CERAMIC MATERIALS I

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Metallurgical and Materials Engineering Department
## Liquid Phase Synthesis

### Fine Ceramic Powders Synthesis Methods

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### Solvent Evaporation
- spray drying
- freeze drying
- emulsion drying
- spray pyrolysis

### Precipitation
- direct precipitation
- coprecipitation
- homogenous precipitation
- multi-step precipitation

### Citrate Gel Process
A variety of fine oxide powders have been made by the liquid-phase method. Recent progress in this technique has been remarkable and new processes have been developed for purification, precise control of chemical composition, uniformity on an atomic scale and particle size.

Preparation of fine ceramic particles from a liquid phase depends on their nucleation from supersaturated solutions and subsequent growth.

The supersaturated solution results from solubility change, chemical reaction and solvent evaporation.

Nucleation and growth are important processes for responsible for the size of crystallites and particles.
Introduction

The sol-gel process is very long known since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glasses were produced without high temperature melting processes.

This made possible the organic modification of silicon compounds (ORMOSIL), which cannot withstand high temperatures.

Sol-gel is a chemical solution process used to make ceramic and glass materials in the form of thin films, fibers or powders.

The sol-gel approach is interesting in that it is a cheap and low-temperature technique that allows for the fine control on the product’s chemical composition, as even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up in the final product finely dispersed.
Sol-gel process refers to a low-temperature method using chemical precursors that can produce ceramics and glasses with **better purity and homogeneity**.

This process is becoming a common technique to produce **ultra fine and pure ceramic powders, fibers, coatings, thin films, and porous membranes**.
Compare to the conventional methods, the most attractive features and advantages of sol-gel process include

(a) molecular-level homogeneity can be easily achieved through the mixing of two liquids;
(b) the homogeneous mixture containing all the components in the correct stoichiometry ensures a much higher purity; and,
(c) much lower heat treatment temperature to form glass or polycrystalline ceramics is usually achieved without resorting to a high temperature.
(d) More recently, the sol-gel method has been extensively developed and used in biotechnology applications.
Liquid solutions

SOL-GEL PROCESS

What is Sol ? Gel ? Colloidal sols ?

• Colloid means :
  – A suspension containing dispersed particles of 1~1000 nm
  – Gravitational force are negligible
  – Interactions are dominated by short-range forces.
  – Require adjustment of pH to prepare good dispersive particles
  – Colloidal sol sometime is called particulate sols.

• Sol :
  – A homogenous dispersion of soluble solids and miscible liquids, is consisted of finely divided, discrete particles of 1~10 nm in diameter
  – A “colloidal sol” consists of dense (oxide or hydroxide) particles 1~1000 nm which therefore include colloidal dispersion and colloidal suspension.
  – Line which distinguishes a dispersion (1~10 nm) from a suspension (>10 nm) is generally accepted at an equivalent spherical diameter, 10 nm
A sol consists of a liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment.

Agglomeration of small particles are due to van der Waals forces and a tendency to decrease the total surface energy. Van der Waals forces are weak, and extend only for a few nanometers.

In order to counter the van der Waals interactions, repulsive forces must be established.
Repulsive forces may be accomplished by:

**Electrostatic repulsion:** By adsorption of charged species onto the surface of the particles, repulsion between the particles will increase and agglomeration will be prevented. Most important for colloidal systems.

**Steric hindrance:** By adsorbing a thick layer of organic molecules, the particles are prevented from approaching each other reducing the role of the van der Waals forces. Works best in concentrated dispersions. Branched adsorbates works best. Usual for nanomaterials.
### SOL-GEL PROCESS

<table>
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<th>Term</th>
<th>Description</th>
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<tr>
<td><strong>Sol</strong></td>
<td>a stable suspension of colloidal solid particles or polymers in a liquid</td>
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<tr>
<td><strong>Gel</strong></td>
<td>porous, three-dimensional, continuous solid network surrounding a continuous liquid phase</td>
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<tr>
<td><strong>Colloidal (particulate) gels</strong></td>
<td>agglomeration of dense colloidal particles</td>
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<tr>
<td><strong>Polymeric gels</strong></td>
<td>agglomeration of polymeric particles made from subcolloidal units</td>
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Sol-gel process usually consists of 4 steps:

- The desired colloidal particles once dispersed in a liquid to form a sol.

- The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.

- The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.

- The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.
Liquid solutions

SOL-GEL PROCESS

Sol

Gel

Flocculation And Precipitation
Liquid solutions

Sol-gel processing options
If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed.

If drying is performed under supercritical conditions, the network structure may be retained and a gel with large pores may be formed. This is called an aerogel, and the density will be very low. A record is $< 0.005 \text{ g/cm}^3$. 
Liquid solutions

SOL-GEL

Schematic diagram illustrating the enormous shrinkages accompanying the drying by liquid evaporation and sintering of a polymeric gel

ΔL / L₀ = 50 %
ΔV / V₀ = 90 %

Drying

ΔL / L₀ = 20 %
ΔV / V₀ = 50 %

Sintering

Dried Gel

Gelled material

Dense Product

ΔL / L₀ = linear shrinkage
ΔV / V₀ = volumetric shrinkage

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It can be used in ceramics manufacturing processes and producing very thin films of metal oxides for various purposes.

Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology. One of the more important applications of sol-gel processing is to carry out zeolite synthesis.

Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicalite sol formed by this method is very stable.

Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration, pervaporation and reverse osmosis.
**Liquid solutions**

**SOL-GEL PROCESS**

- **Sol-gel alumina, Al\(_2\)O\(_3\)**

  - **Starting precursors**
    - Aluminium alkoxides
      - Al(OC\(_3\)H\(_7\))\(_3\) aluminium isopropoxide
      - Al(OC\(_4\)H\(_9\))\(_3\) aluminium secbutoxide
      - i.e. Al (OR)\(_3\)......
  
  - **Excess water . Vigorous stirring**
    - (80\(^o\)C, hydrolysis reaction)
  
  - **Deflocculation**
    - Add acid (HCl, HNO\(_3\), CH\(_3\)COOH)
    - Non-complexing anion with Al, and
    - Produce a charge effect at low conc.
  
  - **Monohydroxide**
  
  - **Polymerized gel Al\(_2\)O\(_3\)**
The idea behind sol-gel synthesis is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner.

Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds.

The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction.

Enables mixing at an atomic level.

Results in small particles, which are easily sinterable.
# Liquid Phase Synthesis

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Hydrothermal synthesis

- High solvent pressure in an autoclave – known as the *hydrothermal method*
- Using a high pressure of a reactive gas
- Directly applied hydrostatic pressure on solids

The hydrothermal method involves heating the reactants in a closed vessel (an autoclave).
- an autoclave is constructed from thick stainless steel and fitted with safety valves.
- typically lined with a non-reactive material such as teflon.
- the autoclave is heated to above its normal boiling point, the pressure is increased and is called ‘super heated water’.
- these hydrothermal conditions also exist in nature and many minerals are formed in this process (e.g. zeolites, emeralds, etc.)
- low temperatures are one advantage of the method.
- unusual oxidation states may be stabilized.
- Superheated water may dissolve some metal oxides that are insoluble under ambient conditions
Hydrothermal synthesis of quartz

Uses a temperature gradient to dissolve the reactant at higher temperature, which is transported up the reaction tube by convection, then crystallizes out at a lower temperature.

Hydrothermal synthesis of CrO₂

Cr₂O₃ is the stable oxide of chromium at normal conditions.

\[
\begin{align*}
\text{Cr}_2\text{O}_3 & + \text{CrO}_3 \rightarrow 3\text{CrO}_2 \\
\text{CrO}_3 & \rightarrow \text{CrO}_2 + \frac{1}{2} \text{O}_2
\end{align*}
\]
Liquid solutions

Hydrothermal synthesis

Hydrothermal synthesis of zeolite A, $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]\cdot27\text{H}_2\text{O}$.

- Hydrated alumina, $\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$ is dissolved in concentrated $\text{NaOH}$.
- The cooled solution is mixed with sodium metasilicate, $\text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O}$ and a thick white gel forms.
- The gel is placed in a closed teflon bottle and heated to 363 K over 6 hours.
- Changes in the form of alumina, pH of the solution, type of base used, and proportions of alkali, aluminum compound, and silica lead to the production of different zeolites.
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### Citrate Gel Process
**Spray pyrolysis**

A solution or slurry is atomized and passes through a heated area.

Solvents evaporate, particles pyrolyze or react to form the product powder.

The size of the particles depends on the size of the droplets and the concentration.

Often hollow spheres are formed.
Porosity of the product is controlled e.g. by concentration and thermal profile.

**Flame reactors:** A combustion reaction is used to heat the spray. Short residence time, maximum use of energy. Risk of contamination by combustion reactants.

**Heating reactors:** Spray into a hot furnace. Good control of temperature and residence time. Growth on walls, formation of hard aggregates.

**Laser reactors:** Heated by a laser; efficient transfer of heat to gaseous species.

**Plasma reactors.**
**Liquid solutions**

**Spray pyrolysis**

**Products**

**Large scale:** Titania, silica, alumina powders. (from the chlorides by flame pyrolysis)

**Smaller scale:** Bi$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, GeO$_2$, NiO, MoO$_2$, SnO$_2$, V$_2$O$_5$, WO$_3$, ZrO$_2$, AlBO$_3$, Al$_2$TiO$_5$, AlPO$_4$...
Nitrides, carbides, borides, silicides….  

**Metal synthesis:**

\[ \text{SiCl}_4(g) + 4\text{Na}(g) \rightarrow \text{Si} + 4\text{NaCl} \]
\[ 2\text{NbCl}_5(g) + 5 \text{Mg} \rightarrow 2\text{Nb} + 5\text{gCl}_2 \]

*Formation of dense (left) and hollow particles (right) by spray pyrolysis*
Liquid solutions

PRECIPITATION METHODS

- Precursors such as nitrates and carbonates can be used as starting materials instead of oxides.

- Co-precipitation involves taking a stoichiometric mixture of soluble salts of the metal and precipitating them as hydroxides, citrates, oxalates, or formates. The mixture is filtered, dried, and then heated to give the final product.

- Precursor method involves atomic level mixing by forming a solid compound (precursor) in which the metals of the desired compound are present in the proper stoichiometry.

  - the precursor is heated to decompose it to the desired product.
  - homogeneous products are formed at relatively low temperatures.
  - it is not always possible to find a suitable precursor.
Precursor method example

Ti(OBu)₄(aq) + 4H₂O(l) → Ti(OH)₄(s) + 4BuOH(aq)

Excess oxalic acid redissolves the precipitate.

Ti(OH)₄(s) + (COO)₂²⁻(aq) → TiO(COO)₂(aq) + 2OH⁻(aq) + H₂O(l)

Ba²⁺(aq) + (COO)₂²⁻(aq) + TiO(COO)₂(aq) → Ba[TiO((COO)₂)₂](s)

Decomposition by heating (920 K) gives the desired oxide phase.

Ba[TiO((COO)₂)₂](s) → BaTiO₃(s)

Decomposition of oxalates is also used to form ferrites (MFe₂O₄).
Products from precursor methods often contain small particles with a large surface area, which is desired for certain applications.
Liquid solutions

PRECIPITATION METHODS

Precipitation is easy ...

Control over crystallite size, size distribution, morphology ... is hard
Processes which may be involved in precipitation:

- Nucleation
- Crystal growth
- Ostwald ripening
- Recrystallization
- Coagulation
- Agglomeration

It is necessary to control each of these steps in order to e.g. form monodisperse particles with a well-defined and reproducible morphology.

Monodisperse materials are interesting e.g. for formation of stable dispersions, uniform ceramics powders, pigments with reproducible colour, catalysts and nano-objects.

The solvent is usually water, but may be other solvents or molten salts.
**Precipitation Methods**

**Nucleation and growth**

In melts, temperature was the decisive factor. In solutions, concentration must be increased:

- Direct reaction of ions (e.g. adding bromine ions to a solution containing silver cations)
- Redox reactions (e.g. reduction of HAuCl$_4$ with formaldehyde to give colloidal gold)
- Precipitation by poor solvents (e.g. adding water to an ethanolic solution of sulphur)
- Decomposition of compounds (e.g. adding acid to an aqueous solution of thiosulphate to precipitate sulphur)
- Hydrolysis

**Decomposition or removal of complexing agents:**

Precipitation and growth of large crystals of Ag$_2$CO$_3$ from NH$_3$(aq)

Precipitation of $\alpha$-TiHPO$_4$ H$_2$O using complexing by HF

**Temperature control**
Growth

If new nuclei form during growth, a range of particle sizes is obtained.

In order to obtain monodisperse crystals, nucleation and growth must be separated.

The rate of growth may be controlled by diffusion of dissolved species to the particles or by the rate of condensation.

Another source of particle forming species is dissolution of smaller particles (more soluble due to surface curvature.)

Ostwald ripening effects usually work up to 5 nm particles.
**Liquid solutions**

**PRECIPITATION METHODS**

**Soft Agglomerates:**
Assemblies of primary particles physically held together by weak interactions.

**Coagulation:**
Attachment of two particles when they collide

A *hydrolysis* may involve addition of metal alkoxides to water, which are hydrolyzed to give the oxide as a colloidal product.
Liquid solutions

PRECURSOR METHODS

Intimate mixing of components in solution, precipitation, filtration, washing, drying, calcination

- High degree of homogenization
- Large contact area
- Reduction of diffusion distances
- Faster reaction rates
- Lower reaction temperatures
- Metastable phases, smaller grain size, larger surface area
Liquid solutions

Coprecipitation Method

Coprecipitation applicable to nitrates, acetates, oxalates, hydroxides, alkoxides, beta-diketonates and so forth

Requires: similar salt solubilities
- similar precipitation rates
- no supersaturation

Washing: water, organic solvents

Drying: evaporation, azeotropic distillation, freeze-drying
Spinels

oxalates: $\text{Zn(CO}_2\text{)}_2/\text{Fe}_2[(\text{CO}_2\text{)}_3]/H_2O$ 1:1 mixing, $H_2O$ evaporation, salts coprecipitation
Solid-solution mixing on atomic scale, filter, calcine in air

$\text{Zn(CO}_2\text{)}_2 + \text{Fe}_2[(\text{CO}_2\text{)}_3] \rightarrow \text{ZnFe}_2\text{O}_4 + 4\text{CO} + 4\text{CO}_2$

$\text{Al}_2\text{O}_3$ Bayer Process

$\text{NaOH, p}$ bauxite $\rightarrow \text{Al(OH)}_4^- + \text{CO}_2 \rightarrow \text{Al(OH)}_3 \rightarrow \alpha-\text{Al}_2\text{O}_3$

Fe(OH)$_3$, TiO$_2$, SiO$_2$

$\text{BaTiO}_3$

$\text{BaCl}_2 + \text{TiOCl}_2 + 2\text{H}_2\text{C}_2\text{O}_4 + 4\text{H}_2\text{O} + \text{Ln dopants} \rightarrow \text{BaTiO(C}_2\text{O}_4\text{)}_2\cdot 4\text{H}_2\text{O} + 4\text{HCl}$

filtration, washing, drying, calcination @ 730 °C
Liquid solutions

Spinel

\[ \text{Al(NO}_3\text{)}_3 + \text{Mg(NO}_3\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{MgAl}_2\text{O}_4 + 6 \text{NO}_x + (10-3x)\text{O}_2 \]

freeze-drying gives amorphous mixture, calcination @ 800 °C !!! low T

Ruby

Ion exchange

\[ \text{Al(NO}_3\text{)}_3 + \text{Cr(NO}_3\text{)}_3 \rightarrow \text{Al(OH)}_3 + \text{Cr(OH)}_3 \text{ sol} \]

freeze drying gives solid (Al/Cr)(OH)_3 @ LN_2 temperature, 5 Pa

anealing @ 950 °C for 2.5 h gives solid solution Al_{2-x}Cr_xO_3

Zirconia

\[ \text{ZrSiO}_4(\text{zircon}) + \text{NaOH} \rightarrow \text{Na}_2\text{ZrO}_3 + \text{Na}_2\text{SiO}_3 \]

\[ \text{ZrOCl}_2 \xrightarrow{\text{OH, YCl}_3} \text{Zr(OH)}_4 / \text{Y(OH)}_3 \xrightarrow{\text{azeot. dist. calcination}} \text{nano-Y/ZrO}_2 \]
Liquid solutions

High-\(T_c\) Superconductors

\[
\text{La}^{3+} + \text{Ba}^{2+} + \text{Cu}^{2+} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{ppt} \quad \rightarrow \quad \text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4
\]

Magnetic garnets, tunable magnetic materials

\[
\text{Y(NO}_3)_3 + \text{Gd(NO}_3)_3 + \text{FeCl}_3 + \text{NaOH} \rightarrow \text{Y}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}
\]

Firing @ 900 °C, 18-24 hrs, pellets, regrinding, repelletizing, repeated firings, removes REFeO\(_3\) perovskite impurity

Isomorphous replacement of \(\text{Y}^{3+}\) for \(\text{Gd}^{3+}\) on dodecahedral sites, solid solution, similar rare earth ionic radii

complete family accessible, \(0 < x < 3\), \(2\text{Fe}^{3+}\) \(O_h\) sites, \(3\text{Fe}^{3+}\) \(T_d\) sites, \(3\text{RE}^{3+}\) dodecahedral sites
Chemical precipitation techniques of the type used for classical wet quantitative analyses can be used to prepare a wide variety of inorganic salts.
• In some cases, it may be possible to precipitate a specific compound containing two cations, and the composition of the precipitate will be uniform regardless of the concentration of ions in solution.
  
  • An example of the latter is

\[
\text{BaCl}_2 + \text{TiCl}_4 + 2\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\text{H}_2\text{O}(20^\circ\text{C})} \text{BaTiO(C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O} + 6\text{H}_3\text{O}^+ + 6\text{Cl}^- \]

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• The thermal decomposition of the barium titanyl oxalate salt produces barium titanate indirectly, but at a relatively low temperature (700 °C), because of the fine particle size and mixedness:

\[
\begin{align*}
\text{BaTiO(C}_2\text{O}_4\text{)}_2 \cdot 4\text{H}_2\text{O}(s) \\
\text{BaTiO(C}_2\text{O}_4\text{)}_2(s) + \frac{1}{2}\text{O}_2(g) \\
\end{align*}
\]

\[
\begin{align*}
(25-225°C) \\
(225-456°C) \\
\end{align*}
\]

\[
\begin{align*}
\text{BaCO}_3(s) + \text{TiO}_2(s) + \text{CO}(g) + 2\text{CO}_2(g) \\
\text{BaCO}_3(s) + \text{TiO}_2(s) \xrightarrow{(465-700°C)} \text{BaTiO}_3(s) + \text{CO}_2(g) \\
\end{align*}
\]
Thanks for your kind attention

THE END
Any Questions