed. In this thermodynamic model, proton exchange (and the associated electron transfer) between metal ions and solution occurs until the mean electronegativity of the hydrolysed species becomes equal to the mean electronegativity of the surrounding aqueous solution. The ability to predict solution species and their condensation behaviour is a very useful tool for understanding the chemistry of sol–gel processes.

Sol–gel processing of metal–organic compounds

The phrase sol–gel has been used inaccurately in the scientific literature and is often assigned to all wet chemical methods for ceramic synthesis even though there are only two sol–gel processing techniques. The second[35] sol–gel technique involves ceramic synthesis by hydrolysis of metal–organic compounds, in particular metal alkoxides,[36] $M(OR)_z$ where R is an alkyl group, and at the present time publications on sol–gel dominate the literature on ceramic synthesis. This method is particularly associated with non-fusion routes to oxide glasses. For preparation of multicomponent oxides, alkoxides are mixed together in alcohol and a component unavailable as an alkoxide is introduced as a salt, for example an acetate, so that the resulting solution has the required ceramic composition. Hydrolysis is carried out under controlled conditions of pH, added H_2O, alkoxide and alcohol concentration. The reaction conditions can result in the solution forming a solid monolithic gel (known as an alcogel) which is dried and calcined to an oxide powder, or precipitation of powders directly from solution. The reactions occurring in solution are complex[32] but involve hydrolysis and condensation to polymeric species as represented by the equations

$$\mathrm{M(OR)}_z + \mathrm{H_2O} \rightarrow \mathrm{M(OR)}_{z-1}(\mathrm{OH}) + \mathrm{ROH} \tag{4}$$

$$2\mathrm{M(OR)}_{z-1}(\mathrm{OH}) \rightarrow \mathrm{M_2O(OR)}_{2z-2} + \mathrm{H_2O} \tag{5}$$

$$\mathrm{M(OR)}_z + \mathrm{M(OR)}_{z-1}(\mathrm{OH}) \rightarrow \mathrm{M_2O(OR)}_{2z-2} + \mathrm{ROH} \tag{6}$$

Metal–oxygen–metal (M—O—M) bonds are formed in solution by self-condensation or by cross-condensation when different alkoxides are used, thus M′—O—M. Sol–gel processing with alkoxides shares the same versatility and benefits as the use of colloids but has some additional advantages. Because many alkoxides are liquids or volatile solids they can be purified to form extremely pure oxide sources which is important for electroceramic synthesis, while improved chemical homogeneity is obtained owing to mixing of components at the molecular level. The improved homogeneity is associated with lower crystallisation temperatures than for use of colloids, often between 400 and 800 °C for gel→oxide conversion. However, alkoxides are relatively expensive compared to precursors for sol–gel processing of colloids, a limited range of them are commercially available and their use involves a solvent-based rather than a water-based process. There are certainly requirements[37] to develop economical syntheses for large quantities of alkoxides to fully exploit the process. Many chemical studies have been carried out on characterising alkoxide solutions in order to relate the solution properties of the precursors to the ceramic properties. Techniques[35] have included light scattering, small-angle X-ray scattering, NMR spectroscopy, liquid chromatography and this characterisation is an active area of sol–gel studies. As for all chemical syntheses the success of a sol–gel synthesis is ultimately judged by the performance of the chemically derived ceramic.

Sol–gel processing of metal alkoxides has been widely used for the preparation of submicrometre oxide powders. For example, $Y_3Fe_5O_{12}$ was prepared[38] by hydrolysis of a mixture of $Fe(OC_2H_5)_3$ in C_2H_5OH and $Y(OC_4H_9)_3$ in xylene. The resulting gel was, after drying, converted at 700 °C to $Y_3Fe_5O_{12}$ with a mean diameter of 9 nm. Alkoxides have differing hydrolysis rates and the benefits of improved homogeneity can thus be lost during hydrolysis of mixed alkoxides. Modification of hydrolysis rates which affect particle formation, growth and aggregation can be made by complexing the alkoxide with a chelating ligand. For example, $Zr(OC_3H_7)_4$ can be complexed with acetylacetone and hydrolysis of this alkoxide with[39] toluene-*p*-sulfonic acid in the presence of acetylacetone yielded ZrO_2 particles around 3 nm in diameter after ageing the reactants at 60 °C. Monodispersed spherical powders, usually submicrometre, can be obtained by controlled hydrolysis of alkoxide solutions and are known as Stöber spheres.[40,41] An example of a powder made by controlled hydrolysis (also known as homogeneous nucleation) is shown in Fig. 2 and the mechanism of particle formation and growth is of relevance to other ceramic syntheses. While powder formation by homogeneous nucleation has often been considered to involve nucleation from supersaturated solutions at a critical particle size followed by diffusion of molecular species onto growing nuclei, recent studies[42–44] suggest an alternative mechanism in which nucleation followed by aggregation of small particles takes place during particle growth.

Many electroceramics are used in the form of thin coatings, around 1 μm, and the development of sol–gel coatings is an area of expanding activity; a sol–gel $PbTiO_3$ coating is shown in Fig. 3. Alkoxide-derived coatings include $Pb_{1-x}La_{2x/3}TiO_3$ where x is between 0 and 0.2 for pyroelectric applications,[45] and $La_{0.5}Sr_{0.5}CoO_3$ electrode materials[46] while the ability of chemical methods to tailor the properties of ceramics is highlighted by fabrication of ceramic membranes.[47–49] While polymer membranes are widely available, ceramic membranes have operating advantages, in particular superior chemical and thermal durabilities. Nanofiltration membranes have pore diameters in the separation layer around 2 nm and have been prepared[48] by controlled hydrolysis of $Zr(OC_5H_{11})_4$ to ZrO_2 particles less than 5 nm in diameter. These particles were then deposited from a dispersion onto a substrate to produce the membrane layer. Alcogels can be dried and sintered to crack-

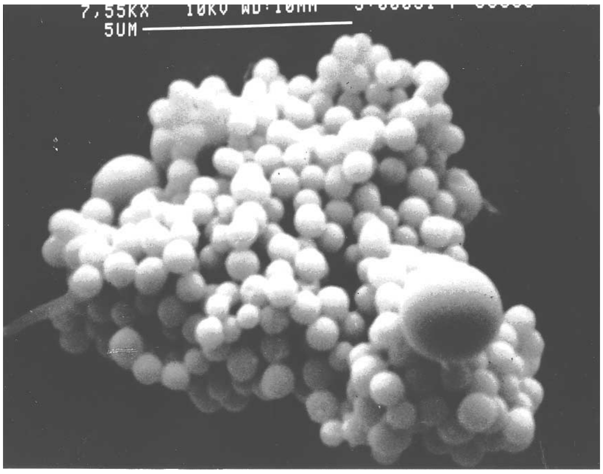

Fig. 2 Titania spheres by controlled hydrolysis of an alkoxide

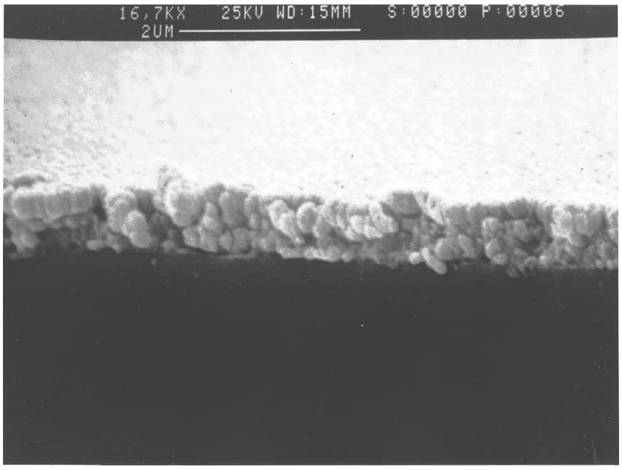

Fig. 3 Sol–gel lead titanate coating

free monolithic components. Silica alcogels were prepared[50] from hydrolysed $Si(OC_2H_5)_4$ solutions in the presence of a drying control chemical additive, formamide, which modified the pore size distribution in the alcogel producing an average pore size around 5 nm. This modification allowed conversion of the alcogel to crack-free silica components. Alcogels can also be converted by supercritical drying to aerogels[51,52] which are transparent, porous solids with high surface area and densities as low as 0.003 g cm^{-3}. In supercritical drying, pore fluid is removed directly above its critical point. For C_2H_5OH, the common solvent in sol–gel processing, the critical temperature and pressure are 243 °C and 6.4 MPa respectively, but recently a low-temperature method has been introduced[52] in which ethanol is replaced by CO_2 and the latter is removed above its critical point, 31 °C and 7.2 MPa; the lower critical temperature is a processing advantage.

Ceramics are hard, brittle solids whereas polymers are tough, flexible and ductile. Hybrid polymer–ceramic materials can share the advantages of these two types of materials while minimising the disadvantages. These materials have been called ceramers[53] to indicate a material that has a unique combination of ceramic and polymer properties, ormosils[54] which refers specifically to an organically modified silicate for a SiO_2-based system but are now more generally known as ormocers[55] (organically modified ceramics). Alkoxides have a central role in the synthesis of ormocers. While the use of alkoxides for oxide synthesis involves precursors where all attached alkoxy groups can be replaced on hydrolysis, preparation of ormocers uses precursors in which some attached groups are retained on reaction. These hybrid materials contain an inorganic backbone and organic components that produce chemical or structural modification of the inorganic network. Low-temperature curing (*ca.* 150 °C) produces the ormocer solid in contrast with high crystallisation temperatures required for oxide ceramics. As an example, an ormocer was prepared[54] by reaction of a silanol-terminated polydimethylsiloxane (molecular mass 1750) with acidified $Si(OC_2H_5)_4$ at 80 °C and gelation occurred at ambient temperature. Potential applications of ormocers are many,[56] including optoelectronics, sensors, coatings, elastomers and porous materials. Development of ormocers is an exciting area of materials science where there is considerable scope for innovative sol–gel chemistry to produce novel materials with tailored properties.

Hydrothermal synthesis

Hydrothermal techniques are widely used in industrial processes for the dissolution of bauxite prior to precipitation of gibbsite in the Bayer process and for the preparation of aluminosilicate zeolites. Interest in this method for synthesis of ceramic powders, as measured by the number of publications, is much less than in the two sol–gel processes. This is surprising because hydrothermal synthesis offers a low-temperature, direct route to submicrometre, oxide powders with a narrow size distribution avoiding the calcination step required in sol–gel processing. When applied to ceramic powders hydrothermal techniques often involve heating metal salts, oxides or hydroxides as a solution or suspension in a liquid at elevated temperature and pressure up to about 300 °C and 100 MPa. Syntheses that offer a lower temperature route[57] than solid-state reactions to compounds are frequently described as soft chemistry routes or *chimie douce* reactions, although these terms have not been widely used in the ceramic literature. The advantage of hydrothermal synthesis is illustrated by the preparation of $BaFe_{12}O_{19}$[58] from a suspension of $Ba(OH)_2$ and α-FeOOH. Single-phase submicrometre ferrite particles were obtained at 325 °C compared with a temperature between 1150 and 1250 °C in the conventional solid-state synthesis by firing a mixture of α-Fe_2O_3 and $BaCO_3$. For $SrFe_{12}O_{19}$, coprecipitated mixed strontium(II) and iron(III) hydroxides were heated in the temperature range 160–220 °C for up to 5 h, yielding strontium hexaferrite[59] powder, about 2 µm in diameter with a platelet morphology. This reaction temperature is low compared to 1250 °C for the conventional solid-state reaction between $SrCO_3$ and Fe_2O_3 and 800 °C for coprecipitation. The hydrolysis reaction represented in eqn. (3) can become more pronounced under hydrothermal conditions compared to ambient temperatures leading to direct formation of oxide powders from electrolyte solutions. This type of reaction is known as forced hydrolysis. As an example, monoclinic ZrO_2 powder with particle diameters in the range 1–10 nm was produced[60] by heating a 0.2 mol dm^{-3} solution of $ZrO(NO_3)_2$ at pH 0.5. Hydrothermal techniques have also been used for fabrication of thin films, for example $BaTiO_3$[61] on Ti substrates.

Understanding the reaction mechanism of hydrothermal syntheses and the nature of solution species can help in the production of powders with well defined properties. Dissolution–recrystallisation processes are considered important in particle nucleation and growth under hydrothermal conditions while polynuclear ions that are precursors for sol–gel processes are important for forced hydrolysis reactions. For example a tetrameric species $[Zr(OH)_2{\cdot}4H_2O]_4^{8+}$ has been considered[60] to form particles of critical size which nucleated from solution and grew by aggregation. Thermodynamic modelling of hydrothermal processes has been carried out, particularly for $BaTiO_3$,[62] and these calculations indicate the stability of the desired product under different conditions, namely pH, temperature and reagent concentrations. Although many chemical syntheses are very different from a practical viewpoint, they are often related by underlying chemical themes. Hence a greater knowledge of the formation and structure of solution species will be useful in increasing understanding of powder formation in sol–gel and hydrothermal processes.

Polymer pyrolysis

Polymer pyrolysis refers to the synthesis of a polymeric compound, sometimes called a preceramic polymer, which is then fabricated into a shape and pyrolysed to the ceramic. Polymer pyrolysis is particularly associated with the synthesis of high-tensile strength β-SiC fibre as a result of pioneering work[63,64] carried out in the 1970s. This work involved thermal rearrangement of polysilanes to polycarbosilanes. For example, $(CH_3)_2SiCl_2$ was converted by reaction with Li to dodecamethylcyclohexasilane, $[(CH_3)_2Si]_6$ which underwent ring-opening and polymerisation at 400 °C under Ar to yield a polycarbosilane. Continuous polycarbosilane fibre could be prepared[65] either by drawing from solution or by melt-spinning and was pyrolysed to β-SiC fibres although the molecular mass distribution of the polycarbosilane affected the fibre quality. These studies also led to a process for the manufacture[7] of continuous polycrystalline β-SiC fibre and an important step in the process is curing of polycarbosilane fibres in O_2 which cross-links molecular chains of the polymer preventing melting during polymer decomposition. Conversion of polycarbosilanes to fibre is a further example of powderless processing. Besides their use in the preparation of fibres, preceramic polymers can be applied as films and moulded into shapes that can be cured and pyrolysed to near net-shape ceramic components with high purity and compositional homogeneity at relatively low temperature. They are also used to build-up the matrix, by impregnation, of fibre-reinforced ceramic matrix composites. These benefits for fabrication have led to increased interest in the chemical design of preceramic polymers that can be converted directly to ceramic fibres and monoliths. Another preceramic polymer is polysilastyrene,[66] a soluble phenylmethylpolysilane made by reaction of $(CH_3)_2SiCl_2$ and $C_6H_5CH_3SiCl_2$ with Na in toluene. Solubility, melting point, the curing process (whether by heat treatment or by ultraviolet irradiation) and, in particular, ceramic yield on pyrolysis are all important properties for successful use of preceramic polymers, and further examples of the range of materials developed are shown[67] in Table 2. This area of ceramics where synthesis has a crucial role is under increasing[68,69] investigation.

Polymer pyrolysis is not restricted to Si-based systems. Thus, reaction of $B_{10}H_{14}$ with diamines such as $NH_2CH_2CH_2NH_2$ yielded a solid preceramic polymer[70] which was pyrolysed in NH_3 at 1000 °C to a BN-containing powder. For AlN, anodic dissolution of Al in acetonitrile containing a primary amine and a tetraalkylammonium salt (for increasing the solution conductivity) produced[71] a liquid with composition $Al(NHR)_3$ that underwent polymerisation to a solid gel with composition $Al_2(NR)_3$. The latter was pyrolysed above 800 °C in NH_3 to AlN powder with a crystallite size of 25 nm. Although this last example involves polymer pyrolysis it can also be classified as a non-aqueous liquid-phase reaction.

Non-aqueous liquid-phase reactions

Liquid-phase reactions take place in a non-aqueous solvent, which may be inert or one of the reactants, and are associated with the synthesis of non-oxide powders, particularly Si_3N_4. An interfacial reaction[7,72] occurs between $SiCl_4(l)$ in a mixed cyclohexane–benzene solvent and $NH_3(l)$ at −40 °C producing an amorphous solid, silicon diimide $Si(NH)_2$, which decomposes on heating to 1400 °C to α-Si_3N_4. This reaction forms the basis for a commercial route to Si_3N_4 powder (Ube Industries) which consists of equiaxed particles, about 0.1–0.2 μm in size, containing 95% of the α-phase and 5% of β-Si_3N_4; this powder contains lower levels of impurities than those from other syntheses for Si_3N_4 such as solid-state reaction, as the reactants can be readily purified. Other metallic nitrides have been[73] made by similar interfacial reactions, for example cubic vanadium nitride with a particle size of 0.1–1 μm is formed by decomposition of the product of the reaction of $VCl_4(l)$ and $NH_3(l)$ at 1500 °C in NH_3. For borides, $Ti(BH_4)_3$, obtained from the reaction[6] of B_2H_6 with $Ti(OC_4H_9)_4$, decomposed at 140 °C in xylene according to the equation

$$2Ti(BH_4)_3 \rightarrow 2TiB_2 + B_2H_6 + 9H_2 \qquad (7)$$

to give an aggregated TiB_2 powder of high purity with a particle size of 0.1–0.2 μm, while cubic ZnS was obtained[74] on passing H_2S through a diethylzinc solution at ambient temperature. In an extension of sol–gel processing to non-oxides, amorphous GeS_2 was obtained[75] by reaction of H_2S with $Ge(OC_2H_5)_4$ at ambient temperature and crystallised on heating, although it was easily contaminated with GeO_2. Low-temperature decomposition is an advantage of non-aqueous reactions that have been extended to oxides and include condensation between metal chlorides and metal alkoxides, which has been referred[76] to as a non-hydrolytic sol–gel reaction represented by the equation

$$MCl_z + M(OR)_z \rightarrow Cl_{z-1}MOM(OR)_{z-1} + RCl \rightarrow 2MO_{z/2} + zRCl \qquad (8)$$

For example, $TiCl_4$ and $Ti(OC_3H_7)_4$ were heated together at 110 °C and the resulting monolithic gel was decomposed to anatase at 500 °C. Non-hydrolytic reactions can be carried out by reaction of a metal chloride with an ether[77] which forms an intermediate adduct and then a metal chloroalkoxide. This approach has a processing advantage as the use of alkoxides, which may be difficult to synthesise, is avoided. For example, $VOCl_3$ was reacted with $(C_3H_7)_2O$ at 110 °C and the resulting gel was decomposed at 500 °C to orthorhombic V_2O_5 powder.

Table 2 Ceramic product and yield from preceramic polymers[67]

precursor	temperature/°C; atmosphere	product	yield (mass%)
polymethylvinylsilane	1000; Ar	SiC	83
polytitanocarbosilane	1300; N_2	$SiC_xO_yTi_w$	75
polyhydridosilazane	1200; N_2	Si_3N_4	74
polymethylsilazane	800; NH_3	Si_3N_4	85
polyvinylsilazane	1200; N_2	SiC_xN_y/C	85
polyvinylphenylsilazane	1000; N_2	Si_3N_4	85
polycyclomethylsilazane	1000; Ar	Si_3N_4/SiC	88
polyborosilazane	1000; Ar	BN/Si_3N_4	90
polyboronsiliconimide	1250; NH_3	SiB_xN_y	72
polymethylsiloxane	1000; He	SiO_xC_y	85
polyphenylsilsesquioxane	1400; Ar	SiC_xO_y	78

Aerosol-derived powders

Two aerosol routes are used for powder preparation. The first involves generation of a supersaturated vapour from a reactant followed by homogeneous nucleation, while the second involves generation of liquid droplets by various methods which undergo a heat treatment to solid particles. For example,[78] the silazane precursor $[CH_3SiHNH]_n$ where $n = 3$ or 4, which was made by ammonolysis of CH_3SiHCl_2, was decomposed to a vapour at about 1000 °C in NH_3. Rapid condensation of the gaseous product produced nanometre-sized ceramic powders in the Si(N,C) system. Liquid droplets can be generated by use of pneumatic jet atomisation or ultrasonic atomisation after which the droplets are dried and transported by a carrier gas to a furnace where they are decomposed to oxide powders. Decomposition of droplets in this way is often referred[79] to as spray-pyrolysis. Compared to conventional powder synthesis, aerosol methods have the ability to produce spherical particles with sizes ranging from micrometres down to 100 nm with high purity and chemical homogeneity for complex metal oxides. An example[80] of an aerosol-derived cathodoluminescent phosphor, $Y_{2.82}Tb_{0.18}Ga_{2.5}Al_{2.5}O_{12}$, made by ultrasonic atomisation is shown in Fig. 4. Other materials made by aerosol methods include submicrometre $SrFe_{12}O_{19}$,[81] while electrostatic atomisation has been used for synthesis of ZrO_2 powder.[82]

Spray-drying[24] is used in industrial processes for converting a liquid feed into a dry powder. When applied to ceramic powders the feed can consist of oxide colloids or salt solutions and when these precursors are used spray-drying is analogous to aerosol techniques. Spray-dried powders are often larger than aerosol-derived powders, around 10 μm in diameter. This technique is a convenient way to prepare multicomponent oxides with good chemical homogeneity. For example, $GdAl_2B_4O_{10.5}$, which could not be obtained[3] in high yield by solid-state reactions between oxides owing to its decomposition above 1050 °C, was readily prepared as a single phase by

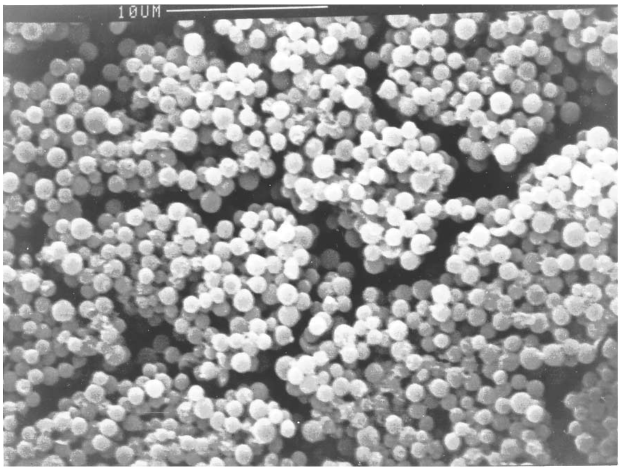

Fig. 4 Aerosol-derived $Y_{2.82}Tb_{0.18}Ga_{2.5}Al_{2.5}O_{12}$ powder

spray-drying mixed electrolyte solutions followed by calcination at 950 °C. Spray-roasting or spray-calcination involves converting a liquid feed to droplets that are fed directly to a furnace and powder sizes obtained from this technique and spray-drying are similar. Spray-roasting has been used to manufacture[83] multicomponent ceramics, for example ferrites such as $MnFe_2O_4$.

Gas-phase reactions

Reactions between gases have been used to prepare both oxides and non-oxide powders on the laboratory and industrial scale. These reactions are characterised[1] by the use of a variety of heating techniques including furnace heating, lasers, gas plasmas and flame propagation, while the underlying chemical principle that determines particle formation is homogeneous nucleation from supersaturated vapours. In flame-hydrolysis,[84] volatile compounds such as $SiCl_4$ are passed through an oxygen–hydrogen stationary flame. Molten primary oxide particles formed by nucleation grow by coalescence to larger droplets. As particles solidify they stick together on collision, forming solid aggregates which then associate to loosely bound agglomerates. Flame-hydrolysed silicas have been used[23] in sol–gel processing while examples of other flame-hydrolysed oxides are shown in Table 3. Pioneering work[85] on the use of high-powered lasers to heat gases yielded Si_3N_4 with a particle size between 10 and 25 nm and nitrogen surface area of 117 m^2 g^{-1} from a mixture of SiH_4 and NH_3. Silane has a strong absorbance band at 10.6 μm, near the wavelength of CO_2 lasers, and was decomposed to a supersaturated Si vapour which reacted with NH_3. These reactions are characterised by fast heating and cooling rates (10^6 K s^{-1} and 10^5 K s^{-1} respectively) and reaction times around 10^{-3} s. Different precursors have been used in laser-driven reactions; for example,[86] mixed Si_3N_4–SiC powders with an average particle size of 20 nm were obtained from a mixture of hexamethyldisilazane, $(CH_3)_3SiNHSi(CH_3)_3$ and NH_3. Direct current argon plasmas have been used to prepare[87] TiN powders with diameters around 10 nm by heating a mixture of $TiCl_4$ and NH_3 at 1100 °C. Plasma-derived powders which had a much finer particle size than commercial TiN (size around 0.5–1.0 μm) prepared by nitridation of Ti could be pressureless sintered at 1400 °C whereas the conventional powder is difficult to sinter and requires hot-pressing at temperatures higher than 1800 °C.

Table 3 Oxides made by flame hydrolysis[84]

oxide	raw material	boiling point/°C
SiO_2	$SiCl_4$	57
Al_2O_3	$AlCl_3$	180[a]
TiO_2	$TiCl_4$	137
Cr_2O_3	CrO_2Cl_2	117
Fe_2O_3	$Fe(CO)_5$	103
GeO_2	$GeCl_4$	84
NiO	$Ni(CO)_4$	42
SnO_2	$SnCl_4$	114
V_2O_5	$VOCl_3$	127
ZrO_2	$ZrCl_4$	331[a]

[a] Sublimation temperature.

Pechini and citrate gel methods

In the Pechini method,[88] polybasic chelates are formed between α-hydroxycarboxylic acids containing at least one hydroxy group, for example citric acid, $HOC(CH_2CO_2H)_2 \cdot CO_2H$ with metallic ions. The chelate undergoes polyesterification on heating with a polyfunctional alcohol, for example ethylene glycol, $HOCH_2CH_2OH$. Further heating produces a viscous resin, then a rigid transparent, glassy gel and finally a fine oxide powder. Advantages of the Pechini method are the ability to prepare complex compositions, good homogeneity through mixing at the molecular level in solution and control of the stoichiometry. Low firing temperatures are required for decomposition of the resin to the oxide, thus 650 °C for $BaTiO_3$ compared to 1000 °C for the conventional solid-state reaction. This is a versatile method for the synthesis of multicomponent oxides, for example $Pb_3MgNb_2O_9$.[89] The citrate gel[90,91] method shares the advantages of the Pechini method with respect to chemical homogeneity and compositional control. For the synthesis[92] of $YBa_2Cu_3O_{7-x}$ metal nitrate solutions of Y, Ba and Cu were added to citric acid solution and the pH raised to between 6.5 and 7.0 in order to dissolve insoluble barium citrate but not to precipitate metal hydroxides. The solution, which contained polybasic chelates, was concentrated to a viscous resin and dried to a transparent gel that was pyrolysed to a fine powder. The citrate gel method is also a versatile method for synthesis of multicomponent oxides, for example $SrCo_{0.8}Fe_{0.2}O_{3-x}$.[93]

A claimed advantage of many chemical syntheses is their improved homogeneity although evidence for this is not always available. However, a recent study using Raman and ^{13}C NMR spectroscopy indicated that during the preparation[94] of $BaTiO_3$ by the Pechini method the coordination of Ba and Ti in the mixed metal complex remained almost unchanged on polymerisation and that molecular-level mixing was retained at the resin stage and probably in the pyrolysed resin. There is further scope for using characterisation techniques for monitoring changes in homogeneity at different stages of the wide range of chemical syntheses.

Emulsion-derived powders

Emulsions have been used widely in aqueous sol–gel processes for converting sols to gel powders by dehydration, internal gelation and external gelation as was described earlier. Powders made by these methods have sizes in the range of 1 μm or larger and emulsion methods have been extended to include use of microemulsions, enabling preparation of ceramic particles in the nanometre size range. Thus Fe_3O_4 powders were made[95] by precipitation from Fe^{3+}/Fe^{2+} salts with NH_3 (aq) in microemulsions of sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT)–heptane–H_2O while TiO_2 particles with diameters less than 10 nm were prepared[96] by controlled hydrolysis of $Ti(OC_3H_7)_4$ in reverse micelles of Aerosol OT produced in an Aerosol OT–hexane–H_2O solution; the TiO_2 nanoparticles aggregated into sols with sizes of 20 to 200 nm, eventually forming gelatinous precipitates.

Conclusions

Studies on ceramics are interdisciplinary and chemistry has an increasingly important role in the research, development and manufacture of these materials. Chemical methods for ceramic synthesis, a selection of which have been described, are also known as soft chemistry routes and offer a lower temperature route to ceramic materials compared to conventional solid-state reactions between oxide powders. They also allow direct fabrication of ceramics as coatings, fibres and monoliths. For the syntheses under discussion, molten salt reactions offer a straightforward route to ceramic powders using readily available precursors, although their extension to a wide range of compositions requires further study. Sol–gel processing with both aqueous oxide colloids and alkoxides has attracted tremendous attention as measured by the numbers of publications. Aqueous sol–gel processing methods avoid the use of organic solvents, which is a practical advantage, and involve low-cost precursors. Full exploitation of the alkoxide route, particularly for powders, requires economical synthesis of metal alkoxides but this method is very useful for fabrication of thin oxide coatings where the cost of the precursor is not a critical factor. A major development of sol–gel processing has been on organic–inorganic hybrids and there is considerable potential here for innovative chemical synthesis of new materials with tailored properties. Other gel methods, the Pechini and citrate gel techniques, have been shown to be very useful for synthesis of multicomponent electroceramic powders.

Sol–gel processing has been applied mainly to oxide ceramics. There is scope for extending sol–gel processing of alkoxides to non-oxide ceramics which links sol–gel to non-aqueous liquid-phase reactions. The latter have been widely applied to non-oxide powders, in particular for the manufacture of silicon nitride. Hydrothermal synthesis and sol–gel processing, although very different from a practical viewpoint, involve hydrolysis of solution species. Increased knowledge about the formation of hydrolysis products in solution would enhance understanding of the processes involved in particle formation from solution. Hydrothermal synthesis is an established industrial process and offers a direct route to oxide powders, but it has not attracted the attention given to sol–gel methods. There is potential for extending hydrothermal methods to a wide range of compositions for both oxide and non-oxide powders. Control of powder aggregation, for example in coprecipitation and molten salt reactions, is important for ceramic applications and needs to be considered when carrying out a synthesis. A key advantage of polymer pyrolysis over other methods is its ability to yield high-strength non-oxide fibres, and there is considerable scope for chemical design of polymers suitable for conversion to fibres, coatings and monolithic ceramics. Chemical methods have the ability to produce powders with an exceptionally small size in the nanometre range; gas-phase reactions, microemulsions and aerosol methods are particularly suited for preparation of nanoparticles. However, the success of chemical syntheses of ceramic materials can be judged primarily by whether they result in improved materials properties and performance. In order to fully exploit chemical methods now and in the next century a close interaction is required between ceramic studies carried out in the disciplines of chemistry and materials science.

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