SOL-GEL AND ORGANIC CHEMISTRY

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MATR 4350

Outline of the topics:

- Sol-gel processing
- Structure and synthesis of alkoxides
- Properties of alkoxides
- Sol-gel process using metal alkoxides
  - Preparing the sol
  - Hydrolysis and condensation
  - Sol-gel transition
  - Drying and firing
- Characterization of the sol-gel process
- Powders, coating, fibers, crystalline or glass?
  - Powders
  - Coating and films
  - Fibers
  - Glassess
  - Monolithic Ceramics
  - Particles in sol gel films

Sol gel processing

- The sol–gel process consists of 2 steps:
  - Form a sol.
  - Transform the sol into a gel.
- In ceramic synthesis, 2 different sol–gel routes depend on the gel structure:
  - Particulate gel—using a network of colloidal particles
  - Polymeric gel—using an array of polymeric chains
- The process that occurs depends on the form of the sol:
  - a solution
  - a suspension of fine particle

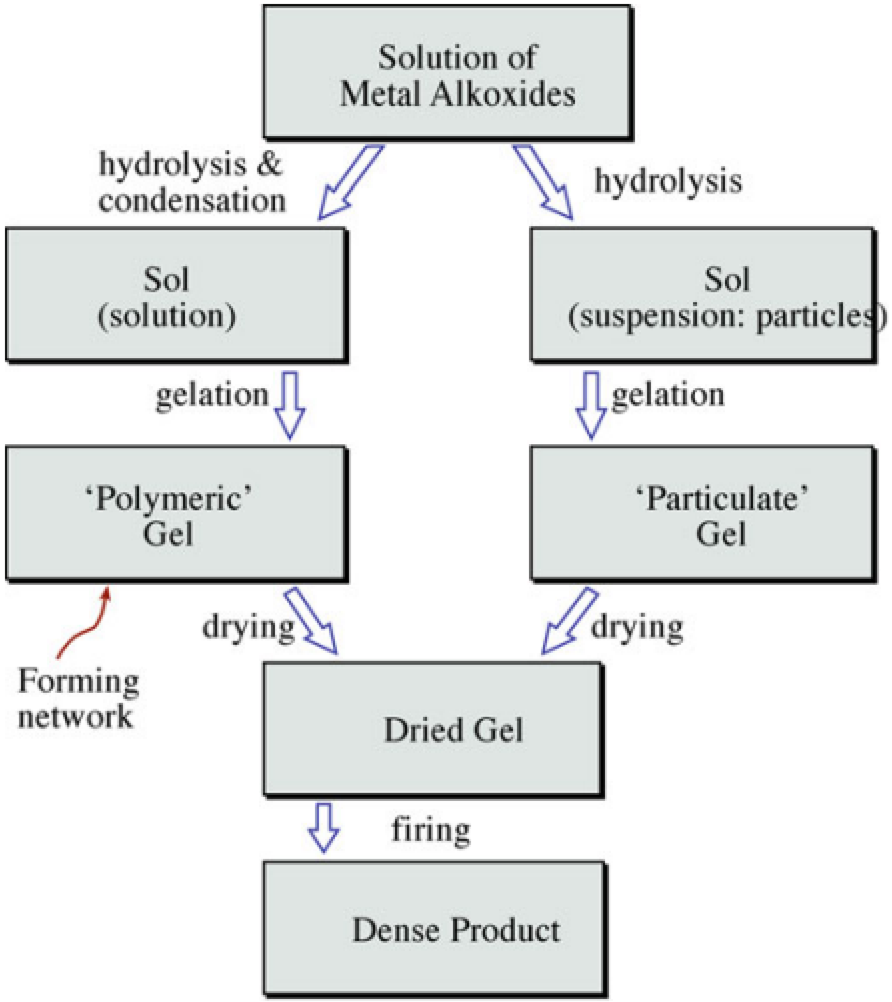


FIGURE 22.1 Flow chart comparing sol–gel processing using a solution and a suspension of fine particles.

- The advantage of sol–gel processing of ceramic powders
  - homogeneous compositions can be prepared at temperatures lower than required for conventional powder processes.
  - 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.
- Advantages using metal alkoxides as precursors for ceramic powders:
  - Most of the alkoxides of interest can be easily prepared or are commercially available & can be readily purified prior to use.
  - Interaction of alkoxides with water yields precipitates of hydroxides, hydrates, & oxides.
  - The size of the precipitate particles usually 0.01~1.0 mm -depend on the hydrolysis conditions.
  - can easily produce nanoparticles.

Structure and synthesis of alkoxides

- Alkoxides have the general formula M(OR)z
  - M – metal/nonmetal (Si)
  - R – alkyl chain
- In these molecular formulae, the superscripts n, t, s, and i refer to normal, tertiary, and secondary or iso alkyl chains

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 3D network, a "*gel*".

METAL ALKOXIDE

M(OR)
For convenience we will say "metal alkoxide" even when referring to alkoxides of non-metals such as silicon and boron.

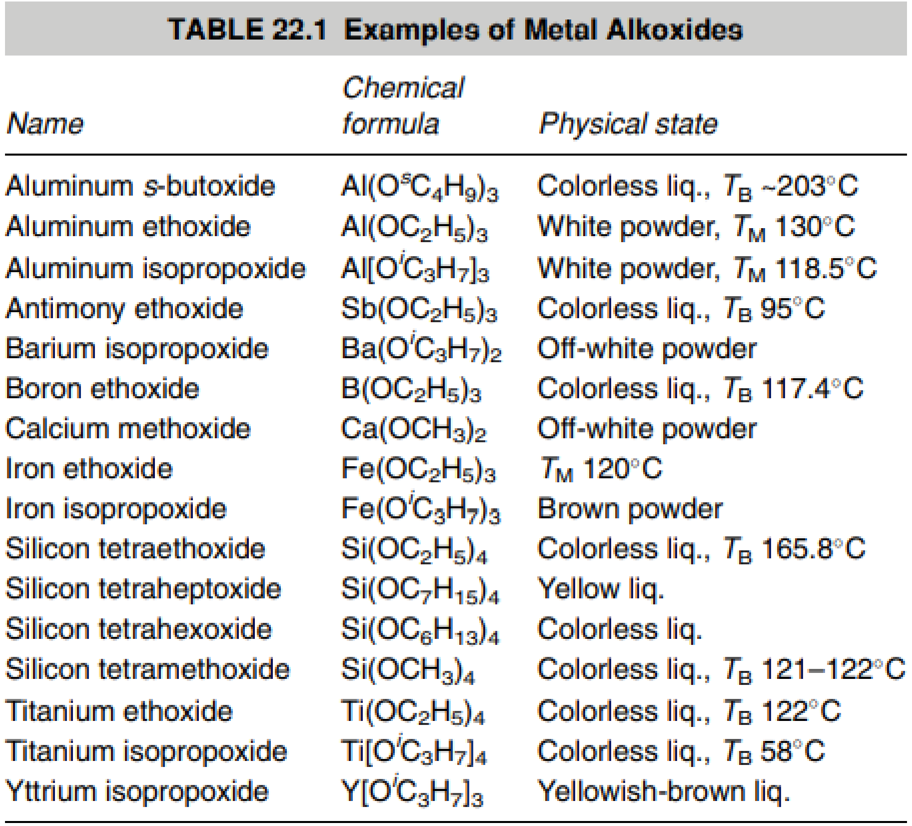
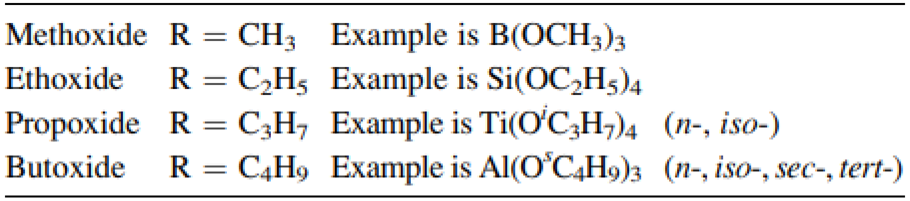


TABLE 22.1 Examples of Metal Alkoxides

Name	*Chemical formula*	*Physical state*
Aluminum *s*-butoxide	$Al(O^sC_4H_9)_3$	Colorless liq., T_B ~203°C
Aluminum ethoxide	$Al(OC_2H_5)_3$	White powder, T_M 130°C
Aluminum isopropoxide	$Al[O^iC_3H_7]_3$	White powder, T_M 118.5°C
Antimony ethoxide	$Sb(OC_2H_5)_3$	Colorless liq., T_B 95°C
Barium isopropoxide	$Ba(O^iC_3H_7)_2$	Off-white powder
Boron ethoxide	$B(OC_2H_5)_3$	Colorless liq., T_B 117.4°C
Calcium methoxide	$Ca(OCH_3)_2$	Off-white powder
Iron ethoxide	$Fe(OC_2H_5)_3$	T_M 120°C
Iron isopropoxide	$Fe(O^iC_3H_7)_3$	Brown powder
Silicon tetraethoxide	$Si(OC_2H_5)_4$	Colorless liq., T_B 165.8°C
Silicon tetraheptoxide	$Si(OC_7H_{15})_4$	Yellow liq.
Silicon tetrahexoxide	$Si(OC_6H_{13})_4$	Colorless liq.
Silicon tetramethoxide	$Si(OCH_3)_4$	Colorless liq., T_B 121–122°C
Titanium ethoxide	$Ti(OC_2H_5)_4$	Colorless liq., T_B 122°C
Titanium isopropoxide	$Ti[O^iC_3H_7]_4$	Colorless liq., T_B 58°C
Yttrium isopropoxide	$Y[O^iC_3H_7]_3$	Yellowish-brown liq.



Methoxide	$R = CH_3$	Example is $B(OCH_3)_3$	
Ethoxide	$R = C_2H_5$	Example is $Si(OC_2H_5)_4$	
Propoxide	$R = C_3H_7$	Example is $Ti(O^iC_3H_7)_4$	(*n*-, *iso*-)
Butoxide	$R = C_4H_9$	Example is $Al(O^sC_4H_9)_3$	(*n*-, *iso*-, *sec*-, *tert*-)

Properties of alkoxides

- Most metal alkoxides contain lower aliphatic alkyl groups and are coordinated complexes, not single molecules
- Many alkoxides are available commercially, particularly those of Si, Al, Ti, B, and Zr.
- The properties of metal alkoxides depend on the electronegativity of metal
- Alkoxides of alkali metals & alkaline earth metals are ionic solids.
- Alkoxides of Ge, Al, Si, Ti, and Zr are often covalent liquids.
- Because most alkoxides are either liquids or volatile solids they can be purified by distillation to form exceptionally pure oxide sources

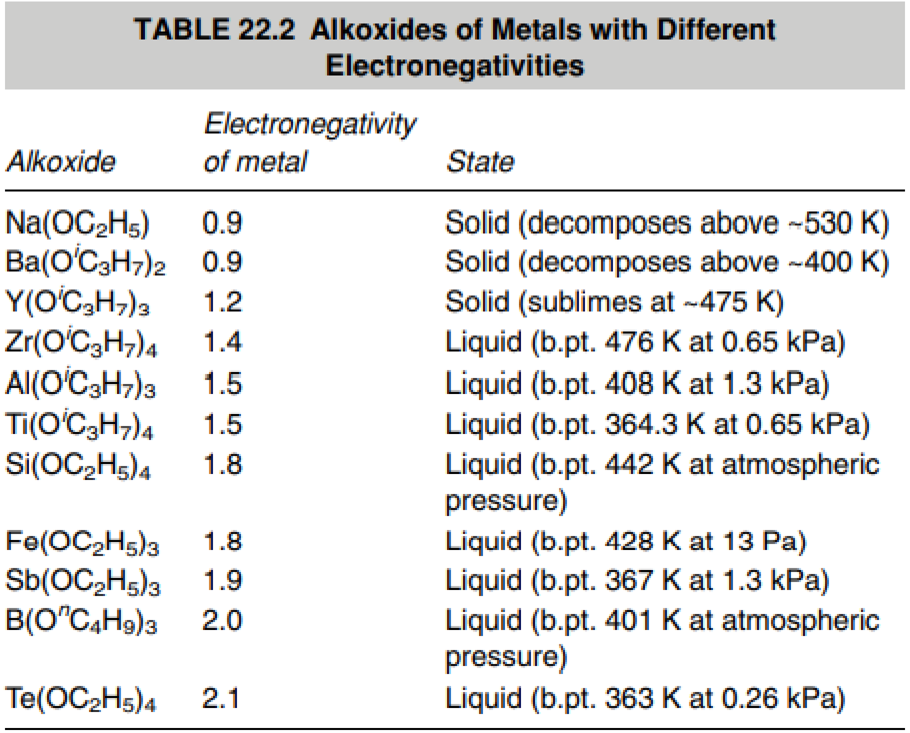
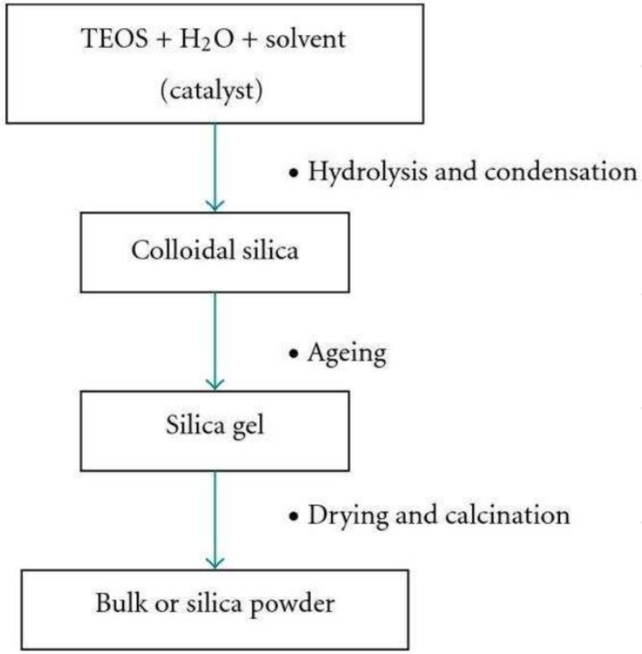
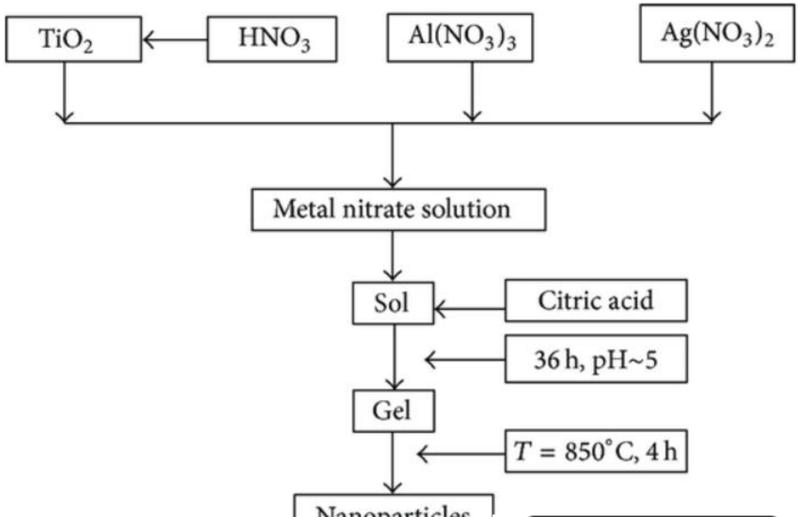


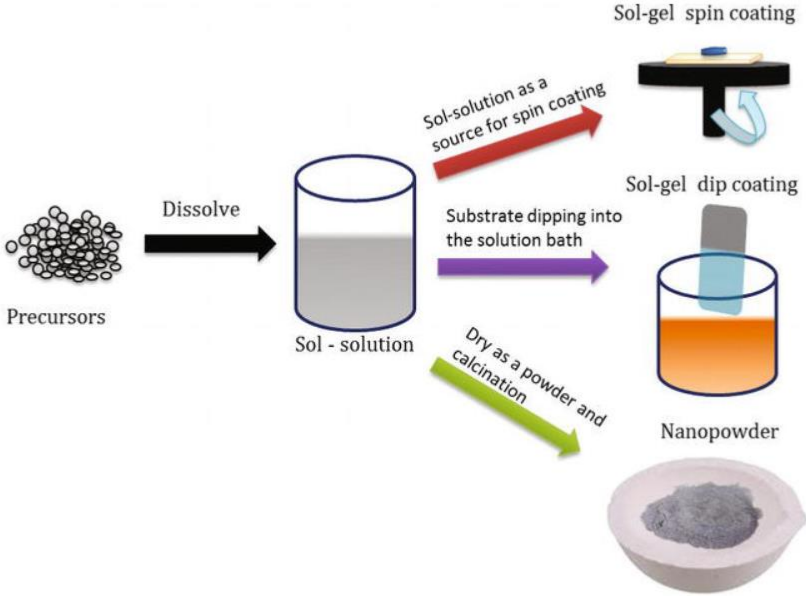
TABLE 22.2 Alkoxides of Metals with Different Electronegativities

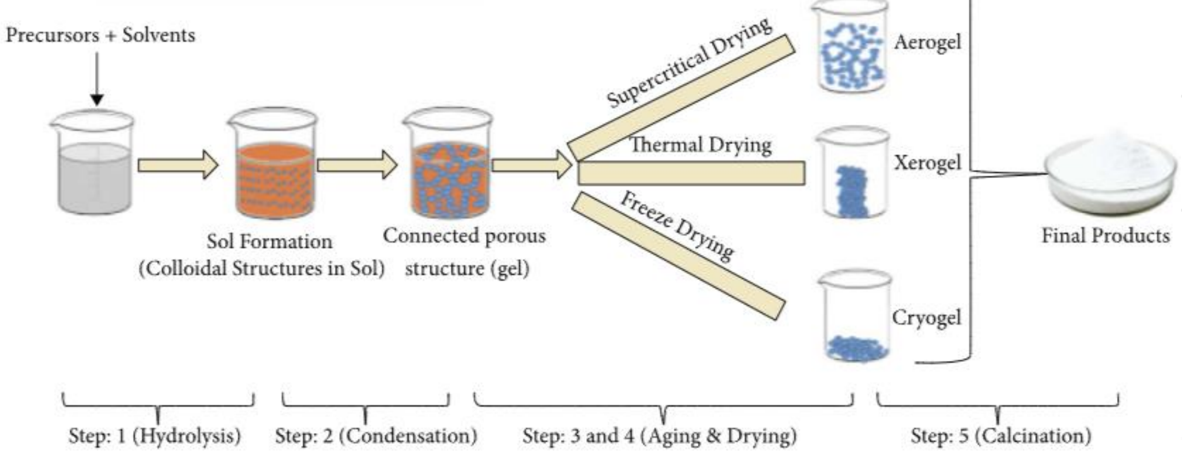
Alkoxide	*Electronegativity of metal*	*State*
$Na(OC_2H_5)$	0.9	Solid (decomposes above ~530 K)
$Ba(O^iC_3H_7)_2$	0.9	Solid (decomposes above ~400 K)
$Y(O^iC_3H_7)_3$	1.2	Solid (sublimes at ~475 K)
$Zr(O^iC_3H_7)_4$	1.4	Liquid (b.pt. 476 K at 0.65 kPa)
$Al(O^iC_3H_7)_3$	1.5	Liquid (b.pt. 408 K at 1.3 kPa)
$Ti(O^iC_3H_7)_4$	1.5	Liquid (b.pt. 364.3 K at 0.65 kPa)
$Si(OC_2H_5)_4$	1.8	Liquid (b.pt. 442 K at atmospheric pressure)
$Fe(OC_2H_5)_3$	1.8	Liquid (b.pt. 428 K at 13 Pa)
$Sb(OC_2H_5)_3$	1.9	Liquid (b.pt. 367 K at 1.3 kPa)
$B(O^nC_4H_9)_3$	2.0	Liquid (b.pt. 401 K at atmospheric pressure)
$Te(OC_2H_5)_4$	2.1	Liquid (b.pt. 363 K at 0.26 kPa)

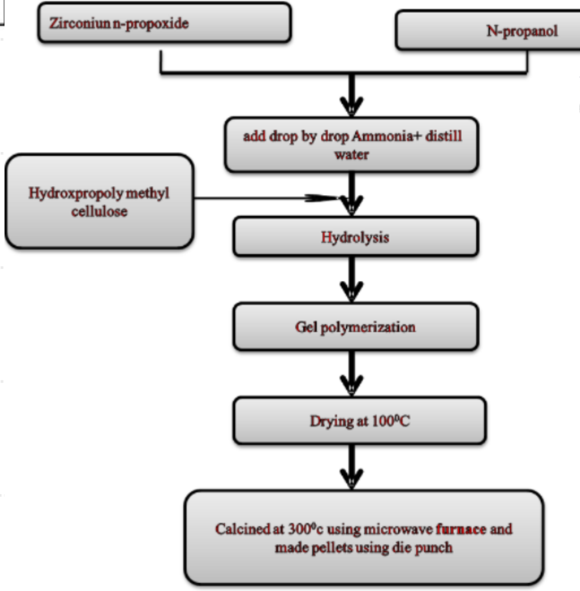
Sol-gel process using metal alkoxides

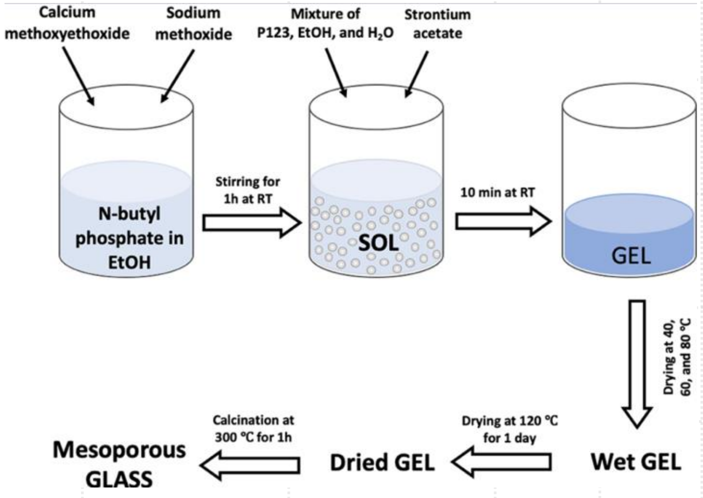


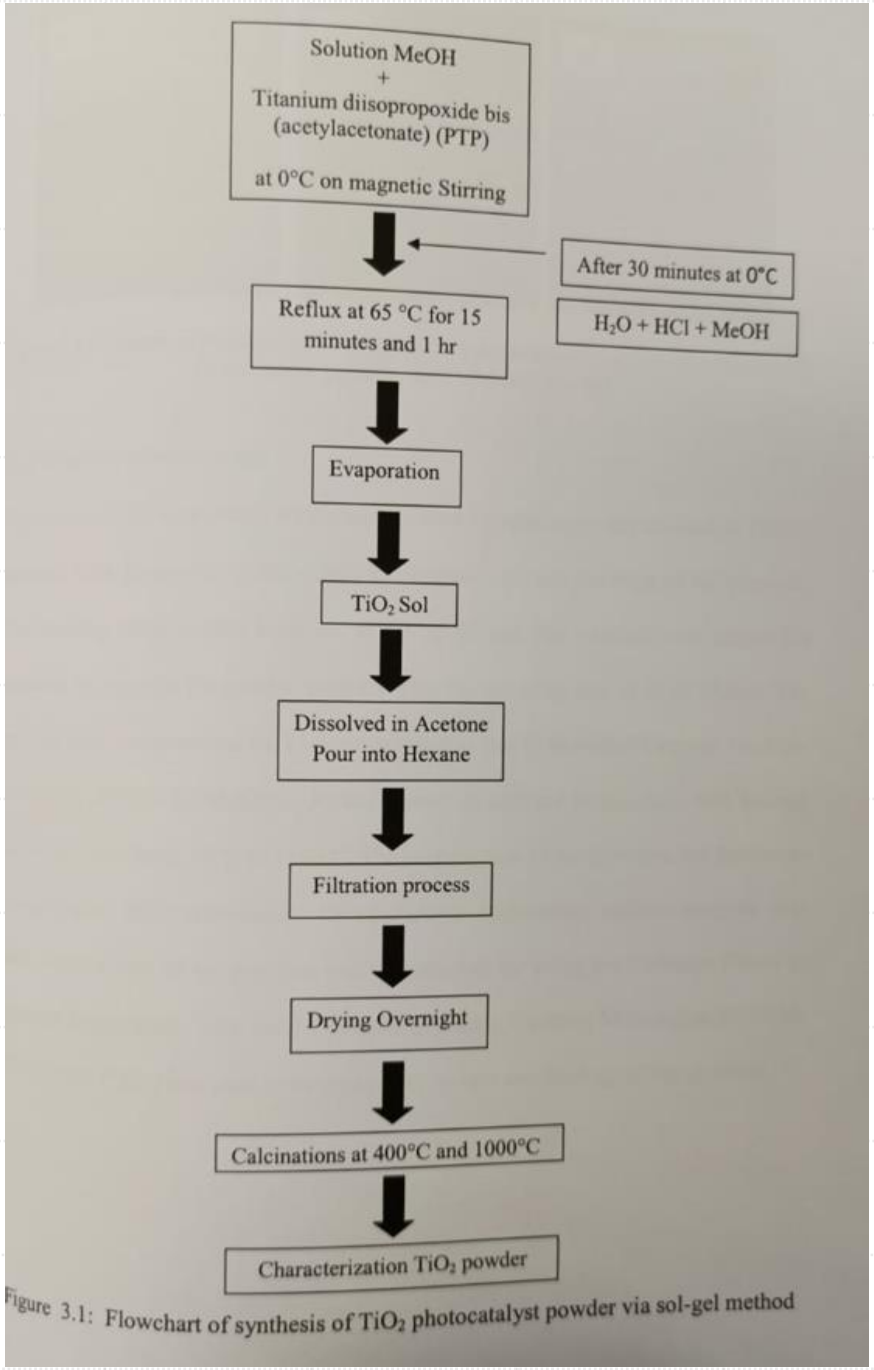












Solution MeOH
+
Titanium diisopropoxide bis (acetylacetonate) (PTP)
at 0°C on magnetic Stirring

After 30 minutes at 0°C

H_2O + HCl + MeOH

Reflux at 65 °C for 15 minutes and 1 hr

Evaporation

TiO_2 Sol

Dissolved in Acetone
Pour into Hexane

Filtration process

Drying Overnight

Calcinations at 400°C and 1000°C

Characterization TiO_2 powder

Figure 3.1: Flowchart of synthesis of TiO_2 photocatalyst powder via sol-gel method

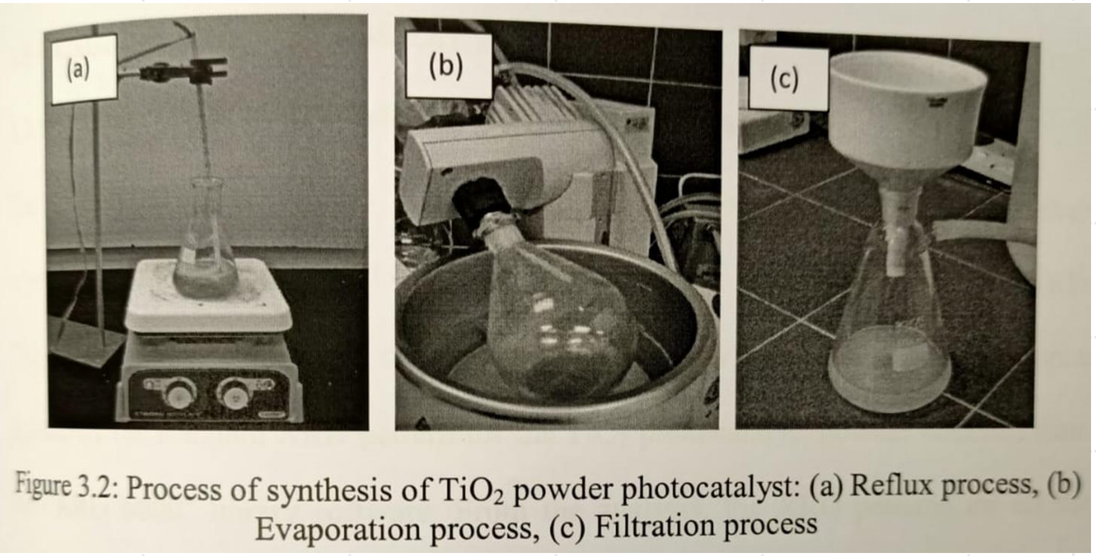
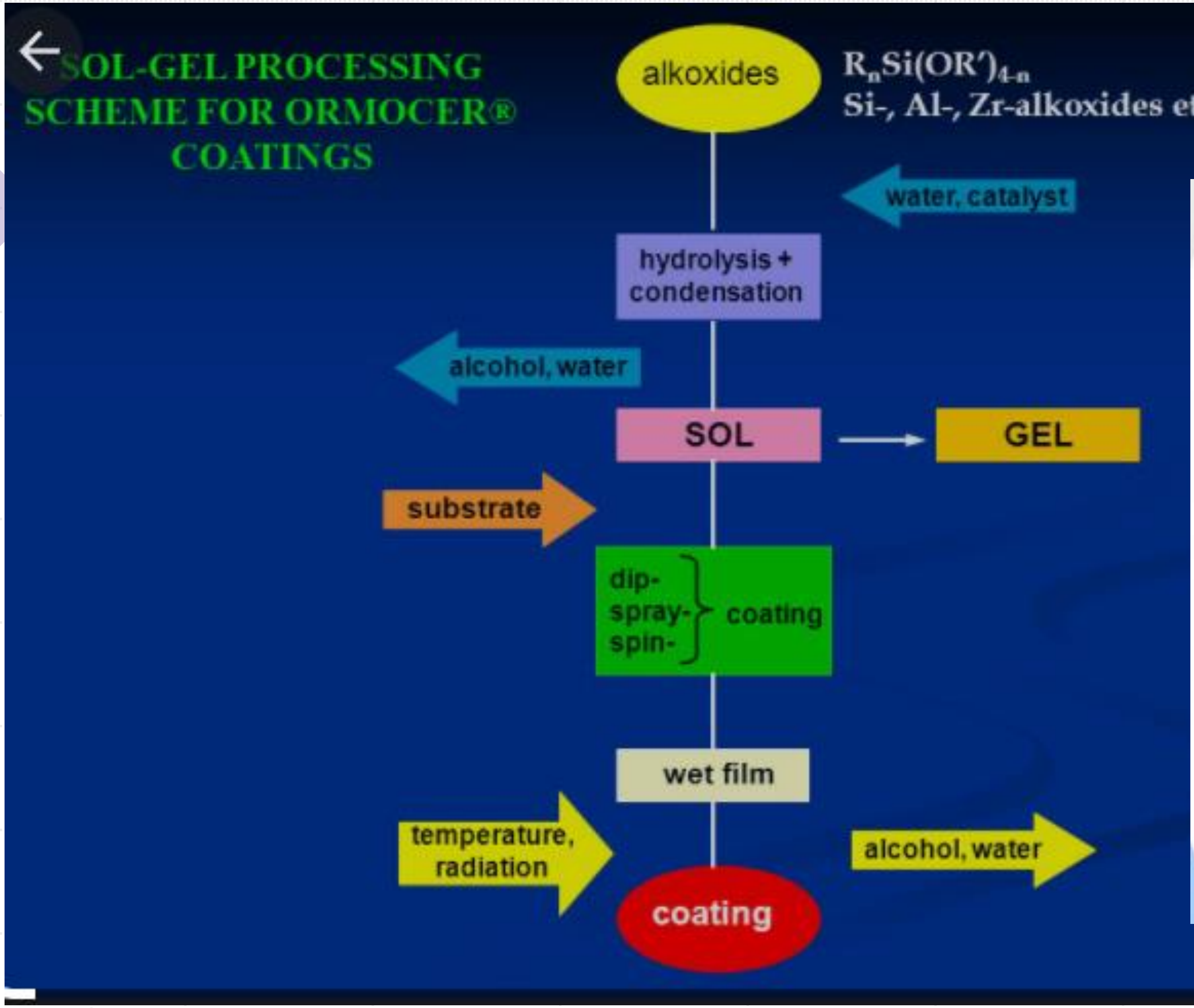


Figure 3.2: Process of synthesis of TiO_2 powder photocatalyst: (a) Reflux process, (b) Evaporation process, (c) Filtration process



SOL-GEL PROCESSING SCHEME FOR ORMOCER® COATINGS

alkoxides

$R_nSi(OR')_{4-n}$

Si-, Al-, Zr-alkoxides etc.

water, catalyst

hydrolysis + condensation

alcohol, water

SOL → GEL

substrate

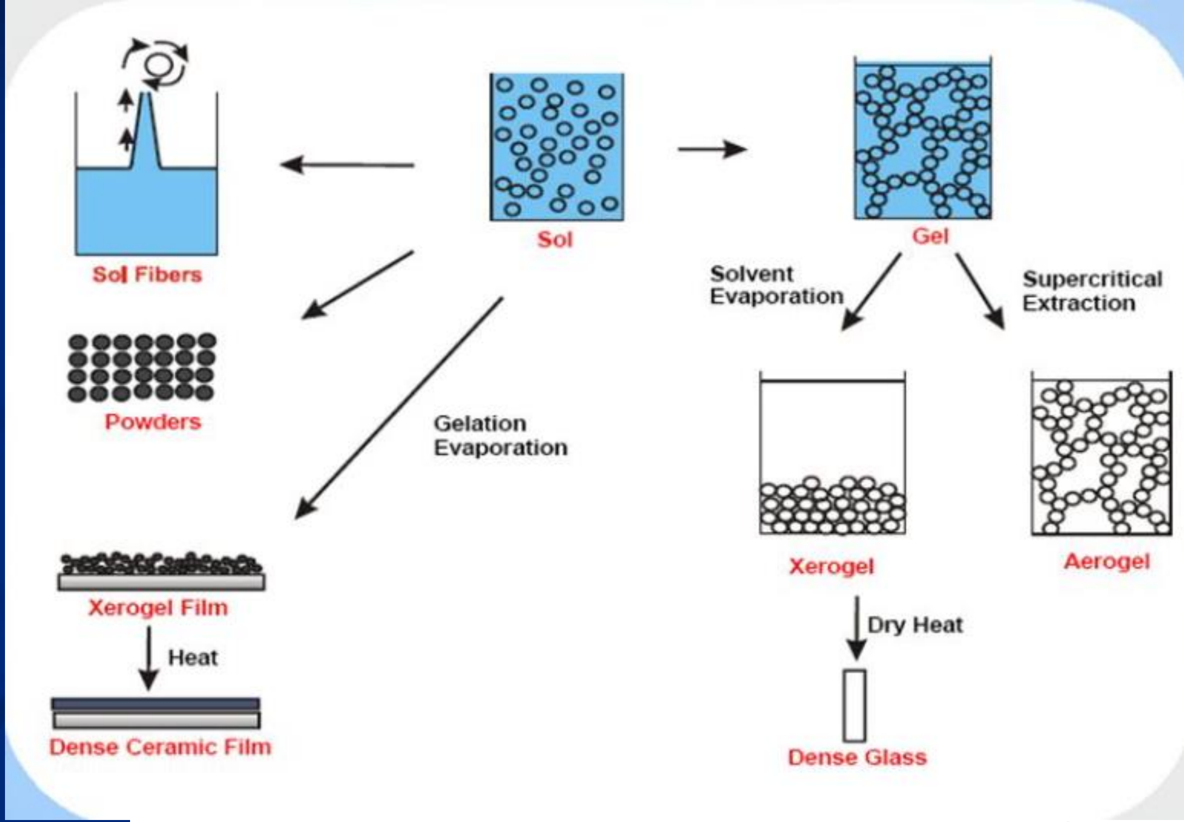
dip-
spray-
spin-
coating

wet film

temperature, radiation

alcohol, water

coating



Preparing the sol

- The sol–gel process can be used to make **single or multicomponent oxides**.
- First, we consider the case of a one component system—silica.
- Of the many available **silicon alkoxides, TEOS** is commonly used.
- TEOS is **insoluble in water**, but water is necessary for the hydrolysis reaction
  - **need to select a solvent** for both the alkoxide and water.
- **Ethanol** is a suitable solvent, contains 3 components: 43 vol% $Si(OC_2H_5)_4$ 43 vol% C_2H_5OH 14 vol% H_2O

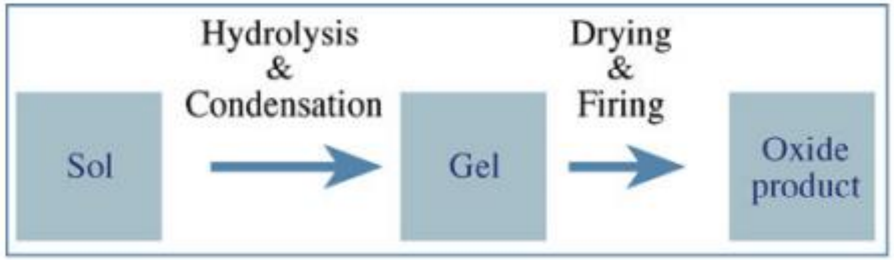


FIGURE 22.4 Basic steps in the sol–gel process using metal alkoxides.

Hydrolysis and condensation

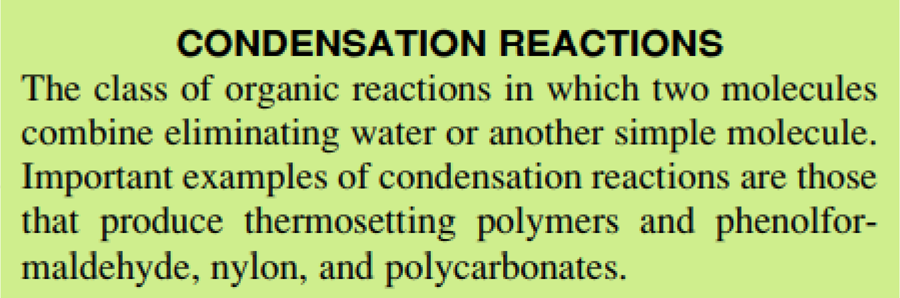
- Metal alkoxides undergo hydrolysis very easily (meaning they react with water)
- During the initial stage of hydrolysis an **alcohol molecule, ROH,** is expelled

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

- 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.

$$M(OH)(OR)_{z-1} + M(OR)_z \\ \rightarrow (RO)_{z-1}MOM(OR)_{z-1} + ROH$$

$$2M(OH)(OR)_{z-1} \rightarrow (RO)_{z-1}MOM(OR)_{z-1} + H_2O$$

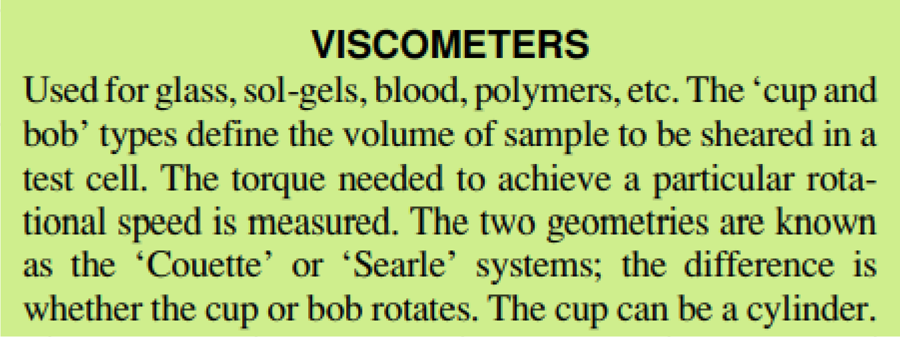


CONDENSATION REACTIONS

The class of organic reactions in which two molecules combine eliminating water or another simple molecule. Important examples of condensation reactions are those that produce thermosetting polymers and phenolformaldehyde, nylon, and polycarbonates.

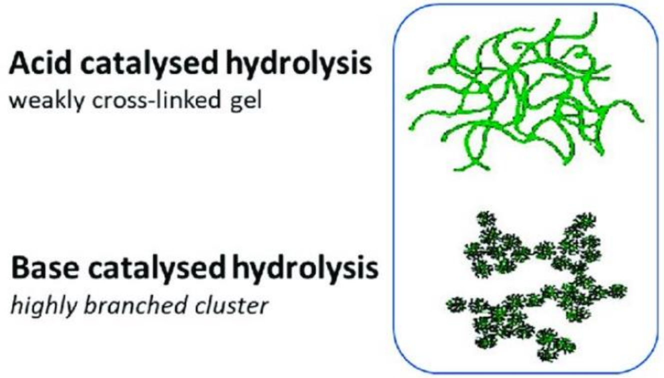
Sol-gel transition

- **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 reaction**



VISCOMETERS

Used for glass, sol-gels, blood, polymers, etc. The ‘cup and bob’ types define the volume of sample to be sheared in a test cell. The torque needed to achieve a particular rotational speed is measured. The two geometries are known as the ‘Couette’ or ‘Searle’ systems; the difference is whether the cup or bob rotates. The cup can be a cylinder.



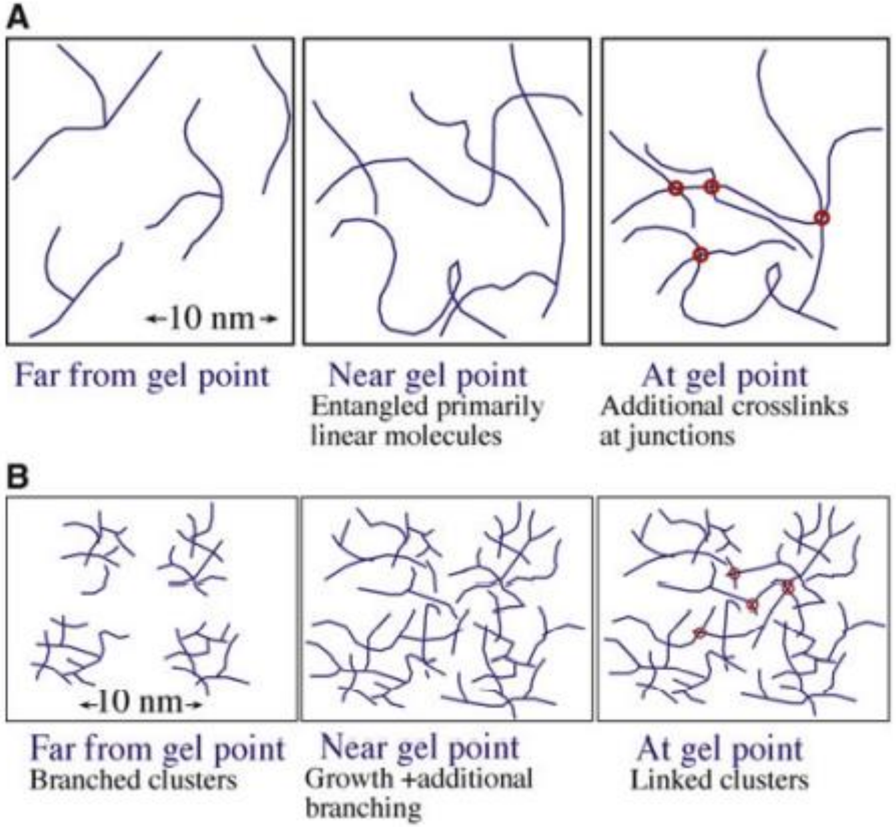


FIGURE 22.7 Acid-catalyzed (A) and base-catalyzed (B) polymerization and gelation.

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
- During firing, further changes occur as the gel densifies

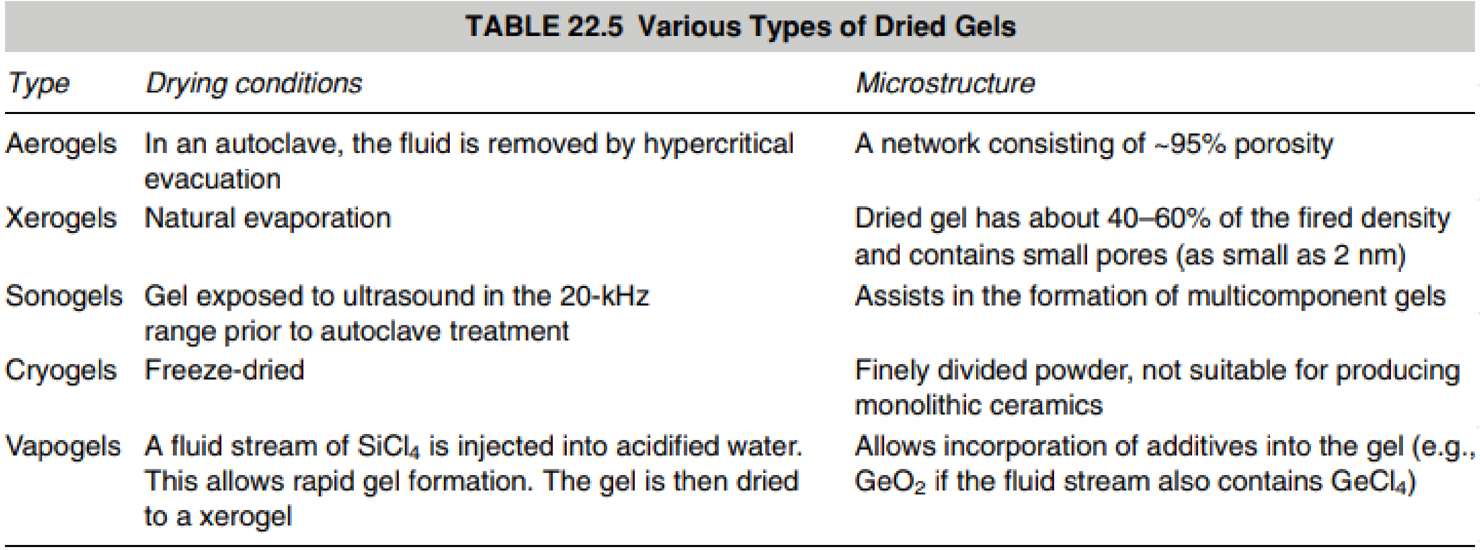
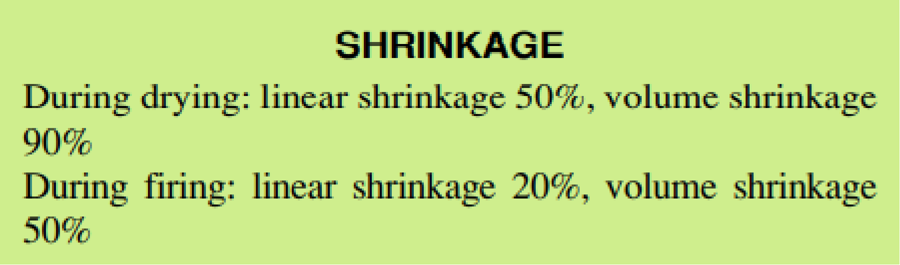


TABLE 22.5 Various Types of Dried Gels

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 $GeCl_4$)



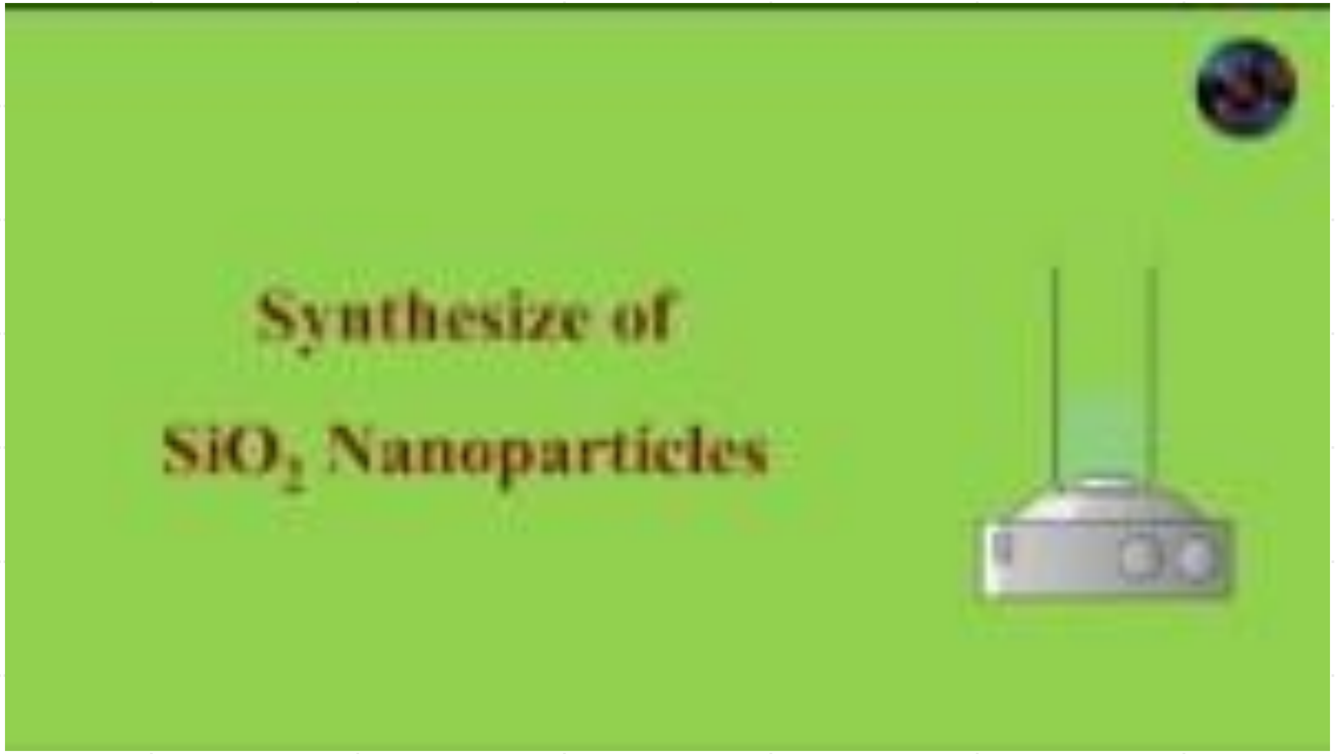
SHRINKAGE

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

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

Sol Gel Method for the synthesis of silica nanoparticles

https://www.youtube.com/watch?v=RCGavOWKYxk



https://www.youtube.com/watch?v=dlCCNMtoJvk
TiO Nanoparticle

Characterization of the sol-gel process

Measuring viscosity changes

The transitions during sol-gel processing

1) Transition from sol to gel

2) Transition from gel to oxide

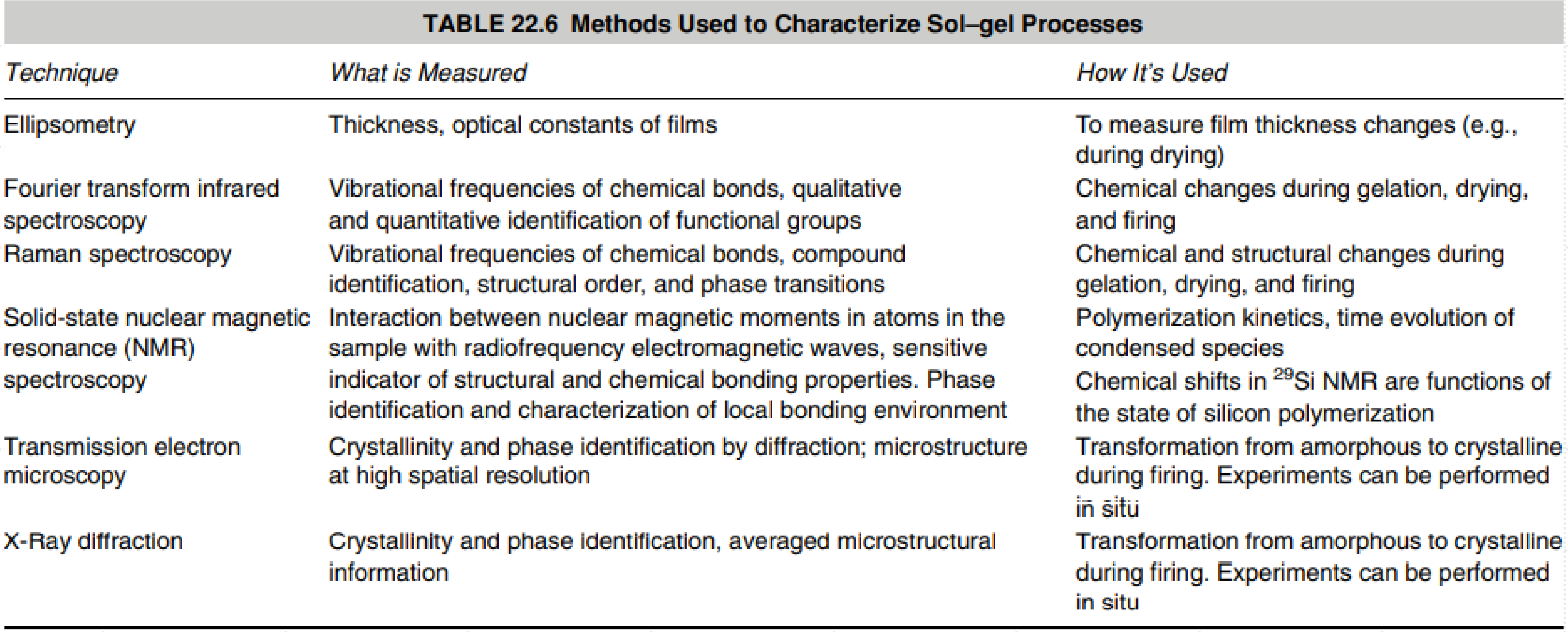


TABLE 22.6 Methods Used to Characterize Sol–gel Processes

Technique	*What is Measured*	*How It's Used*
Ellipsometry	Thickness, optical constants of films	To measure film thickness changes (e.g., during drying)
Fourier transform infrared 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 radiofrequency 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 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 in situ
X-Ray diffraction	Crystallinity and phase identification, averaged microstructural information	Transformation from amorphous to crystalline during firing. Experiments can be performed in situ

Powders, coating, fibers, crystalline/ glass?

Powder- Can make very small particles & control the composition

Bioactive glass powders, with a composition of SiO_2–CaO–P_2O_5

Coatings—The sol is a viscous liquid & can be applied to a substrate by spinning

1) TiO_2-based antiglare coatings on glass

2) Coat steel with alumina to improve wear resistance

Crystalline or glass?

High-purity porous silica glass for filtration

Fibers— Can pull a thread out that is liquid & dry it, coat it

SiO_2 fibers used for space shuttle tiles

Powders

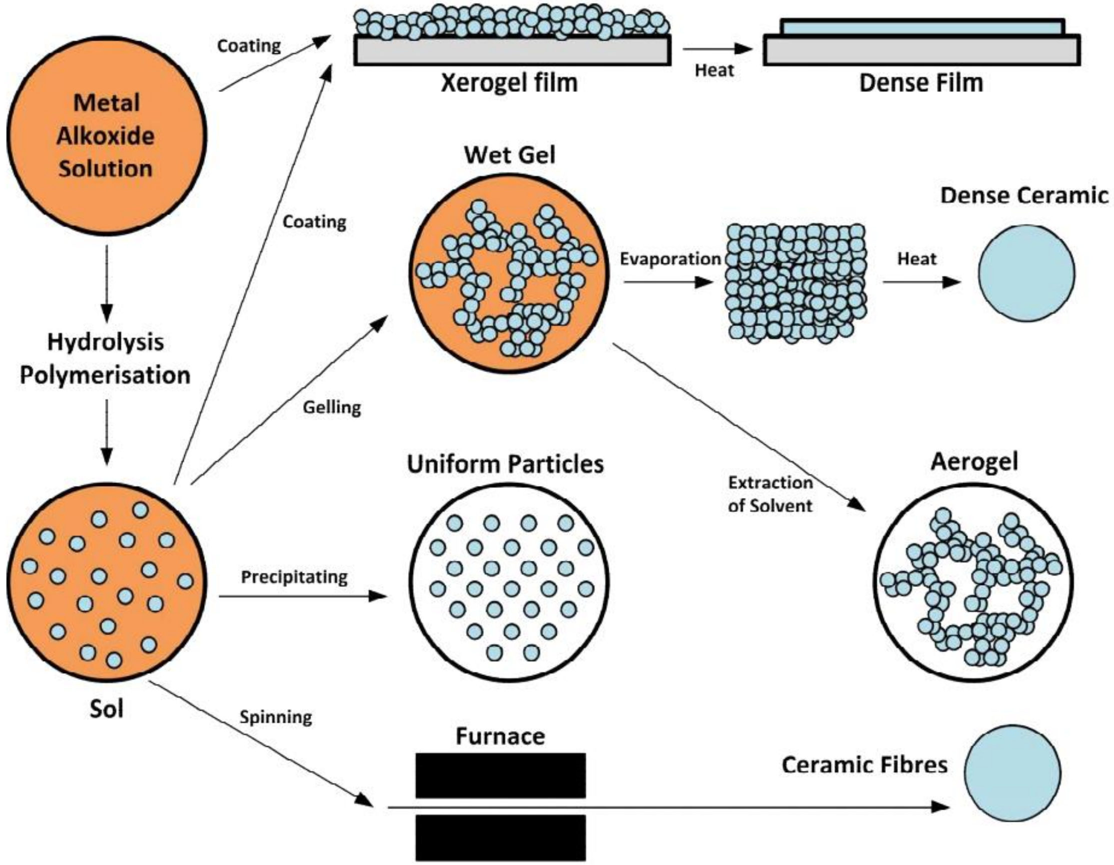
- Powders obtained via a sol–gel process using **metal alkoxides**/ combination of **metal alkoxides & metal salts.**
  - The mixing of the constituents is achieved at a molecular level
  - The powders are chemically **homogeneous**
- Powders produced by the sol–gel method are usually **amorphous.**
- **High surface area**, allows them to be **sintered to nearly full density** at **lower temperatures** than are normally required when the particles have been made by other techniques.
- Example: **Gel-derived mullite powders** can be sintered to full density

Coating

- 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:
    - substrate remains stationary, & the liquid is lowered
- Spinning is widely used for applying sol–gel coatings.
- 1 particular application is to produce thin coatings of PZT for micro-electro-mechanical systems (MEMS).
- Alkoxide-derived coatings are used for both
  - antireflective layers on glass substrates
  - solar reflecting coatings on flat glass

The sol-gel coating process

- Therefore, usually consists of 4 steps:
    - The desired colloidal particles are dispersed in a liquid to form a sol.
    - The deposition of sol solution to produce 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.



- The advantages of forming coatings via sol–gel reactions:
  - Large areas
  - Uniform composition
  - Conformal coating of irregularly shaped substrates (fibers)
  - High purity
  - Microstructural control
    - pore volume (0–65%), pore size (<0.4 to >5.0 nm), & surface area (<1 to 250 m^2/g)
  - Less expensive than vapor-phase processes (chemical vapor deposition & sputtering)

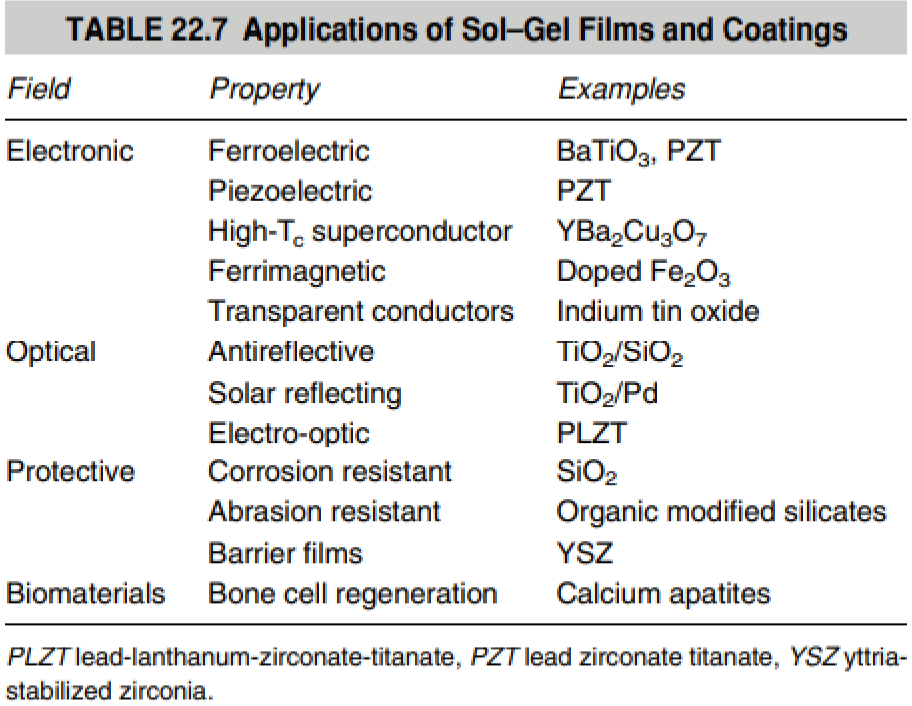


TABLE 22.7 Applications of Sol–Gel Films and Coatings

Field	*Property*	*Examples*
Electronic	Ferroelectric	$BaTiO_3$, PZT
	Piezoelectric	PZT
	High-T_c superconductor	$YBa_2Cu_3O_7$
	Ferrimagnetic	Doped Fe_2O_3
	Transparent conductors	Indium tin oxide
Optical	Antireflective	TiO_2/SiO_2
	Solar reflecting	TiO_2/Pd
	Electro-optic	PLZT
Protective	Corrosion resistant	SiO_2
	Abrasion resistant	Organic modified silicates
	Barrier films	YSZ
Biomaterials	Bone cell regeneration	Calcium apatites

PLZT lead-lanthanum-zirconate-titanate, *PZT* lead zirconate titanate, *YSZ* yttria-stabilized zirconia.

Ceramic fiber

- Fibers can be drawn directly from viscous sols
  - made by acid-catalyzed hydrolysis using low H_2O:M ratios.
- At viscosities greater than ~1 Pas, the sol is sticky; and the fiber can be produced by forcing the sol through a spinnerette.
- The spinnerette can be rotated to produce a yarn. This process is used commercially to produce polymer fiber
- **Applications for sol–gel** derived fibers include:
  - Reinforcement in composites
  - Refractory textiles
  - High-temperature superconductors
- **Examples of fibers** produced by sol–gel:
  - SiO_2
  - SiO_2–TiO_2 (10–50 mol% TiO_2)
  - SiO_2–Al_2O_3 (10–30 mol% Al_2O_3)
  - SiO_2–ZrO_2 (10–33 mol% ZrO_2)
  - SiO_2–Na_2O–ZrO_2 (25 mol% ZrO_2)

Glasses

- Glasses can be synthesized using the sol–gel process.
- This process allows the possibility of **forming the 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. The advantages that they found were:
  - **Lower melting temperatures** could be used (the gel is already amorphous).
  - It was **not necessary to stir the melt** (the gel is homogeneous).
  - It was found that glasses fabricated **from gels** & those of the same composition made **from oxide powders** had essentially the **same physical properties**.
- 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.
- However, **glass coatings** made by the sol–gel process are still important commercially

Monolithic ceramics

- 2 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 to dry the gel without introducing cracks in the dried body**.
- The advantages of using a sol–gel route compared to conventional ceramic methods
  - working in **uncontaminated conditions** and using **lower temperature**
- 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 when forming powders using this method.

Particle in sol-gel films

- Because the sol–gel films are essentially amorphous in their as-prepared state:
  - **Heat treat them to grow nanoparticles**
  - **Embedded inside an amorphous matrix**
- The amorphous SiO(C) film was produced by **pyrolysis of a sol–gel precursor.**
  - The co-hydrolysis of triethoxysilane & methyldiethoxysilane used the addition of acidic water to produce the xerogel.
  - The xerogel was pyrolyzed at 1,000C for 1 h to produce a **Si-rich glass**.
  - The films were heated for another 10 h and then 100 h to produce the images:

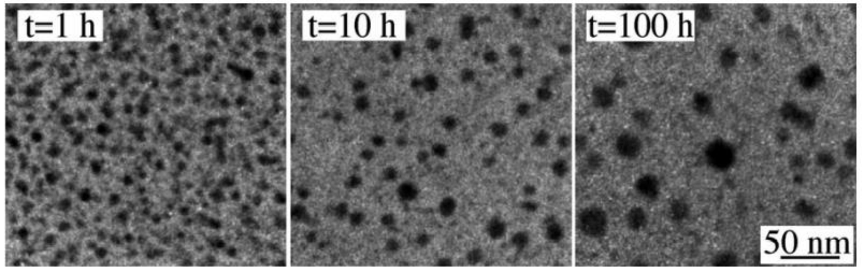


FIGURE 22.10 Use of sol–gel processing to produce Si nanoparticles in a glass matrix. The time indicates the length of the heat treatment.

- The **dark regions** in the images are **O-depleted and Si-rich**.
- High resolution transmission electron microscopy showed that these were **crystalline Si nanoparticles**