

## Chapter 3. Preparative Methods



### 3.1 Introduction

- methods for preparing depend on 1) the composition of the solid  
2) the form in for its proposed use  
e.g) silica glass for fiber optics vs. silica glass for lab using  
↓  
should be much freer of impurities
- not the stable form under normal condition  
e.g) diamond → high pressure
- unusual oxidation state  
e.g)  $\text{CrO}_2$  by the hydrothermal method
- for industrial use → no high temp. method could be favored  
due to the ensuring energy savings.

## Chapter 3. Preparative Methods



- special care in the preparation of solids: - use stoichiometric quantities  
- pure starting materials  
- the reaction has gone to completion  
↳ ∴ not possible to purify a solid once it has formed.
- in this chapter
  - the ceramic method: simply grinding up + heating until they react  
↳ improve methods for the better uniformity of the reaction and  
reducing the reaction temp.
  - alternative method: microwave heating  
: combustion synthesis
  - less well-known method: using high pressures  
: gas-phase reaction
  - to produce pure solid: important in the semiconductor industry  
: a single crystal

## 3.2 High Temperature Ceramic Methods

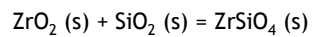


### 3.2.1 Direct heating of solid

#### ■ The Ceramic Method

- The direct method: the simplest and most common way of preparing solid
  - heating together two non-volatile solids which react to form the product
  - industrial + lab
  - whole range of materials → mixed metal oxides, sulfides, nitrides,,

e.g.)  $\text{ZrSiO}_4$  (zircon) → for a high temp. pigment



Direct heating of these @ 1300 °C

- 1) take stoichiometric amount of the binary oxides
- 2) grind them to give a uniform small particle size
- 3) heat in a furnace for several hours in an alumina crucible



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### 3.2.1 Direct Heating of Solids



#### ▪ Disadvantages

- 1) requires a high-temperature ( large input of energy, 500 - 2000 °C)

↳ ∴ high coordination # of reactants (4 - 12)

↳ take a lot of  $E$  to overcome the lattice  $E$  so that a cation can leave its position in the lattice and diffuse to a diff. site

- 2) unstable or decomposition of the phase or compounds at hi-temp.

- usually slow reaction

↳ temp. ↑ → diffusion rate of the ions ↑

- reaction occurs in the solid-state (no higher than m.p.)
- reaction occurs only at the interface through diffusion
- 2/3 of m.p. → gives a reasonable reaction time
- importance of grinding the starting materials

{ a small particle size → { to maximize the surface contact area  
{ well-mixed → { to minimize the diffusion distance



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### 3.2.1 Direct Heating of Solids



- pelletizing the mixed powders in the press

↳ heating → regrinding → heating  
(bring fresh surfaces & speed up the reaction)

but, still the reaction time → in hours

e.g.)  $\text{CuFe}_2\text{O}_4$ : 23 hrs.

- product is usually not homogeneous in composition
- grind → reheat (x several times) for a phase pure product
- trial and errors for the best reaction condition

- heating method: up to 2300 K → resistant heating

(resistant of a metal element

↳ electrical  $E \rightarrow$  heat

: above 2300K → electric arc

: up to 4300 K → carbon dioxide laser

### 3.2.1 Direct Heating of Solids



- containers: 1) withstand high-temp.

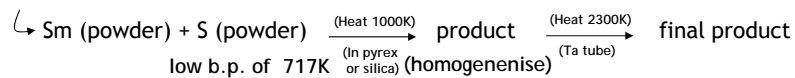
2) sufficient inert not to react

- silica (1430 K)
- alumina (2200 K)
- zirconia (2300 K)
- magnesia (2700 K)
- metals (Pt, Ta,,,) )
- graphite linings

- Sealed Tube Method

: when the products/ reactants are sensitive to air or water or are volatile

e.g.) SmS



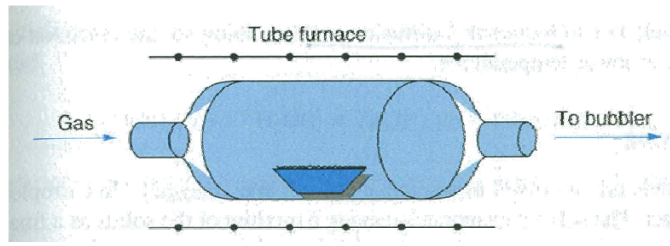
↳ electric current through tube → resistance of the heating

### 3.2.1 Direct Heating of Solids



#### Special atmosphere

- 1) inert gas (Ar): to prevent oxidation to a higher oxidation states
- 2) oxygen: to encourage the formation of high oxidation state
- 3) hydrogen: to produce a low oxidation state



small boat w/ reactant solids

- gas: 1) to expel all the air
- 2) to flow over the reactants during the heating and cooling cycles

### 3.2.2 Reducing the Particle Size and Lowering the Temp.



- In a polycrystalline mixture of solid reactants: particle size  $\rightarrow \sim 10 \mu\text{m}$  :
  - more careful & persistent grinding  $\rightarrow \sim 0.1 \mu\text{m}$
- $\therefore$  diffusion:  $\sim 100$  &  $10,000$  unit cell
- Need better way of bringing the components
  - into more intimate contact or
  - into contact at an atomic level
  - reduce this diffusion path
  - lower temp.

### 3.2.2 Reducing the Particle Size and Lowering the Temp.



#### ■ Spray - Drying

: dissolve the reactant in solvents  
↓  
spray as fine droplet into a hot chamber  
↓  
solvent evaporate  
↓  
leave a mixture of solids as a fine powder  
↓  
product

#### ■ Freeze -Drying

: dissolve the reactants in solvents  
↓  
freeze in liquid nitrogen (-77K)  
↓  
remove the solvent by pumping  
↓  
fine powder

### 3.2.2 Reducing the Particle Size and Lowering the Temp.



#### ■ The Co-Precipitation & Precursor Methods

- precursor: at a simple level - precursor (e.g. nitrates & carbonates) can be used as starting

↳ materials instead of oxides  
↓  
decomposed to the oxides on heating @ low temp.  
↓  
lose gaseous species  
↓  
leave fine & more reactive powders

- co-precipitation: even more intimate mixture of starting materials

↳ metal ions soluble salts as a stoichiometric mixture  
↓  
dissolve  
↓  
precipitate as hydroxides, citrates, formates  
↓  
filtered, dried, heated  
↓  
final product

### 3.2.2 Reducing the Particle Size and Lowering the Temp.



- e.g.) (1) the precursor method: mixing at the atomic level

↳ metals of the desired compound are present in the correct stoichiometry

- $MM'_2O_4$ : salt of an acetate containing M & M' mixing in the ratio 1:2

↓ heat

decompose to the product

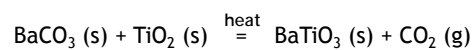
↳ homogeneous products at low-temp

- disadvantage: not always possible to find a suitable precursor

### 3.2.2 Reducing the Particle Size and Lowering the Temp.



- e.g.) (2) Barium titanite ( $BaTiO_3$ ) -ferroelectric materials



need to control grain size → precursor method (oxalate)

- 1) prepare an oxalate of titanium

↳ titanium butoxide + excess oxalic acid solution

↓ hydrolyses

precipitate

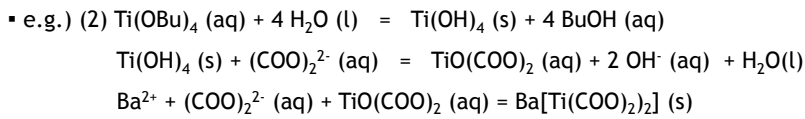
↓ re-dissolves in the excess oxalic acid

+  $BaCl_2$  (aq)

↓

barium titanyl oxalate/ precipitates

### 3.2.2 Reducing the Particle Size and Lowering the Temp.



↓ Heat (920 K)  
 easily decompose to give the oxide



- $\text{MFe}_2\text{O}_4$  (ferrite) can be prepared using the same method.
- crystalline solids containing small particles of large surface area  
 ↳ catalysis, capacitors

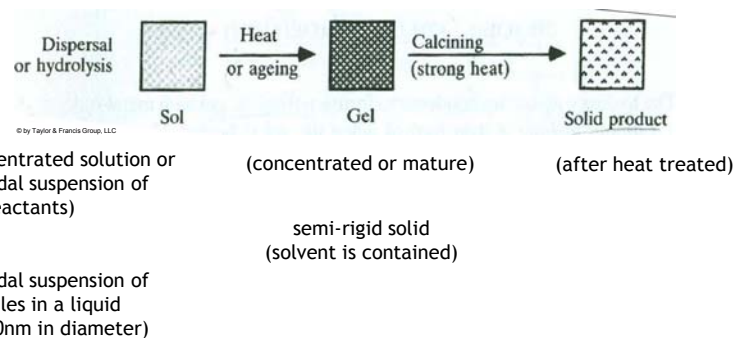
### 3.2.2 Reducing the Particle Size and Lowering the Temp.



#### ■ Sol-Gel Method

- disadvantage of the precipitation method: the stoichiometry of the precipitate may not be exact

- sol-gel: reactants never precipitate out



### 3.2.2 Reducing the Particle Size and Lowering the Temp.

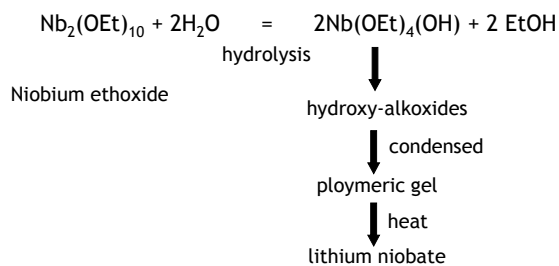


- preparation: 1) dispersal of an insoluble solid or  
(e.g.) dispersal of oxides or hydroxides in water
- 2) addition of a precursor which reacts w/ the solvent to form a colloidal product  
(e.g.) addition of metal alkoxide to water
- sol: treated/left to form a gel by dehydrating and/or polymerizing
- gel: heated - to remove the solvent
  - decomposes anion (alkoxides or carbonates) → oxide
  - rearrangement of the structure
  - crystallization
- advantage of sol-gel: time & temp. can be reduced

### 3.2.2 Reducing the Particle Size and Lowering the Temp.



- Lithium Niobate ( $\text{LiNbO}_3$ )
- : ferroelectric materials → optical switch
- : if ceramic method → { incorrect stoichiometry  
mixture of phase





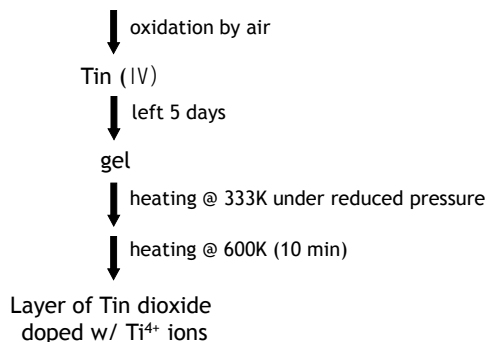
### 3.2.2 Reducing the Particle Size and Lowering the Temp.



#### ■ Doped Tin Dioxide (SnO<sub>2</sub>)

- : oxygen-deficient n-type semiconductor
- : dopant such as Sb<sup>3+</sup> increases the conductivity

↳ for Ti-doped SnO<sub>2</sub>: Ti(OBu)<sub>4</sub> + SnCl<sub>2</sub>·2H<sub>2</sub>O → hydroxy complexes

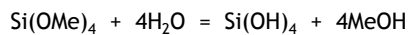


### 3.2.2 Reducing the Particle Size and Lowering the Temp.



#### ■ Silica for optical Fibers

- : should be free of impurities → conventional methods are inadequate
- ↳ sol- gel method (use volatile compd. of silicon)



↓ condense

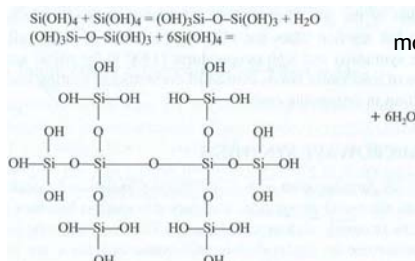
Si-O-Si bonds



more SiO<sub>4</sub> tetrahedra are linked



eventually SiO<sub>2</sub>

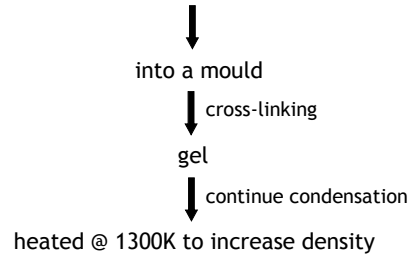


### 3.2.2 Reducing the Particle Size and Lowering the Temp.



#### ■ Silica for optical Fibers

: as condensation reach a certain size → colloidal particles (sol)



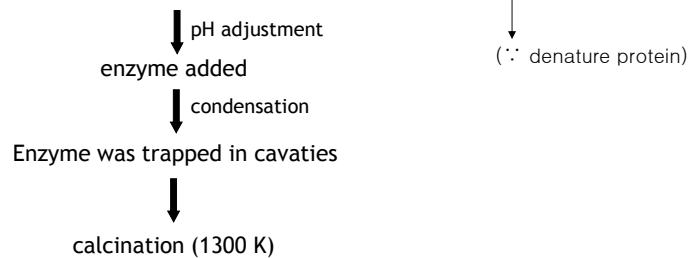
### 3.2.2 Reducing the Particle Size and Lowering the Temp.



#### ■ Biosensor

: often use an enzyme trapped w/ its microenvironment in a silica-gel

sol of silica from  $\text{Si}(\text{OMe})_4$  w/ water (instead of methane)



### 3.3 Microwave Synthesis



- In a liquid or solid: microwave or ions → not free to rotate
  - ↳ heating is not the result of the rotational transition

- acting in two different ways

- 1) conduction heating: charged particle moving by an oscillating electric current

↓  
resistance to their movement → heat

- 2) dielectric heating: no charged particle, but dipole moments

↓  
alignment of the dipole moments by the electric field  
↳ domestic microwave: act on water

### 3.3 Microwave Synthesis



- In solid: don't change alignment of dipole moment instantaneously
  - ↳, but w/ a characteristic time,  $\tau$

↳ if oscillating slow → <sup>same order of  $\tau$</sup>  the dipole can follow  
↓ solid absorb microwave radiation  
dipole realignment → heat (small heating effect)

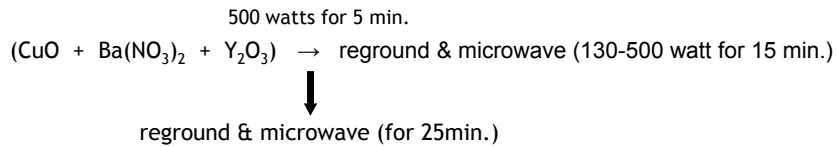
↳ at least one component must absorb microwave radiation

### 3. 3. 1 The High Temperature Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$



: using a conventional ceramic method → 24 hrs.

: microwave method → 2hrs.



- CuO: microwave active

↳ 5-6 g, 500 watt, 30 min. → 1074 K

other examples)  $\text{ZnO}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MnO}_2$ ,  $\text{PbO}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{WO}_3$ ...

- CaO: less active

5-6 g, 500 watt, 30 min. → 356K

other examples)  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{SnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$

weak point of microwave synthesis: chemical inhomogeneity, reaction temp. increases

strong point of microwave synthesis: less problem w/ cracking

### 3. 4 Combustion Synthesis



: self-propagating high temp. Synthesis

- alternative route to the ceramic method

↳ repeated heating and grinding is required!!!

- exothermic/even explosive reactions to maintain a self-propagating high temp.

→ borides, nitrides, oxides, silicides, intermetallics, ceramics

- mix → pellet → ignite (laser, electric arc, heating coil) → synthetic wave → ~ 3000 K during the reaction

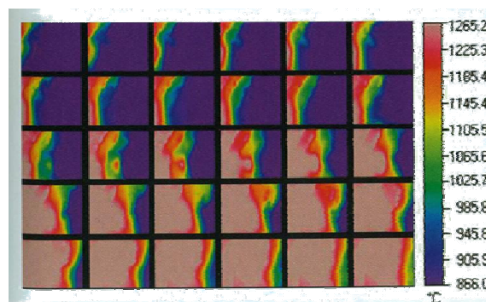


Fig.3.4

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### 3. 4 Combustion Synthesis



- ball milling: Russia, Korea, Spain use
  - ↳ fast, high-purity, economical
- e.g.) Hydrides (e.g.  $\text{MgH}_2$ ) for hydrogen storage
- Borides (e.g.  $\text{TiB}_2$ ) for abrasives and cutting tools
- Carbides (e.g.  $\text{SiC}$  and  $\text{TiC}$ ) for abrasive and cutting tools
- Nitrides (e.g.  $\text{Si}_3\text{N}_4$ ) for high strength, heat resistant ceramic
- ...