Inorganic Materials
Chemistry Desk Reference

INORGANIC MATERIALS CHEMISTRY
Desk Reference

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ABOUT THE AUTHOR

Dr. D. Sangeeta* is a materials scientist with the Ceramics Laboratory of the General Electric Corporate Research and Development Center, conducting a variety of inorganic materials chemistry–related projects. Prior to joining General Electric in March 1994, she was a research scientist at Battelle in Columbus, Ohio. There, she conducted research and development in the areas of sol-gel processing, metal organic chemical vapor deposition, and supercritical drying to produce ceramic films, powders, and monolithic composites.

Dr. Sangeeta was a research associate in the Materials Science Department at the University of Illinois, Urbana, in 1989. As a research associate she conducted research relating to sol-gel processing of ferroelectric thin films and zirconia powders. She completed her Ph.D. in chemistry with Professor W. G. Klemperer at the School of Chemical Sciences, University of Illinois, Urbana-Champaign. Her thesis work involved understanding the molecular growth pathways in silica sol-gel processing. She obtained her Masters in chemistry from the Indian Institute of Technology, Kanpur, in 1984 and her Bachelors in science from Christ Church College Kanpur, India, in 1982.

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PREFACE

This *Inorganic Materials Chemistry Desk Reference* is meant to be a resource to assist in the preparation of solid state inorganic materials by chemical processing techniques. Ceramic materials can be prepared by a variety of chemical routes and this handbook provides a brief introduction to inorganic materials chemistry and these processing routes, along with definitions of most commonly used terms in the field. The focus of the desk reference is a compilation of property data on inorganic precursors and on inorganic solids to assist in the selection of candidate precursors and materials for a variety of applications.

The idea for such a resource for inorganic materials chemistry was conceived from my personal experience with initiating new materials chemistry-related projects, all of which began by necessity with the painstaking effort required to collect relevant information from a multitude of sources, including textbooks, handbooks, journals, proceedings, and magazines. Beginning with my thesis and postdoctoral work on sol-gel processing at the University of Illinois with Professors W. G. Klemperer and D. A. Payne, I found myself devoting a considerable fraction of my efforts to collecting relevant information in the area of materials chemistry. During my work at Battelle in Columbus, Ohio, and subsequently following my move to the General Electric Corporate Research and Development Center, it was clear to my colleagues and to me that there is a pressing need for a resource that not only explains the terms frequently used in the inorganic materials chemistry field, but also provides data on the physical properties of the precursors available for use in chemical processing techniques. Such questions as "What precursor can I select to prepare this inorganic solid?" and "Which precursor (from the processing point of view) is suitable or viable for this process?" are the types of questions that scientists and engineers need quick answers to in order to initiate a successful materials chemistry project. This resource provides a rapid reference to help answer these and other such questions. In addition, it provides physical property data on inorganic solids to answer questions such as "What kind of properties should I expect from this or similar materials?"

The desk reference begins with a general introduction to the area of inorganic materials chemistry with an emphasis on chemical processing routes. Several sources of additional information are provided for newcomers to the field and for the experienced practitioners as well. The second chapter provides a quick reference to many commonly used terms in the field of inorganic materials chemistry. The primary purpose of the desk reference, that of providing data on inorganic precursors and ceramic materials, is served in Chapters 3 and 4. The third chapter is a compilation of physical property data on various organometallic, metal organic, and inorganic salt precursors used in the processes described in Chapter 1. The fourth chapter consists of seven sections detailing physical property data on inorganic solids, including oxides, carbides, nitrides, borides, selenides, tellurides, and sulfides, among others.

As with any new idea, this resource is a start at compiling and organizing the information currently available. A concerted effort has been made to include all of the relevant information referenced in the multitude of published sources. However, in an emerging area such as this, new processes and products are being invented and discovered every

day making it impossible to include every piece of information. With time, as more relevant information is published, this desk reference will be expanded and revised. Suggestions and input from readers are welcome and will be acknowledged gratefully.

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Chapter 1

INTRODUCTION TO INORGANIC
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·I. INTRODUCTION

The area of inorganic materials chemistry encompasses technologies which have tradi-
tionally existed in both inorganic chemistry and ceramics. Inorganic materials chemistry
applies the expertise developed over the years in inorganic chemistry to developing
ceramic and glassy materials with improved properties and relative ease of processing.
Growing acceptance in recent years of the importance of chemistry to materials prepara-
tion and processing has resulted in the recognition of materials chemistry as a distinct
subdiscipline of chemistry. *Materials chemistry*, in general, can be defined as the chemical
science which deals with the preparation, processing, and analysis of solid state materials.
Inorganic materials chemistry, in particular, relates to the preparation, processing, and prop-
erties of inorganic materials, such as metal carbides, borides, nitrides, oxides, sulfides,
selenides, tellurides, and their combinations.[1]

In contrast to conventional ceramic and glass processing which require high temper-
atures and/or high pressures, inorganic materials chemistry involves preparation and
processing of inorganic materials under relatively milder temperature and pressure con-
ditions. The chemical route to ceramic materials not only can provide a milder route to
ceramic and glassy materials, but also an opportunity to prepare unusual forms of existing
materials such as, for example, epitaxial films, transparent films of otherwise opaque
material, stable colloidal suspensions, submicron powders, microporous membranes.
Inorganic materials chemistry can also provide the opportunity to prepare novel multi-
component systems that are otherwise difficult to prepare by conventional techniques.
Multicomponent systems such as Y, Ba, and Cu (1-2-3) oxide superconductors, for exam-
ple, can be prepared in various forms, including films and powders prepared using novel
chemical routes such as sol-gel and colloidal processing. Also, some materials, such as
crystalline lead zirconate titanate, $Pb(Zr,Ti)O_3$, which could previously be prepared only
in a monolithic form or as single crystals can now be fabricated, using chemical processing
techniques, as polycrystalline films having properties similar to single crystals.

Another important aspect of materials chemistry research is the study of the interaction
between materials and their environment. Types of interactions may include corrosion,
adhesion, oxidation, mechanical or chemical abrasion, thermal shock, chemical sensing,
and thin-film deposition. A complete understanding of such topics requires expertise in
surface science, analytical chemistry, chemical kinetics, thermodynamics, and modeling
of chemical processes. A common focus of such studies is the application of chemical
methodologies to provide both an understanding on the molecular level, as well as

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improved control over the properties of the resultant materials and the interaction of these materials with the environment.

The preparation and characterization of novel materials are currently the most popular research topics among the many areas of research in materials chemistry. Topics of interest include the development of precursors for glass, ceramic, metal, and semiconductor materials, wet chemical processing, gas phase film deposition and powder preparation, molecular, micro-, and macroscopic characterization of the resultant solid state materials. The processing aspects of materials chemistry present the greatest opportunity for research and may deal with a variety of individual techniques, such as sol-gel processing, surface science, metal organic decomposition (MOD), metal organic chemical vapor deposition (MOCVD), colloidal processing, nanoscale materials synthesis, among others.

II. PREPARATION AND PROCESSING OF INORGANIC MATERIALS

In this section, a variety of materials preparation and processing approaches to solid state materials in various forms are described briefly. The types of processes discussed include the sol-gel process, colloidal processing, hydrothermal processing, freeze-drying process, supercritical drying process, MOD, MOCVD or CVD, and flame hydrolysis. Of these processes, sol-gel, colloidal, and hydrothermal processing are often referred to as wet chemical processing.


A. Sol-Gel Process

The sol-gel process is a wet chemical route to a variety of glass and ceramic compositions. It has been mainly used for compositions and forms, such as certain multicomponent systems and films of specific compositions that are not easily available or possible by the conventional ceramic processing methods.

In the sol-gel process, the precursors are mixed to form sols (clear to cloudy) that undergo polymerization forming a gel. By controlling reaction conditions such as solution pH, type of precursors and solvents, reaction temperature, and additives, a variety of physical forms can be produced including films, fibers, microspheres, and monoliths. For fabricating films or fibers, the viscous liquid is used for coating films or drawing fibers. The viscosity of the liquid is carefully controlled to provide the desired physical characteristics of the film or fiber. Fine ceramic powders are produced by the sol-gel process, sometimes referred as the gel precipitation process, by varying the reaction conditions, such as the solution pH and the type of solvent media used. Monoliths are normally prepared by drying the gel in a mold, taking the shape of the mold.

The sol-gel process has certain advantages and disadvantages over conventional processes. Advantages include the ability to precisely control the stoichiometry, the possibility of producing multicomponent materials not previously available, and the ability to produce high-purity materials for electronics and optics without much investment in equipment. However, drawbacks of the sol-gel process include solvent waste, large-volume shrinkage during drying, and high precursor costs. For each application, the advantages and disadvantages of the sol-gel process must be considered in comparison with other processes. The use of sol-gel techniques for producing films has, in particular, generated considerable commercial interest because of the versatility of the sol-gel process in producing multicomponent homogenous compositions with ease and cost-effectiveness.
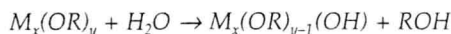
Among ceramic compositions, oxides are the most common composition prepared by the sol-gel process, where the precursors are hydrolyzed in water and are air dried. A

general sol-gel reaction to yield oxide systems with a single component where metal alkoxides are used as precursors is given below:

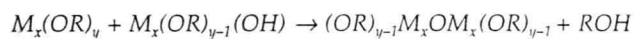$$M_x(OR)_y + y/2H_2O \xrightarrow{ROH} M_xO_{y/2} + yROH$$
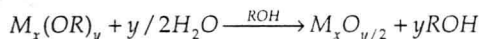
where R is an alkyl or aryl. The above reaction results from two intermediate reactions called hydrolysis and condensation which can be represented by the following equations:

Hydrolysis:

$$M_x(OR)_y + H_2O \rightarrow M_x(OR)_{y-1}(OH) + ROH$$

Condensation:

$$M_x(OR)_y + M_x(OR)_{y-1}(OH) \rightarrow (OR)_{y-1}M_xOM_x(OR)_{y-1} + ROH$$

or

$$M_x(OR)_{y-1}(OH) + M_x(OR)_{y-1}(OH) \rightarrow (OR)_{y-1}M_xOM_x(OR)_{y-1} + H_2O$$
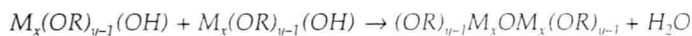
The above condensed species undergo further condensation during drying and heat-treatment processes which results in the formation of oxides. Examples of such single component oxide systems are

$$Si(OCH_3)_4 + 2H_2O \xrightarrow{CH_3OH} SiO_2 + 4CH_3OH$$
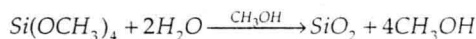
and the hydrolysis and condensation reactions can be represented by

$$Si(OCH_3)_4 + H_2O \rightarrow Si(OCH_3)_3(OH) + CH_3OH$$

$$Si(OCH_3)_4 + Si(OCH_3)_3(OH) \rightarrow (OCH_3)_3SiOSi(OCH_3)_3 + CH_3OH$$

$$Si(OCH_3)_3(OH) + Si(OCH_3)_3(OH) \rightarrow (OCH_3)_3SiOSi(OCH_3)_3 + H_2O$$
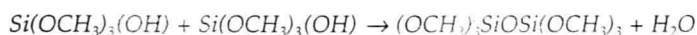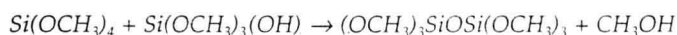
Other materials such as sulfides and other chalcogenides can also be prepared by the above process, with H_2S or thiols normally used as sulfidating agents to form the sulfides. Carbides and nitrides can be prepared by carefully selecting appropriate alkoxide and other precursors which decompose after polymerization into carbides and nitrides with minimal oxide impurities, under reducing or nitridating (ammonia) atmospheres. The preparation process for carbides nitrides and borides can also be classified as an MOD process, as described later in this section.

A variety of precursors have been used in the sol-gel process and their relevant physical properties are tabulated in Chapter 3. The properties of the end products, a variety of different glass or ceramic compositions, are categorized and listed in Chapter 4.

Colloidal Processing can be described as a sol-gel process where the starting material is a colloidal suspension instead of molecular precursors. This wet chemical method is used for preparing solid state inorganic materials from a colloidal system with the size of the dispersed phase particles ranging between 1 nm and 1 μm in at least one dimension. In order to produce a stable colloidal suspension, dispersing agents are employed or the pH of the suspension is adjusted to finely disperse the colloidal particles.

A number of materials have been prepared by the above method, including UO_2–PuO_2 nuclear fuel spheres produced from a stable suspension of uranyl nitrate, plutonium nitrate, a modifying agent, and a gelling agent. In this example, the suspension was gelled with ammonia and washed with water and dried prior to sintering. This route is sometimes also referred to as a *gel-precipitation route*.

Other examples of colloidal processing include the preparation of monodispersed alumina and silica spheres or polydispersed titania and ceria powders from colloidal suspensions of their precursors.

Fine ceramic particles can also be prepared by a *sol-emulsion-gel process*, where the reactants are suspended as micelle[2] in a nonmiscible solvent with an aid of a surfactant and the droplets are then gelled to form ceramic particles. The particles are then isolated by conventional processing routes. The sol-emulsion-gel process can also be classified as a colloidal processing route.

Fine zirconia particles in the range of 4 to 6 nm have been prepared by this process using $ZrO(NO_3)_2$ and NH_3 reactants in xylene solvent. The zirconyl nitrate precursor was dissolved in water and dispersed in xylene using a surfactant, Tween 80. The droplets were then gelled with ammonia gas and the resultant fine zirconia powder was separated by distillation and multiple solvent washing.[3]

B. Hydrothermal Process

The hydrothermal process is a method of forming ceramic powders by heating and pressurizing solutions or suspensions of metal salts, oxides, hydroxides, or metal powders in water and, on occasion, in other solvents. The process is conducted in a pressure vessel called an autoclave. Normally, as the mixture is heated in this closed system the pressure rises and these conditions result in the formation of submicron particles with controlled size and shapes.[6] This route has been used to prepare a variety of monodispersed powders, materials with specific crystalline phases, particles with controlled size and shapes, frequently at temperatures lower than those required in normal processing procedures.

The hydrothermal process promotes the formation of monodispersed spheres by providing the appropriate conditions needed for homogenous nucleation. For example, monodispersed metal oxide powders are formed by homogenous nucleation of metal hydroxide particles which are produced by forced hydrolysis of metal alkoxides using heat and pressure in an autoclave. Forced hydrolysis is normally achieved by controlling the release of the precipitating ion. A route to yttria-stabilized zirconia powder illustrates this concept. The reactants, yttrium chloride, zirconium oxychloride, and urea, $CO(NH_2)_2$, are mixed in an autoclave, where the urea decomposes at temperatures between 160 and 220°C under 5 to 7 MPa releasing ammonia. The ammonia then reacts with the metal salts in water to form hydroxides. These hydroxides are then washed, dried, sintered, and crushed to form fine yttria-stabilized zirconia powder.[4]

In other cases, the hydrothermal process can promote phase transformation. For example, tetragonal zirconia for structural applications can be prepared by such a process. Amorphous zirconia precipitated from $ZrCl_4$ and NH_4OH can be aged in an autoclave between 513 and 1093 K at 100 MPa pressure in water to form a tetragonal phase of zirconia in addition to the normal monoclinic phase.[5]

Metal oxides that cannot be prepared by normal oxidation of metals in an oxidizing atmosphere can also be prepared by hydrothermal processes. For example, hafnium (Hf) particles were only surface oxidized to HfO_2 in water between 300 and 400°C as a result of the formation of an oxide layer which protected the interior of the metal chips.[6] However, under 50 to 150 MPa and between 300 and 700°C in an autoclave Hf was completely

oxidized to HfO_2. Complete oxidation occurs in the autoclave because the hydrides of hafnium are formed under the elevated temperature and pressure conditions, which then quickly convert to the hafnium oxide.

C. Supercritical Drying Process

The supercritical drying process is used for producing fine ceramic powders or monolithic materials with extremely high porosity. The supercritical drying process normally involves preparing a gel containing a large volume fraction of liquid, following which the liquid is removed above its critical point (hence, no surface tension) without collapsing the solid state structure in the gel. As a result a highly porous structure called an *aerogel* is formed with intricate porosity.

An extensive body of information on supercritical drying exists in the area of aerogels.[7] As the term indicates, aerogels are solid state structures where the pores are filled with air and are formed by replacing the liquid in a gel with air. Much of the research work in this area has been focused on silica-type aerogels in both monolithic and powder forms. Some silica aerogels have been prepared with porosities up to 99.99%.[8] Silica gels are normally prepared using alkoxides:

$$Si(OR)_4 + H_2O + ROH \rightarrow SiO_2 + ROH$$

where R is an alkyl (CH_3, C_2H_5, etc.).

In the above sol-gel reaction, the only by-product is a liquid, an alcohol. The gel thus formed by the sol-gel process contains alcohol trapped in the silica solid state network. If the liquid is removed by evaporating the alcohol, the solid state structure would collapse from the capillary pressure developed as a result of the surface tension of the liquid. However, at or above the critical point of the liquid the surface tension of the liquid disappears. Hence, under supercritical conditions the liquid can be removed without collapsing the solid state structure thus forming a highly porous silica material with fine particles. The solid state network is built up of these interconnected primary particles.

Certain ceramic powders have been prepared by a supercritical method called rapid expansion of supercritical solutions (RESS). In this method,[9] solute nucleation and condensation occur within an expanding supercritical jet. For example, SiO_2 particles with diameters less than 5 μm were prepared by rapidly expanding a solution containing 3000 ppm of SiO_2 soluble species at 743 K under 60 MPa through a stainless steel nozzle 60 μm in diameter with flow rates of 0.7 cm^3 s^{-1}. In this method, the experimental conditions can be varied to change the resultant particle size.

D. Freeze-Drying Process

The freeze-drying process is used for preparing porous monolithic materials or unagglomerated powders. This process is similar to the supercritical drying process since the process also involves liquid removal from a mixture at zero surface tension without collapsing the structure. The liquid in the gel or a slurry is first frozen then removed by the sublimation process without collapsing the structure. In the sublimation process, the frozen liquid converts to vapor without going through the liquid stage thus avoiding surface tension–related capillary pressure. During the freezing process, however, some liquids undergo volume change and the freezing process can therefore potentially damage the structure. As a result, this process is limited to preparing unagglomerated powders. A

variety of oxide powders have been prepared by this method with narrow particle size ranges.[9a]

E. Metal Organic Decomposition

Metal organic decomposition (MOD) is a material synthesis method where metal organic compounds are decomposed to form a film or a fiber or a powder without the use of vacuum or gel powder techniques. The precursors, metal organic compounds, used in the MOD process are coordinated covalent molecules with a metal atom bonded to an organic ligand via a bridging oxygen, sulfur, phosphorus, or nitrogen atoms. For example, carboxylates, alkoxides, and thiolates are metal organic compounds that are frequently used as precursors to oxides and sulfides. Some of the above precursors can be used to produce metal coatings by decomposing or heat-treating the precursor itself or its solution in a reducing environment (e.g., H_2, N_2, Ar, etc.). Nitride coatings can also be produced from precursors where the organic ligand is bonded to the metal atom via a nitrogen atom. Nitride coatings produced by this process contain carbon impurities which can be minimized by heat-treating the material under an ammonia or nitrogen atmosphere.

A similar process is used to prepare metal films or metal carbide films from organometallic precursors where the organic ligand is bonded to the metal directly via a carbon atom. The compounds with aryl or alkyl ligands bonded to the metal atom are suitable precursors for metal carbide–type coatings. For example, a carbosilane oligomer mixture (e.g., $[-(R)_2Si-CH_2-Si(R)_2-CH_2-]_n$) with an Si–C backbone, dissolved in a solvent is deposited on a substrate and heat-treated from 600 to 800°C under argon to form an SiC film. The above process where polymers are used instead of compounds or molecules is referred to as *Polymer pyrolysis*. For example, polysilanes, polycarbosilanes, and polysilazanes can be pyrolyzed to form fibers or coatings of silicon carbide or silicon carbonitride.[10] Metal coatings (e.g., platinum) can be prepared from organometallic precursors in reducing atmospheres by the MOD process.

The precursors normally selected for this process should decompose without evaporating, melting, or leaving a carbon residue. To minimize volume change, precursors must also have a high metal content and a high char yield. Solid precursors require high solubility in the chosen solvent. The compounds must be stable under ambient conditions with minimum sensitivity to air or moisture. Compatibility between the decomposition temperatures of precursors in a multicomponent system is also desirable. From a processing prospective, it is also desirable that the decomposition of the precursors not result in the formation of toxic gases. Considering the above requirements, precursors with carboxylate ligands with or without alkoxide or amide ligands are typically suitable.[11]

The MOD process should not be confused with the MOCVD method of depositing film from gases or vaporized liquid precursors under vacuum conditions.[12] The techniques used for depositing and curing the films in the MOD process are very similar to the techniques used for photoresist coating or screen printing in the electronics industry. Factors critical to achieving uniform continuous films include substrate wettability, solution or liquid viscosity, solvent type, and the curing mechanisms needed to convert an amorphous film to a crystalline film. The solutions are normally filtered to remove any particles that may cause defects in the film. The curing or pyrolysis methods used in the process can alter the crystalline phase, grain size, and the resultant properties of the film. Nonconventional curing techniques, such as rapid thermal annealing, electron beam annealing, and lasers, have been used to alter the physical properties of the film.

Compositions such as $BaTiO_3$, $SrTiO_3$, $PbTiO_3$, ITO (indium-tin oxide), SnO_x, $YBa_2Cu_3O_7$, Pt, Au, Ag, and Pd have been deposited as films on a variety of substrates using the MOD method. Coating compositions containing dopants have also been prepared by this method.

The MOD technique has been successfully used in composite preparation. For example, SiC composites are prepared by impregnating the preforms with carbosilane polymers which are then decomposed to yield silicon carbide.

F. Metal Organic Chemical Vapor Deposition

The MOCVD process is a type of CVD technique where metal organic compounds, often in combination with hydrides or other reactants, are used as volatile precursors to deposit coatings on substrates. The CVD process can be defined as a method to fabricate films or a method to coat particles in a fluidized bed, where the chemical constituents react near or on the heated surface. The CVD process utilizes volatile precursors capable of evaporating without decomposition. In contrast to the established CVD precursors, the MOCVD precursors typically vaporize at much lower temperatures. In most cases, MOCVD reactions occur in the 500 to 1000°C temperature range and at pressures ranging from 1 torr to atmospheric pressure, whereas the conventional precursors for CVD process require at least 900°C and higher temperatures.[13] Recently, research has shown that some metal organic precursors can be decomposed at even lower temperatures.[13a]

The precursors used in the MOCVD process can also be activated by plasma using electromagnetic radiation which is particularly useful in systems with heat-sensitive substrates or surfaces. The thermal activation process, however, is the most commonly used method of activating precursors. The chemical reactions occurring during the MOCVD process may include thermal decomposition (pyrolysis), reduction, hydrolysis, disproportionation, oxidation, carburization, nitridation, or their combinations.

The MOCVD technique has been most commonly used for fabricating thin films of III-V semiconductor compounds, such as gallium arsenide (GaAs), indium arsenide (InAs), indium phosphide (InP), and gallium aluminum phosphide (GaAlP), particularly in epitaxial form. To prepare the above compositions metal alkyls or aryls, e.g., $In(CH_3)_3$, $As(CH_3)_3$, and hydrides, e.g., PH_3, AsH_3, are commonly used as volatile precursors. For example, fabrication of GaAs film involves a reaction between trimethyl gallium and arsine which can be represented by the following equation:

$$Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + 3CH_3$$
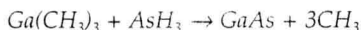
MOCVD precursors and processing equipment are relatively expensive, thus limiting the use of the technology to applications where cost is not a barrier and high quality is desired. Due to this limitation, MOCVD is currently used extensively only in the electronics industry,[14] and in applications for producing advanced lasers and infrared detector–type applications.

Chemical vapor infiltration (CVI) is a type of CVD technique used for a porous structure like a foam or a fibrous mat or weave. As the hot gases infiltrate through the porous media, they react and deposit on the hot surfaces and in some cases continuous deposition eventually fills up the pores to make a composite.[6]

The CVI process is frequently used for fabricating composites at lower temperature and pressure conditions than traditional composite-forming processes like hot pressing and hot isostatic pressing. The milder conditions help retain the mechanical and chemical integrity of the substrate. However, a major limitation of the CVI process is the length of time it takes to fill up the preform pores and to prepare a composite. Due to the tortuous paths in the substrate samples, films must be deposited at lower temperatures and at a slower rate compared with the CVD process to avoid choking the channels. However, recent developments have improved the commercial viability of the CVI process. *Forced CVI* is one technique where the gas flow is restricted to the sample, hence forcing all of

the gases through the channels in the sample and filling them up at a faster rate. Temperature gradients across the sample have also been used to speed up the CVI process. The CVI technique has been extensively used in fabricating SiC composites, where SiC pre-forms are filled with SiC material by chemical vapor infiltration of hydrocarbon and silane vapors.

Fluidized-bed CVD is a CVD technique where the substrate is a powder particle and the powder is suspended in a flowing gas. In order to achieve the desired coating on the particles, the density and the size of the particles and the velocity, density, and viscosity of the fluidizing gas are balanced so that the particles do not settle and clog the gas inlet.

The oldest application of the fluidized-bed CVD technique is for coating nuclear fuel particles (uranium-thorium carbide) with pyrolytic carbon and silicon carbide. Propane and other hydrocarbon gases are normally used as the volatile precursors for pyrolytic carbon and methyltrichlorosilane is the preferred precursor for SiC. Similarly, a zirconium carbide coating has been deposited by fluidized-bed CVD from zirconium tetrachloride and a hydrocarbon.[6,15]

G. Aerosol Processes

Aerosol processes can be classified as material synthesis via gas-to-particle or droplet-to-particle conversion. In a gas-to-particle conversion, gases or vapors react forming primary particles which further grow by coagulation or surface reactions. Powders produced by this process have a narrow size distribution, and the process can yield nonporous spherical particles. Materials like carbon black, silica, and titania are produced by the gas-to-particle conversion process in flame reactors. Flame hydrolysis which is commonly used for producing fine silica powder can be classified as a gas-to-particle conversion process. Fine ceramic powders can be prepared by the flame hydrolysis method where the precursors are oxidized in a flame to form oxides in a wide range of particle sizes. For example, SiO_2 powders have been prepared by flame hydrolysis from $SiCl_4$ oxidation in an H_2/O_2 stationary flame. After formation of the primary SiO_2 particles in the flame, the tiny droplets of SiO_2 coalesce as they move away from the flame and form larger particles from aggregates to agglomerates of SiO_2. The particles can then be separated by size.

In the droplet-to-particle conversion process, solution or slurry droplets are suspended in a gaseous medium by liquid atomization where the droplets react with gases or pyrolyze at high temperatures to form powders. The particle size distribution is determined by the droplet size or processing conditions such as particle breakup during pyrolysis or drying. The particles are mostly monodispersed and porous. Spray drying and spray pyrolysis are the most common industrial methods of producing powders by the droplet-to-powder conversion process.[16] Freeze-drying of droplets is another technique where powders are produced by droplet-to-particle conversion.

III. PRECURSORS

A variety of precursors used in different chemical processing routes have already been discussed in the previous section with regard to their suitability for individual processes. In this section, precursors used for the processes described in preceding sections are classified by groups. The precursors can be molecular or polymeric or a colloidal suspension of particles. Information on the properties of individual precursor properties is provided in Chapter 3, Physical Properties of Inorganic Materials Precursors.

A. Inorganic Salts

Inorganic salts are often used as molecular precursors in wet chemical processes such as sol-gel, colloidal, and hydrothermal processes. Inorganic salts are ionic compounds and some examples of inorganic salt precursors are listed in Table 1.

TABLE 1

Inorganic Salts	Examples
Metal halides	$MgCl_2$, LiF, KCl, $SiCl_4$, $TiCl_4$, $CuCl_2$, KBr, $ZrOCl_2$
Metal carbonates	$MgCO_3$, $CaCO_3$, Na_2CO_3, $SrCO_3$
Metal sulfates	$MgSO_4$, $BaSO_4$, K_2SO_4, $PbSO_4$
Metal nitrates	$LiNO_3$, KNO_3, $Fe(NO_3)_2$
Metal hydroxides	$Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, $Fe(OH)_3$, $Zr(OH)_4$
Salts with mixed ligands	$(CH_3)_3SnNO_3$, $(C_2H_5)_3SiCl$, $(CH_3)_2Si(OH)_2$

B. Metal Organic Compounds

Metal organic compounds (MOC) are covalent or inorganic coordinate compounds where the metal center is bonded to the ligand via a noncarbon atom, such as oxygen, sulfur, phosphorus, or nitrogen. In the literature, organometallic compounds described later in this chapter are also referred to as MOCs. MOCs are used as precursors for both wet chemical– and dry vapor–related processes. Examples of MOCs are provided in Table 2.

TABLE 2

Metal Organic Compounds	General Formula	Selected Examples
Metal alkoxides	–M(–OR), where R is an alkyl	$Al(OC_3H_7)_3$, $Si(OCH_3)_4$, $Ti(OC_3H_7)_4$, $Zr(OC_4H_9)_4$
Metal carboxylates	–M(–OC(O)R)$_x$, where R is an alkyl	$Al(OC(O)CH_3)_3$, $Pb(OC(O)CH_3)_2$, – acetates $Pb(OC(O)CH_2CH_3)_4$, – propionate $Al(OC(O)C_nH_5)_3$, – benzoate
Metal ketonates	–M(–OC(R)CH(R')CO–)$_x$, where R is an alkyl or aryl	$Ca(OC(CH_3)CH(CH_3)CO)_2$, – pentanedionate $Al(OC(C(CH_3)_3)CH(C(CH_3)_3)CO)_2$ – heptanedionate
Metal amides (sometimes also referred to as amines)	—	$(CH_3)_2AlNH_2$, $(C_2H_5)_2AlN(CH_3)_2$, $(CH_3)BeN(CH_3)_2$, $(iC_3H_7)_3GeNH_2$, $(C_3H_7)_3PbN(C_2H_5)_2$
Metal thiolates	–M(–SR)$_x$, where R is an alkyl or an aryl	$(CH_3)_2Ge(SC_2H_5)$, $Hg(C_4H_5S)_2$, $(SCH_3)Ti(C_5H_5)_2$, $(CH_3)Zn(SC_2H_5)$
Metal azides	–MN_3	$(CH_3)_3SnN_3$, CH_3HgN_3
Metal thiocyanides	–M(–NCS)$_x$	$(C_2H_5)_3Sn(NCS)$
MOCs with mixed functional groups	—	$(C_4H_9)Sn(OC(O)CH_3)_3$, $(C_5H_5)_2TiCl_2$, $(C_5H_5)Ti(OC(O)CH_3)_3$

C. Organometallic Compounds

Organometallic compounds are covalent or coordinate compounds where the ligand is bonded to the metal center via a carbon atom. Like MOCs, organometallic compounds are used as precursors for both wet chemical- and dry vapor-related processes. Commonly used organometallic precursors are listed in Table 3.