

# **Direct Reactions of Solids**

**"HEAT-AND-BEAT" or "SHAKE-AND-BAKE"  
Solid state reactions**

**At least one of the reactants and one of the products are solid**

**Reactions in a lattice of atoms**

**Atomic mobility**

**High temperatures**

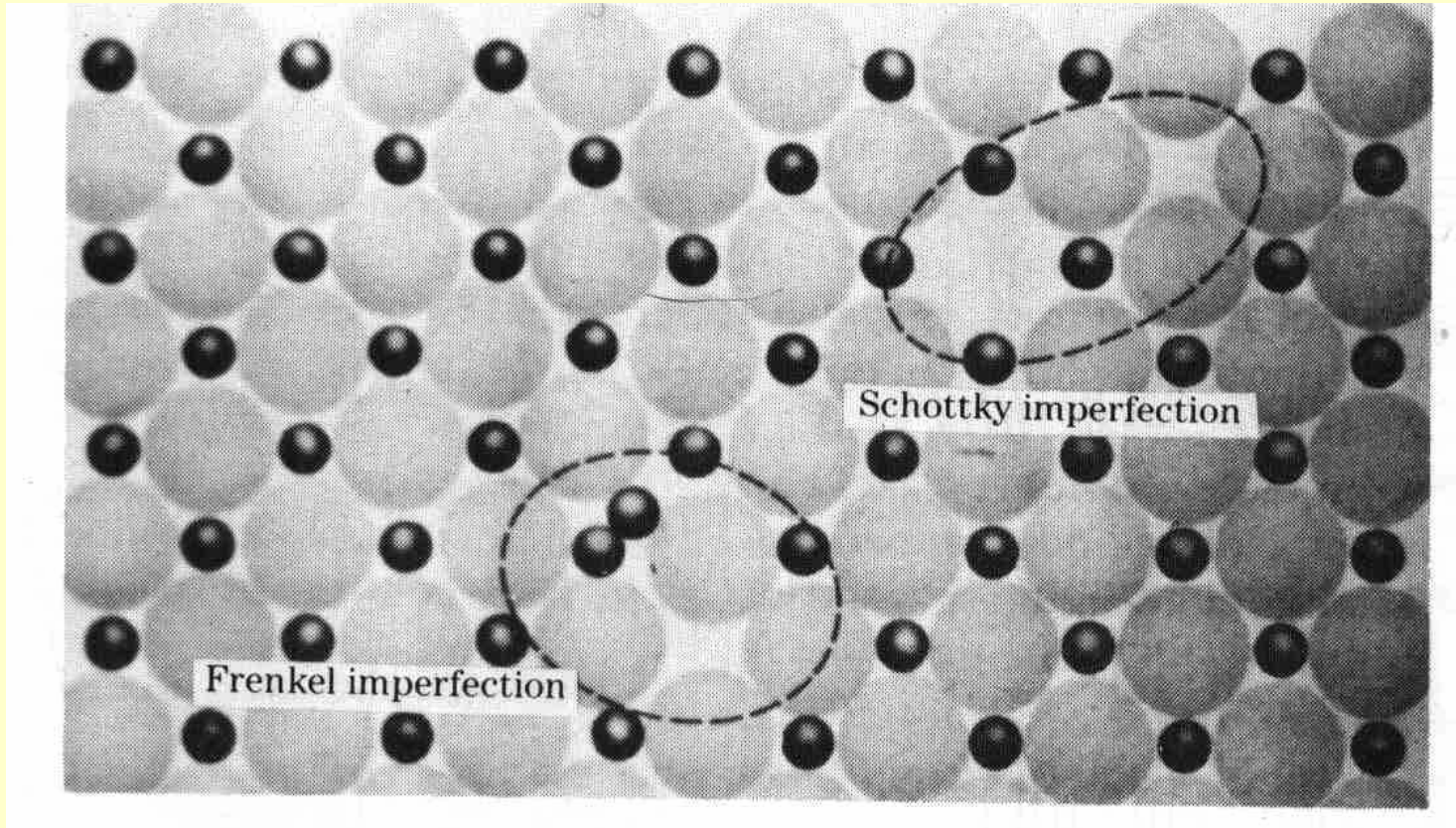
**No mobility without defects – perfect crystal = no chemistry**

**Reactions on the interphase between phases**

**Microstructure**

**Diffusion controls the reaction rate**

# Point Defects

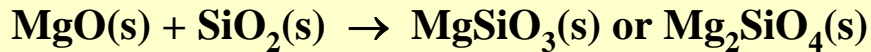
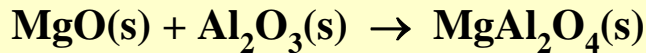
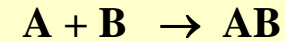


**Schottky-imperfection: vacancy, missing ions moved to the surface**

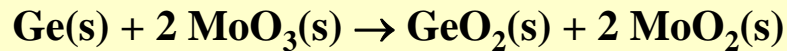
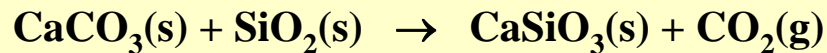
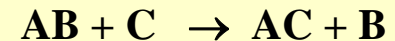
**Frenkel-imperfection: vacancy, missing ions on interstitial positions**

# Reaction Types

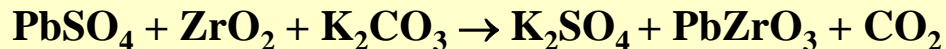
**Solid - solid synthesis - addition**



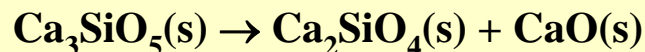
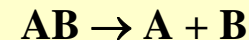
**Solid - solid synthesis – exchange, metathesis**



**Solid - solid synthesis – exchange and addition**

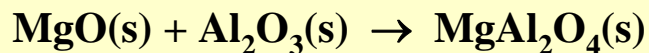
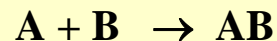


**Solid - solid synthesis - dissociation**

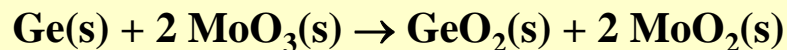
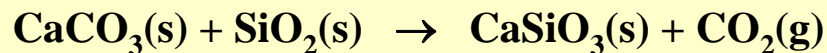
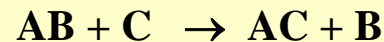


# Reaction Types

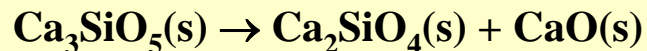
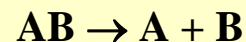
**Solid - solid synthesis - addition**



**Solid - solid synthesis – exchange, metathesis**

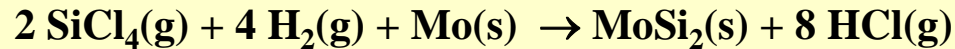
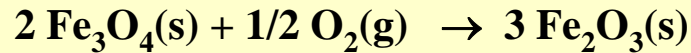


**Solid - solid synthesis - dissociation**



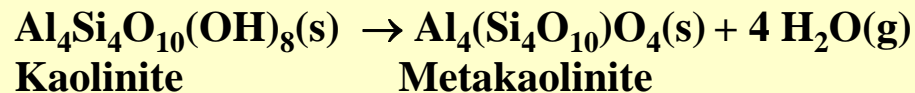
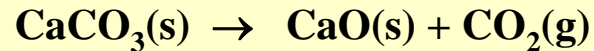
# Reaction Types

**Solid – gas synthesis**                      **A + B → AB**



**High temperature corrosion of metals in air**

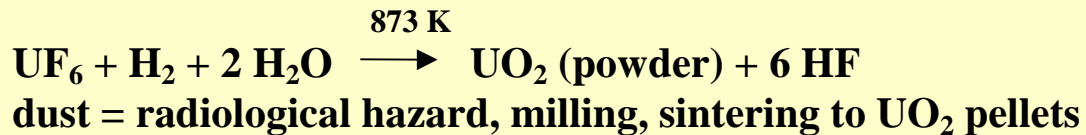
**Solid – gas dissociation**                      **AB → A + B**



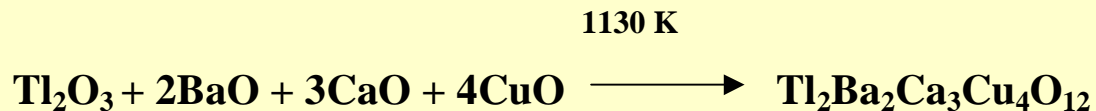
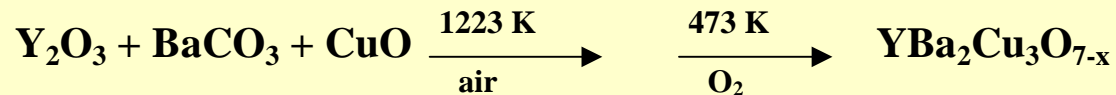
# Direct Reactions of Solids

## Other Examples

### Oxides



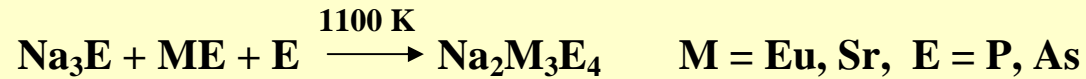
### YBCO 123 Superconductor (1987)



# Direct Reactions of Solids

Other classes than oxides

## Pnictides

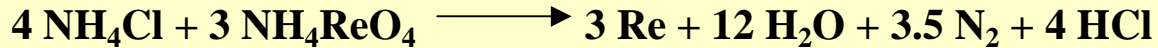
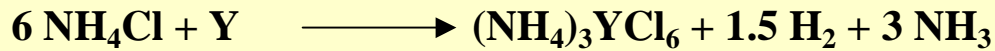
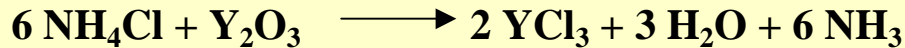
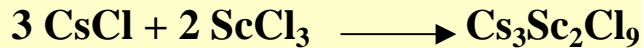


## Metals

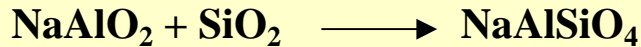


# Direct Reactions of Solids

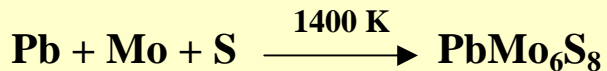
## Chlorides



## Aluminosilicates



## Chalcogenides



**Chevrel phases**

$(\text{ M}_x\text{ Mo}_6\text{ X}_8, \text{ M} = \text{ RE, Sn, Pb, Cu, X} = \text{ S, Se, Te})$



# **Direct Reactions of Solids**

## **Powder Mixing Method**

**Precise weighing for exact stoichiometry**

**Mixing (components, dopants, additives)**

**Milling or grinding (ball mill, mortar)**

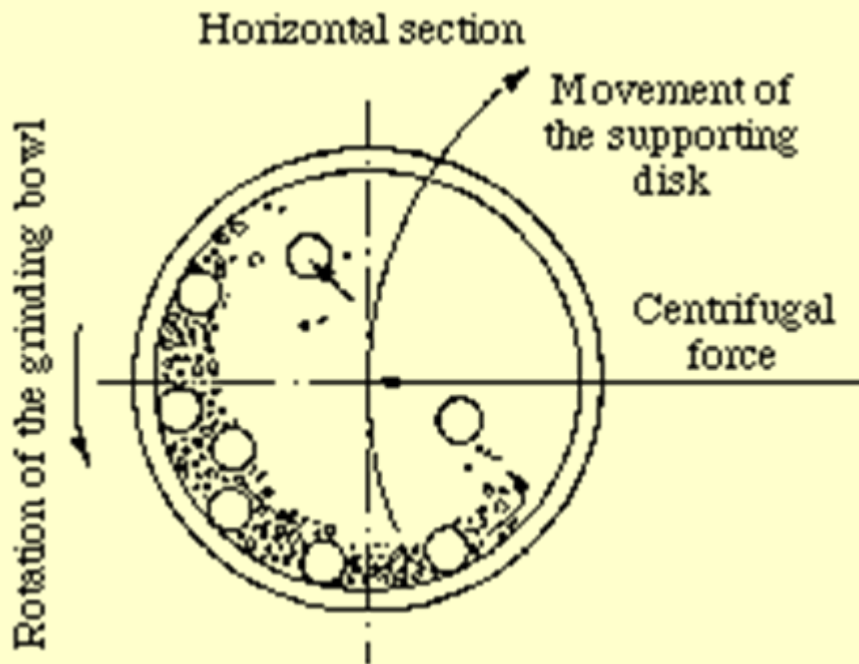
**Compaction (pelleting, organic binders)**

**Calcination @ high temperature ( $> 1000\text{ }^{\circ}\text{C}$ )**

**Firing/grinding cycles**

# Direct Reactions of Solids

Planetary ball mill



**Rotation speed:** up to 400 rpm  
**Milling jars:** alumina, YSZ, tungsten carbide, agate

Planetary ball mill

Rotation and counter-wise spinning





**Atritor mill**

# Compaction - Pressing



**Hydraulic Uniaxial Press**

*Maximum pressure: 120 MPa*



**Warm Isostatic Press**

*Max. pressure: 400 MPa*

*Max. temperature: 80 °C*

*Volume: 2,5 l*



**Hot press**

*Max. temperature: 1250 °C*

*Max. pressure: 100 MPa*

*Max. diameter: 25 mm<sup>2</sup>*

# Calcination



## **Tube Furnace**

in air and in controlled atmosphere

*Maximum temperature: 1450 °C or 1600 °C*

*Furnace-tube diameter: up to 75 mm*



## **Vacuum Furnace**

in vacuum or Ar, N<sub>2</sub>, O<sub>2</sub> atmosphere

*Maximum temperature: 1200 °C*

*Chamber Dimensions: 150x200x250 mm<sup>3</sup>*

# Direct Reactions of Solids

## Advantages

- simple equipment**
- low cost and easily accessible starting materials**
- well studied**

## Disadvantages

- impurities from grinding (Fe, Cr, ...)**
- broad particle size distribution**
- some phases unstable @ high T, decomposition**
- formation of undesirable phases**
- slow formation, diffusion, long reaction times**
- large grain size**
- poor chemical homogeneity:**
  - poor mixing of large crystallites**  
**(milling lower limit ~ 100 nm)**
  - volatility of some components (Na<sub>2</sub>O, PbO, ...)**
  - uptake of ambient gas (O<sub>2</sub> in superconductors)**

# Direct Reactions of Solids

## Experimental Considerations

### ☛ Reagents

**Drying, fine grain powders for maximum SA, surface activation (Mo + H<sub>2</sub>), in situ decomposition (CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>, O<sub>2</sub><sup>2-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) for intimate mixing, precursor reagents, homogenization, organic solvents, grinding, ball milling, ultrasonication**

### ☛ Container Materials

**Chemically inert crucibles, boats, ampoules (open, sealed, welded)**

**Noble metals: Au, Ag, Pt, Ni, Rh, Ir, Nb, Ta, Mo, W**

**Refractories: alumina, zirconia, silica, BN, graphite**

**Reactivities with containers at high temperatures needs to be carefully evaluated for each system, pelleting minimizes contact with container, sacrificial pellet**

## Properties of Common Container Materials

Material	Maximum Working Temp., K	Thermal Shock Resistance	Thermal Conductivity, $W\ m^{-1}\ K^{-1}$	Coefficient of Linear Expansion $\times 10^6, K^{-1}$	Other Properties
Pyrex	770	GOOD	1.13	3.2	Permeable to air at high T
CaF <sub>2</sub>	1420	FAIR	-	24	-
SiO <sub>2</sub>	1530	VERY GOOD	1.38 - 2.67	0.4 - 0.6	Permeable to air at high T, devitrification above 1670 K
Si <sub>3</sub> N <sub>4</sub>	1770	FAIR	10 - 33	6.4	-
Pt	1950	VERY GOOD	73	9.11	Plastic at high T
BN	1970	VERY GOOD	5.02	0.2-3	Oxidizes in air above 970 K
Vitreous C	2070	GOOD	4.19 - 8.37	2-3.5	Oxidizes in air above 900 K
Al <sub>2</sub> O <sub>3</sub>	2170	FAIR	35 - 39	8	Reacts with metals above 1800 K
AlN	2270	FAIR	50 - 170	5.7	-
BeO	2570	GOOD	230	8.4	Reacts with metals above 1800 K
ZrO <sub>2</sub>	2570	GOOD	1.97	4.5	-
Ir	2600	VERY GOOD	148	6.8	-
MgO	2870	FAIR	37.7	25	High vapor pressure
ThO <sub>2</sub>	3070	FAIR	4.19	6	Reacts with C above 2290 K



# Direct Reactions of Solids

## ☛ Heating Program

Slow or fast heating, cooling, holding at a set point temperature

**Tammann's rule:  $T_r > 2/3 T_m$**

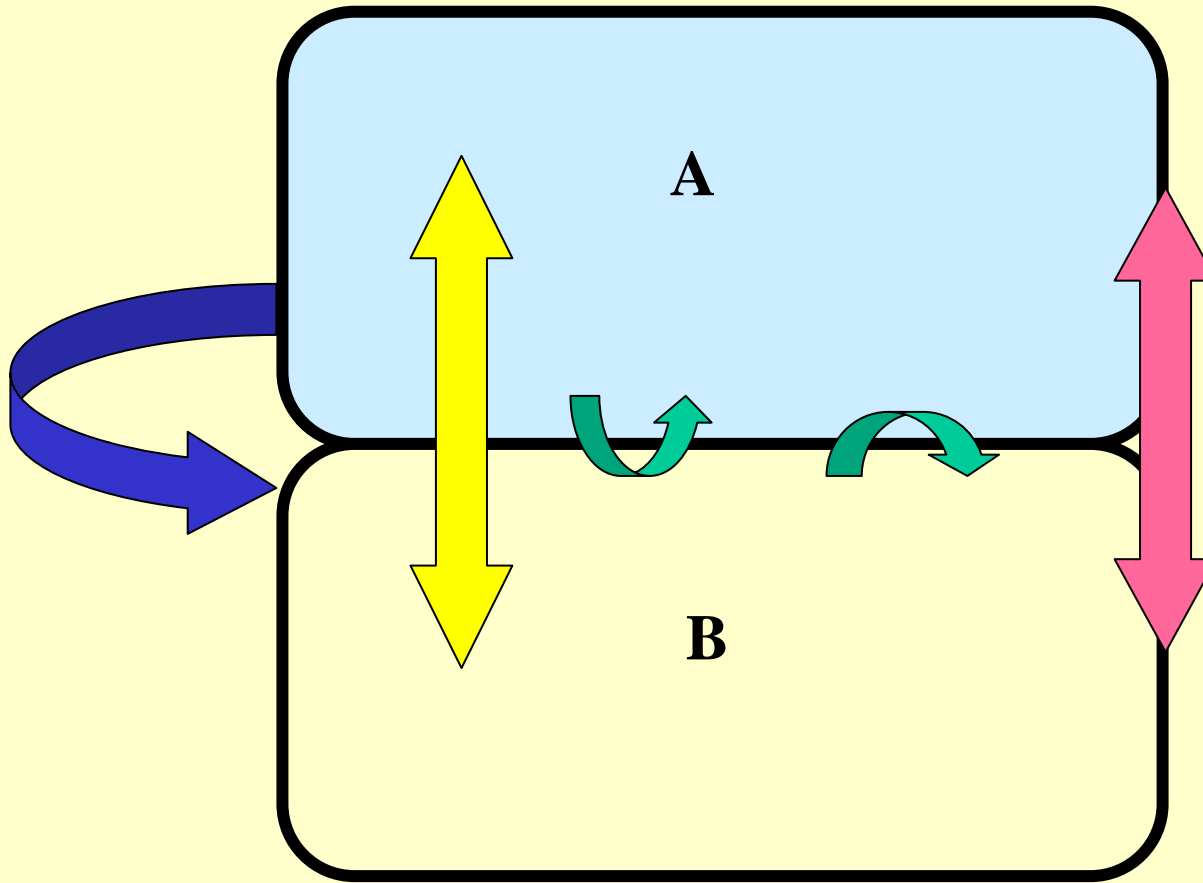
Furnaces, RF, microwave, lasers, ion or electron beam


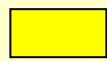
## ☛ Prior decomposition



Initial cycle at lower temperature to prevent spillage or volatilization, frequent cycles of heating, cooling, grinding, boost SA. Overcoming sintering, grain growth, fresh surfaces. Pelleting, hot pressing, enhanced contact area increases rate and extent of reaction

☛ Controlled atmosphere (oxidizing, reducing, inert) or vacuum. Unstable oxidation states, preferential component volatilization if T too high, composition dependent atmosphere ( $O_2$ ,  $NH_3$ ,  $H_2S$ , ...)

# Reaction Paths between Two Solids

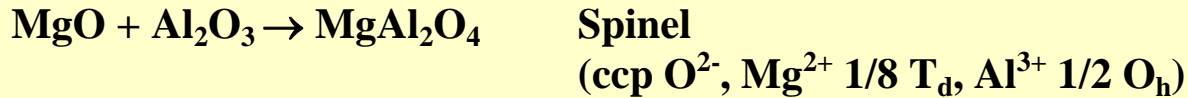


 gas phase diffusion  
 volume diffusion

 interface diffusion  
 surface diffusion

# Direct Reactions of Solids

Model reaction, well studied:



Single crystals of precursors, interfaces between reactant grains

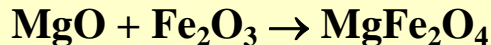
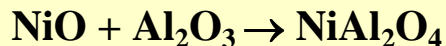
On reaction, new reactant-product  $\text{MgO}/\text{MgAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4$  interfaces are formed

Free energy negative, favors reaction but extremely slow at normal temperatures (several days at 1500 °C)

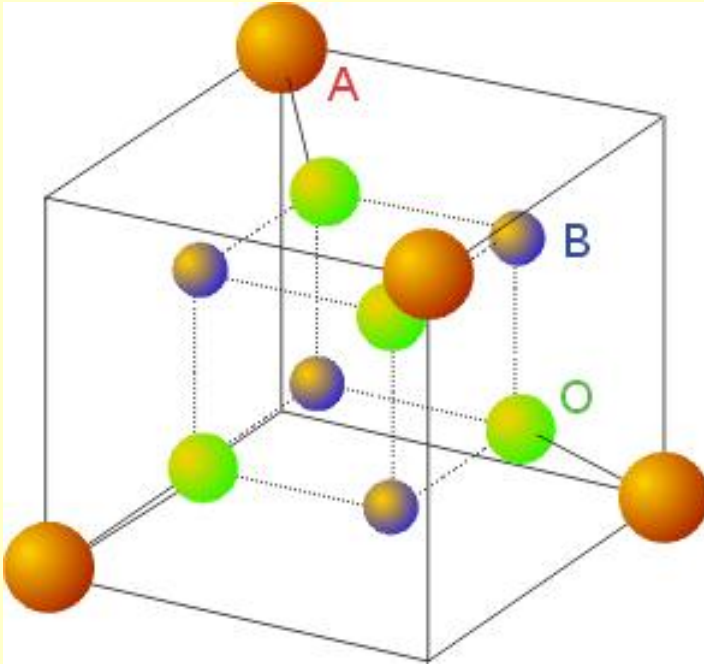
Interfacial growth rates 3 : 1

Linear dependence of interface thickness  $x^2$  versus  $t$

Easily monitored rates with colored product at interface,  $T$  and  $t$



# The Spinel Structure: $AB_2O_4$



fcc array of  $O^{2-}$  ions, A occupies 1/8 of the tetrahedral and B 1/2 of the octahedral holes

→ normal spinel:  $AB_2O_4$

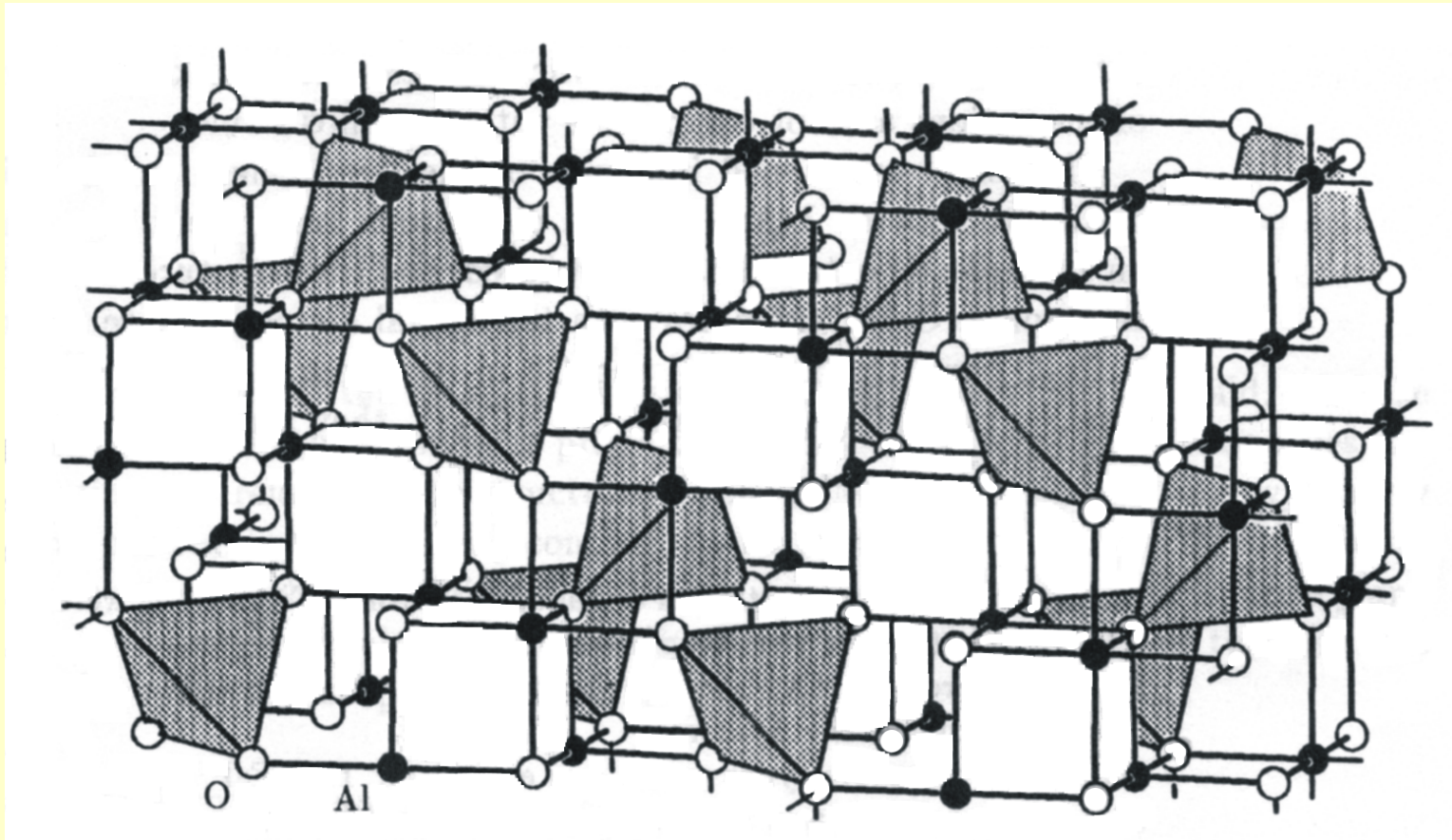
$Co_3O_4$ ,  $GeNi_2O_4$ ,  $WNa_2O_4$

→ inverse spinel:  $B[AB]O_4$

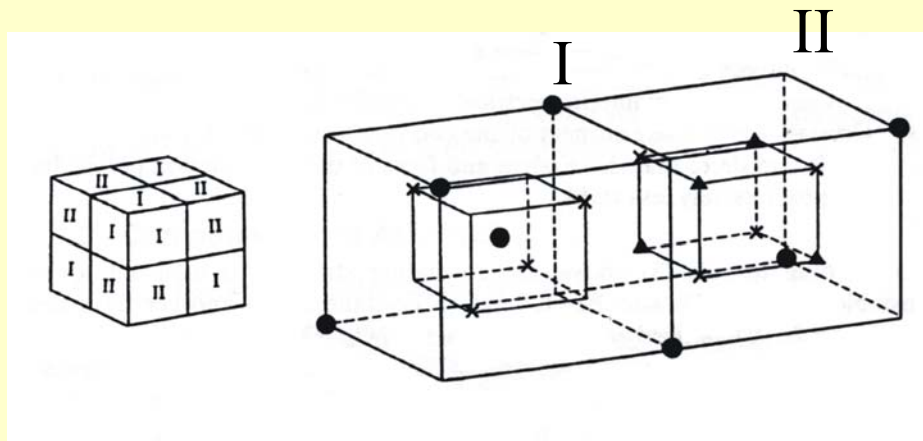
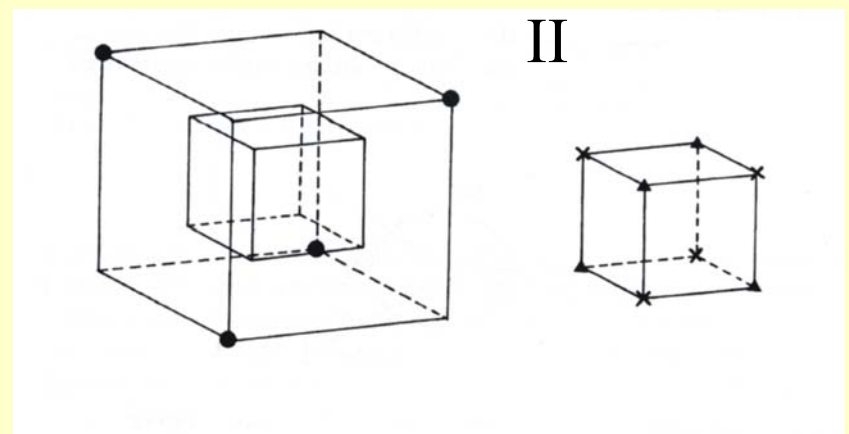
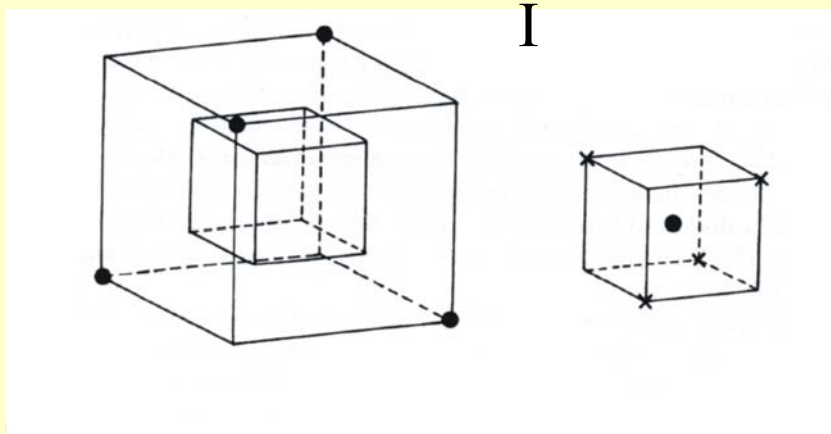
$Fe_3O_4$ :  $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ ,  $TiMg_2O_4$ ,  $NiLi_2F_4$

→ basis structure for several magnetic materials

# The spinel structure: $\text{MgAl}_2\text{O}_4$



# The spinel structure: $\text{MgAl}_2\text{O}_4$



• = Mg

x = O

▲ = Al

# Direct Reactions of Solids

Why is nucleation, mass transport so difficult?

MgO ccp  $O^{2-}$ ,  $Mg^{2+}$  in  $O_h$  sites

$Al_2O_3$  hcp  $O^{2-}$ ,  $Al^{3+}$  in  $2/3 O_h$  sites

$MgAl_2O_4$  ccp  $O^{2-}$ ,  $Mg^{2+}$   $1/8 T_d$ ,  $Al^{3+}$   $1/2 O_h$

- ☛ Structural differences between reactants and products, major structural reorganization in forming product spinel
- ☛ Making and breaking many strong bonds (mainly ionic), high temperature process as  $D(Mg^{2+})$  and  $D(Al^{3+})$  large for small highly charged cations
- ☛ Long range counter-diffusion of  $Mg^{2+}$  and  $Al^{3+}$  cations across interface, usually RDS (= rate determining step), requires ionic conductivity, substitutional or interstitial hopping of cations from site to site to effect mass transport
- ☛ Nucleation of product spinel at interface, ions diffuse across thickening interface, oxide ion reorganization at nucleation site
- ☛ Decreasing rate as spinel product layer thickens

Parabolic rate law:  $dx/dt = k/x$

$$x^2 = kt$$

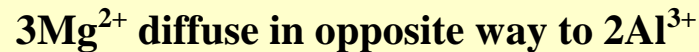
# Direct Reactions of Solids

## Kinetics:

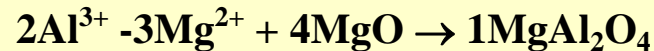
Linear  $x^2$  vs.  $t$  plots observed

$\ln k$  vs.  $1/T$  experiments provide Arrhenius activation energy  $E_a$  for the solid-state reaction

Reaction mechanism requires charge balance to be maintained in the solid state interfacial reaction:



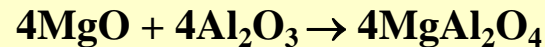
MgO/MgAl<sub>2</sub>O<sub>4</sub> Interface:



MgAl<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> Interface:



Overall Reaction:

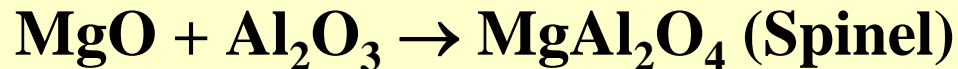


the **Kirkendall** Effect : RHS/LHS growth rate of interface = 3/1

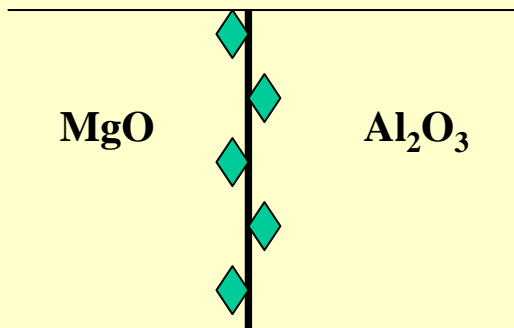


# Direct Reactions of Solids

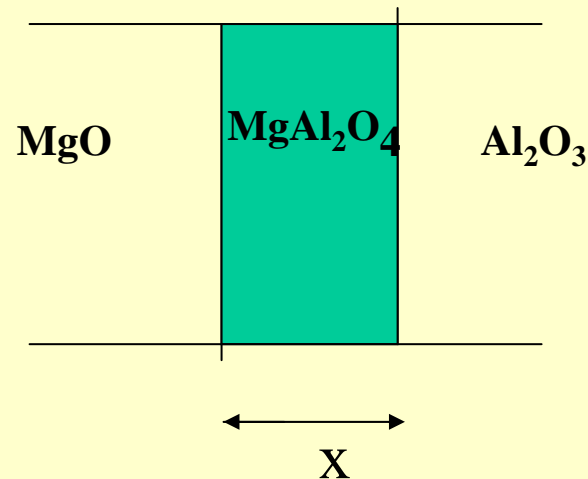
Model for a classical solid-solid reaction (below melting point !):  
Planar interface between two crystals



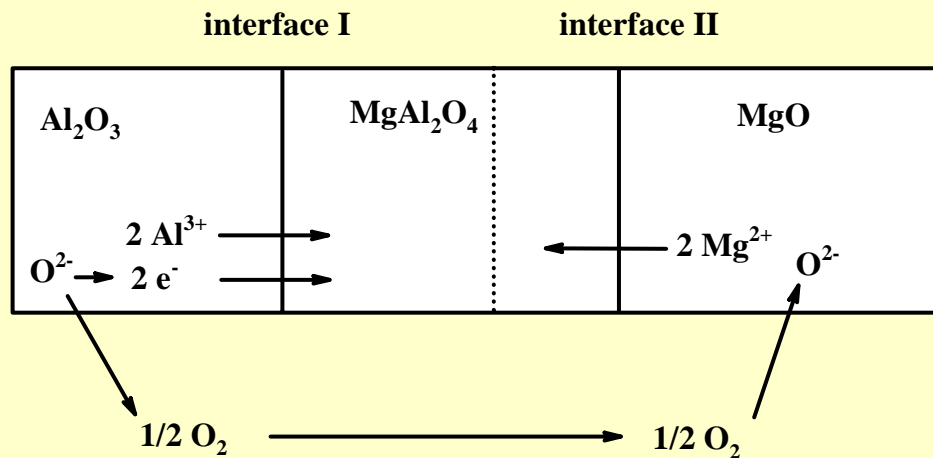
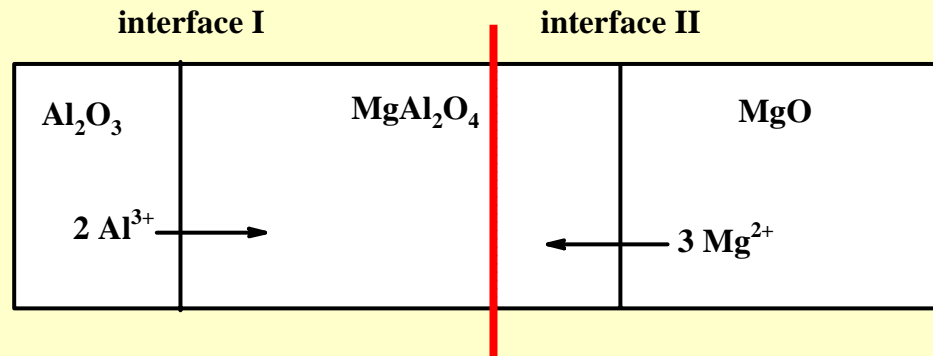
Phase 1:  
nucleation



Phase 2:  
growth of nuclei



# Reaction Mechanism



# Direct Reactions of Solids

Thermodynamic and kinetic factors

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

General kinetic expression

$$g(\alpha) = \int k(T) dt \quad g(\alpha) = k(T) t$$

$$\int \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int k(T) dt$$

$\alpha$  – the molar fraction of the reacted product at a time  $t$

$k(T)$  – the rate constant of the process

Experimentally evaluate  $\alpha$  at different  $t$

Fit data into a  $g(\alpha) = k(T) t$  expression to obtain  $k(T)$  and the type of mechanism model

$$\alpha = \frac{P_t - P_0}{P_e - P_0}$$

$P_t$  = the value of a property at time  $t$

$P_0$  = the value of a property at the beginning

$P_e$  = the value of a property at the end

$$\alpha = 0 - 1$$

e.g.  $P_t$  = mass loss,  $x$ , .....

# Direct Reactions of Solids

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

$$\int \frac{d\alpha}{f(\alpha)} = \int k(T)dt$$

$$g(\alpha) = \int k(T) dt$$

$$g(\alpha) = k(T) t$$

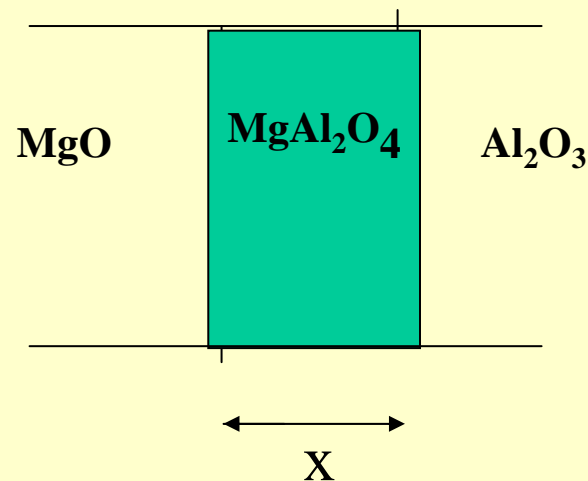
**Decreasing reaction rate as spinel product layer (x) thickens**

**Here  $\alpha = x$**

**Parabolic rate law:**

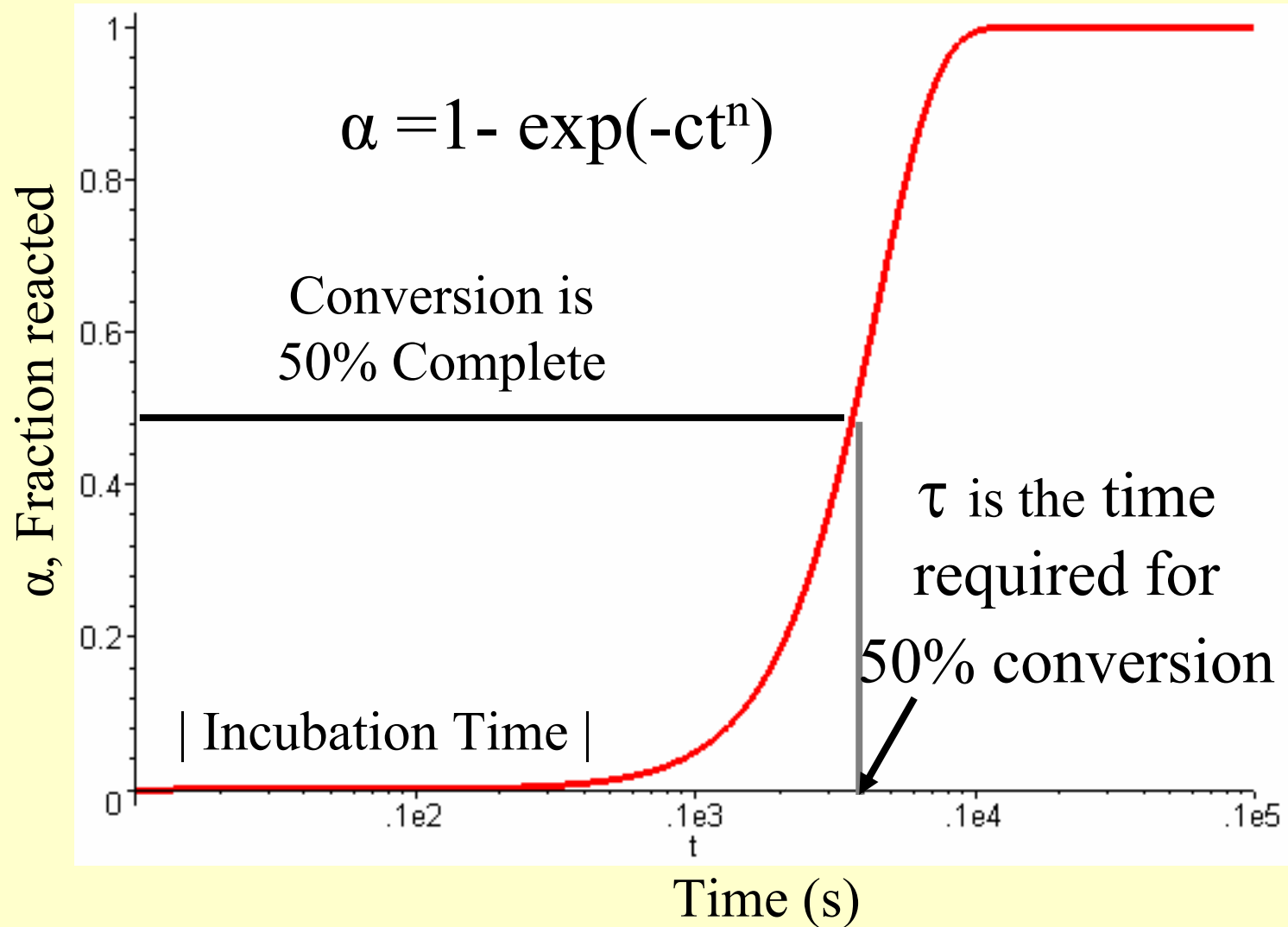
$$dx/dt = k/x$$

$$x^2 = kt$$



<b>Mechanism model</b>	<b><math>g(\alpha)</math></b>
<b>Diffusion controlled</b>	
One-dimensional	$\alpha^2$
Two-dimensional	$\alpha + (1 - \alpha) \ln (1 - \alpha)$
Three-dimensional, Jander	$[1 - (1 - \alpha)^{1/3}]^{2/3}$
Three-dimensional, Ginstling	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$
Three-dimensional, Carter	$(1 + \alpha)^{2/3} + (1 - \alpha)^{2/3}$
<b>Growth controlled</b>	
General	$[1 - (1 - \alpha)^{1-n}]$
First order, $n = 1$	$[- \ln (1 - \alpha)]$
<b>Nucleation controlled</b>	
Power law	$\alpha^{1/n}$
<b>Nucleation-Growth controlled</b>	
Avrami	$[- \ln (1 - \alpha)]^{1/2}$
Erofeev	$[- \ln (1 - \alpha)]^{1/3}$
Planar boundary	$1 - (1 - \alpha)^{1/2}$
Spherical boundary	$1 - (1 - \alpha)^{1/3}$

# Avrami Plot



# Direct Reactions of Solids

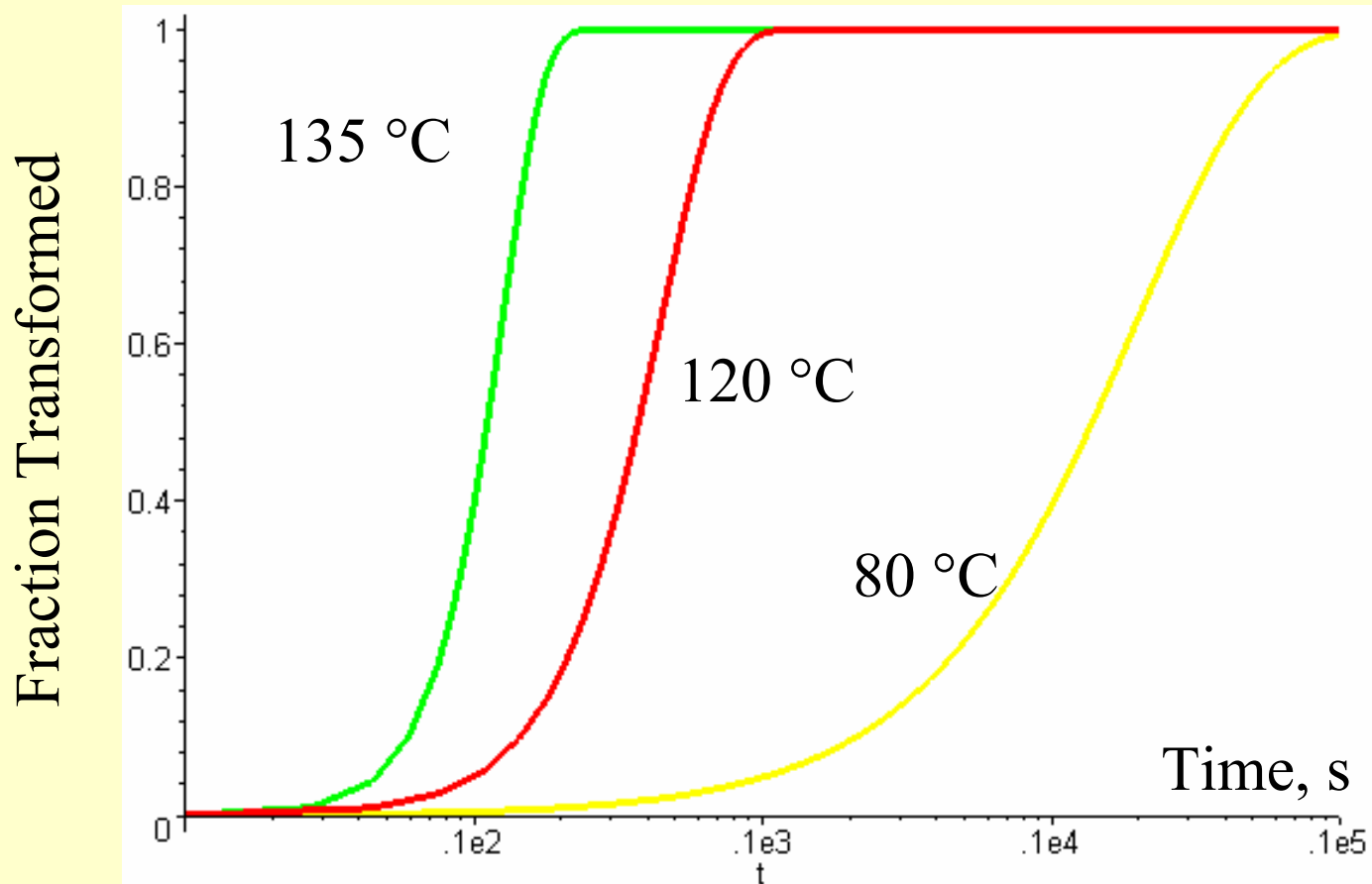
Perform the measurements in a range of temperatures T

use Arrhenius equation to evaluate the activation energy  $E_a$

$$k(T) = k_0 \exp(-E_a/RT)$$

# Direct Reactions of Solids

Perform the measurements in a range of temperatures  $T$   
use Arrhenius equation to evaluate the activation energy  $E_a$   
 $k(T) = k_0 \exp(-E_a/RT)$





# FACTORS INFLUENCING REACTIONS OF SOLIDS

## CONTACT AREA

- ★ Surface area of reactants
- ★ Particle size
- ★ Pelleting, pressing, precursors

## DIFFUSION RATE

- ★ Diffusion rates of atoms, ions, molecules in solids
- ★ Reaction temperature, pressure, atmosphere
- ★ Diffusion length, particle size
- ★ Defect concentration, defect type
- ★ Reaction mechanism

## NUCLEATION RATE

- ★ Nucleation of product phase within the reactant with similar crystal structure
- ★ Epitactic and topotactic reactions
- ★ Surface structure and reactivity of different crystal planes/faces

# Direct Reactions of Solids

## KEY FACTORS IN SOLID STATE SYNTHESIS

**CONTACT AREA and surface area (SA) of reacting solids control:**

→ Rates of diffusion of ions through various phases, reactants and products

→ Rate of nucleation of the product phase

Reaction rate is greatly influenced by the SA of precursors as contact area depends roughly on SA of the particles

**Surface Area (SA) of Precursors**

spherical particles, radius  $r$  [nm], density  $\rho$  [g/cm<sup>3</sup>]

$$SA = A/m = \frac{4\pi r^2}{\frac{4}{3}\pi r^3 \cdot \rho} = 3000/r\rho \quad [m^2/g]$$

# Direct Reactions of Solids

Consider 1 g of a material, density  $1.0 \text{ g/cm}^3$ , cubic crystallites

number of cubes	edge length, cm	SA, $\text{m}^2/\text{g}$
1	1	$6 \cdot 10^{-4}$
$10^9$	$10^{-3}$	0.6
$10^{18}$	$10^{-6}$	600

**Contact area**

not in reaction rate expression for product layer thickness versus time:  $dx/dt = k/x$

**But for a constant product volume**

$x \propto 1/A_{\text{contact}}$  and furthermore  $A_{\text{contact}} \propto 1/d_{\text{particle}}$

**Thus particle sizes and surface area inextricably connected and obviously  $x \propto d$  and SA particle size affect the interfacial thickness**

# Direct Reactions of Solids

**These relations suggest some strategies for rate enhancement in direct reactions:**

**→ Hot pressing densification of particles**

**High pressure squeezing of reactive powders into pellets (700 atm)  
Pressed pellets still 20-40% porous. Hot pressing improves densification**

**→ Atomic mixing in composite precursor compounds**

**→ Coated particle mixed component reagents, corona/core precursors**

**→ Decreasing particle size, nanocrystalline precursors**

**Aimed to increase interfacial reaction area  $A$  and decrease interface thickness  $x$ , minimizes diffusion length scales**

$$dx/dt = k/x = k'A = k''/d$$

# DIRECT REACTION OF SOLIDS

## DIFFUSION RATE

Fick's law  $J = -D(dc/dx)$

$J$  = flux of diffusing species,  $\#/cm^2s$

$(dc/dx)$  = concentration gradient,  $\#/cm^4$

$D$  = diffusion coefficient,  $cm^2/s$ , for good reaction rates  $> 10^{-12}$

$D$  increases with temperature, rapidly as you approach the melting point

**Tammann's rule: Extensive reaction will not occur until the temperature reaches at least 2/3 of the melting point of one or more of the reactants.**

Factors influencing cation diffusion rates:

→ Charge, mass and temperature

→ Interstitial versus substitutional diffusion

→ Number and types of defects in reactant and product phases

All types of defects enhance diffusion of ions

(intrinsic or extrinsic, vacancies, interstitials, lines, planes, dislocations, grain boundaries)

# Diffusion

Diffusion coefficients show an exponential temperature dependence (Arrhenius type):

$D_{\infty}$ :  $D$  for  $T \rightarrow \infty$ ,

$Q$ : activation energy of diffusion

$R$ : the gas constant

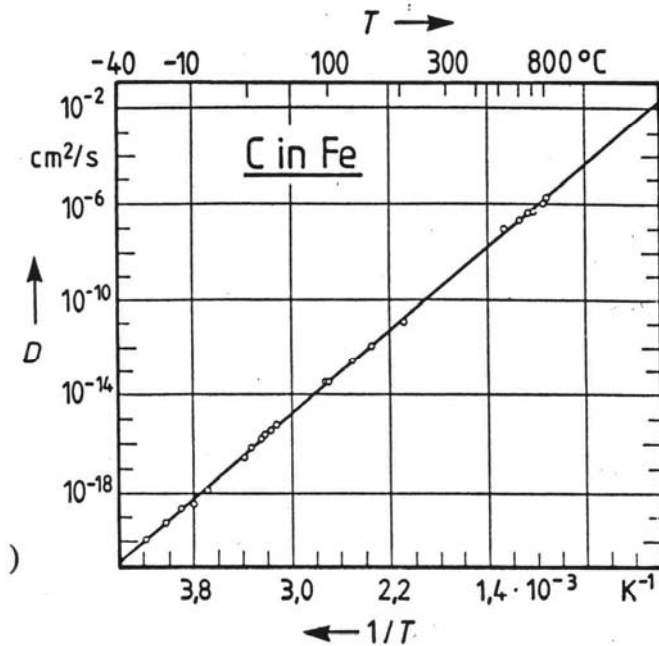
$$D = D_{\infty} \exp\left(-\frac{Q}{RT}\right)$$

The logarithmic representation of  $D$  versus  $1/T$  is linear

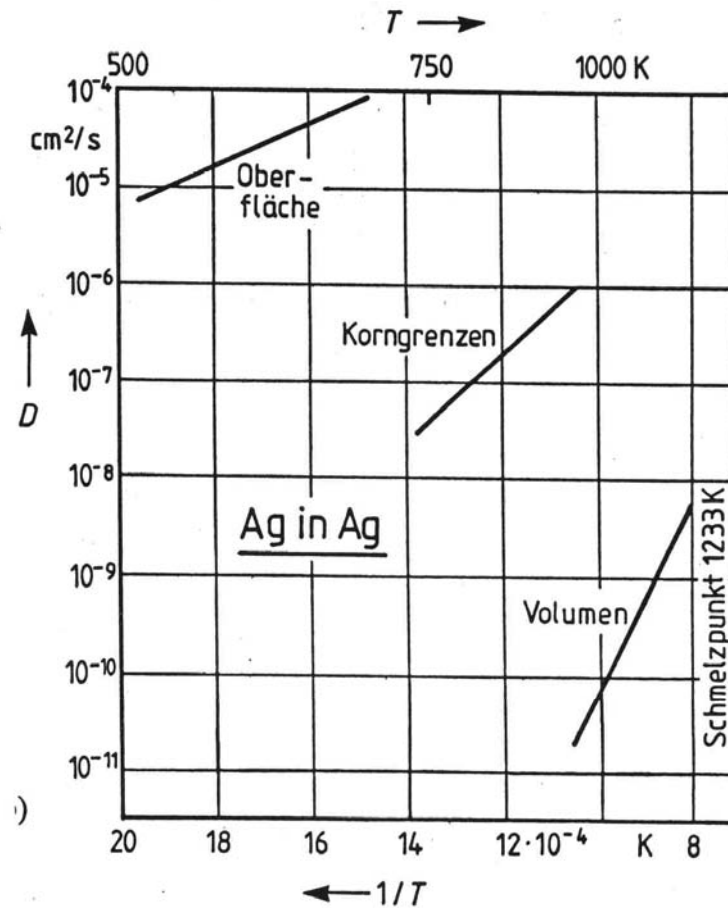
the slope corresponds to the activation energy  $Q$  and the intercept to  $D_{\infty}$ .

# Diffusion

C in Fe



Ag in Ag



# Direct Reactions of Solids

NUCLEATION RATE

$$n = n_0 \exp\left(-\frac{(\Delta G_N + \Delta G_D)}{kT}\right)$$

**Nucleation rate  $n$**

**Nucleation rate = const.  $\times \exp\{- (\Delta G_N + \Delta G_D)/kT\}$**

**$\Delta G_N$  = thermodynamic barrier to nucleation**

**$\Delta G_D$  = kinetic barrier to diffusion across the liquid/nucleus interface**

$$\Delta G_N = \Delta G_S + 4/3\pi r^3 \Delta G_V$$

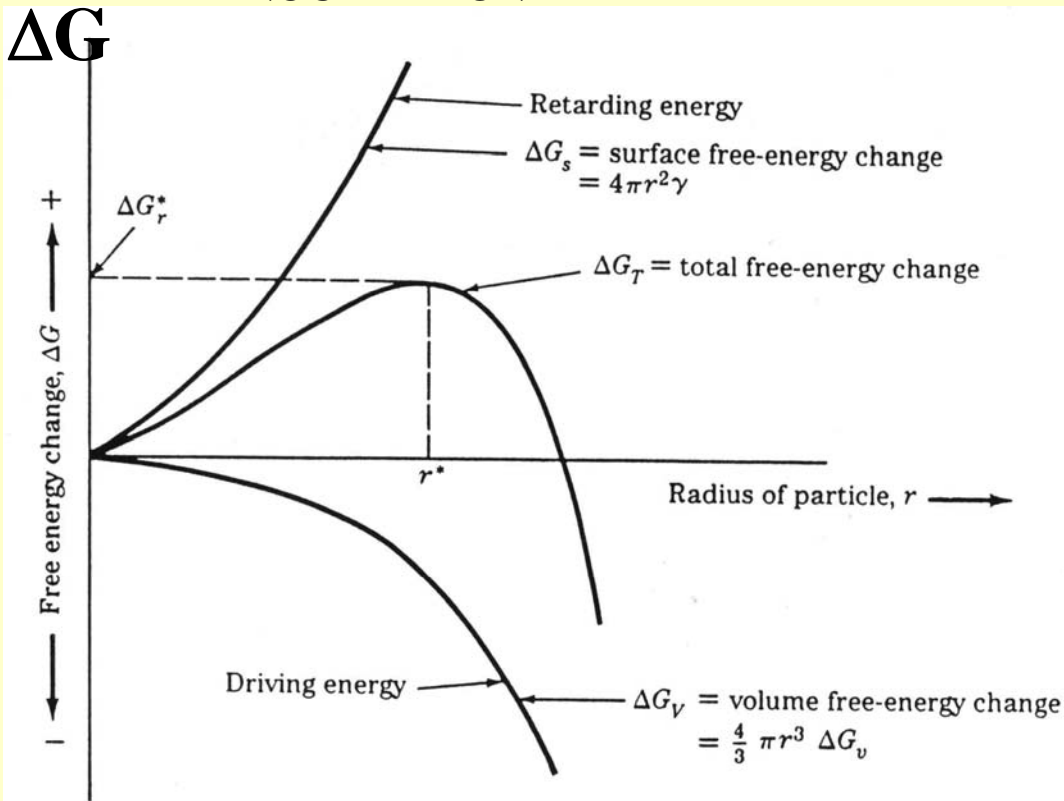
**$\Delta G_S = 4\pi r^2 \gamma$  surface free energy change      positive**

**$4/3\pi r^3 \Delta G_V$  volume free energy change      negative, l to s lowers energy**



# Nucleation rate $n$

## NUCLEATION RATE



$r$ : radius of spheric seed

$r^*$ : critical radius

( $r > r^*$  seed grows by itself)

$\Delta G_N$ : total free energy change

$\Delta G_s$ : surface free energy change

$\Delta G_v$ : volume free energy change

$$\Delta G_N = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v$$

# Direct Reactions of Solids

## Solidification

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma$$

- Volume free energy + surface energy

## One solid phase changing to another

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma + \frac{4}{3} \pi r^3 \varepsilon$$

- Volume energy + surface energy + strain energy
- the new solid does not take up the same volume as the old solid

# **Nucleation vs. Crystal Growth (solution or melt)**

**Undercooling – cooling below the melting point**

**relations between undercooling, nucleation rate and growth rate of the nuclei**

**large undercooling:            many small nuclei  
(spontaneous nucleation)  
growth rate small - high viscosity, slow diffusion**

**small undercooling:            few (evtl. small) nuclei  
growth rate high – fast diffusion close to the m.p.**

# Nucleation vs. Crystal Growth

**Rate of nucleation**

**Rate of growth**

$T_a$  = small undercooling, slow cooling rate  
rate

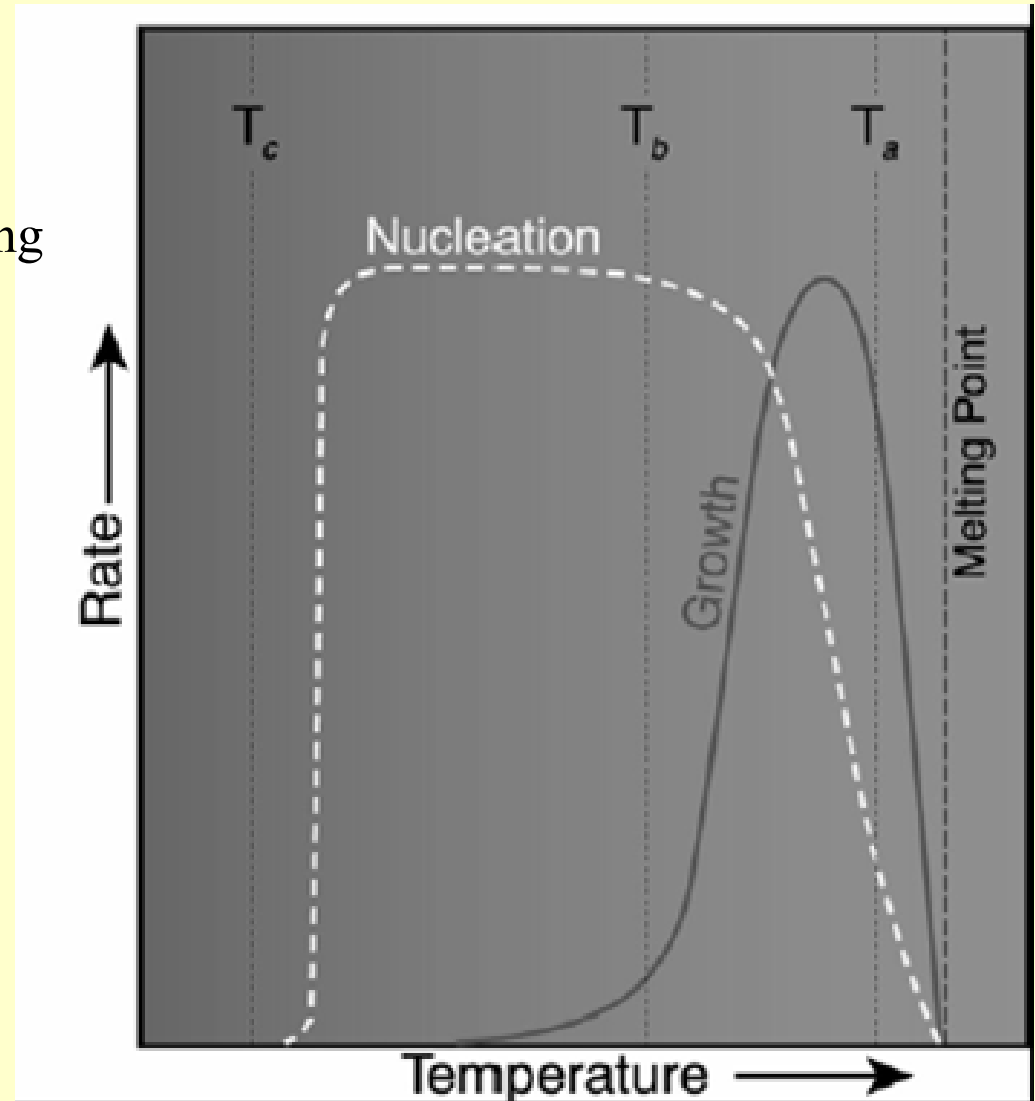
Fast growth, slow nucleation = Few coarse crystals

$T_b$  = larger undercooling, rapid cooling rate

Rapid nucleation, slow growth = many fine-grained crystals

$T_c$  = very rapid cooling

Nearly no nucleation = glass



# DIRECT REACTION OF SOLIDS

## NUCLEATION RATE

**Nucleation requires structural similarity of reactants and products  
less reorganization energy = faster nucleation of product phase  
within reactants**

**MgO, Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> example**

**MgO (rock salt) and MgAl<sub>2</sub>O<sub>4</sub> (spinel) similar ccp O<sup>2-</sup>  
but distinct to hcp O<sup>2-</sup> in Al<sub>2</sub>O<sub>3</sub> phase**

**Spinel nuclei, matching of structure at MgO interface**

**Oxide arrangement essentially continuous across MgO/MgAl<sub>2</sub>O<sub>4</sub>  
interface**

**Bottom line: structural similarity of reactants and products  
promotes nucleation and growth of one phase within another  
Lattice of oxide anions, mobile Mg<sup>2+</sup> and Al<sup>3+</sup> cations**

**Topotactic and epitactic reactions**

**Orientation effects in the bulk and surface regions of solids**

**Implies structural relationships between reagent and product**

**Topotaxy occurs in bulk, 1-, 2- or 3-D**

**Epitaxy occurs at interfaces, 2-D**

# DIRECT REACTION OF SOLIDS

## Epitactic reactions

require 2-D structural similarity, lattice matching within 15% to tolerate oriented nucleation otherwise mismatch over large contact area, strained interface, missing atoms

**Example: MgO/BaO, both rock salt lattices, cannot be lattice matched over large contact area**

## Lattice matched crystalline growth

**Best with less than 0.1% lattice mismatch. Causes elastic strain at interface**

**Slight atom displacement from equilibrium position.**

**Strain energy reduced by misfit-dislocation**

**Creates dangling bonds, localized electronic states, carrier scattering by defects, luminescence quenching, killer traps, generally reduces efficacy of electronic and optical devices, can be visualized by HR-TEM imaging**

# Direct Reactions of Solids

## Topotactic reactions

**More specific, require interfacial and bulk crystalline structural similarity, lattice matching**

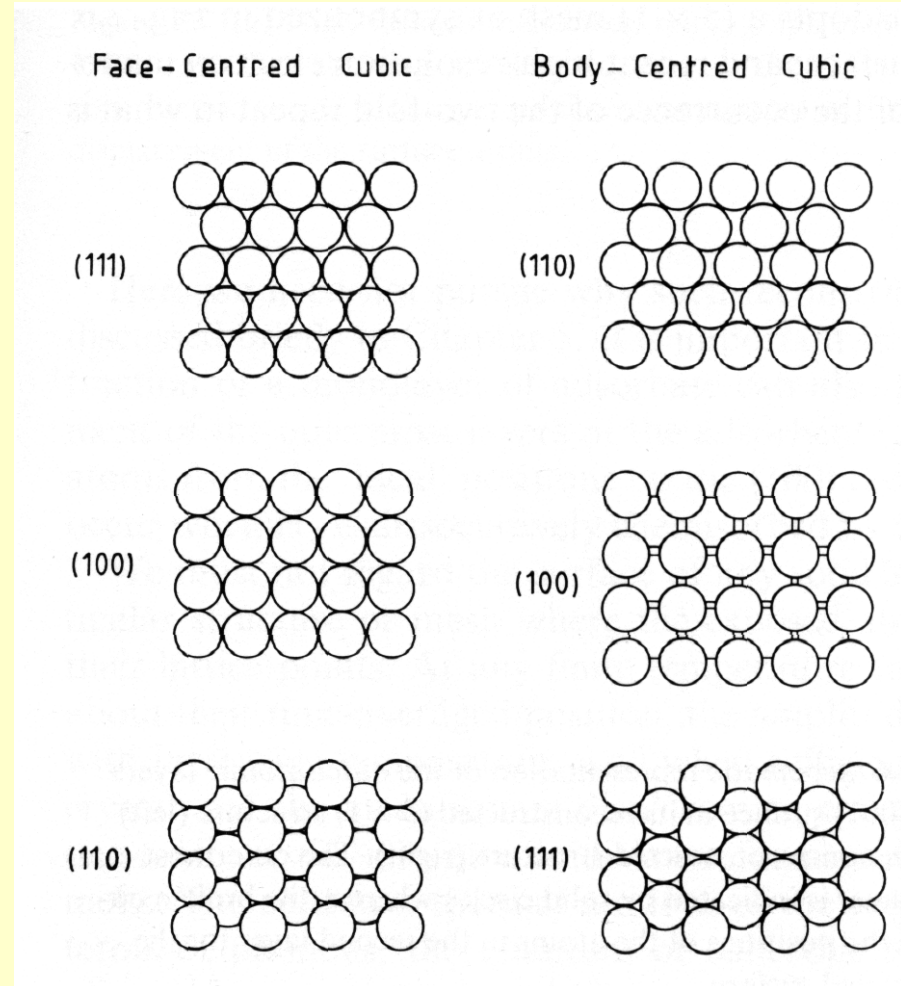
**Topotaxy: involves lock-and-key ideas of self-assembly, molecule recognition, host-guest inclusion, clearly requires available space or creates space in the process of adsorption, injection, intercalation etc.**

# Direct Reactions of Solids

**Surface structure and reactivity**

**Nucleation depends on actual surface structure of reacting phases.**

**Different Miller index faces exposed, atom arrangements different, different surface structures, implies distinct surface reactivities.**



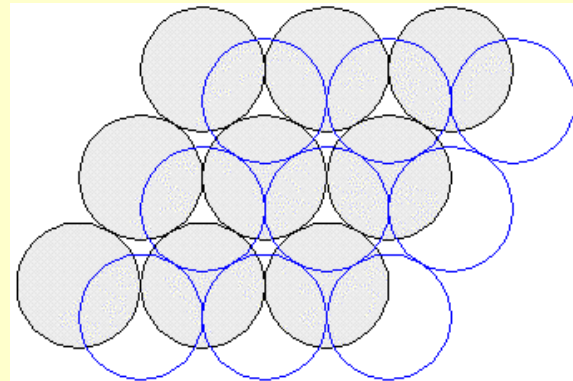
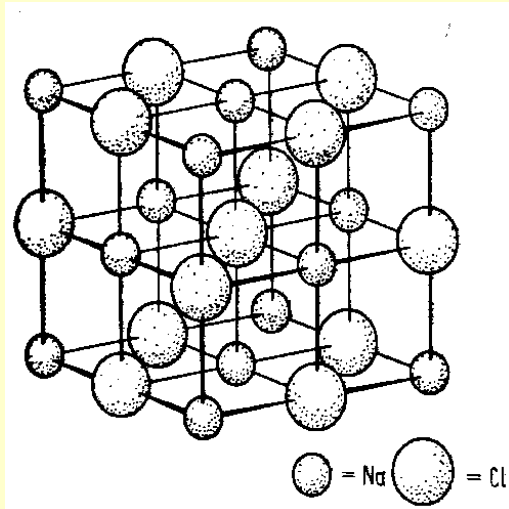


# Direct Reactions of Solids

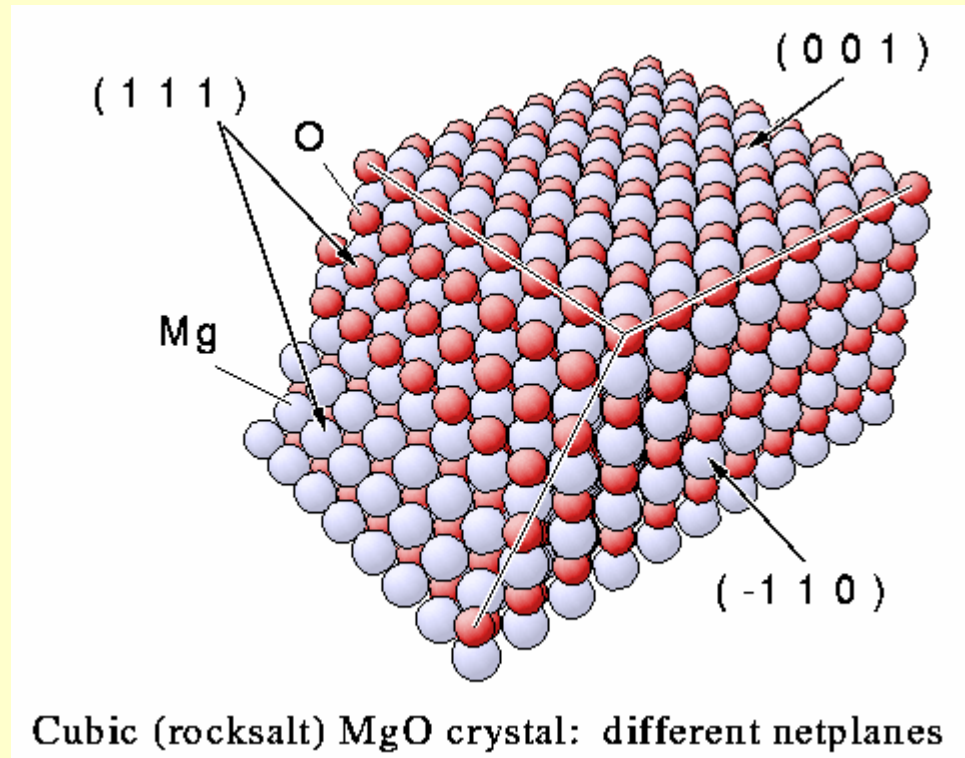
**Example: MgO (rock salt)**

**{100} MgO alternating  $\text{Mg}^{2+}$ ,  $\text{O}^{2-}$  at corners of square grid**

**{111} MgO,  $\text{Mg}^{2+}$  or  $\text{O}^{2-}$  hexagonal arrangement**



# Direct Reactions of Solids



# Direct Reactions of Solids

**Different crystal habits possible, depends on rate of growth of different faces,  
octahedral, cubooctahedral, cubic possible and variants in between**

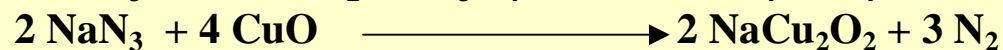
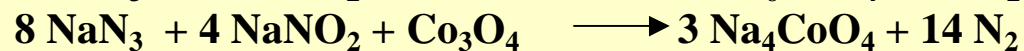
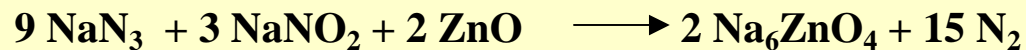
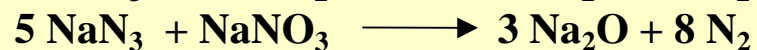
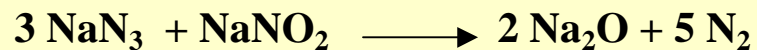
## **CRYSTAL GROWTH**

**Most prominent surfaces, slower growth  
Growth rate of specific surfaces controls morphology  
Depends on area of a face, structure of exposed face, accessibility of a face, adsorption at surface sites, surface defects**

**Play major role in reactivity, nucleation, crystal growth, materials properties (electronic, optical, magnetic, charge-transport, mechanical, thermal, acoustical etc)**

## DIRECT REACTION OF SOLIDS

### Azide Method



# **Self-Sustained High-Temperature Synthesis (SHS)**

**Mixing**

**Metal powders (Ti, Zr, Cr, Mo, W, ....) + other reactants**

**Pressing into pellets**

**Ignition by energy pulse (W wire)**

**S.S. reactor, under Ar**

**Exothermic reaction**

**Byproduct removal**

# DIRECT REACTION OF SOLIDS

## SHS reactions:

- \* heterogeneous
- \* exothermic, high temperatures,  $T_f = 1500 - 3000 \text{ }^\circ\text{C}$
- \* high thermal gradients
- \* redox
- \* frontal mode, reaction wave velocity  $u = 1 - 10 \text{ mm}\cdot\text{s}^{-1}$
- \* metastable phases

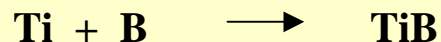
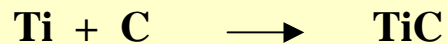
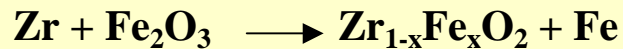
## State of the substance in the reaction front:

solid ( $T_f < T_m$ ,  $p < p_0$ ) „solid flame“

liquid, melt ( $T_f > T_m$ )

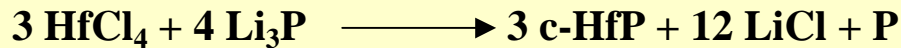
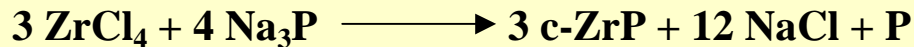
gaseous

## Thermite reaction



# Self-Propagating Metathesis

**Grinding of components in a glove box  
addition of NaCl, KCl or NH<sub>4</sub>Cl as a heat sink,  
S.S. vessel, ignition by a resistively heated wire, reaction time 1 s,  
washing products with MeOH, water, drying**

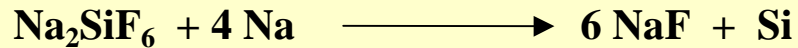


**c-ZrP and c-HfP hard and chemically inert materials,  
hexagonal to cubic transitions: ZrP 1425 °C, HfP 1600 °C**

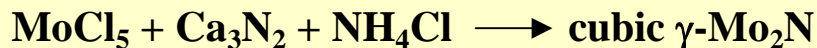
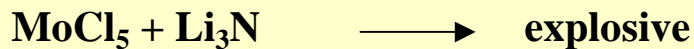
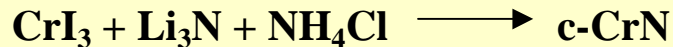
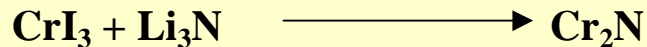
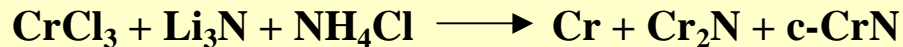
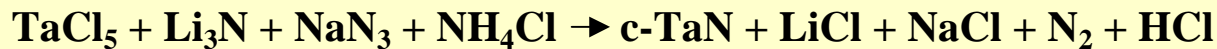
## DIRECT REACTION OF SOLIDS

# Self-Propagating Metathesis

### Silicon production



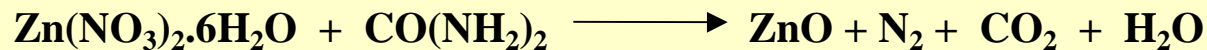
### Hard materials production





# Combustion Synthesis

**Oxidizing reagents (metal nitrates) mixed with fuel (urea, glycine) by melting or in solution**  
**drying**  
**combustion ignited at 300-500 °C**  
**exothermic self-propagating non-explosive reaction (excess of fuel)**  
**reaction time 1 min, flame temperature 1000 °C**  
**product dry foam, crumbles to a fine powder.**



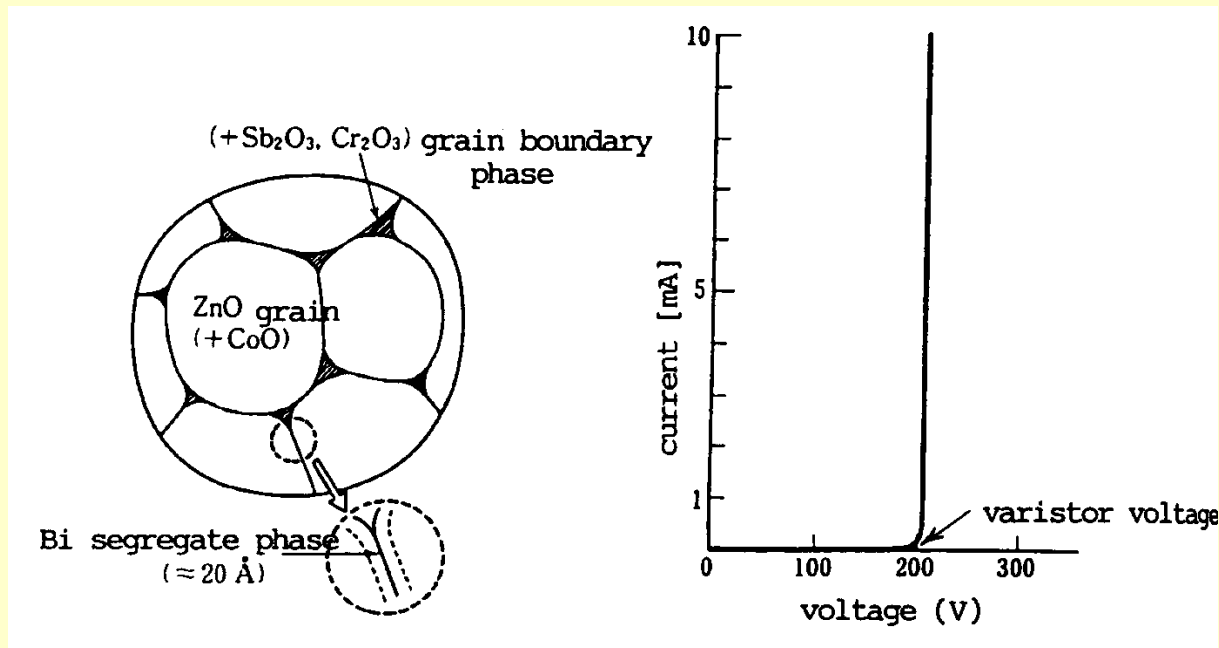
# Combustion Synthesis

## Examples

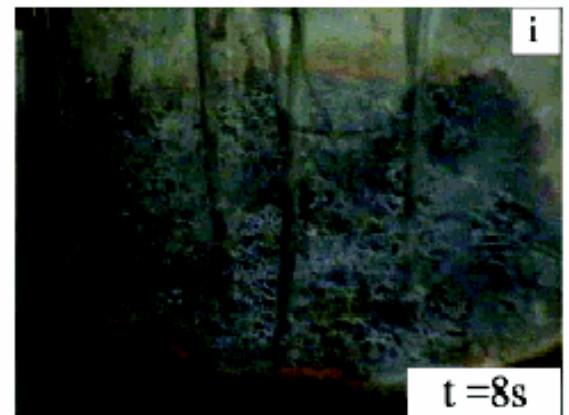
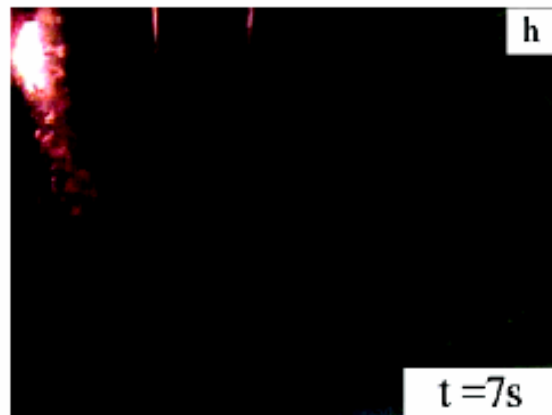
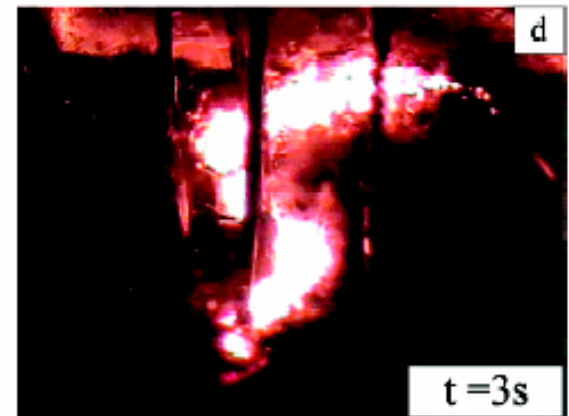
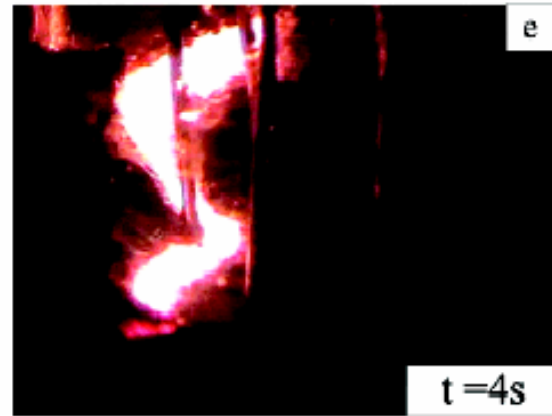
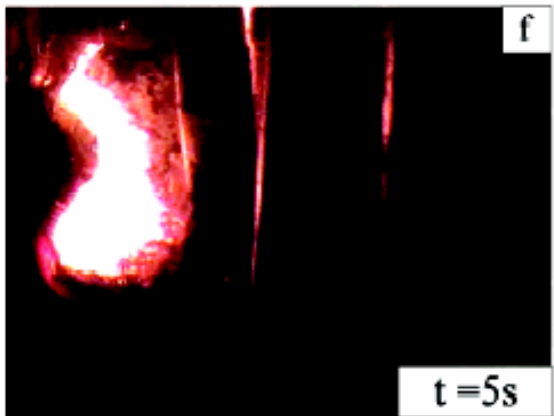
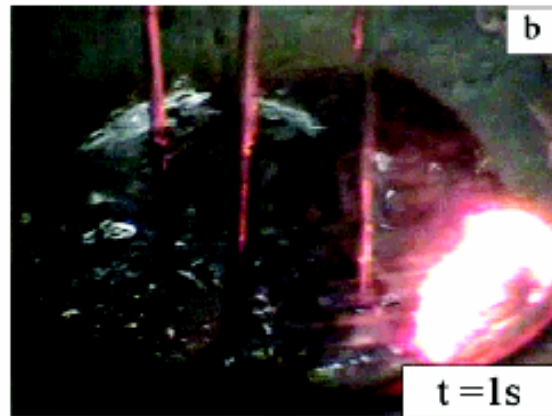
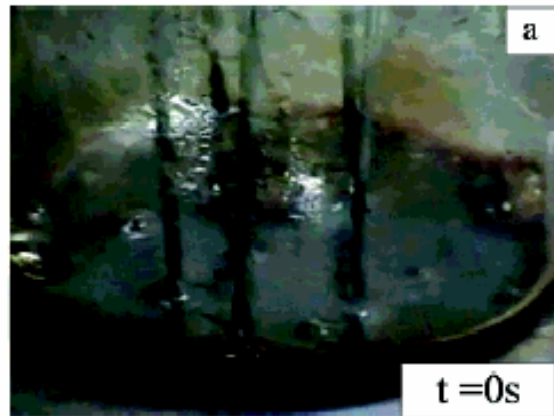
ZnO(90%) - Bi<sub>2</sub>O<sub>3</sub> - Sb<sub>2</sub>O<sub>3</sub>

Non-Ohmic behavior  $I = (U/C)^a$  C, a = constants, a = 50

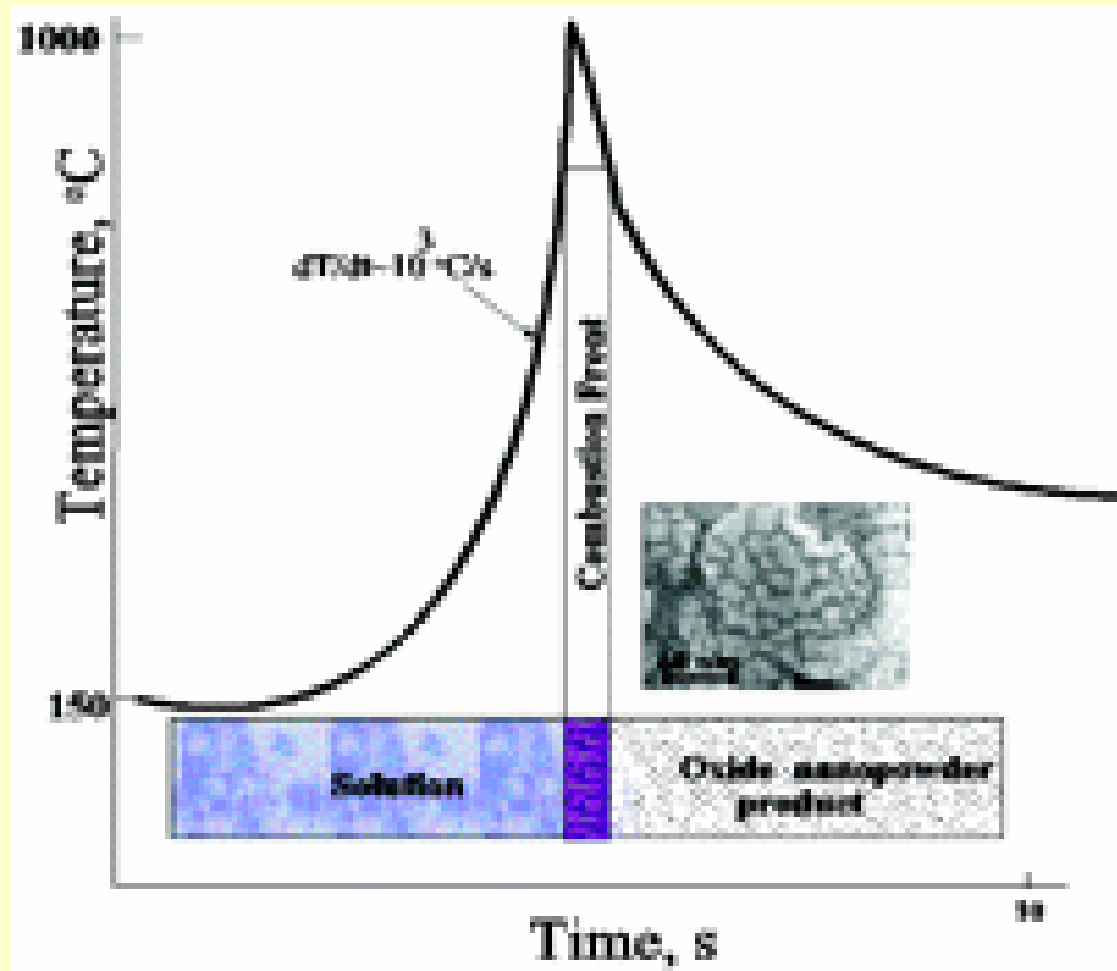
Voltage stabilization, surge absorption



# Reaction front propagation: glycine-iron nitrate



# Self-Propagating Metathesis



# Combustion Synthesis

## Examples



**mixing 1:1:1 in aqueous solution, drying at 90 °C**

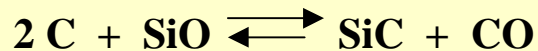
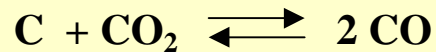
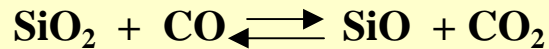
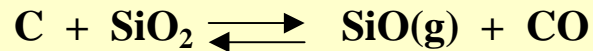
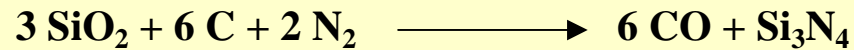
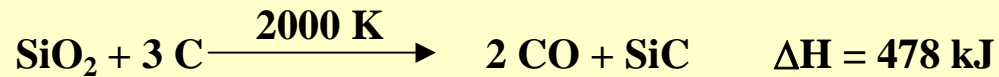
**combustion at 250 °C**

**calcination to LiVMoO<sub>6</sub> cathode material for Li-ion**

# DIRECT REACTION OF SOLIDS

## Carbothermal Reduction

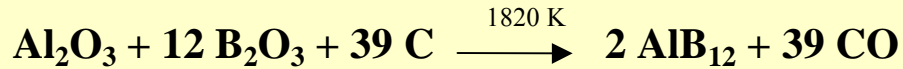
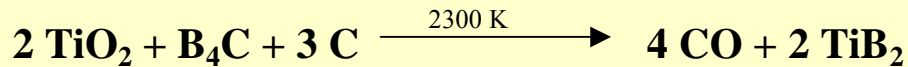
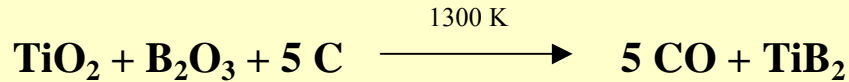
### Acheson



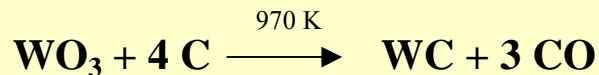
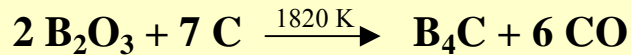
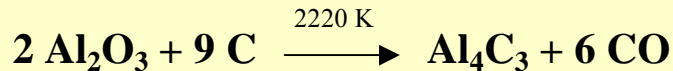
# DIRECT REACTION OF SOLIDS

## Carbothermal Reduction

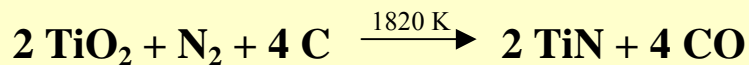
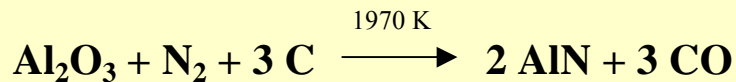
### Borides



### Carbides



### Nitrides



## DIRECT REACTION OF SOLIDS

# Fusion-Crystallization from Glass

## Fusion-Crystallization from Glass

**Mixing powders**

**Melting to glass: single phase, homogeneous (T, C), amorphous**

**Temperature limits:**      **mp of reagents**  
   **volatility of reagents**

**Nucleation agent**

**Homogeneous nucleation, few crystal seeds**

**Slow transport of precursors to seed**

**Lowest possible crystallization temperature**

**Crystallizing a glass above its glass transition**

**Metastable phases accessible, often impossible to prepare by other methods**



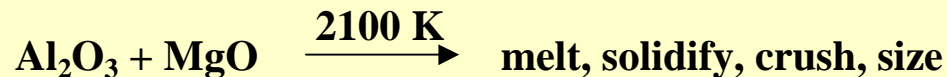
## DIRECT REACTION OF SOLIDS

# Fusion-Crystallization from Glass

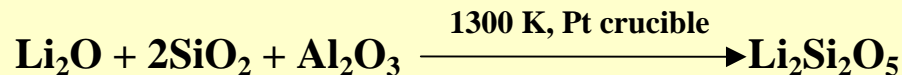
## Fusion-Crystallization from Glass

Production of window glass

Abrasive grains



Crystallizing an inorganic glass, lithium disilicate

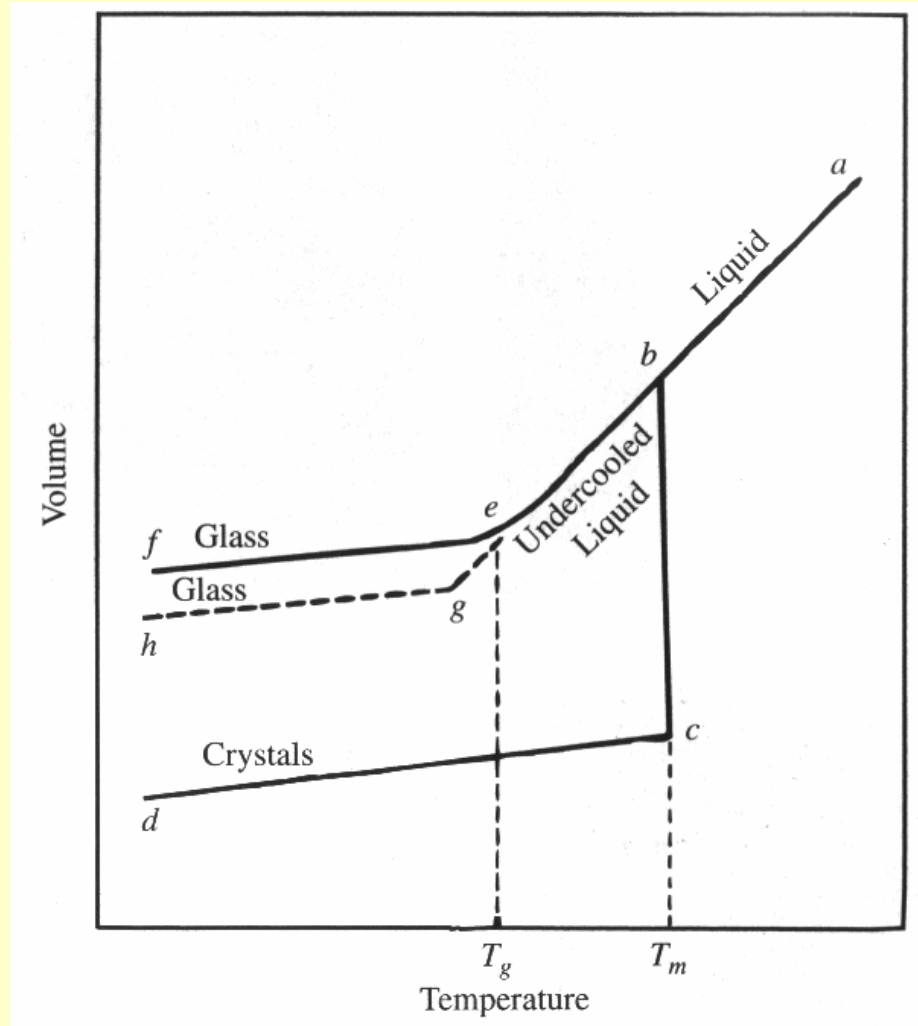


$\text{Li}_2\text{Si}_2\text{O}_5$  forms as a melt. Hold at  $1100^\circ\text{C}$  for 2-3 hrs. Homogeneous, rapid cooling, fast viscosity increase, quenches transparent glass

$\text{Li}_2\text{Si}_2\text{O}_5$ , glass  $500\text{-}700^\circ\text{C}$ ,  $T_g \sim 450^\circ\text{C}$  from DSC  $\rightarrow$   $\text{Li}_2\text{Si}_2\text{O}_5$ , crystals in 2-3 hrs.,

principle of crystallizing a glass above its glass transition

# Fusion-Crystallization from Glass



## DIRECT REACTION OF SOLIDS

# Fusion-Crystallization from Glass

## Fusion-Crystallization from Glass

### Glass Ceramics

polyxtalline materials made by controlled xtallization of glasses

### Cooking utensils

$\text{Li}_2\text{O}/\text{SiO}_2/\text{Al}_2\text{O}_3(>10\%)$     nucl.  $\text{TiO}_2$      $\beta$ -spodumene

### Vacuum tube components

$\text{Li}_2\text{O}/\text{SiO}_2/\text{Al}_2\text{O}_3(<10\%)$     nucl.  $\text{P}_2\text{O}_5$     Li-disilicate, quartz

### Missile radomes

$\text{MgO}/\text{SiO}_2/\text{Al}_2\text{O}_3$     nucl.  $\text{TiO}_2$     cordierite, cristobalite