

Sols, Gels, and Organic Chemistry

CHAPTER PREVIEW

Extensive research and development in the past decade have resulted in increasing awareness of the importance of chemical synthesis, particularly using organic precursors, in the processing and fabrication of ceramics. The sol-gel process is one method that is used commercially in many applications, such as forming coatings on window glass. It is also used, as we have previously described, for forming powders and fibers. The process gives us excellent control of product purity and composition for the simple reason that we start with pure materials. It allows us to deposit films and coatings on a range of different surfaces, enabling a flexibility that is not present in many vapor-phase methods.

We can summarize the key advantages offered by the sol-gel process.

- It uses relatively low temperatures.
- It can create very fine powders.
- It produces compositions not possible by solid-state fusion.

There are some disadvantages of the sol-gel process.

- The cost of the raw materials (the chemicals) may be high. As an example, MgO powder with a purity of 98% is available in small quantities for \$30/kg. Magnesium ethoxide, a chemical source for making MgO, costs about \$200/kg.
- There is often a large volume shrinkage and cracking during drying (we have to remove the “organics”).
- Organic chemistry often uses confusing terminology and is avoided by ceramists whenever possible.

In Chapter 20 we described how sol-gel processing (and other chemical methods) is used to make ceramic powders and fibers. So, why do we need another chapter on this topic? There are two main reasons. First, to use sol-gel processing scientifically you must understand the chemistry (the terminology and the reactions). Second, chemical methods for making powders are going to be even more important in the future because they can be used to make nanoparticles and even to coat them.

22.1 SOL-GEL PROCESSING

The sol-gel process consists of two steps. First we form a *sol*. Then we transform this into a *gel*. In ceramic synthesis, two different sol-gel routes have been identified and depend on the gel structure.

- Particulate gel—using a network of colloidal particles
- Polymeric gel—using an array of polymeric chains

THE TERM SOL-GEL

It is convention to use the term “sol-gel” rather than “sol/gel,” although the latter might be more correct; “sol” and “gel” are two independent concepts.

DEFINITION OF SOL AND GEL

Colloidal particles or molecules are suspended in a liquid or solution, a “*sol*.” The sol is mixed with another liquid, which causes formation of a continuous three-dimensional network, a “*gel*.”

The process that occurs depends on the form of the sol, i.e., whether it is a solution or a suspension of fine particles. A flow diagram indicating each of

the processes is shown in Figure 22.1.

In this chapter we are concerned only with the polymeric gel route because this is the approach that is most useful to ceramists. This method has been successful in preparing a range of advanced ceramics such as lead zirconate titanate (PZT) and the high- T_c oxide superconductors.

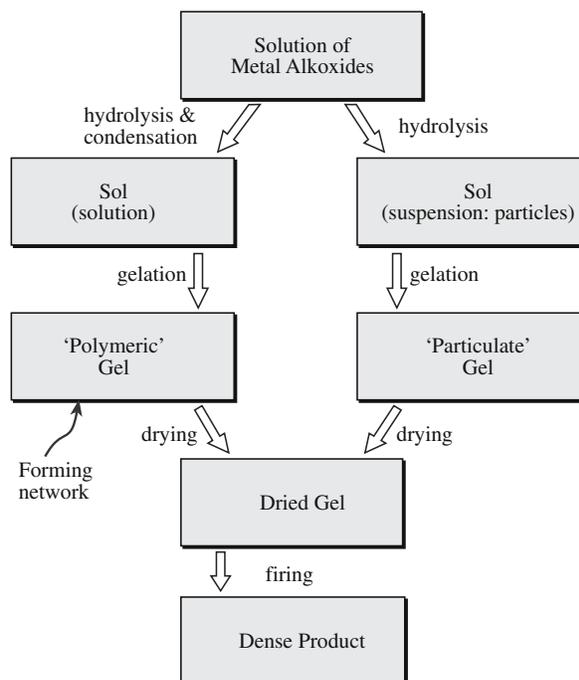


FIGURE 22.1 Flow chart comparing sol-gel processing using a solution and a suspension of fine particles.

The significant advantage of sol-gel processing of ceramic powders is that homogeneous compositions can be prepared at temperatures lower than required for conventional powder processes. Furthermore, the reactants used in sol-gel processing are available in very high purities, which allows the formation of high-purity powders of crystalline ceramics and glasses.

A commonly studied approach for synthesizing oxides has been to hydrolyze the appropriate metal alkoxides. There are several advantages to using metal alkoxides as precursors for ceramic powders. Most of the alkoxides of interest can be easily prepared or are commercially available and can be readily purified prior to use. Interaction of alkoxides with water yields precipitates of hydroxides, hydrates, and oxides. The precipitate particles usually range in size from 0.01 to 1 μm , depending on the hydrolysis conditions. So we can easily produce nanoparticles.

22.2 STRUCTURE AND SYNTHESIS OF ALKOXIDES

Alkoxides have the general formula $\text{M}(\text{OR})_z$, where M is usually a metal, but can also be a nonmetal such as Si, and R is an alkyl chain. Table 22.1 lists some common alkoxides used in the preparation of ceramics.

The nomenclature adopted for the simple alkoxides follows the basic rules of organic chemistry:

METAL ALKOXIDE $\text{M}(\text{OR})_z$

For convenience we will say “metal alkoxide” even when referring to alkoxides of nonmetals such as silicon and boron.

TABLE 22.1 Examples of Metal Alkoxides

Name	Chemical formula	Physical state
Aluminum <i>S</i> -butoxide	$\text{Al}(\text{O}^\circ\text{C}_4\text{H}_9)_3$	Colorless liquid, $T_B \sim 203^\circ\text{C}$
Aluminum ethoxide	$\text{Al}(\text{OC}_2\text{H}_5)_3$	White powder, $T_M 130^\circ\text{C}$
Aluminum isopropoxide	$\text{Al}(\text{O}^\circ\text{C}_3\text{H}_7)_3$	White powder, $T_M 118.5^\circ\text{C}$
Antimony ethoxide	$\text{Sb}(\text{OC}_2\text{H}_5)_3$	Colorless liquid, $T_B 95^\circ\text{C}$
Barium isopropoxide	$\text{Ba}(\text{O}^\circ\text{C}_3\text{H}_7)_2$	Off-white powder
Boron ethoxide	$\text{B}(\text{OC}_2\text{H}_5)_3$	Colorless liquid, $T_B 117.4^\circ\text{C}$
Calcium methoxide	$\text{Ca}(\text{OCH}_3)_2$	Off-white powder
Iron ethoxide	$\text{Fe}(\text{OC}_2\text{H}_5)_3$	$T_M 120^\circ\text{C}$
Iron isopropoxide	$\text{Fe}(\text{O}^\circ\text{C}_3\text{H}_7)_3$	Brown powder
Silicon tetraethoxide	$\text{Si}(\text{OC}_2\text{H}_5)_4$	Colorless liquid, $T_B 165.8^\circ\text{C}$
Silicon tetraheptoxide	$\text{Si}(\text{OC}_7\text{H}_{15})_4$	Yellow liquid
Silicon tetrahexoxide	$\text{Si}(\text{OC}_6\text{H}_{13})_4$	Colorless liquid
Silicon tetramethoxide	$\text{Si}(\text{OCH}_3)_4$	Colorless liquid, $T_B 121\text{--}122^\circ\text{C}$
Titanium ethoxide	$\text{Ti}(\text{OC}_2\text{H}_5)_4$	Colorless liquid, $T_B 122^\circ\text{C}$
Titanium isopropoxide	$\text{Ti}(\text{O}^\circ\text{C}_3\text{H}_7)_4$	Colorless liquid, $T_B 58^\circ\text{C}$
Yttrium isopropoxide	$\text{Y}(\text{O}^\circ\text{C}_3\text{H}_7)_3$	Yellowish-brown liquid

Methoxide	$\text{R} = \text{CH}_3$	Example is $\text{B}(\text{OCH}_3)_3$
Ethoxide	$\text{R} = \text{C}_2\text{H}_5$	Example is $\text{Si}(\text{OC}_2\text{H}_5)_4$
Propoxide	$\text{R} = \text{C}_3\text{H}_7$	Example is $\text{Ti}(\text{O}^\circ\text{C}_3\text{H}_7)_4$ (<i>n</i> - and <i>iso</i> -)
Butoxide	$\text{R} = \text{C}_4\text{H}_9$	Example is $\text{Al}(\text{O}^\circ\text{C}_4\text{H}_9)_3$ (<i>n</i> -, <i>iso</i> -, <i>sec</i> -, and <i>tert</i> -)

In these molecular formulas, the superscripts *n*, *t*, *s*, and *i* refer to normal, tertiary, and secondary or isoalkyl chains, each of which is illustrated for the butoxide group in Figure 22.2. These are common names and do not follow the Commission on the Nomenclature of Organic Chemistry of the International Union of Pure and Applied Chemistry (IUPAC). In the case of higher alkoxides, i.e., those with five or more C atoms, the nomenclature is derived strictly from IUPAC conventions. For example, the alkoxide group $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{O}^-$ would be referred to as 2,2-dimethylbutoxide. The old name is neohexoxide.

Most metal alkoxides contain lower aliphatic alkyl groups and are coordinated complexes and not single molecules. Figure 22.3 shows an example of a coordination complex of aluminum isopropoxide consisting of three molecules.

Even when using the IUPAC convention there is still the distinct possibility of encountering confusion when reading the literature. For example, silicon tetraethoxide

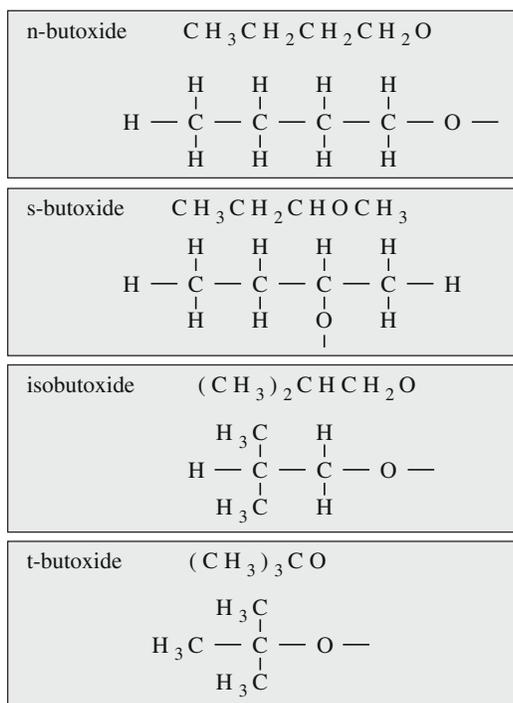


FIGURE 22.2 Illustration of nomenclature for metal alkoxides.

may be referred to as tetraethylsilicate, tetraethylorthosilicate (TEOS), and tetraethoxysilane!

The first alkoxide to be synthesized was silicon tetraisopentoxide (formerly called silicon tetraisomyloxide), made by a reaction between silicon tetrachloride and isopentanol (formerly isoamyl alcohol):



Many alkoxides are available commercially, particularly those of Si, Al, Ti, B, and Zr. These are not generally

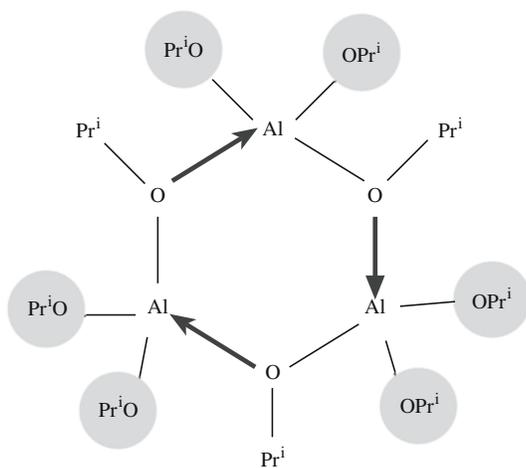


FIGURE 22.3 Three-molecule coordination complex of aluminum isopropoxide.

TABLE 22.2 Alkoxides of Metals with Different Electronegativities

Alkoxide	Electronegativity of metal	State
$\text{Na}(\text{OC}_2\text{H}_5)$	0.9	Solid (decomposes above ~530 K)
$\text{Ba}(\text{O}^i\text{C}_3\text{H}_7)_2$	0.9	Solid (decomposes above ~400 K)
$\text{Y}(\text{O}^i\text{C}_3\text{H}_7)_3$	1.2	Solid (sublimes at ~475 K)
$\text{Zr}(\text{O}^i\text{C}_3\text{H}_7)_4$	1.4	Liquid (boiling point 476 K at 0.65 kPa)
$\text{Al}(\text{O}^i\text{C}_3\text{H}_7)_3$	1.5	Liquid (boiling point 408 K at 1.3 kPa)
$\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$	1.5	Liquid (boiling point 364.3 K at 0.65 kPa)
$\text{Si}(\text{OC}_2\text{H}_5)_4$	1.8	Liquid (boiling point 442 K at atmospheric pressure)
$\text{Fe}(\text{OC}_2\text{H}_5)_3$	1.8	Liquid (boiling point 428 K at 13 Pa)
$\text{Sb}(\text{OC}_2\text{H}_5)_3$	1.9	Liquid (boiling point 367 K at 1.3 kPa)
$\text{B}(\text{O}^i\text{C}_4\text{H}_9)_3$	2.0	Liquid (boiling point 401 K at atmospheric pressure)
$\text{Te}(\text{OC}_2\text{H}_5)_4$	2.1	Liquid (boiling point 363 K at 0.26 kPa)

expensive materials, for example, TEOS, a colorless liquid, costs about \$40/kg. However, nonstandard alkoxides, for example, $\text{Ba}(\text{OC}_2\text{H}_5)_2$, are more expensive. Barium isopropoxide is an off-white powder and costs about 250 times as much as TEOS (\$10/g). A 10% w/v solution of $\text{Ba}(\text{OC}_2\text{H}_5)_2$ in ethanol will cost about \$2/ml.

22.3 PROPERTIES OF ALKOXIDES

The properties of metal alkoxides depend on the electronegativity of the metal. Pauling's electronegativity scale was given in Chapter 3.

Alkoxides of alkali metals, e.g., sodium alkoxides, and alkaline earth metals are ionic solids. Alkoxides of Ge, Al, Si, Ti, and Zr are often covalent liquids. Since most alkoxides are either liquids or volatile solids (examples are given in Table 22.2), they can be purified by distillation to form exceptionally pure oxide sources as shown in Table 22.3.

TABLE 22.3 Effect of Distillation on the Purity of Silicon Tetraethoxide

Form/impurity	Mn	Cr	Fe	Co	Ni	Cu
As supplied (ppb)	10	15	86	0.7	<200	<200
Once distilled (ppb)	0.8	2	31	0.3	11	<20

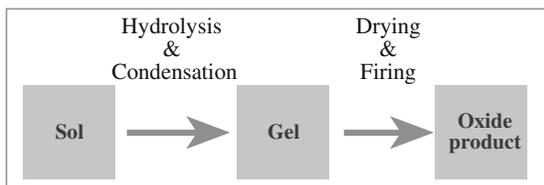


FIGURE 22.4 The basic steps in the sol-gel process using metal alkoxides.

22.4 THE SOL-GEL PROCESS USING METAL ALKOXIDES

The three basic steps in the sol-gel process are summarized in Figure 22.4. The conversion of the sol to a gel occurs by hydrolysis and condensation reactions. The gel is converted into the oxide by drying and firing. We will now look at each of these steps in a little more detail.

Preparing the Sol

The sol-gel process can be used to make single or multi-component oxides. First we will consider the case of a one-component system—silica. Of the many available silicon alkoxides, TEOS is commonly used. It is insoluble in water, but water is necessary for the hydrolysis reaction; hence we need to select a solvent for both the alkoxide and water. Ethanol is a suitable solvent, and a typical formulation contains three main components: 43 vol% $\text{Si}(\text{OC}_2\text{H}_5)_4$, 43 vol% $\text{C}_2\text{H}_5\text{OH}$, and 14 vol% H_2O .

For small-scale sol-gel processing in the laboratory the equipment is relatively simple and inexpensive:

- Three-necked flask (contains the mixed solutions)
- Mechanical stirrer (the mixture is stirred constantly)
- Reflux condenser (needed to prevent the solution from evaporating)
- Constant temperature bath (the rate of hydrolysis depends on temperature)

Multicomponent sols can be prepared by mixing different precursors, which are selected to give eventually an oxide of the desired composition. Table 22.4 gives examples of typical formulations for both single-component and multicomponent alkoxide solutions. There may be problems if the hydrolysis rates of the precursors are different, and this can create inhomogeneities in the subsequent gel. We can allow for this possibility by partially hydrolyzing the less reactive component [e.g., $\text{Si}(\text{OC}_2\text{H}_5)_4$] before adding the more reactive one [e.g., $\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$].

For some metals, such as the alkali metals and alkaline earth metals, it is not possible or it is inconvenient to use alkoxides because they are either unavailable or difficult to prepare. You can see from Table 22.2 that alkoxides of these metals are solids

with low volatility. In many cases they also have low solubility. In these situations alternative reactants must be found. Metal salts such as acetates and citrates, which are soluble in organic solvents, are a viable alternative. Many of these can be obtained in a high-purity analytical grade. In cases in which we use both alkoxides and metal salts it is usual to first form a solution of all the components that are to be added as alkoxides. Then add the salts as solutions in alcohol or, if this is not possible, in the water that is to be used for the hydrolysis reaction. The final solution is homogenized by stirring.

SAMPLE RECIPE

PZT thin films can be prepared using a solution of zirconium butoxide [$\text{Zr}(\text{O}^i\text{C}_4\text{H}_9)_4$] and titanium propoxide [$\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$] in 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$) mixed with lead acetate trihydrate [$(\text{CH}_3\text{CO}_2)_2\text{Pb} \cdot 3\text{H}_2\text{O}$] that is also dissolved in 2-methoxyethanol.

TABLE 22.4 Formulations for Single-Component and Multicomponent Alkoxide Solutions

Precursor	One component: 100 mol% SiO_2				Two components: 94 mol% SiO_2 + 6 mol% TiO_2				Three components: 15 mol% Li_2O + 3 mol% Al_2O_3 + 82 mol% SiO_2			
	Solution concentration (wt%/100 g)	Oxide content (vol%/100 ml)	mol	g/mol	Solution concentration (wt%/100 g)	Oxide content (vol%/100 ml)	mol	g/mol	Solution concentration (wt%/100 g)	Oxide content (vol%/100 ml)	mol	g/mol
$\text{Si}(\text{OC}_2\text{H}_5)_4$	45	43			11	11			35	34		
$\text{Ti}(\text{OC}_3\text{H}_7)_4$					1	1						
$\text{Al}(\text{OC}_4\text{H}_9)_3$									1	1		
LiNO_3									3	1		
$\text{C}_2\text{H}_5\text{OH}$	40	43	4		36	41	14		29	34	4	
H_2O	16	14	4		52	47	50		33	30	8	
Oxide (Si + Ti + Al + Li)			1	11.3			1	3.15			1	10.6

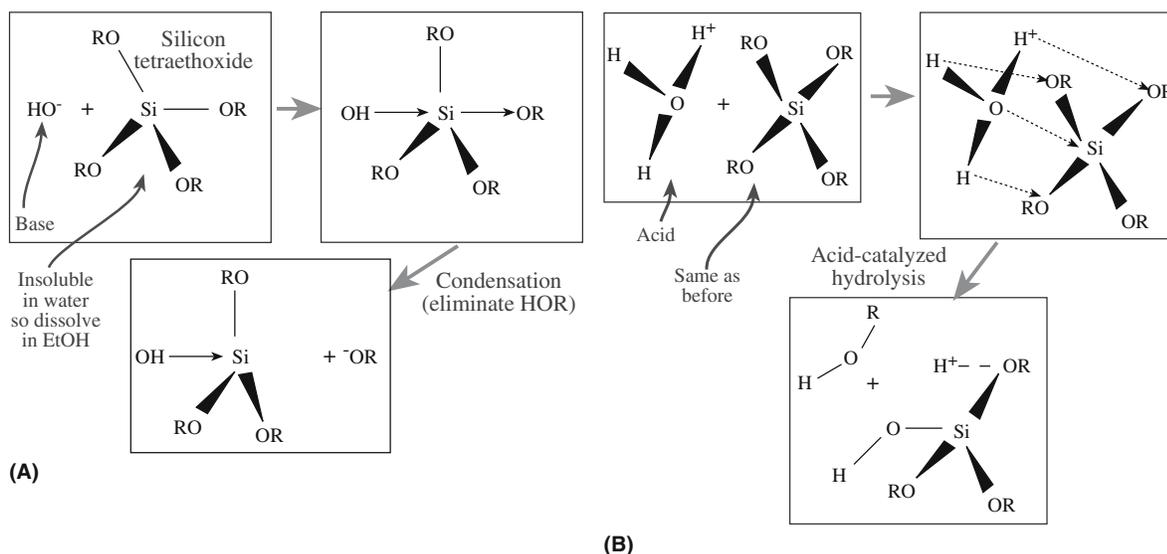


FIGURE 22.5 Schematic showing reaction mechanisms for (a) acid- and (b) base-catalyzed hydrolysis of silicon alkoxides.

Hydrolysis and Condensation

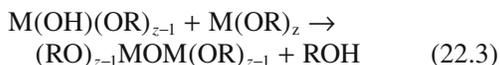
Metal alkoxides undergo hydrolysis very easily (meaning they react with water). In many cases they are so sensitive to moisture that special precautions must be taken in handling and storage (e.g., the use of an N_2 glove box and dehydrated solvents). The product vendor will provide information on the sensitivity of the compound.

During the initial stage of hydrolysis an alcohol molecule, ROH, is expelled.



This is an example of a condensation reaction involving the elimination of an alcohol (e.g., ethanol).

The hydroxy metal alkoxide product can react by a further condensation reaction to form polymerizable species.



Hydrolysis can be carried out either under basic or acidic conditions as shown in Figures 22.5 for TEOS. In the context of sol-gel processing, acid-catalyzed conditions are defined as $pH < 2.5$; base-catalyzed conditions are defined as $pH > 2.5$. Of course, this is not our usual definition of acid and base, where a neutral pH is 7, but corresponds to the point of zero charge (PZC) at which the surface is electrically neutral.

Hydrolysis may go to completion leading to the formation of the silicic acid monomer. But this generally does not occur except at low pH and high water concentrations.

CONDENSATION REACTIONS

The class of organic reactions in which two molecules combine eliminating water or another simple molecule. This produces thermosetting polymers and phenolformaldehyde, nylon, and polycarbonates.

The silicic acid monomer is not stable and condensation of silanol groups (Si–OH) leads to polymer formation before silanol groups substitute for all the alkoxy groups. This

process is illustrated for a general case in Figure 22.6a.

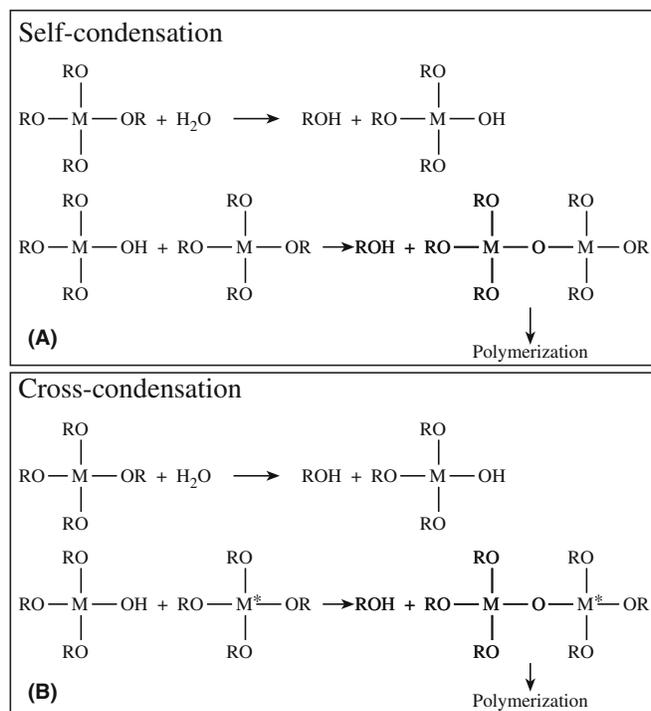


FIGURE 22.6 Schematic showing condensation reactions in (a) single metal alkoxide solutions and (b) mixed metal alkoxide solutions.

For different metal alkoxides the situation is shown in Figure 22.6b.

The experimental variables used in the first stage of the sol-gel process determine the kinetics of the hydrolysis of the sol to form a gel and have a major influence on gel structure. The relevant variables are

- Alkoxide concentration
- Reaction medium
- Concentration of catalyst [The rates of hydrolysis and condensation can be affected by the addition of small amounts of acid (e.g., HCl) or base (e.g., NH₄OH), respectively.]
- Temperature

The Sol-Gel Transition

Viscosity is a key parameter that is used to determine when the sol-gel transition occurs. At the transition there is an abrupt increase in viscosity. The structural changes that occur during gelation for acid-catalyzed and base-catalyzed reactions are illustrated in Figure 22.7.

Viscosity can be measured by two simple methods:

- Capillary flow—most common
- Rotation—using “Couette flow”

The Ostwald viscometer, illustrated in Figure 22.8, is an example of a capillary method used to study the sol-gel

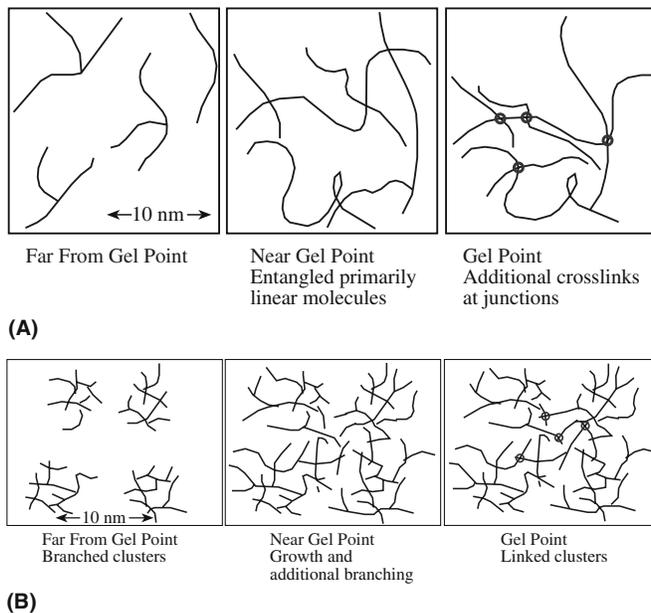


FIGURE 22.7 Illustration of (a) acid- and (b) base-catalyzed polymerization and gelation.

transition. The solution is introduced into the viscometer such that it reaches levels B and C. Liquid is then drawn up into the left-hand limb until the liquid levels are above A and at the bottom of the right-hand bulb. When the liquid is released the time for the left-hand meniscus to pass between marks A and B is measured. Since the pressure at any instant driving the liquid through the capillary is proportional to its density we write

$$\eta = k\rho t \quad (22.5)$$

where k is a constant known as the viscometer coefficient, ρ is the density of the liquid, and t is the flow time. The capillary measurement is simple to operate and quite precise (0.01–0.1%).

Rotational methods are particularly suitable for studying the flow of non-Newtonian liquids. An

example is the concentric cylinder (or Couette) viscometer. The liquid is sheared between concentric cylinders, which are moving relative to one another. The outer cylinder can be rotated (or oscillated) at a constant rate and the shear measured in terms of the deflection of the inner cylinder, which is suspended by a torsion wire. Alterna-

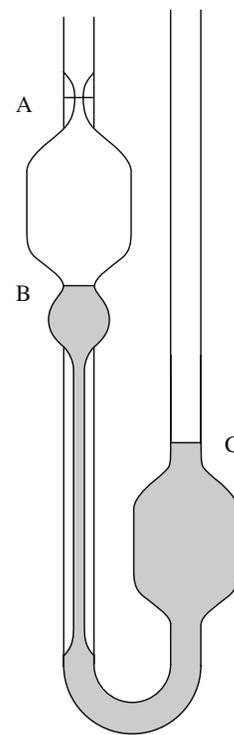


FIGURE 22.8 An Ostwald viscometer. The liquid is initially at B and C, then is drawn up to A.

tively, the inner cylinder can be rotated with the outer cylinder stationary and the resistance offered by the motor measured. The coefficient of viscosity is given by

$$\eta = K\theta/\omega h \quad (22.6)$$

where K is an instrument constant (usually obtained by calibration with a liquid of known η), ω is the angular velocity of the rotating cylinder, and h is the effective height of the liquid in contact with the cylinders. This method is essentially the same as the Mergules viscometer (Section 21.3) that is used to measure the viscosity of glass melts; the temperature is very different.

Drying and Firing

After gelation, the gel usually consists of a weak skeleton of amorphous material containing an interconnected network of small liquid-filled pores. The liquid is usually a mixture of alcohol and water, which must be removed. Shrinkage during this step is usually large.

There are several different methods used to dry gels. Each method produces a dried gel with a specific microstructure. In most cases we obtain either an aerogel or a xerogel, but other microstructures are possible as shown in Table 22.5.

The drying process is complicated, particularly when we want to form monolithic ceramics. One problem is cracking, which is more likely with high drying rates and thick (>1 cm) gels. A number of procedures have been developed to increase drying rates while avoiding cracking:

- Increase the pore size of the gel.
- Decrease the liquid/vapor interfacial energy; e.g., use a solvent with a low γ_{lv} .
- Strengthen the gel.
- Use supercritical (hypercritical) drying: the liquid is removed above its critical temperature, T_c , and critical pressure, p_c . The values of T_c and p_c for the commonly

used sol-gel liquids are water: 647 K and 22 MPa, and ethanol: 516 K and 6.4 MPa.

During firing, further changes occur as the gel densifies. The driving forces for these changes are as follows:

- The large surface area of the dried gel. A xerogel has a solid/vapor interfacial area of 100–1000 m²/g. Reduction of the surface area provides a driving force for densification.
- The low cross-linked density of the dried gel. The free energy, ΔG_f (298 K), of the polymerization reaction (Eq. 22.7) is -14.9 kJ/mol, and this acts as a driving force for increasing the amount of cross-linking.



- Structural relaxation of the solid skeletal phase of the gel as the structure approaches that of a supercooled liquid (if the gel forms a glass) or a crystal line solid (if the gel forms a crystalline ceramic).

SHRINKAGE

During drying: Linear shrinkage 50%, volume shrinkage 90%

During firing: Linear shrinkage 20%, volume shrinkage 50%

22.5 CHARACTERIZATION OF THE SOL-GEL PROCESS

Many techniques, in addition to measuring viscosity changes, have been used to follow the transitions that occur during sol-gel processing. There are the two parts of the process in which we are interested:

1. The transition from sol to gel
2. The transition from gel to oxide

Examples of techniques used to characterize sol-gel processes and the type of information they can provide are listed in Table 22.6. We described most of these techniques in Chapter 10.

TABLE 22.5 The Various Types of Dried Gels

Type	Drying conditions	Microstructure
Aerogels	In an autoclave, the fluid is removed by hypercritical evacuation	A network consisting of ~95% porosity
Xerogels	Natural evaporation	Dried gel has about 40–60% of the fired density and contains small pores (as small as 2 nm)
Sonogels	Gel exposed to ultrasound in the 20-kHz range prior to autoclave treatment	Assists in the formation of multicomponent gels
Cryogels	Freeze dried	Finely divided powder, not suitable for producing monolithic ceramics
Vapogels	A fluid stream of SiCl ₄ is injected into acidified water; this allows rapid gel formation; the gel is then dried to a xerogel	Allows incorporation of additives into the gel, e.g., GeO ₂ if the fluid stream also contains GeCl ₄

TABLE 22.6 Methods Used to Characterize Sol-Gel Processes

<i>Technique</i>	<i>What is measured</i>	<i>How it is used</i>
Ellipsometry	Thickness, optical constants of films	To measure film thickness changes, for example, during drying
Fourier transform IR spectroscopy	Vibrational frequencies of chemical bonds, qualitative and quantitative identification of functional groups	Chemical changes during gelation, drying, and firing
Raman spectroscopy	Vibrational frequencies of chemical bonds, compound identification, structural order and phase transitions	Chemical and structural changes during gelation, drying, and firing
Solid-state nuclear magnetic resonance (NMR) spectroscopy	Interaction between nuclear magnetic moments in atoms in the sample with rf electromagnetic waves, sensitive indicator of structural and chemical bonding properties; phase identification and characterization of local bonding environment	Polymerization kinetics, time evolution of condensed species The chemical shifts in ²⁹ Si NMR are functions of the state of silicon polymerization
Transmission electron microscopy	Crystallinity and phase identification by diffraction, microstructure at high spatial resolution	Transformation from amorphous to crystalline during firing; experiments can be performed <i>in situ</i>
X-ray diffraction	Crystallinity and phase identification, averaged microstructural information	Transformation from amorphous to crystalline during firing; experiments can be performed <i>in situ</i>

22.6 POWDERS, COATINGS, FIBERS, CRYSTALLINE, OR GLASS?

Sol-gel processing is versatile because it can be used to produce ceramics in a number of different forms:

Powders—because we can make very small particles and control the composition

Example application: bioactive glass powders, with a composition of SiO₂-CaO-P₂O₅

Coatings—because the sol is a viscous liquid and can be applied to a substrate by spinning

Example application: TiO₂-based antiglare coatings on glass

Example application: coat steel with alumina to improve wear resistance

Fibers—because we can pull a thread out that is liquid and dry it, coat it, etc.

Example application: SiO₂ fibers used for space shuttle tiles

Crystalline or Glass? We have the choice.

Example application: high-purity porous silica glass for filtration

Powders

Powders can be obtained via a sol-gel process using metal alkoxides or a combination of metal alkoxides and metal salts. Because the mixing of the constituents is achieved at a molecular level, the powders are chemically homogeneous. Powders produced by the sol-gel method are usually amorphous. This characteristic, together with their high surface area, allows them to be sintered to nearly full

density at temperatures lower than are normally required when the particles have been made by other techniques. For example, gel-derived mullite powders can be sintered to full density at <1300°C, whereas the sintering temperature is ~1600°C for crystalline mullite powders. However, the cost of the raw materials limits the use of the sol-gel method in producing many ceramic powders except for those used for specialty applications.

Coatings and Films

Ceramic coatings can be prepared using a sol-gel process involving metal alkoxides. The coatings may be formed by

- Dipping
- Spinning
- Spraying
- Lowering (similar to dipping except the substrate remains stationary and the liquid is lowered)

Spinning is widely used for applying sol-gel coatings, and one particular application is to produce thin coatings of PZT for microelectromechanical systems (MEMS). Alkoxide-derived coatings are used for both antireflective layers on glass substrates and solar reflecting coatings on flat glass. Table 22.7 lists a number of applications for sol-gel films and coatings.

The advantages of forming coatings via sol-gel reactions are

- Large areas
- Uniform composition

TABLE 22.7 Applications of Sol-Gel Films and Coatings

Field	Property	Examples
Electronic	Ferroelectric	BaTiO ₃ , PZT
	Piezoelectric	PZT
	High-T _c superconductor	YBa ₂ Cu ₃ O ₇
	Ferrimagnetic	Doped Fe ₂ O ₃
	Transparent conductors	Indium tin oxide
Optical	Antireflective	TiO ₂ /SiO ₂
	Solar reflecting	TiO ₂ /Pd
	Electrooptic	PLZT
	Corrosion resistant	SiO ₂
Protective	Abrasion resistant	Organic modified silicates
	Barrier films	YSZ
Biomaterials	Bone cell regeneration	Calcium apatites

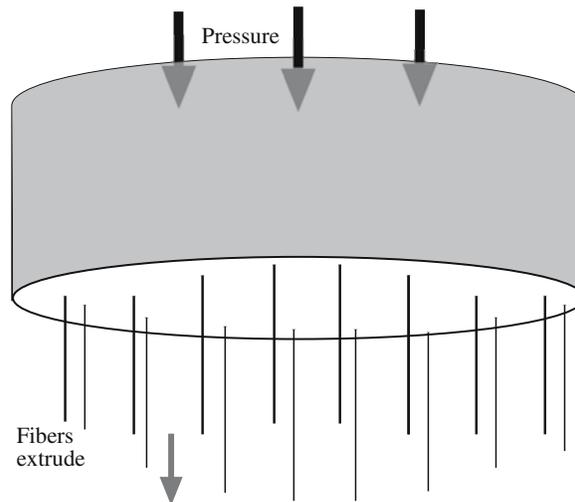
- Conformal coating of irregularly shaped substrates, e.g., fibers
- High purity
- Microstructural control, i.e., pore volume (0–65%), pore size (<0.4 nm to >5.0 nm), and surface area (<1–250 m²/g)
- Less expensive than vapor-phase processes such as chemical vapor deposition (CVD) and sputtering
- Fibers

In Chapter 20 we described various methods of making ceramic fibers including the sol-gel process. Fibers can be drawn directly from viscous sols, which are usually made by acid-catalyzed hydrolysis using low H₂O:M ratios. At viscosities greater than about 1 Pa·s (glycerine has a viscosity of ~1 Pa·s at room temperature) the sol is sticky and we can produce fibers by forcing the sol through a spinnerette, illustrated in Figure 22.9. The spinnerette can be rotated to produce a yarn. This process is used commercially to produce polymer fibers.

Applications for sol-gel-derived fibers include

- Reinforcement in composites
- Refractory textiles
- High-temperature superconductors

Examples of fibers produced by sol-gel are


FIGURE 22.9 Illustration of a spinnerette used to produce fibers and yarn.

- SiO₂
- SiO₂–TiO₂ (10–50 mol% TiO₂)
- SiO₂–Al₂O₃ (10–30 mol% Al₂O₃)
- SiO₂–ZrO₂ (10–33 mol% ZrO₂)
- SiO₂–Na₂O–ZrO₂ (25 mol% ZrO₂)

The properties of some commercial sol-gel fibers are given in Table 22.8.

Glasses

Glasses can be synthesized using the sol-gel process. This process makes it possible to form a disordered glass network, not directly at high temperatures from the melt, but at low temperatures by chemical polymerization in a liquid.

The Owens-Illinois Company started an investigation of bulk glass systems formed by the sol-gel process in 1967. The dried gels were melted and fabricated by conventional techniques. They found the following advantages:

- Lower melting temperatures could be used (the gel is already amorphous).

TABLE 22.8 Properties of Commercial Gel-Derived Ceramic Fibers

Producer	Name	Composition	Tensile strength (MPa)	Tensile modulus (GPa)	Density (g/cm ³)
3M	Nextel 312	Al ₂ O ₃ , SiO ₂ , B ₂ O ₃	1750	154	2.70
3M	Nextel 440	Al ₂ O ₃ , SiO ₂ , B ₂ O ₃	2100	189	3.05
3M	Nextel 480	Al ₂ O ₃ , SiO ₂ , B ₂ O ₃	2275	224	3.05
Du Pont	PRD-166	Al ₂ O ₃ , ZrO ₂	2100	385	4.20
Du Pont	FP	α-Al ₂ O ₃	1400	3853	3.90
Sumitomo		Al ₂ O ₃ , SiO ₂	Average 2200	Average 230	3.20

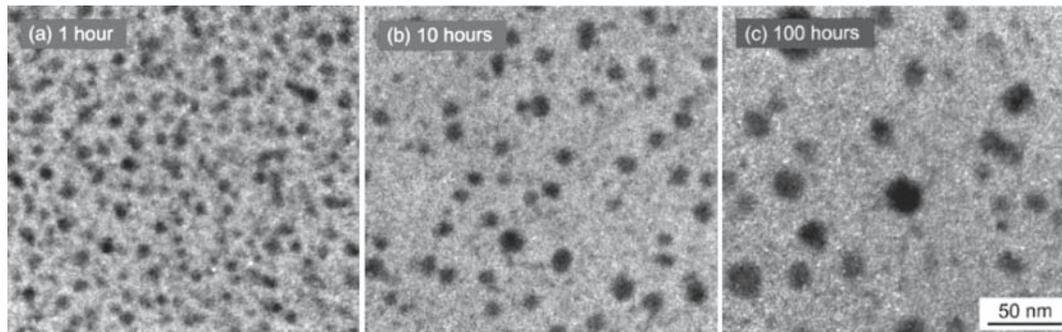


FIGURE 22.10 Use of sol-gel processing to produce Si nanoparticles in a glass matrix. (a–c) The time indicates the length of the heat treatment.

- It was not necessary to stir the melt (the gel is homogeneous).

It was also found that glasses fabricated from gels and those of the same composition made from oxide powders had essentially the same physical properties. But the work was discontinued because of the high cost of the gels compared to the cost of the traditional powders. And, in terms of processing considerations, the gel must be heated very slowly to the melting temperature to ensure that any residual organics and water are removed, otherwise a very seedy and foamy melt can be obtained.

Sol-gel processing can really be justified only for glasses of certain compositions such as those with high melting temperatures and high viscosity glasses that are difficult to melt conventionally. But glass coatings made by the sol-gel process are still important commercially.

Monolithic Ceramics

There are basically two routes that can be used to produce monolithic ceramics via a sol-gel process:

- Firing: use xerogels or aerogels
- Compaction and firing: use gel-derived powders

Making monolithic ceramics directly by a sol-gel process is still a challenge. The main issue is how the gel can be dried without introducing cracks in the dried body. The advantages of using a sol-gel route compared

to conventional ceramic methods is that we are working in uncontaminated conditions and using lower temperatures.

The compaction-and-firing process is similar to traditional methods for producing ceramics from powders except that the powders are derived from the sol-gel process. The pros and cons are the same as those mentioned in forming powders using this method.

Particles in Sol-Gel Films

Since the sol-gel films are essentially amorphous in their as-prepared state, we can heat treat them to grow nanoparticles that are then embedded inside an amorphous matrix. The amorphous SiO(C) film in Figure 22.10 was produced by pyrolysis of a sol-gel precursor. The cohydrolysis of triethoxysilane and methyl-diethoxysilane (in a molar ratio of 9:1) used addition of acidic water (pH 2.25)

to produce the xerogel. The xerogel was pyrolyzed at 1000°C for 1 hour to produce an Si-rich glass. The films were heated for a further 10 hours and then 100 hours to produce the images shown here.

The dark regions in the images are O depleted and Si rich. High-resolution transmission electron microscopy (HRTEM) showed that these were crystalline Si nanoparticles (which have potentially interesting luminescent properties). So not only does this type of study produce an interesting material, but it also sheds light on Ostwald ripening and devitrification of a glass.

MONOLITHIC CERAMICS

The instruction to build a wall in “monolithic” concrete indicates that it should be a wall of concrete built in place and then hardened into a solid unbroken mass. Hence a monolithic ceramic is “built” *in situ*.

CHAPTER SUMMARY

You should know that sols and gels are different concepts and that sol-gel uses both. You cannot avoid learning the basic organic chemistry: it is messy and has confusing terminology but is amazingly versatile and can produce nanomaterials routinely. Sol-gel processing is a method that can be used to form ceramic powders, thin films and coatings, fibers, and monolithic ceramics. The advantages of sol-gel processing are that we have excellent control of the

composition, purity, and homogeneity of our product; how much control depends on the purity of the chemicals with which we start. It also allows us to process materials at lower temperatures than any other method because we have small reactive particles. The disadvantages are that the reactants are often expensive and there are problems in producing bulk ceramic components because of shrinkage. Sol-gel processes are used commercially to produce fibers, coatings, and coated fibers, particularly of ceramics with a high SiO₂ content (because processing temperatures are much lower). It is also particularly suited to producing thin films of multicomponent oxides such as PZT, which have application in MEMS; and how can you put a more uniform coating on a nanoparticle?

PEOPLE IN HISTORY

- Couette, Maurice Frédéric Alfred (1858–1943) was professor of physics at the University of Angers in France. During his lifetime he published only seven papers. The idea for a viscometer based on shearing a liquid between two surfaces came from his Ph.D. thesis.
- Ostwald, Wilhelm (1853–1932) won the Nobel Prize in Chemistry in 1909. He held academic positions at several institutions and from 1887 until his retirement in 1906 was Professor of Physical Chemistry at Leipzig University. His famous students included Arrhenius (Nobel Prize 1903), Van't Hoff (Nobel Prize 1901), and Nernst (Nobel Prize 1920).

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- Bradley, D.C., Mehrotra, R.C., and Gaur, D.P. (1978) *Metal Alkoxides*, Academic Press, London. This is essential reading if you want to find out more. It gives a detailed account of the history and synthesis of metal alkoxides, together with a full list of references.
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- Segal, D. (1989) *Chemical Synthesis of Advanced Ceramic Materials*, Cambridge University Press, Cambridge. Concise description of the various chemical routes to fabricate ceramics. Contains a large number of references.

JOURNALS AND CONFERENCES

- For coverage of current sol-gel research, the most widely used journals are *J. Non-Cryst. Solids*, *J. Mater. Res.*, *J. Am. Ceram. Soc.*, *J. Sol-Gel Sci. Techn.*, and *J. Mater. Sci.*
- The Materials Research Society has sponsored meetings since 1984 under the title *Better Ceramics Through Chemistry* and has published proceedings.

SPECIFIC REFERENCES

- Ebelman, J.J. and Bouquet, M. (1846) *Ann. Chem. Phys.* **17**, 54. Ebelman was the first person to describe alkoxide synthesis. This paper reported the synthesis of boron methoxide, ethoxide, and pentoxide by the reaction of boron trichloride with the appropriate alcohol. These alkoxides can be used in the synthesis of borosilicate glasses.
- Piau, J.M., Bremond, M., Couette, J.M., and Piau, M. (1994) "Maurice Couette, one of the founders of rheology," *Rheol. Acta* **33**(5), 357.

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- Scherer, G.W. (1990) "Stress and fracture during drying of gels," *J. Non-Cryst. Solids* **121**, 104. Model for drying gels.

EXERCISES

- 22.1 Sol-gel coatings are usually prepared using either dipping or spinning. What are the advantages and disadvantages of the two methods?
- 22.2 Why would spinning rather than dipping be used to produce PZT films for applications such as MEMS?
- 22.3 The ceramic fibers listed in Table 22.8 are made by sol-gel processing. (a) Why do you think this processing method was chosen? (b) What starting chemicals would be suitable for making these fibers? (c) Are there any alternative approaches that could be used to produce these ceramic fibers? If so, what are they and how do they compare to sol-gel?
- 22.4 Discuss the economic issues involved in using the sol-gel process to form ceramic powders.
- 22.5 Explain why ²⁹Si NMR can be used to study the amorphous-to-crystalline transition in a silica gel. [Note: You may find the following references of use: Brown, I.D. and Shannon, R.D. (1973) "Empirical bond-strength bond-length curves for oxides," *Acta Crystallogr. A* **29**, 266; Smith, K.A., Kirkpatrick, R.J., Oldfield, E., and Henderson, D.M. (1983) "High-resolution ²⁹Si nuclear magnetic-resonance spectroscopic study of rock-forming silicates," *Am. Mineral.* **68**, 1206.]
- 22.6 What is the difference between a particulate gel and a polymeric gel?
- 22.7 What would be appropriate starting chemicals for producing YBa₂Cu₃O₇ films by sol-gel?
- 22.8 Explain briefly the problems with shrinkage as they apply to sol-gel processing.
- 22.9 Compare the raw materials costs of preparing PZT powders by conventional solid-state reactions and sol-gel processing. What are the pros and cons of each approach?
- 22.10 Nylon is prepared by a condensation reaction. Compare this process to that occurring during sol-gel processing of ceramics using metal alkoxides.