

# 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

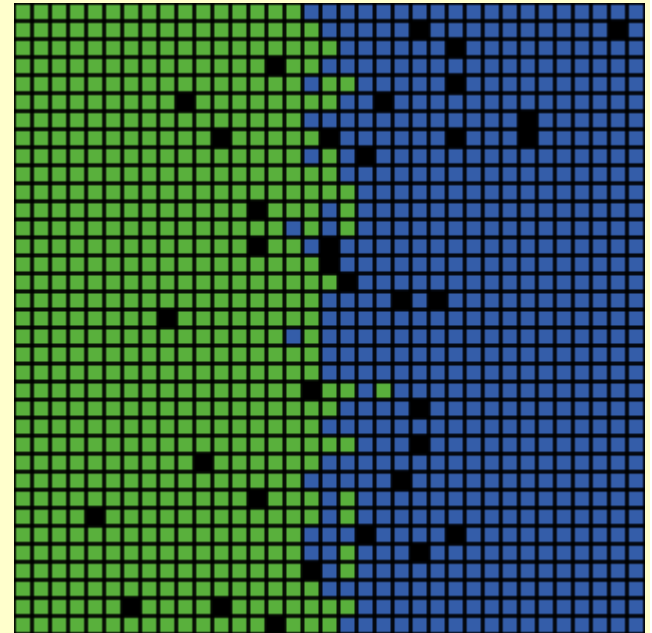
No mobility without defects – perfect crystal = no chemistry

High temperatures

Reactions on the interphase between phases

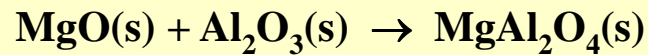
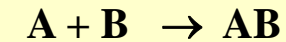
Microstructure - crystallite size, shape, defects

Diffusion controls the reaction rate

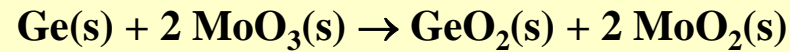
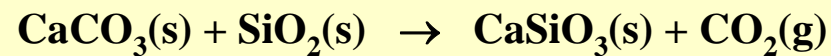
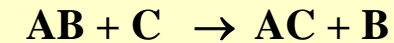


# Reaction Types

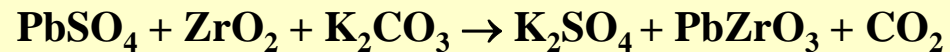
**Solid - solid synthesis - addition**



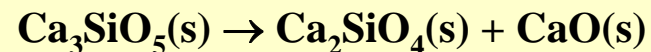
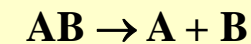
**Solid - solid synthesis – exchange, metathesis**



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

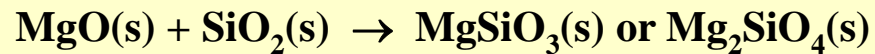
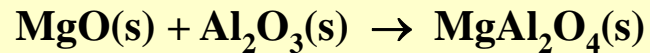
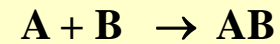


**Solid - solid synthesis - dissociation**

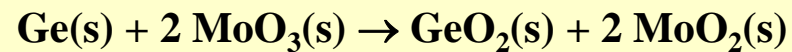
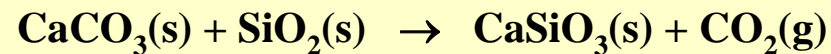
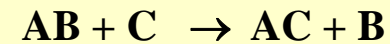


# Reaction Types

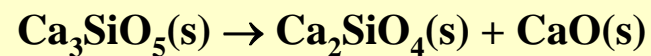
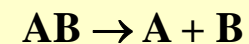
**Solid - solid synthesis - addition**



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

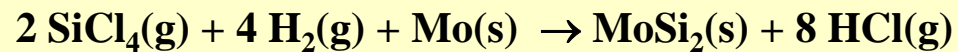
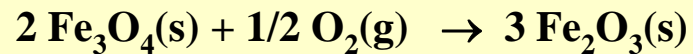


**Solid - solid synthesis - dissociation**



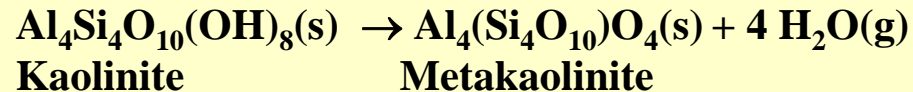
# Reaction Types

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



**High temperature corrosion of metals in air**

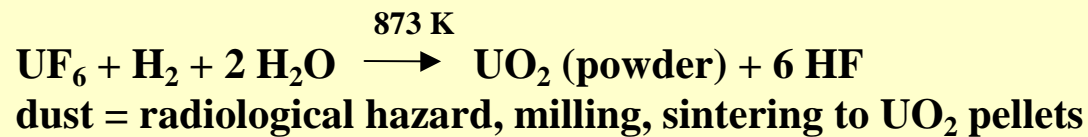
**Solid – gas dissociation**                      **AB → A + B**



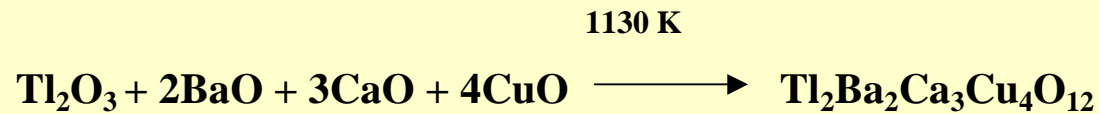
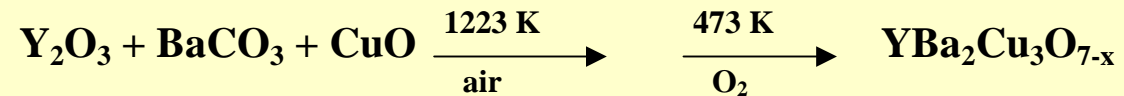
# Reaction Types

## Other Examples

### Oxides



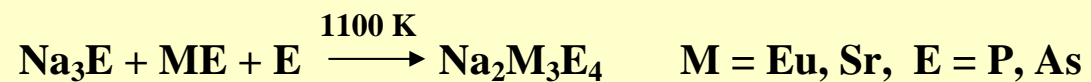
### YBCO 123 Superconductor (1987)



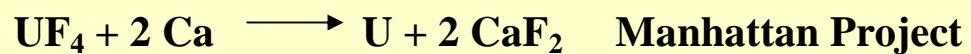
# Reaction Types

Other classes than oxides

## Pnictides

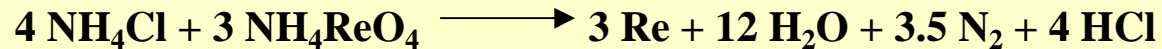
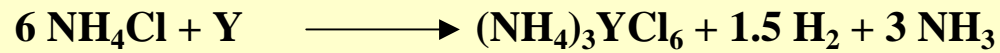
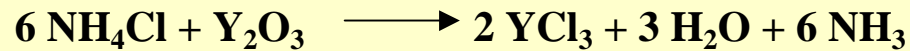
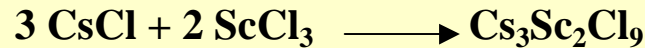


## Metals

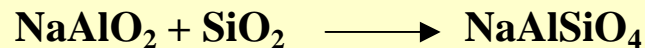


# Reaction Types

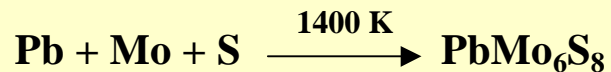
## Chlorides



## Aluminosilicates



## Chalcogenides



**Chevrel phases**

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

# **Experimental Considerations**

## **Powder Mixing Method**

**Precise weighing for exact stoichiometry**

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

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

**Compaction (pelleting, organic binders)**

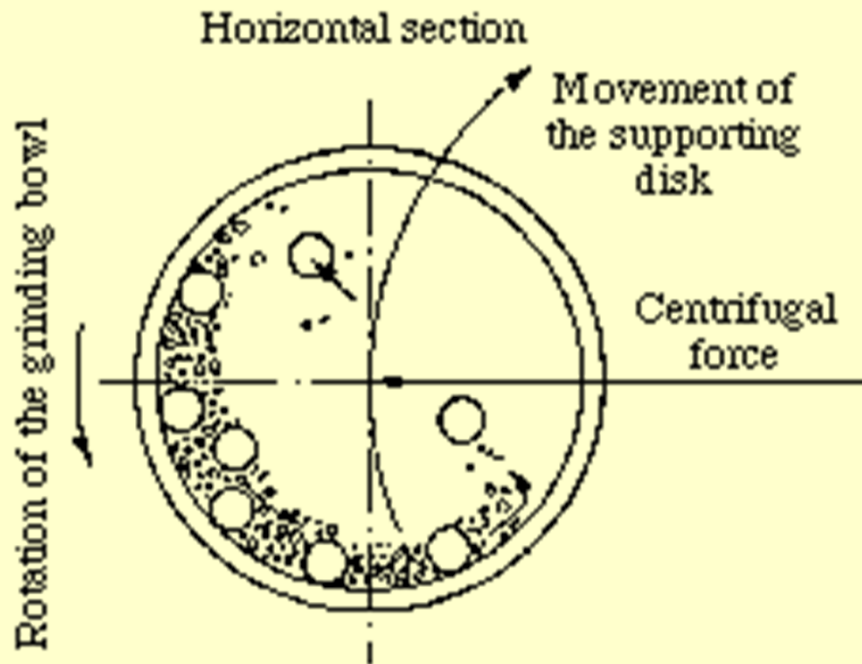
**Calcination @ high temperature ( $> 1000\text{ }^{\circ}\text{C}$ )**

**Firing/grinding cycles**



# Milling

Planetary ball mill



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

Planetary ball mill

Rotation and counter-wise spinning



# Milling

**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*

# 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)

# Experimental Considerations

## Reagents

Drying, fine grain powders for maximum SA, surface activation ( $\text{Mo} + \text{H}_2$ ), in situ decomposition ( $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ,  $\text{O}_2^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ) for intimate mixing, precursor reagents, homogenization, organic solvents, grinding, ball milling, ultrasonication

## 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

## 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



# Experimental Considerations

## 💣 Heating Program

Slow or fast heating, cooling, holding at a set point temperature. Furnaces, RF, microwave, lasers, ion or electron beam

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

## 💣 Controlled atmosphere

oxidizing, reducing, inert or vacuum.

Unstable oxidation states, preferential component volatilization if T is too high, composition dependent atmosphere ( $O_2$ ,  $NH_3$ ,  $H_2S$ , ...)

Fuel and Oxidizer type	Temperature (Celsius)
Fluorescent light	60-80
Incandescent light	100-300
Cigarettes - unventilated conditions	288
Cigarettes - ventilated	400-780
Cigarettes - insulated and smoldering	510-621
Stove element	>550
Match	600-800
Tungsten halogen light	600-900
Candle flame	600-1,400
Electrical spark	1,316
Bunsen burner	1,570
Methanol/air	1,910
Methane/air	1,920-1,949
Butane/air	1,977
Propane/air	1,977
Wood/air (most organics are about here))	~1977
MAPP Gas/air	
Hydrogen/air	2,210
Carbon monoxide/air	2,468
Acetylene/air	2,632
Acetylene/Oxygen	3,300
Hydrogen/Oxygen	
Electrical arcing	<3,750
Plasma torch	~4,700
Lightning	30,000



# Factors Influencing Direct 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 Reactions 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  $> 10^{-12}$

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

$D$  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

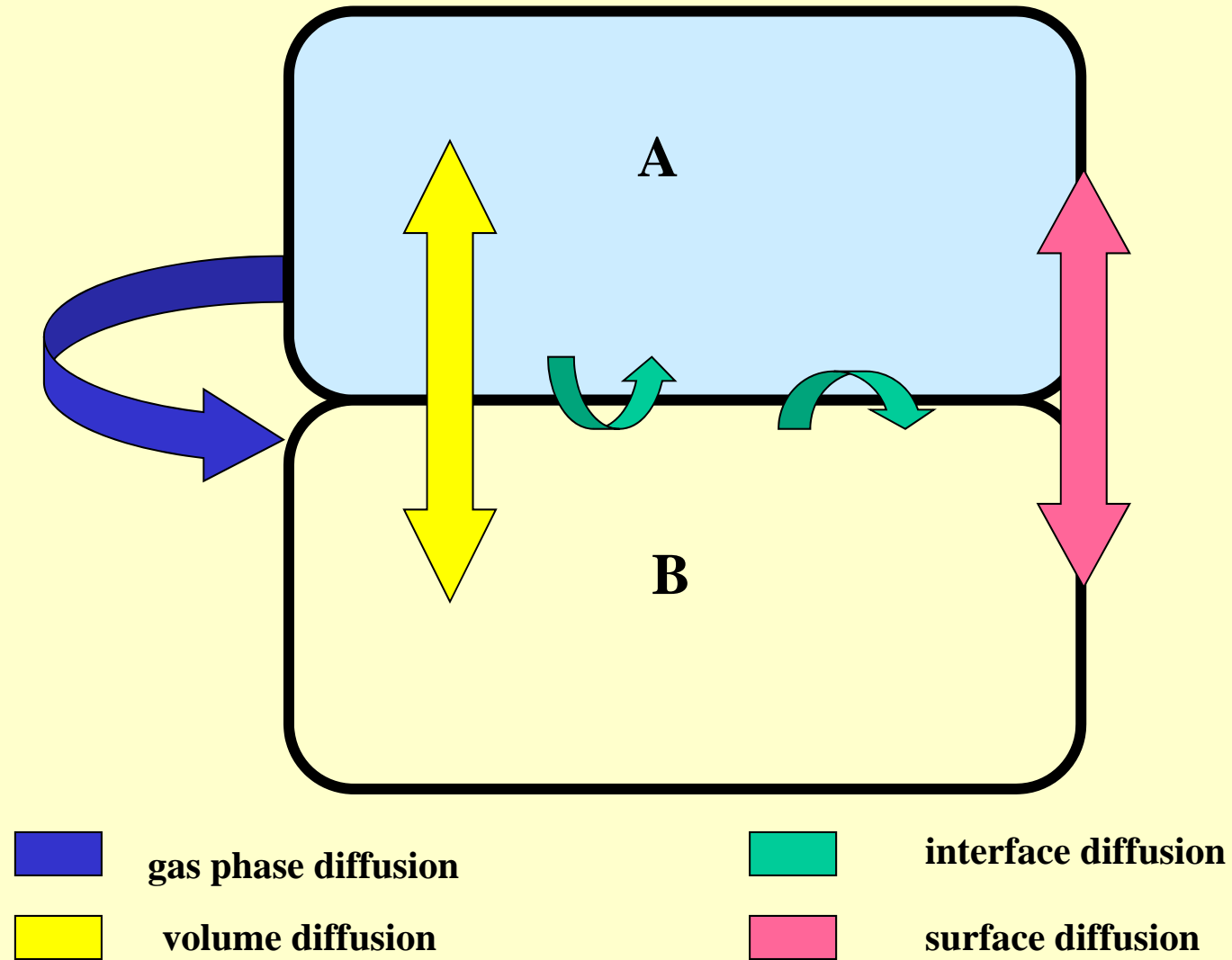
→ Interstitial versus substitutional diffusion

→ 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)

## Reaction Paths between Two Solids



# Direct Reactions of Solids

$A_x B_y O_z$       Stoichiometric formula of spinel

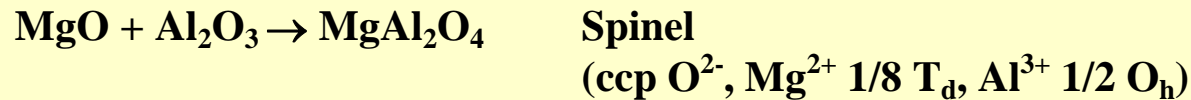
ccp  $O^{2-}$

**A**    occupy  $1/8 T_d$

**B**    occupy  $1/2 O_h$

# Direct Reactions of Solids

**Model reaction, well studied:**



**Single crystals of precursors, interfaces between reactant grains**

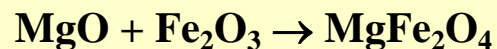
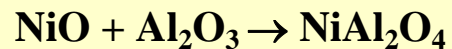
**On reaction, new reactant-product MgO/MgAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> interfaces are formed**

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

**Interfacial growth rates 3 : 1**

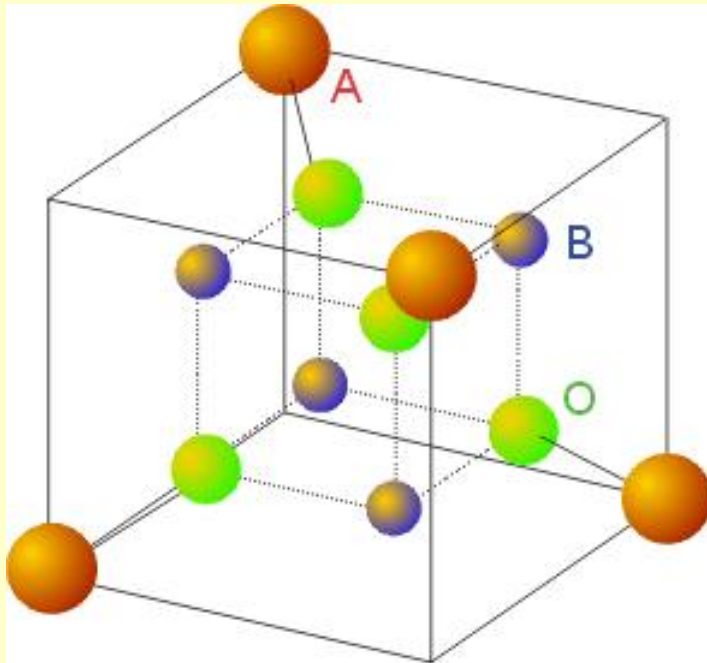
**Linear dependence of interface thickness  $x^2$  versus  $t$**

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





# The Spinel Structure: (A)[B<sub>2</sub>]O<sub>4</sub>



fcc array of O<sup>2-</sup> ions, A occupies 1/8 of the tetrahedral and B 1/2 of the octahedral holes

→ normal spinel: AB<sub>2</sub>O<sub>4</sub>

Co<sub>3</sub>O<sub>4</sub>, GeNi<sub>2</sub>O<sub>4</sub>, WNa<sub>2</sub>O<sub>4</sub>

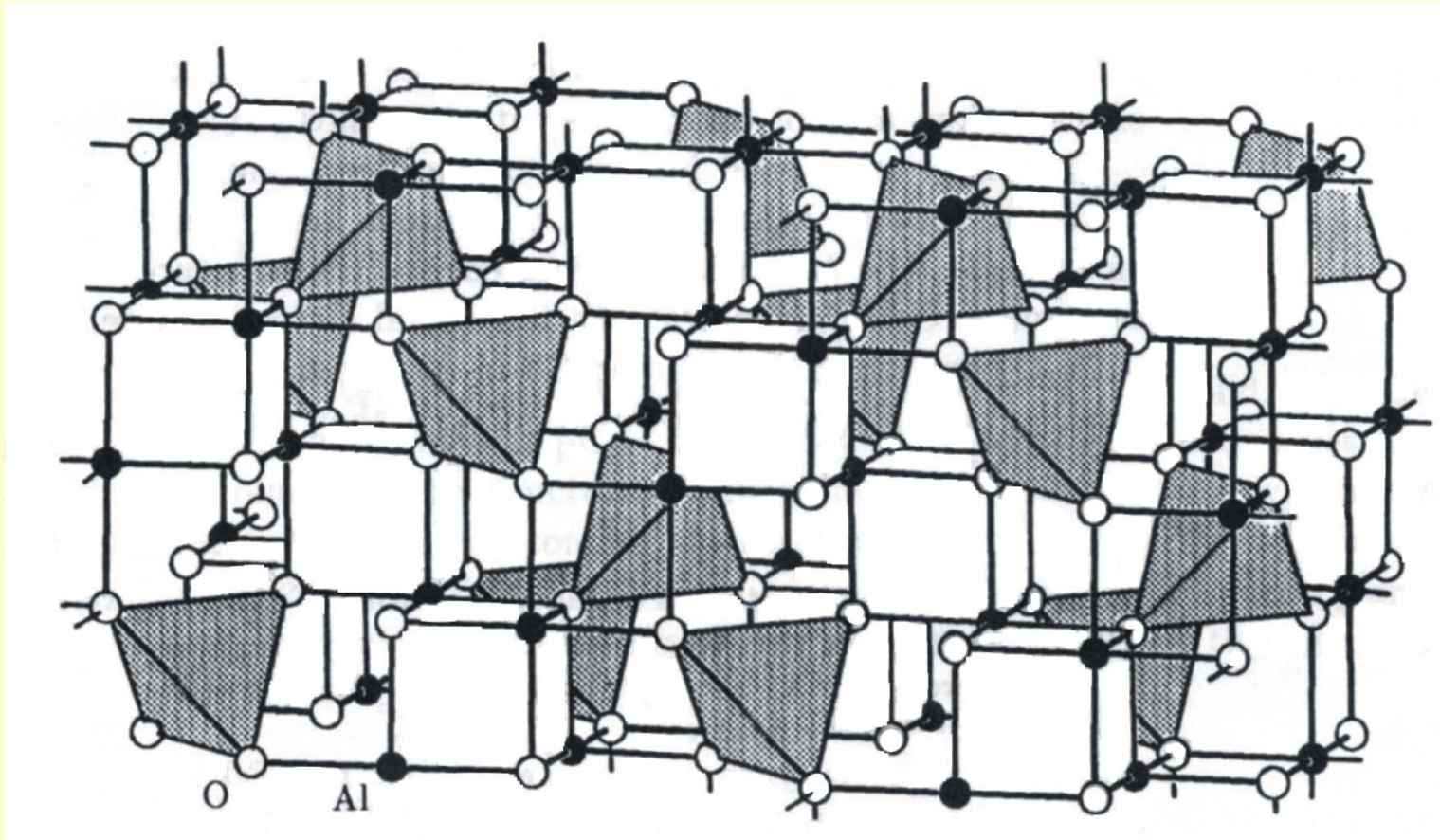
→ inverse spinel: B[AB]O<sub>4</sub>

Fe<sub>3</sub>O<sub>4</sub>: Fe<sup>3+</sup>[Fe<sup>2+</sup>Fe<sup>3+</sup>]O<sub>4</sub>, TiMg<sub>2</sub>O<sub>4</sub>, NiLi<sub>2</sub>F<sub>4</sub>

→ basis structure for several magnetic materials

# The Spinel Structure: $\text{MgAl}_2\text{O}_4$

(A)[ $\text{B}_2$ ] $\text{O}_4$

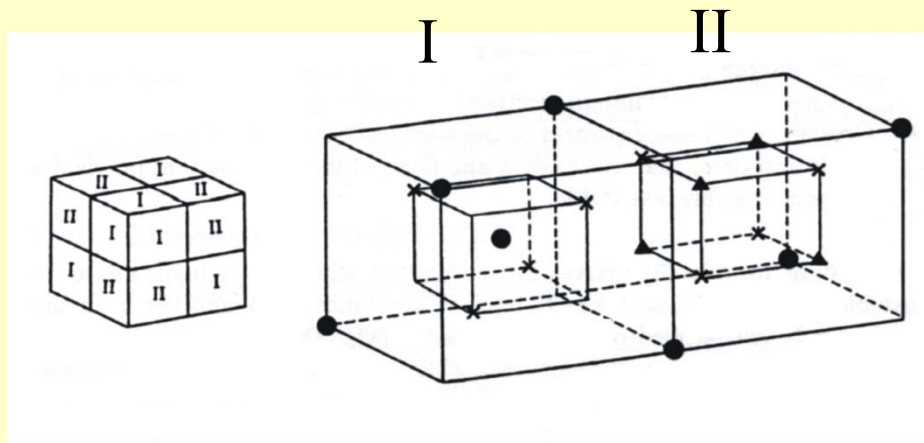
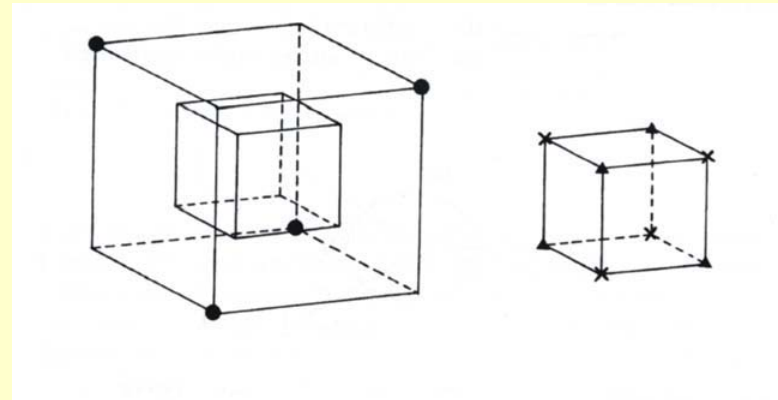
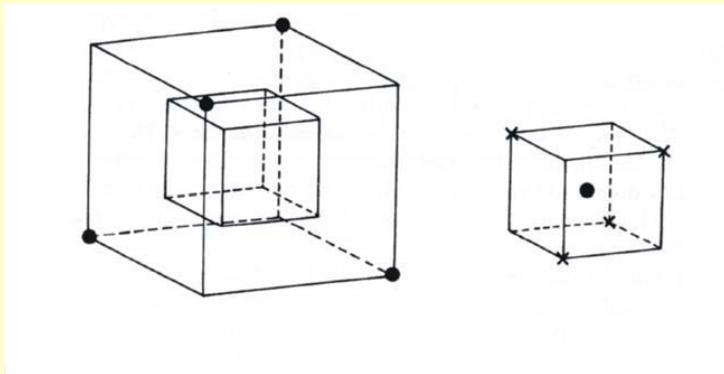


# The Spinel Structure: $\text{MgAl}_2\text{O}_4$



I

II



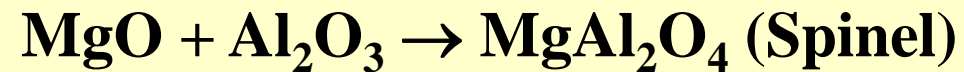
• = Mg

x = O

▲ = Al

# Direct Reactions of Solids

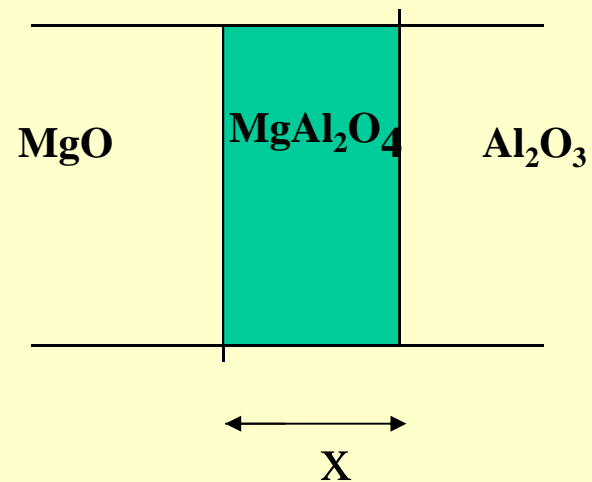
Model for a classical solid-solid reaction (below melting point !):  
Planar interface between two crystals



Phase 1:  
nucleation



Phase 2:  
growth of nuclei



# Direct Reactions of Solids

☛ Structural differences between reactants and products, major structural reorganization in forming product spinel

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

☛ 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:

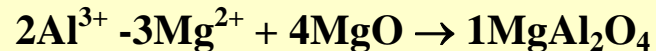
Linear  $x^2$  vs.  $t$  plots observed

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

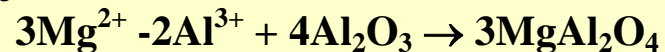
Reaction mechanism requires charge balance to be maintained in the solid state interfacial reaction:



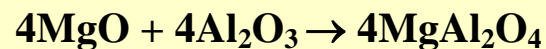
MgO/MgAl<sub>2</sub>O<sub>4</sub> Interface:



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

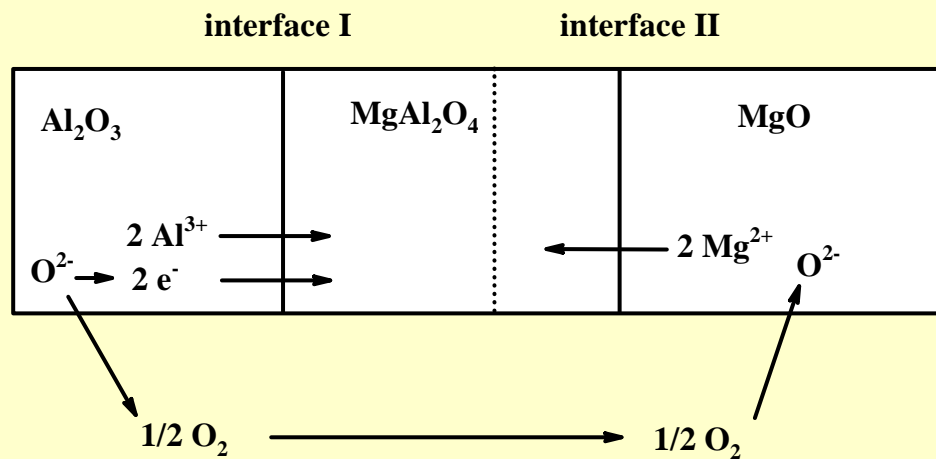
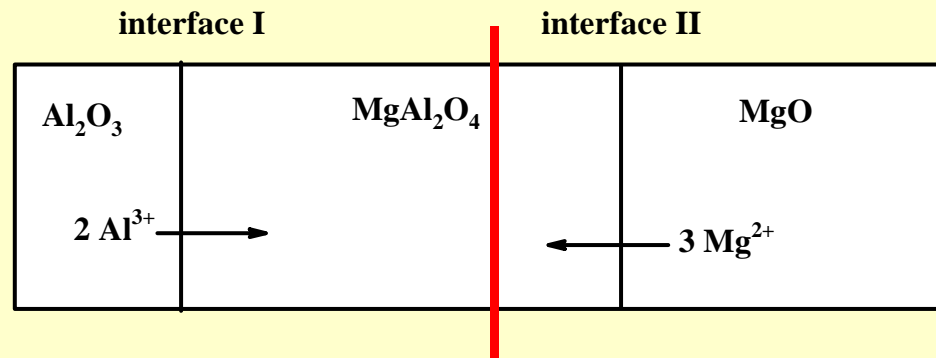


Overall Reaction:



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

# Reaction Mechanism



# Direct Reactions of Solids

## General kinetic expression

Reaction rate

Rate constant

Reaction order

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

$\alpha$  – 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  $\alpha = x$

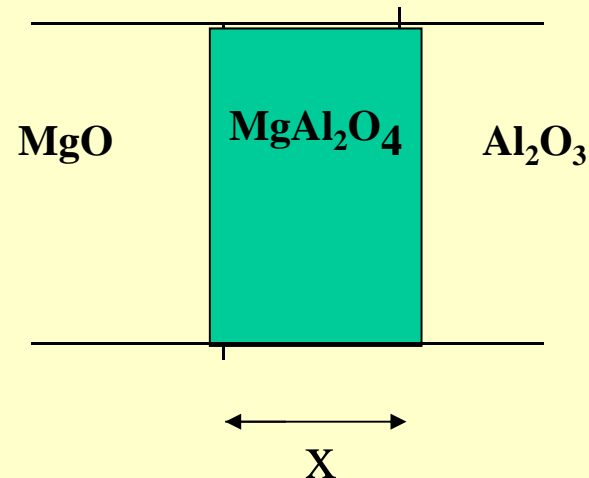
$$\alpha = \frac{P_t - P_0}{P_e - P_0}$$

Parabolic rate law:

$$\alpha = 0-1$$

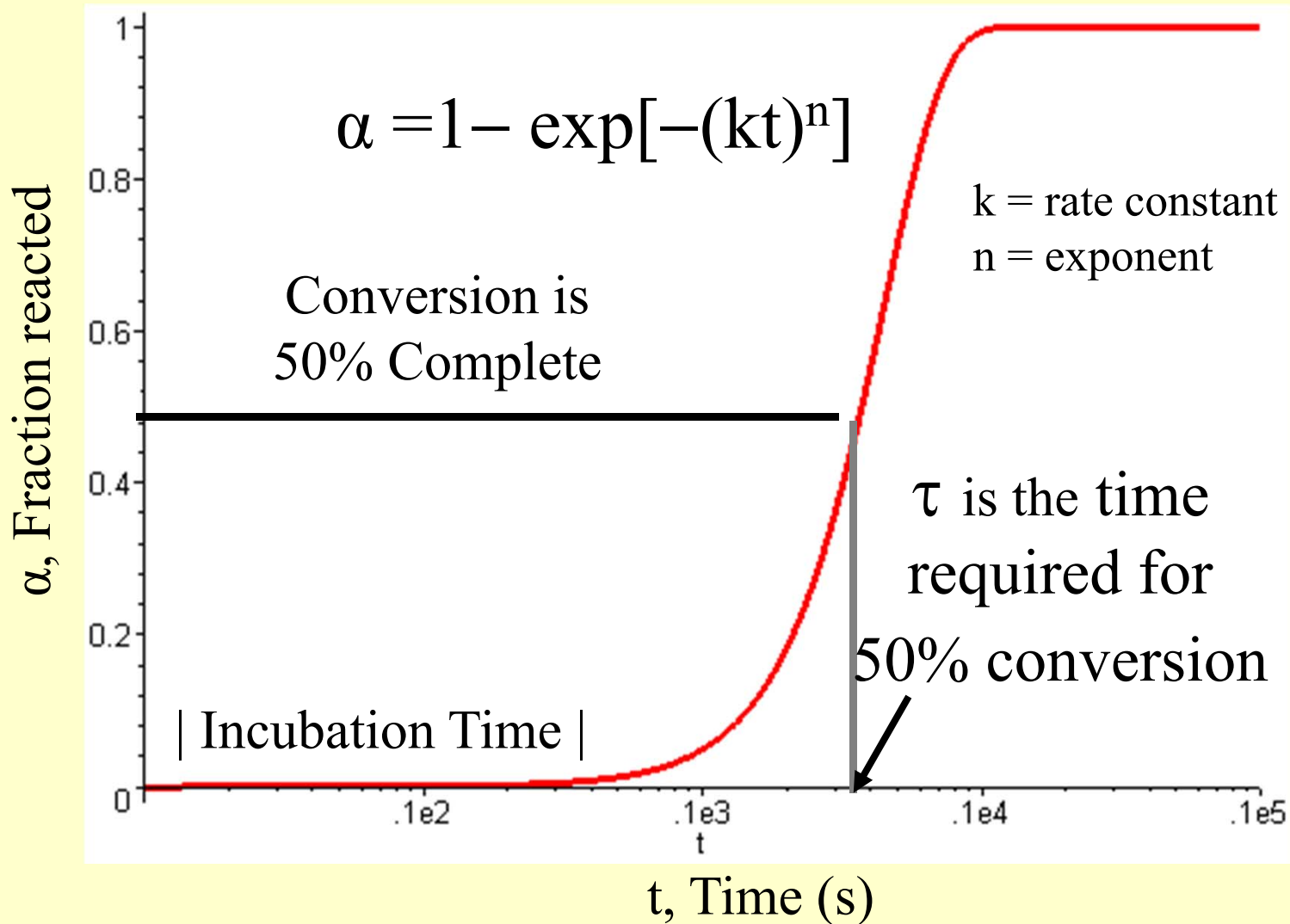
$$dx/dt = k/x$$

$$x^2 = kt$$



<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	$1 - (1 - \alpha)^{1/3}$

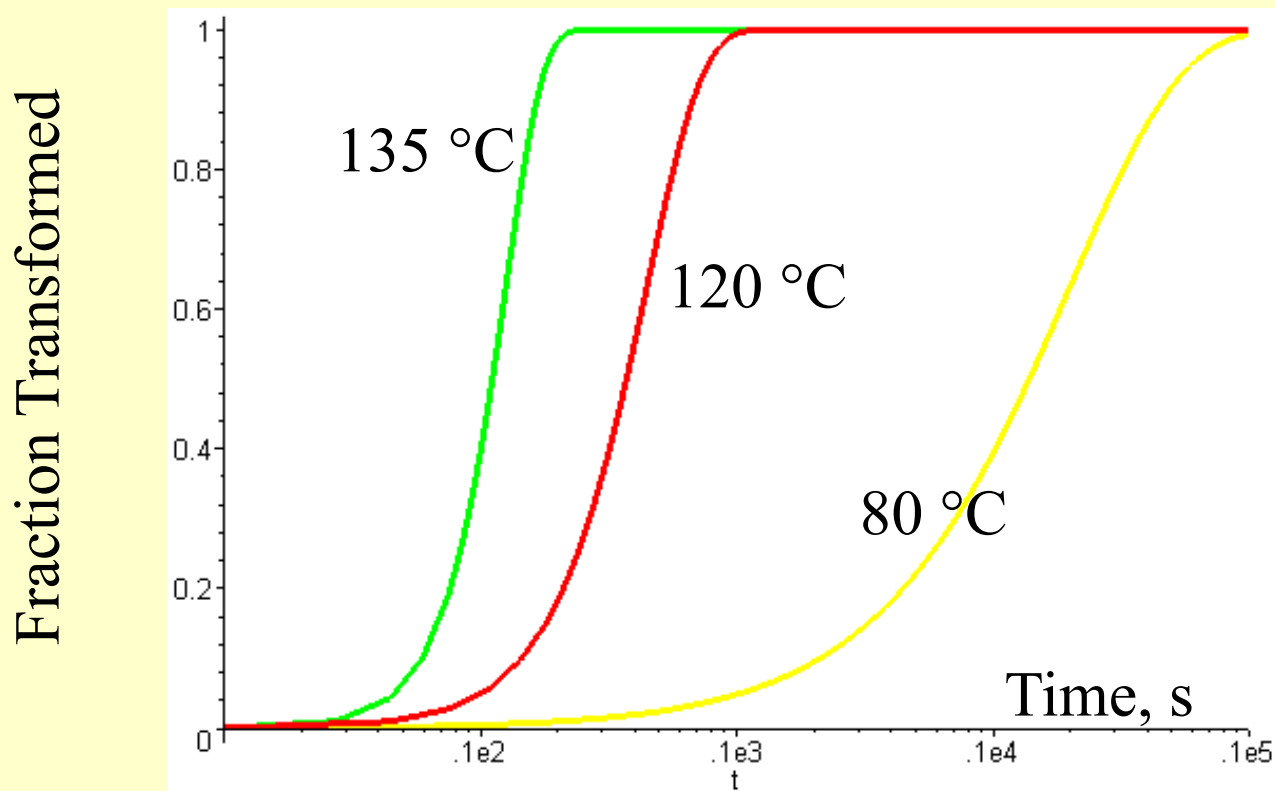
# Avrami Plot



# Direct Reactions of Solids

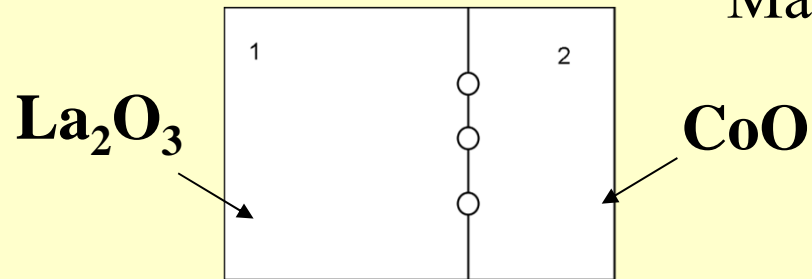
Perform the measurements in a range of temperatures T  
use Arrhenius equation to evaluate the activation energy  $E_a$

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

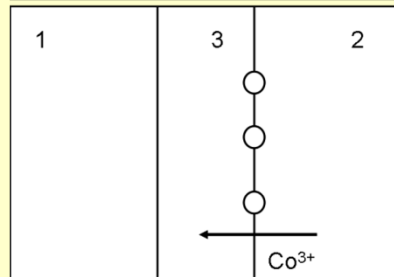


# Cation Diffusion in $\text{LaCoO}_3$

Marker experiments

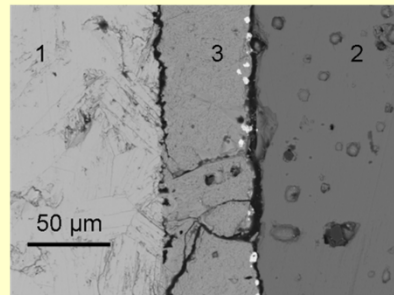


$$D_{\text{Co}} \gg D_{\text{La}}$$



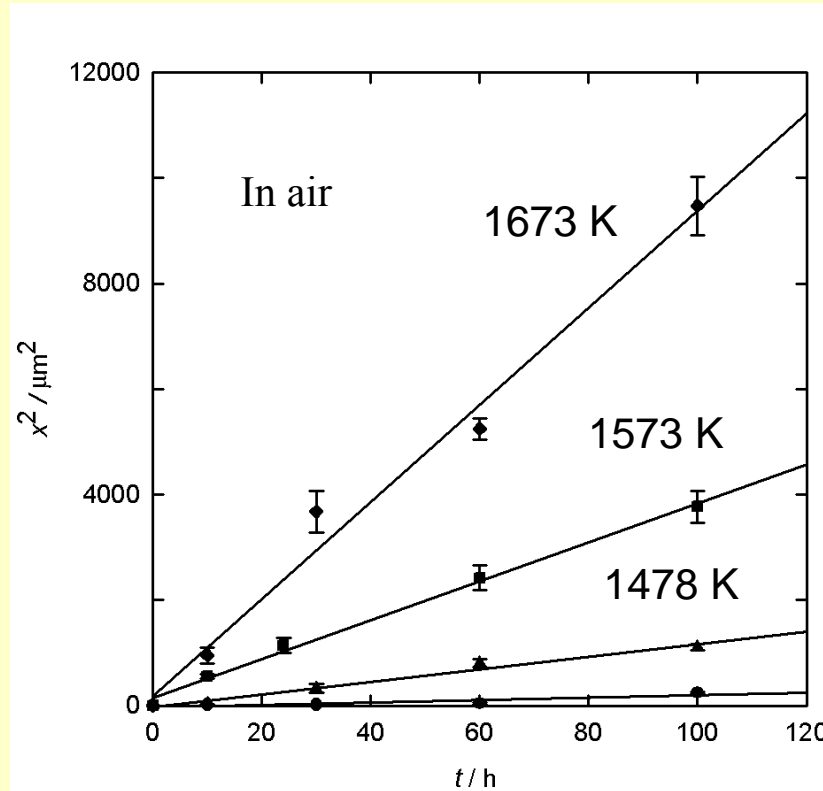
Rate-determining step:

Diffusion of Co cations



$\text{LaCoO}_3$

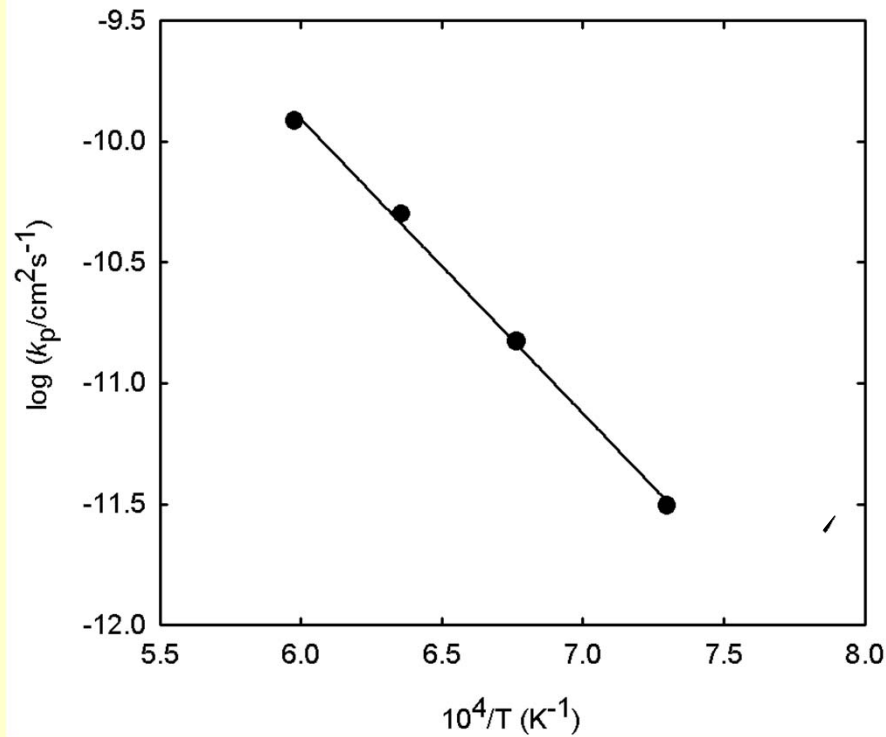
# Growth Kinetics of LaCoO<sub>3</sub>



$$x^2 = kt$$

Parabolic rate law valid = diffusion controlled process

# Growth Kinetics of LaCoO<sub>3</sub>



$T/\text{K}$	$k_p \text{ cm}^2\text{s}^{-1}$	$D \text{ cm}^2\text{s}^{-1b}$
1370	$(3.11 \pm 0.69) \times 10^{-12}$	$3.02 \times 10^{-12}$
1478	$(1.49 \pm 0.14) \times 10^{-11}$	$1.40 \times 10^{-11}$
1573	$(5.01 \pm 0.16) \times 10^{-11}$	$4.55 \times 10^{-11}$
1673	$(1.22 \pm 0.22) \times 10^{-10}$	$1.05 \times 10^{-10}$

$$E_A = (250 \pm 10) \text{ kJ mol}^{-1}$$

# Nucleation

## Homogeneous nucleation

Liquid melt to crystalline solid

Cluster formation

$\Delta G_v$  = driving force for solidification (negative)

below the equilibrium melting temperature,  $T_m$

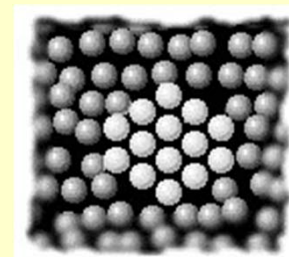
$\Delta T$  = undercooling,  $\Delta H_v$  = enthalpy of solidification (negative)

$$\Delta G_v = \frac{\Delta H_v \Delta T}{T_m}$$

Small clusters of crystallized solid form in a melt because of the random motion of atoms within the liquid

Driving force is opposed by the increase in energy due to the creation of a new solid-liquid interface

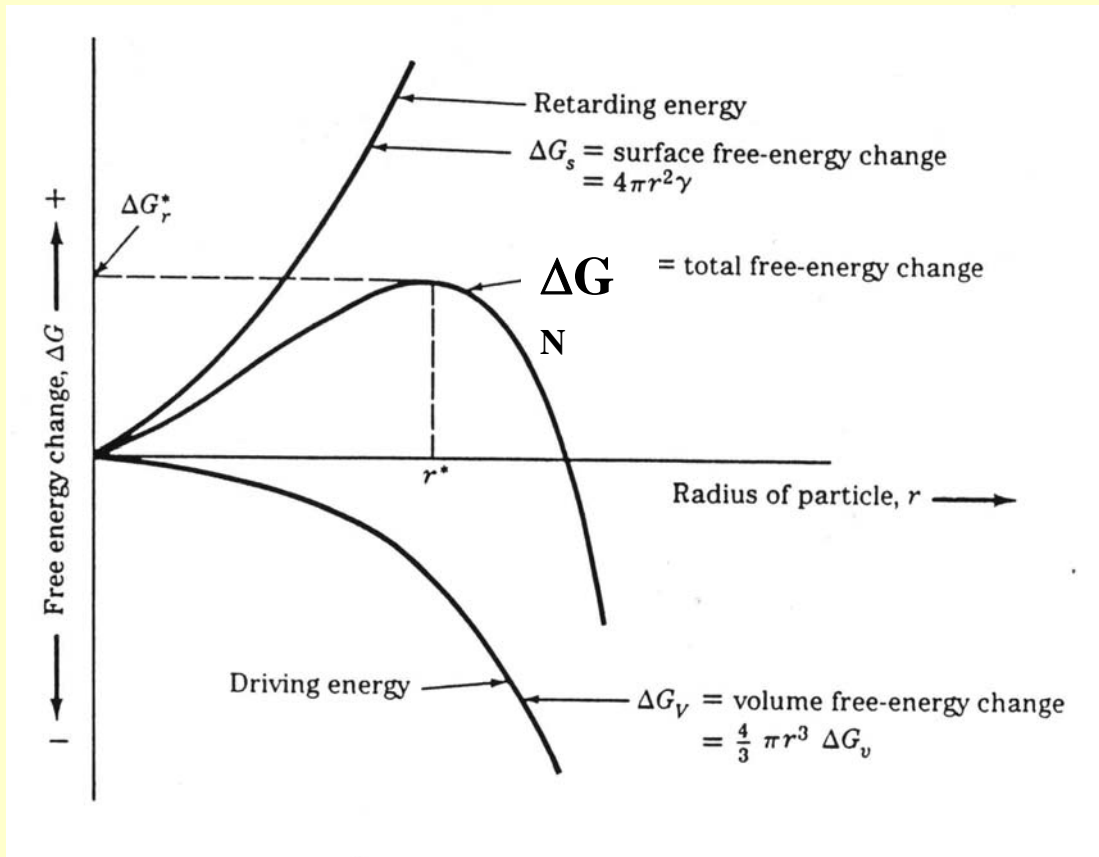
$\gamma_{SL}$  = the solid/liquid interfacial energy





# Nucleation

$\Delta G$



$r$ : radius of spheric seed

$r^*$ : critical radius

$\Delta G_N$ : total free energy change

$\Delta G_s$ : surface free energy change

$\Delta G_v$ : volume free energy change

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

# Critical Radius $r^*$

The critical radius  $r^*$  = the radius at which  $\Delta G_N$  is maximum

$$r^* = \frac{-2\gamma_{SL}}{\Delta G_v} = \frac{-2\gamma_{SL} T_m}{\Delta H_v \Delta T}$$

The energy barrier to homogeneous nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} = \frac{16\pi\gamma_{SL}^3 T_m^2}{\Delta H_v^2 \Delta T^2}$$

The temperature-dependence

$$r^* = 1/\Delta T$$

$$\Delta G^*_r = 1/\Delta T^2$$

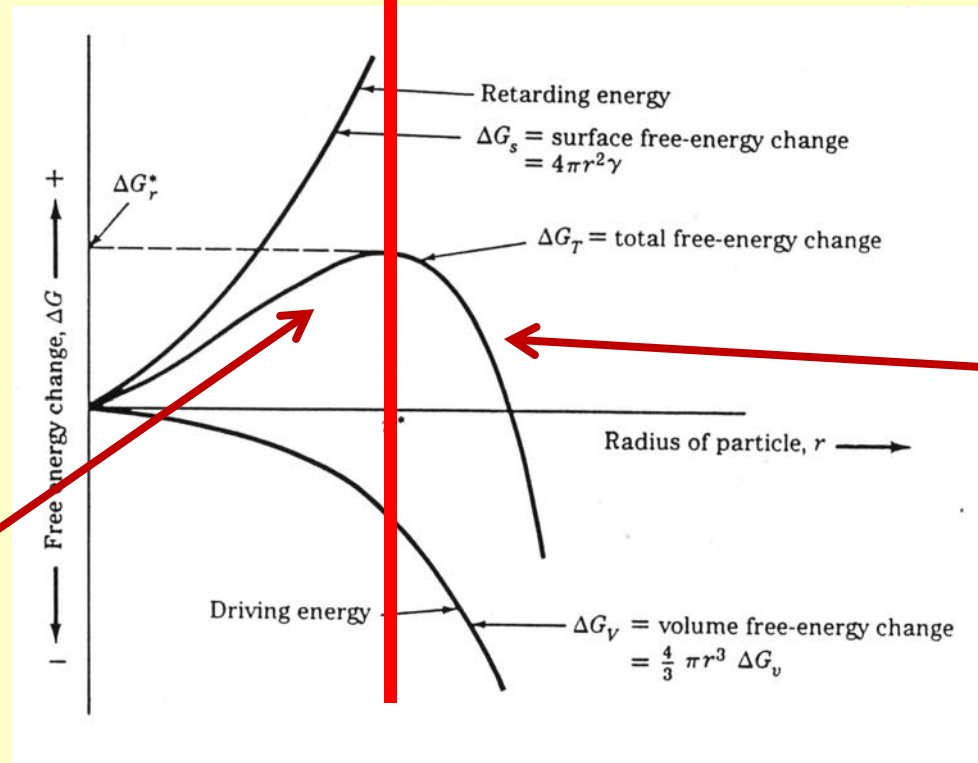
# Nucleation

a sub-critical cluster  
unstable for  $r < r^*$   
the cluster re-dissolves

a nucleus  
stable for  $r > r^*$   
the stable nucleus continues to grow

Increasing  $r$

$\Delta G > 0$



Increasing  $r$

$\Delta G < 0$

# Nucleation rate $n$

Nucleation rate  $n$

*Liquid to solid*

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

$\Delta G_N$  = thermodynamic barrier to nucleation

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

Assume, that solid phase nucleates as spherical clusters of radius  $r$

$\Delta G_N$  = the net (excess) free energy change for a single nucleus

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

$\Delta G_S = 4\pi r^2 \gamma_{SL}$  surface free energy change      positive

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

# Heterogeneous Nucleation

Nuclei can form at preferential sites:  
flask wall, impurities, catalysts, .....

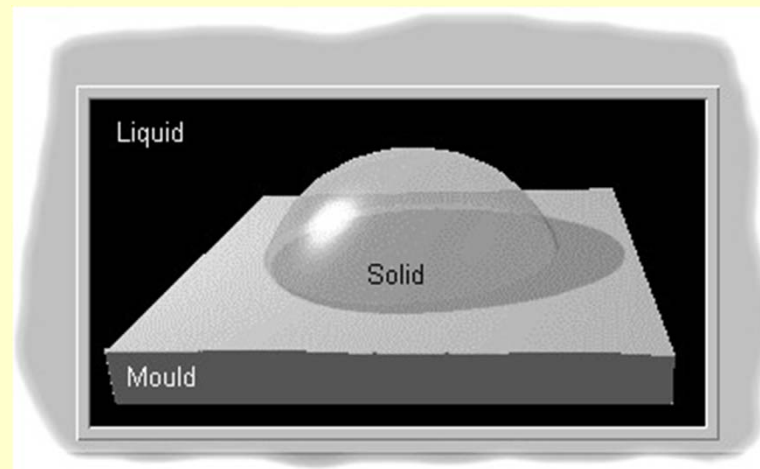
The energy barrier to nucleation,  $\Delta G^*$ , is substantially  
**reduced**

The critical nucleus size,  $r^*$  is the same for both  
heterogeneous and homogeneous nucleation

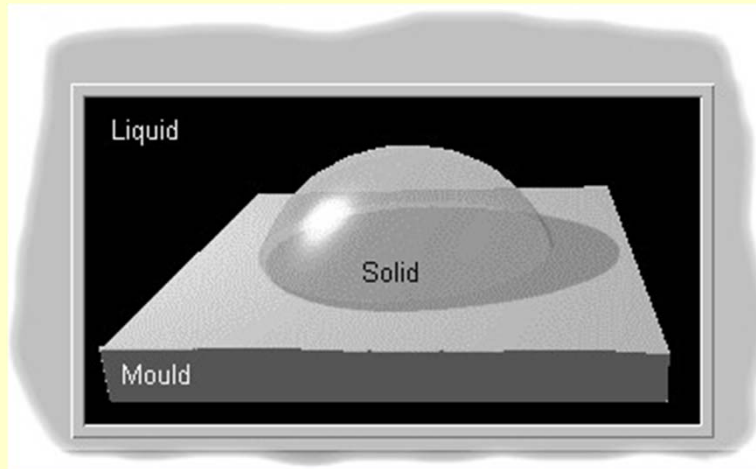
# Heterogeneous Nucleation

a solid cluster forming on a wall:

- the newly created interfaces (i.e. solid-liquid and solid-wall)
- the destroyed interface (liquid-wall)



# Heterogeneous Nucleation



$$r_{\text{het}}^* = \frac{-2\gamma_{\text{SL}}}{\Delta G_{\text{v}}^*} = r_{\text{hom}}^*$$

$$\Delta G_{\text{het}}^* = \frac{16\pi\gamma_{\text{SL}}^3}{3\Delta G_{\text{v}}^{*2}} S(\theta) = \Delta G_{\text{hom}}^* S(\theta)$$

$$\cos \theta = \frac{\gamma_{\text{WL}} - \gamma_{\text{WS}}}{\gamma_{\text{SL}}}$$

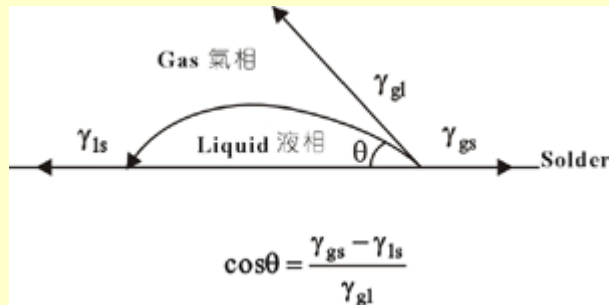
$\theta$  = wetting angle

Shape factor  $S(\theta)$

$$S(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}$$

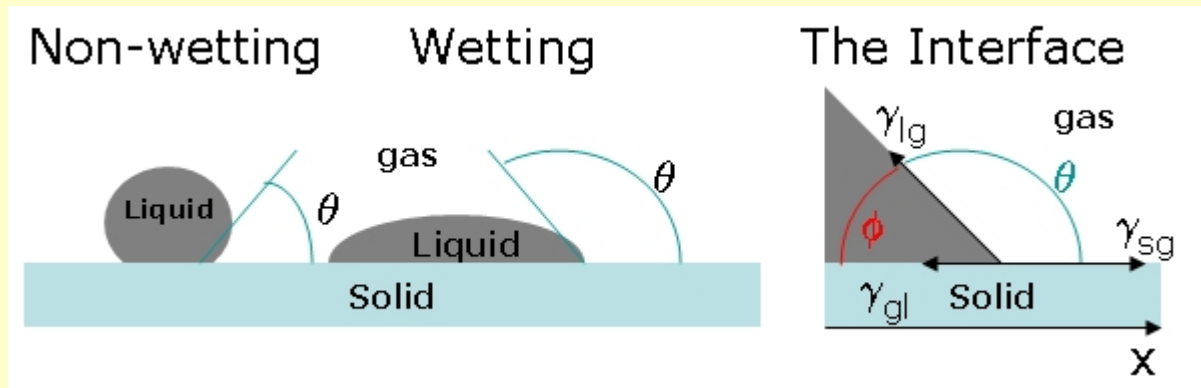
# Wetting Angle

Force equilibrium



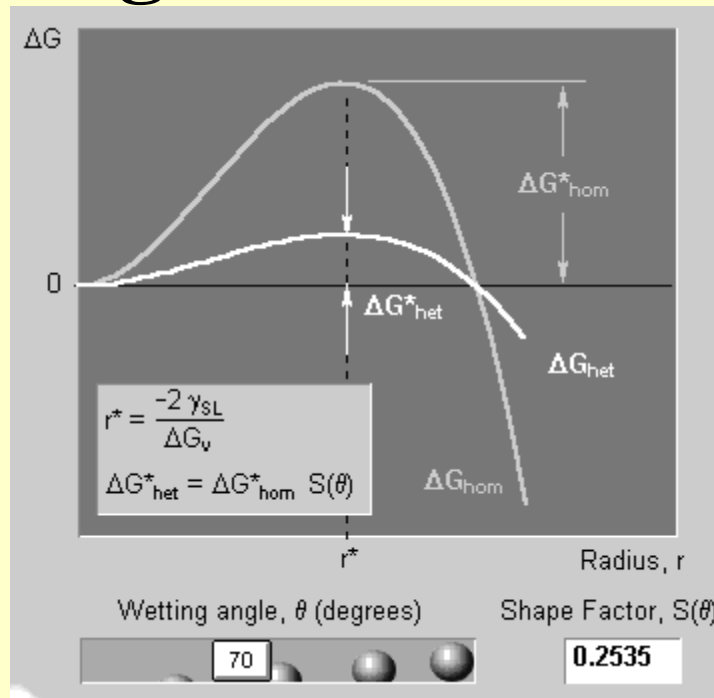
$$\gamma_{GS} = \gamma_{GL} \cos\theta + \gamma_{SL}$$

$$\cos\theta = \frac{\gamma_{GS} - \gamma_{SL}}{\gamma_{GL}}$$





# Heterogeneous Nucleation



The critical radius  $r^*$  is the same for both homogeneous and heterogeneous nucleation

The volume of a critical nucleus and  $\Delta G^*$  can be significantly smaller for heterogeneous nucleation due to the shape factor, depending on the wetting angle,  $\theta$

# Direct Reactions of Solids

## Solidification

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

- Volume free energy + surface energy

## One solid phase changing to another

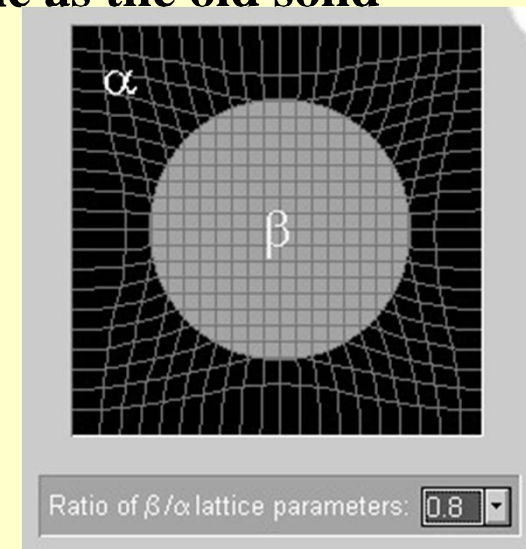
$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma_{SL} + \frac{4}{3} \pi r^3 \varepsilon$$

- Volume energy + surface energy + strain energy
- the new solid does not take up the same volume as the old solid
- a misfit strain energy term,  $\Delta G_s = V \varepsilon$

$$r^* = \frac{-2\gamma_{\alpha\beta}}{(\Delta G_v^* + \Delta G_s)}$$

$$\Delta G^* = \frac{16\pi\gamma_{\alpha\beta}^3}{3(\Delta G_v^* + \Delta G_s)^2}$$

$\gamma_{\alpha\beta}$  = the  $\alpha/\beta$  interfacial energy



# Nucleation

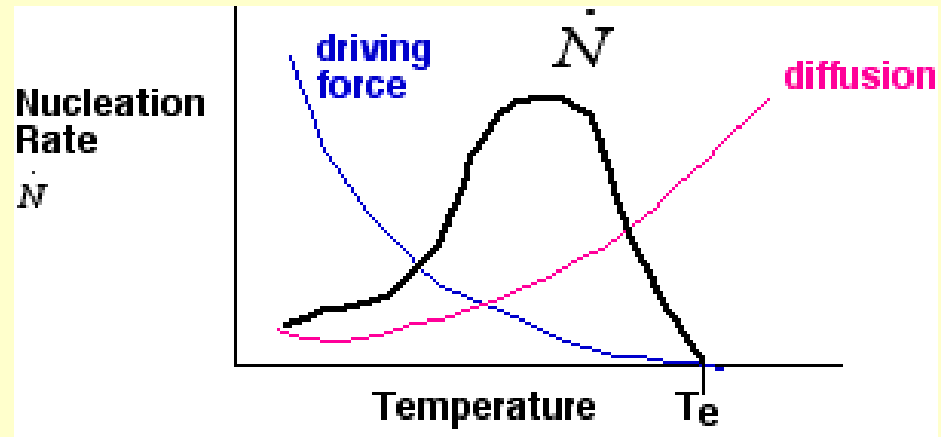
Transformation from liquid to solid phase requires:

- Nucleation of new phase
- Growth of new phase

Nucleation depends on:

- driving force toward equilibrium – cooling of a melt  
increases as we move to lower temperatures
- diffusion of atoms into clusters  
increases at higher temperatures

Combination of these two terms (multiplication)  
determines the total nucleation rate



# Nucleation rate $I$

Nucleation rate [ $\text{m}^{-3} \text{s}^{-1}$ ]  $I = \beta n^*$

$n^*$  = the steady-state population of critical nuclei ( $\text{m}^{-3}$ )

$$n^* = n_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

$n_0$  = the number of potential nucleation sites per unit volume  
 $\Delta G^*$  = the critical free energy of nucleation

$\beta$  = the rate at which atoms join critical nuclei ( $\text{s}^{-1}$ ), thereby making them stable, a diffusion-dependent term

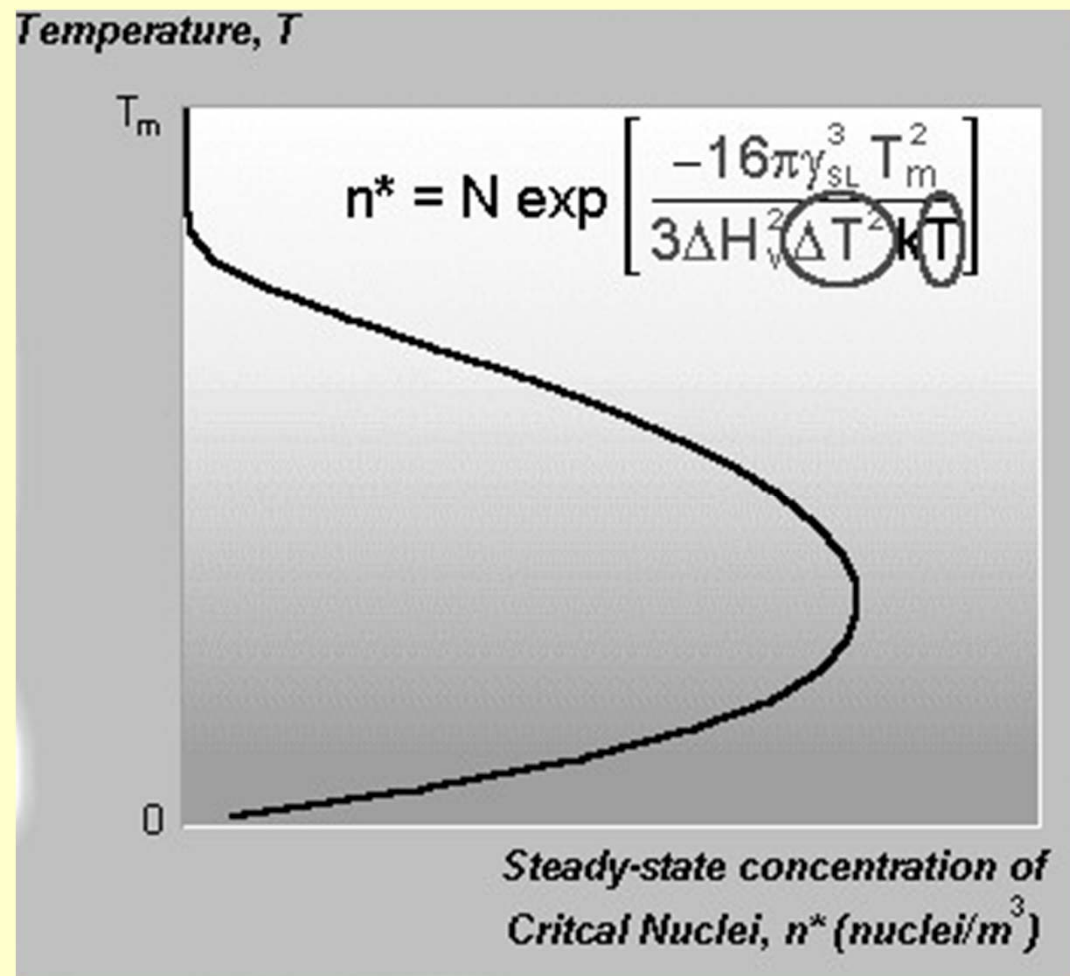
$$\beta = \omega \exp(-Q/kT)$$

$\omega$  = temperature independent term incorporating vibrational frequency and the area to which atoms can join the critical nucleus

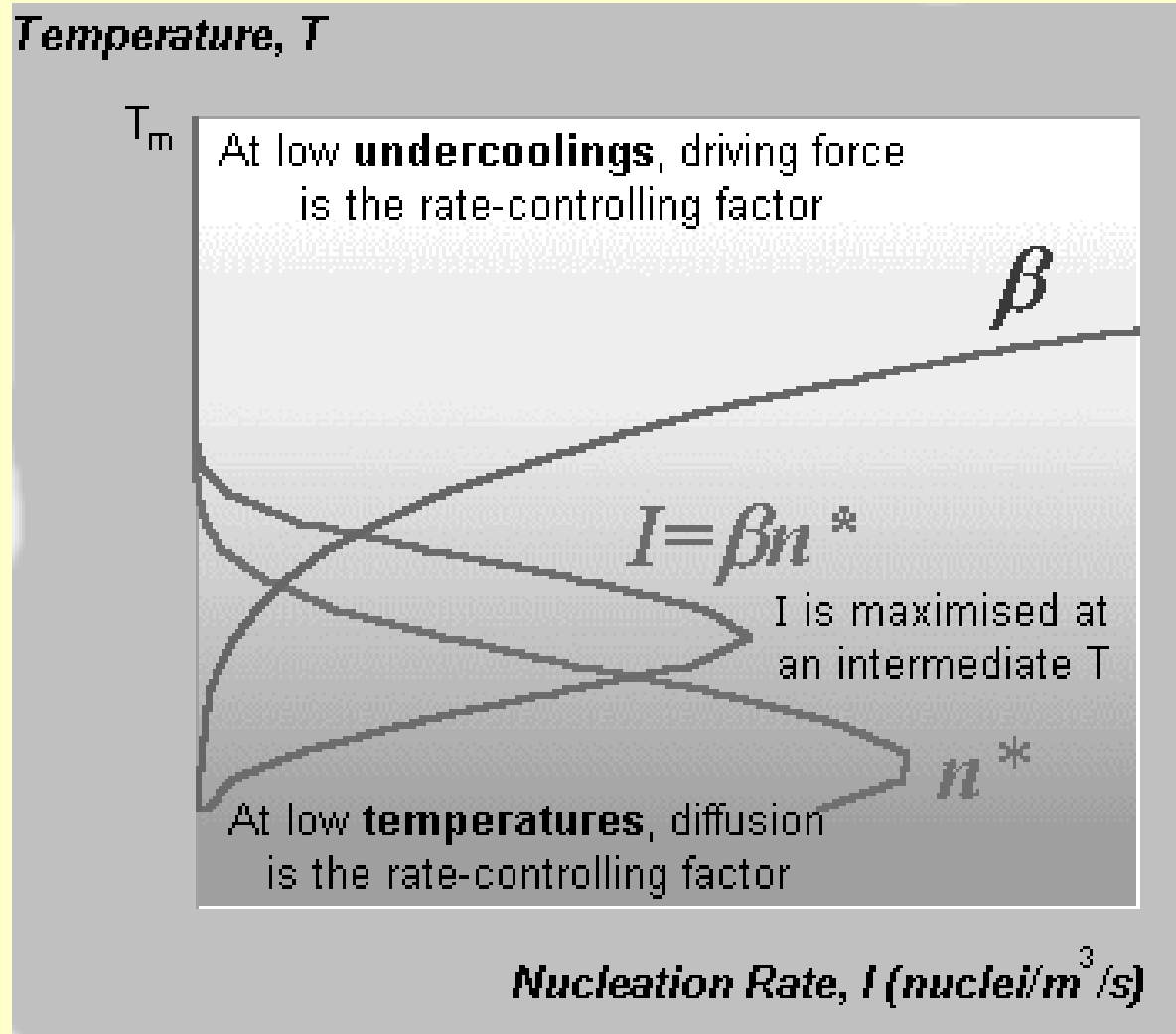
$Q$  = an activation energy for atomic migration

# Nucleation rate $I$

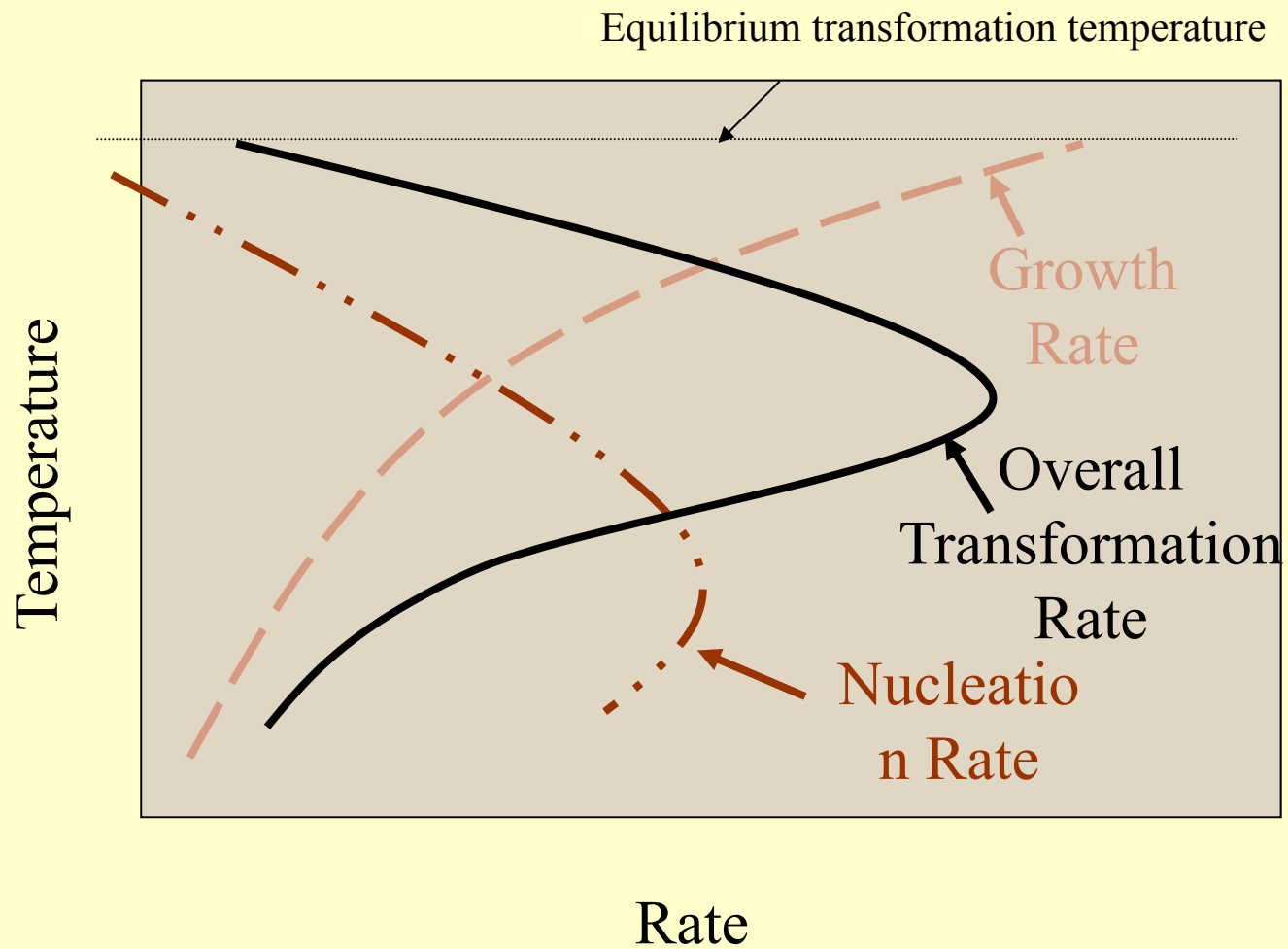
$n^*$  = the steady-state population of critical nuclei ( $\text{m}^{-3}$ )



# Nucleation



# Nucleation vs. Growth



# **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

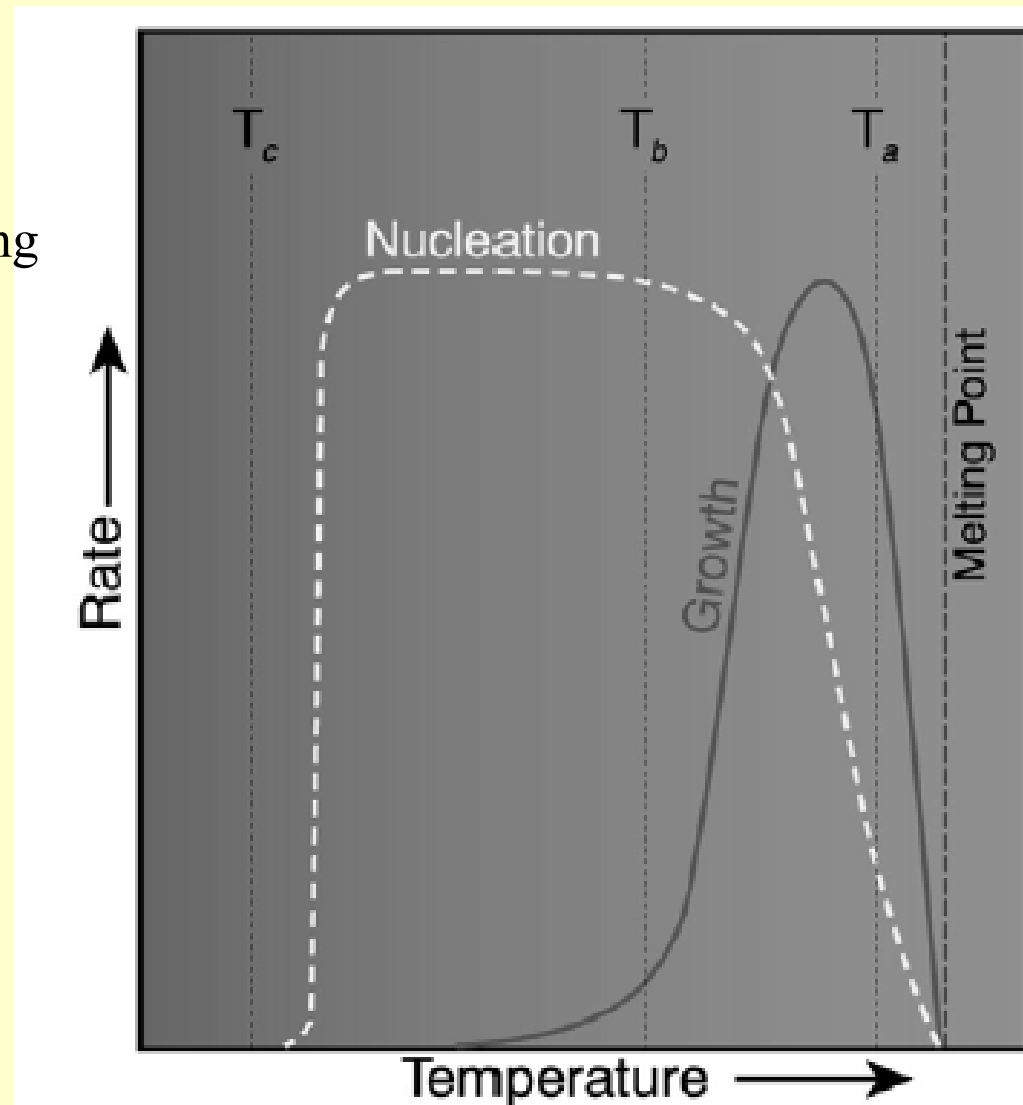
Fast growth, slow nucleation = Few coarse crystals

$T_b$  = 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**

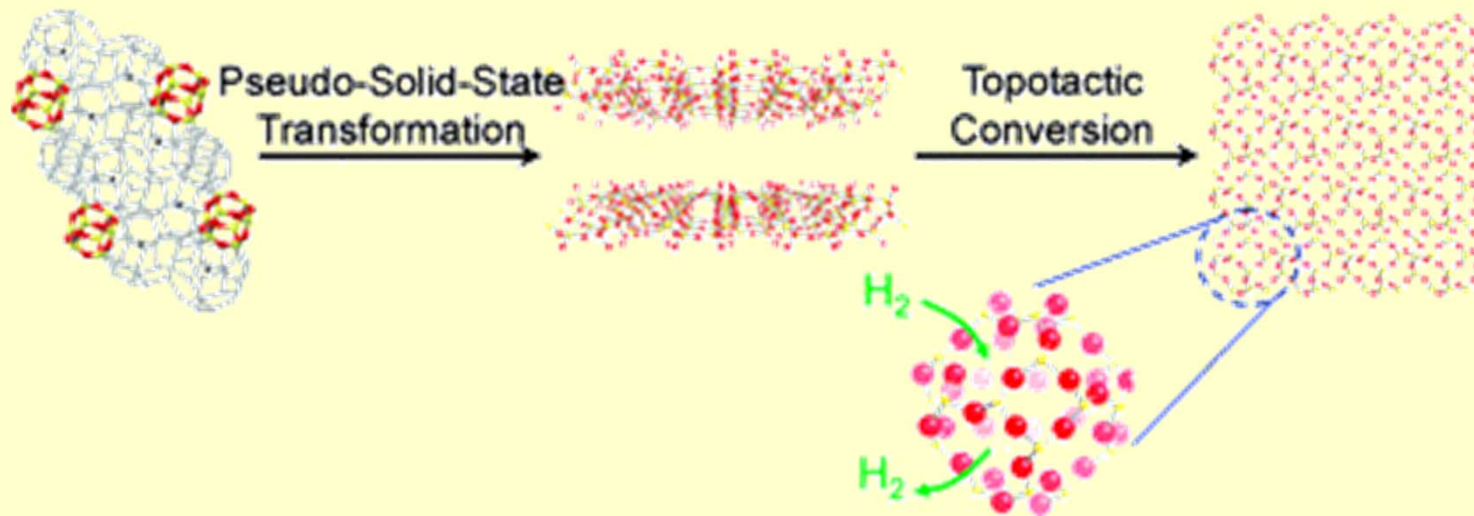
**Creates dangling bonds, localized electronic states, carrier scattering by defects, luminescence quenching, killer traps, generally reduces efficacy of electronic and optical devices, can be visualized by HR-TEM imaging**

# 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.

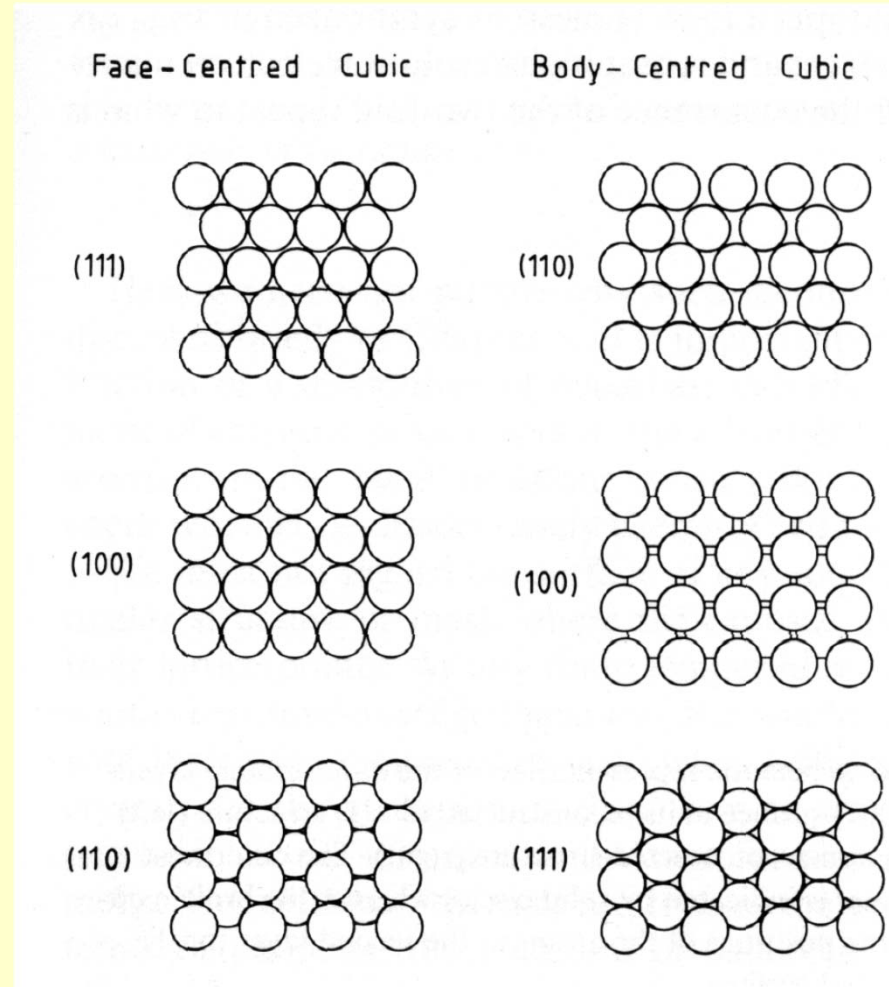


# Direct Reactions of Solids

**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.**

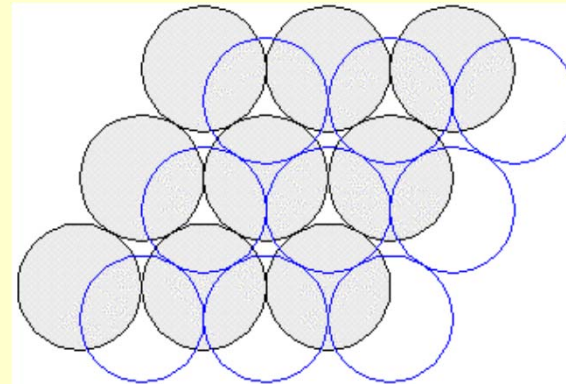
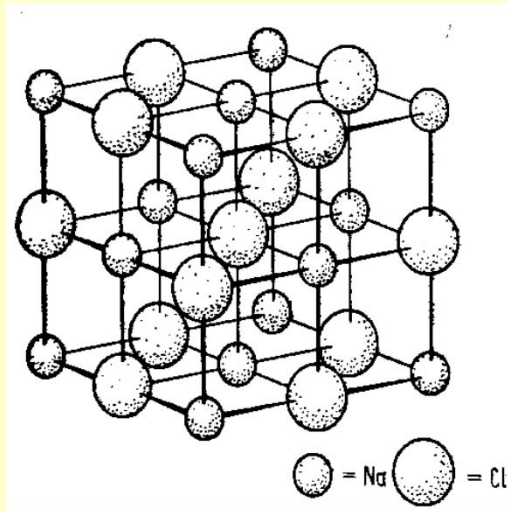


# Direct Reactions of Solids

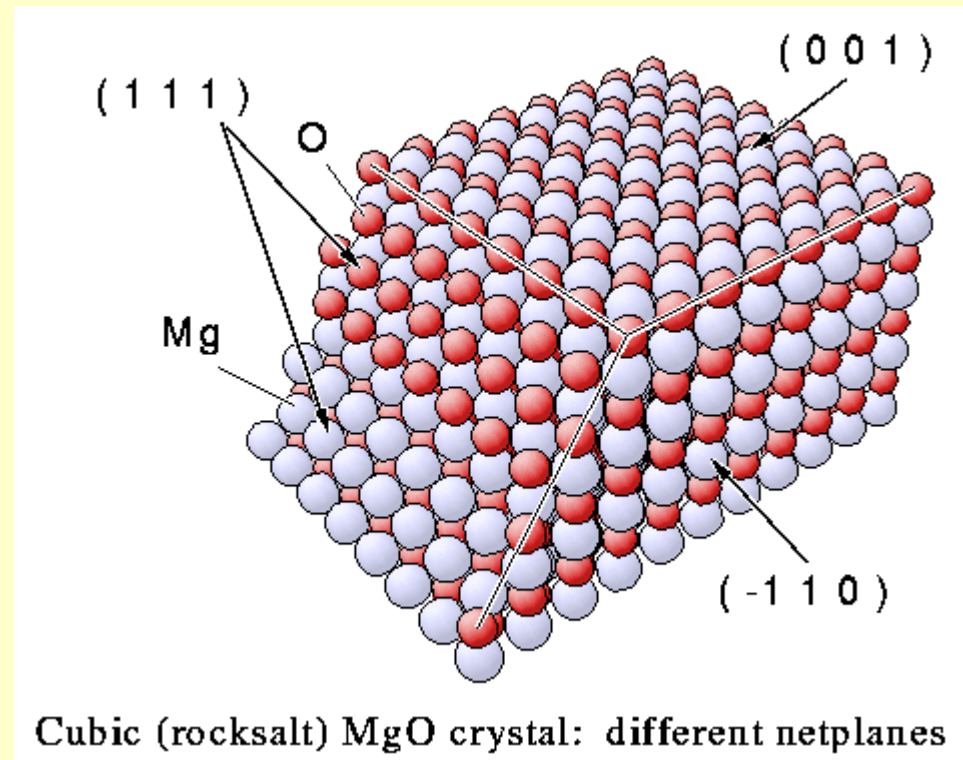
Example: MgO (rock salt)

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

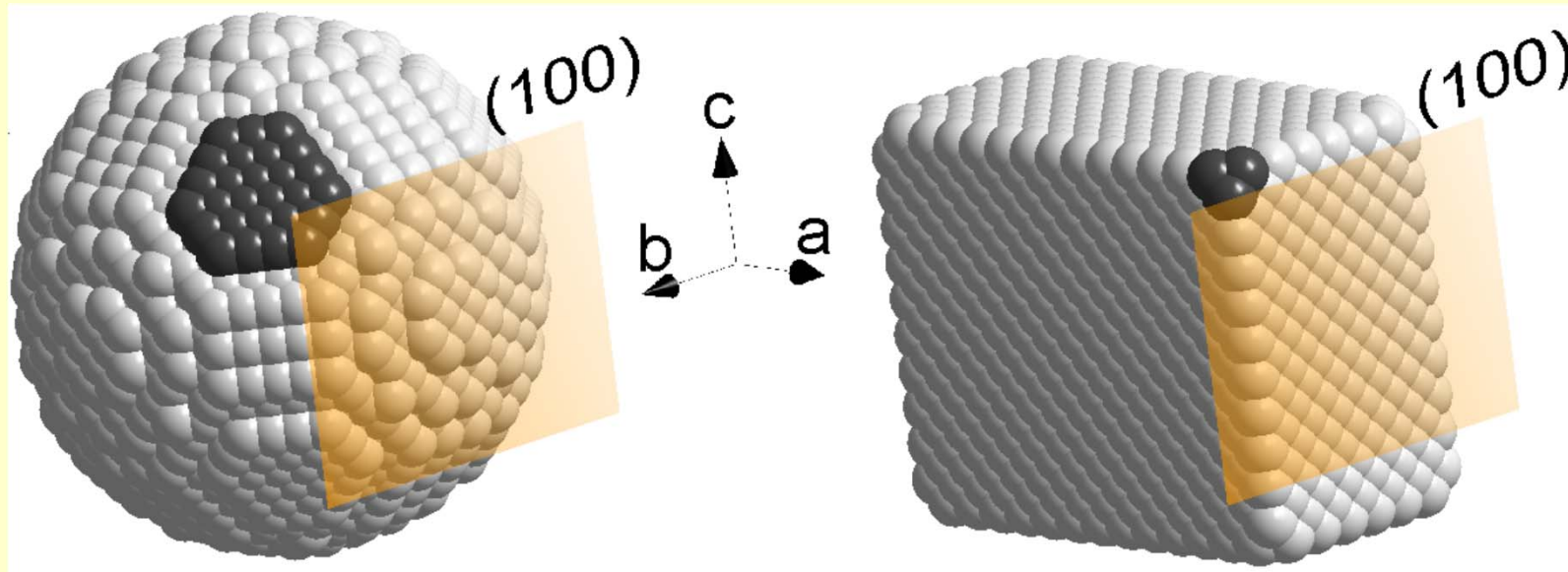
{111} MgO,  $\text{Mg}^{2+}$  or  $\text{O}^{2-}$  hexagonal arrangement



# Direct Reactions of Solids



# Direct Reactions of Solids



**Atoms located in (111) and (100) crystal planes for spherical and cuboid particles**

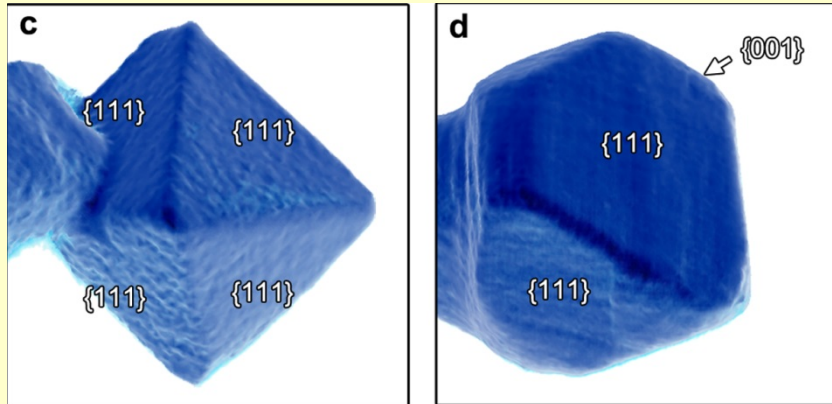
**Model particles = fcc structure of Pt 4 nm size**

**Dark grey = atoms located in (111)-surface**

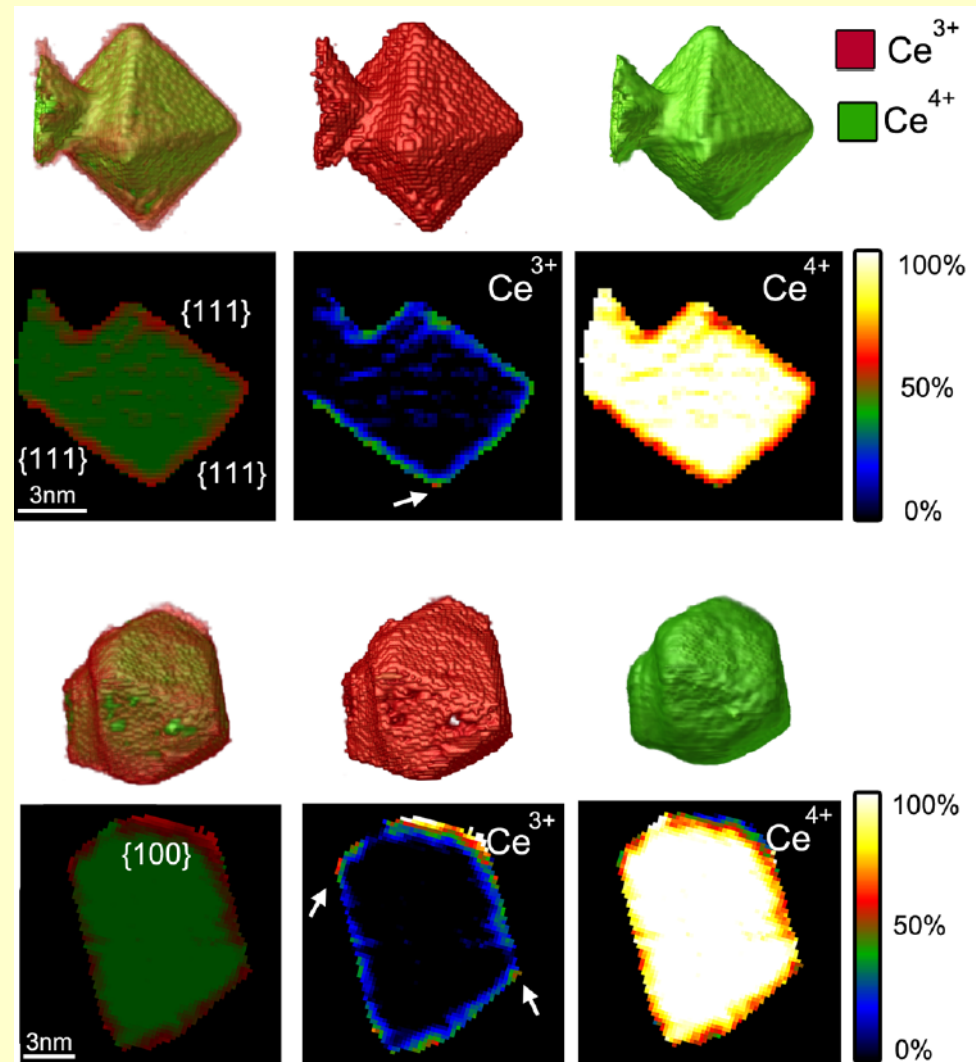
**Light orange = the (100) face**



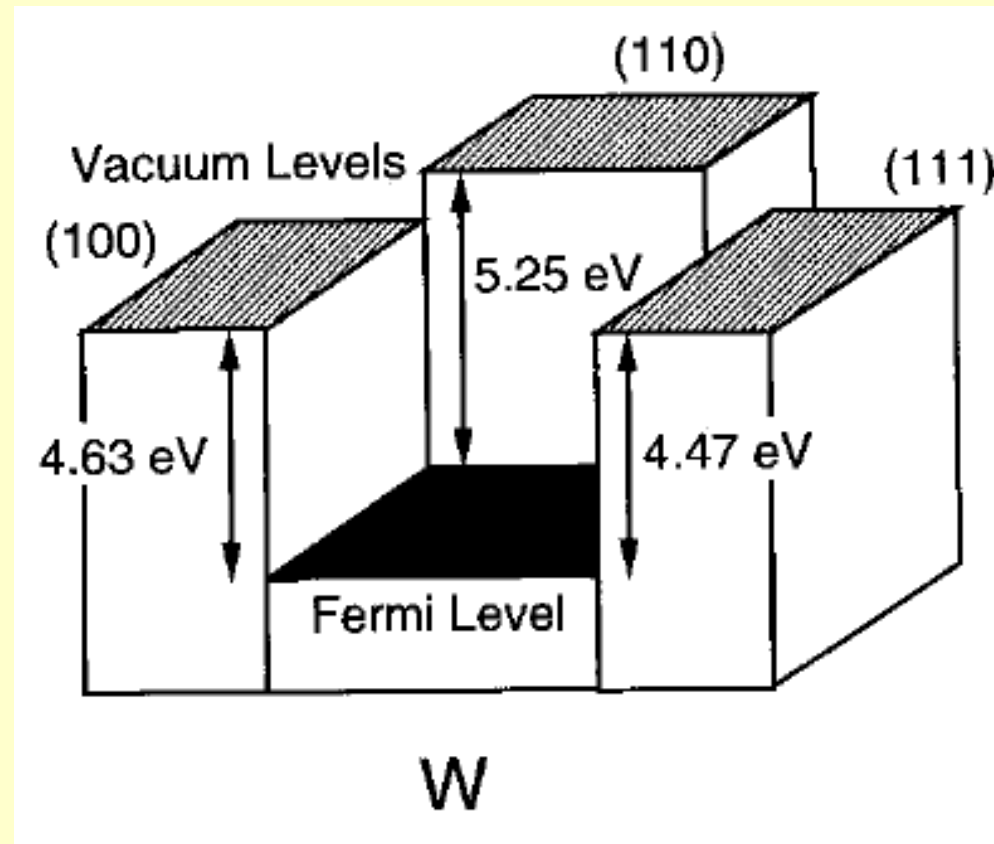
# Surface Facet Reactivity



**Electron tomography and electron energy loss spectroscopy (EELS) map the valency of the Ce ions in  $\text{CeO}_{2-x}$  nanocrystals in 3D. A facet-dependent reduction shell at the surface; {111} facets show a low surface reduction, whereas at {001} surface facets, the cerium ions are more reduced.**

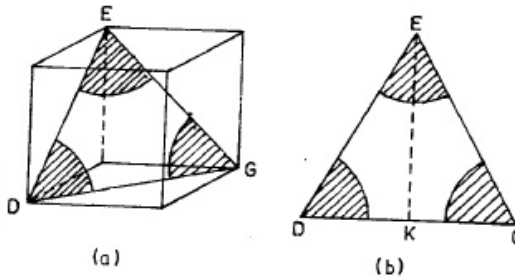


# Work function of different crystal planes



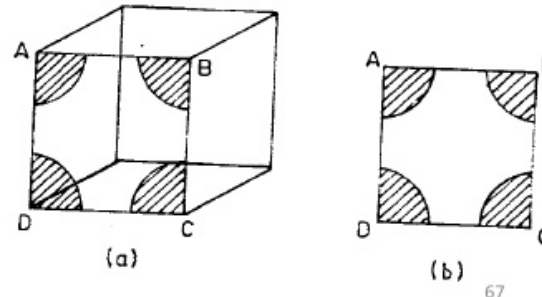
**Planar density on (111) plane in a Simple Cubic Structure:**

- Number of atoms on (111) plane is  $1/6 \times 3 = 0.5$
  - Area of (111) plane (triangle DEF) is  $1/2 \times (\sqrt{2}a) \times (0.866 \times \sqrt{2}a) = 0.866a^2$
- $$PD = 0.5 \text{ atom} / 0.866a^2 = 0.577 / a^2$$



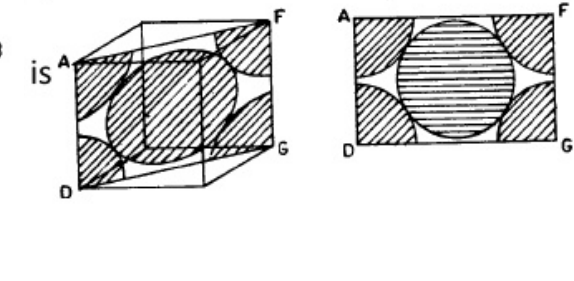
**Planar density on (100) plane in a Body Centred Cubic Structure:**

- Number of atoms on (100) plane is 1
  - Area of (100) plane (square section) is  $a \times a = a^2$
- $$PD = 1 \text{ atom} / a^2 = 1 / a^2$$



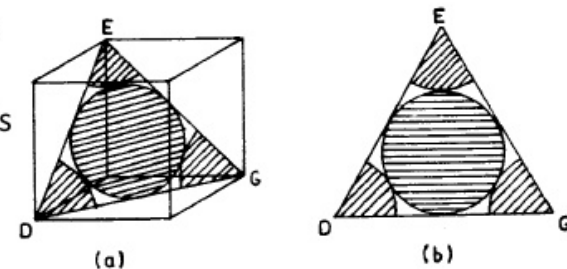
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**Body Centered Cubic Structure:**

- Number of atoms on (111) plane is  $1/6 \times 3 + 1 = 1.5$
  - Area of (111) plane (triangle DEG) is  $1/2 \times \sqrt{2}a \times \sqrt{2}a \sin 60^\circ = 0.866 a^2$
- $$PD = 1.5 \text{ atoms} / 0.866a^2 = 1.732 / a^2$$



# 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**

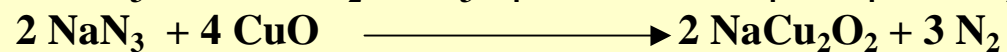
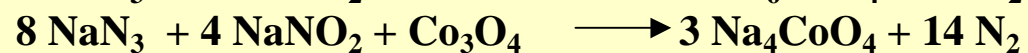
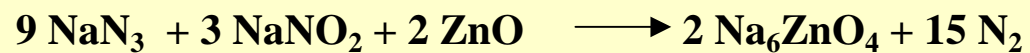
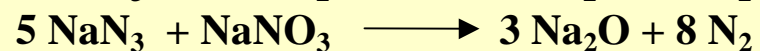
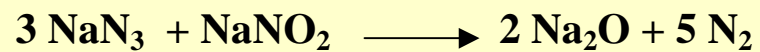
**Growth rate of specific surfaces controls morphology**

**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  $u = 1 - 10 \text{ mm.s}^{-1}$
- \* metastable phases

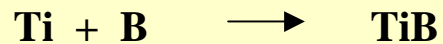
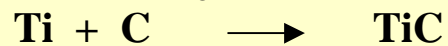
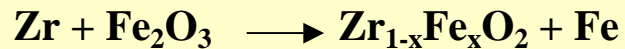
### State of the substance in the reaction front:

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

liquid, melt ( $T_f > T_m$ )

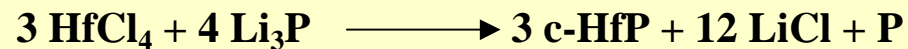
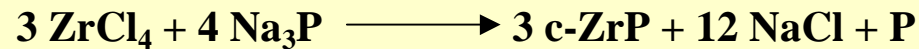
gaseous

### 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**



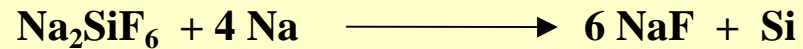
**c-ZrP and c-HfP hard and chemically inert materials,  
hexagonal to cubic transitions: ZrP 1425 °C, HfP 1600 °C**



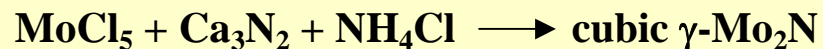
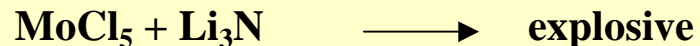
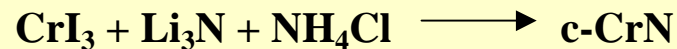
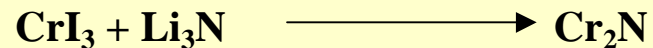
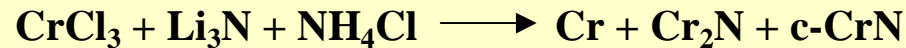
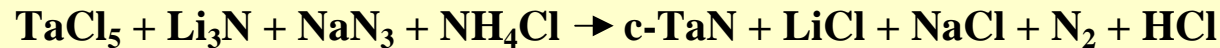
## DIRECT REACTION OF SOLIDS

# Self-Propagating Metathesis

### Silicon production

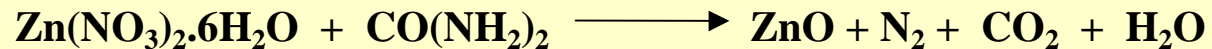


### Hard materials production



# 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.**

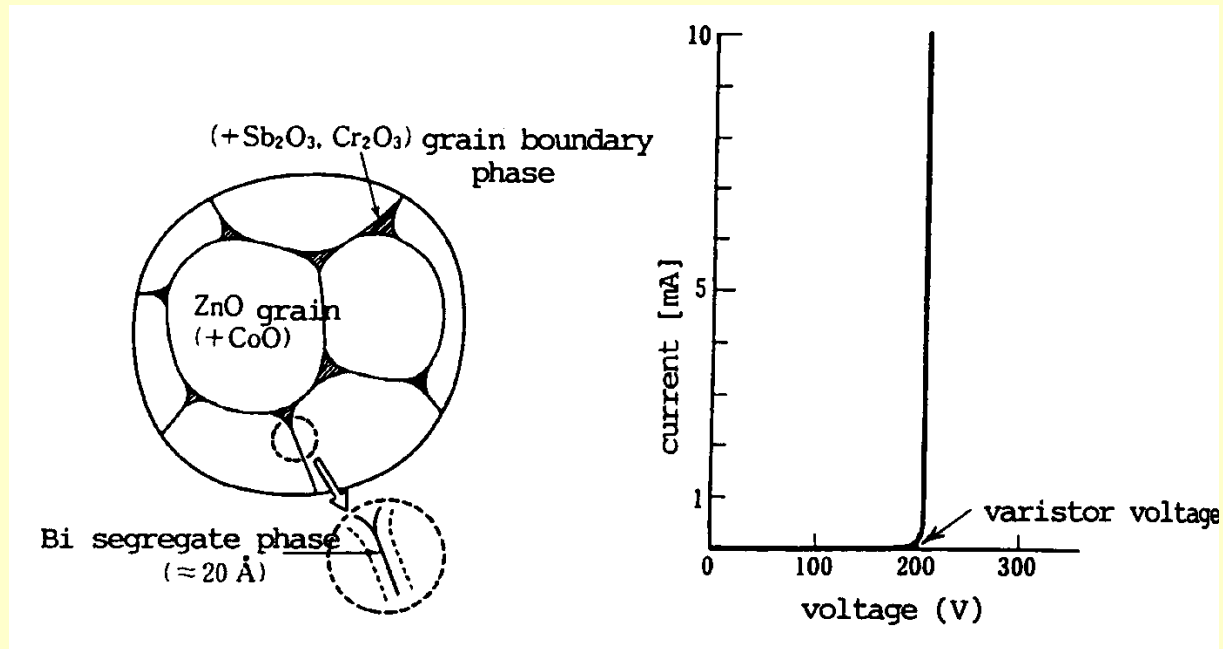


# Combustion Synthesis

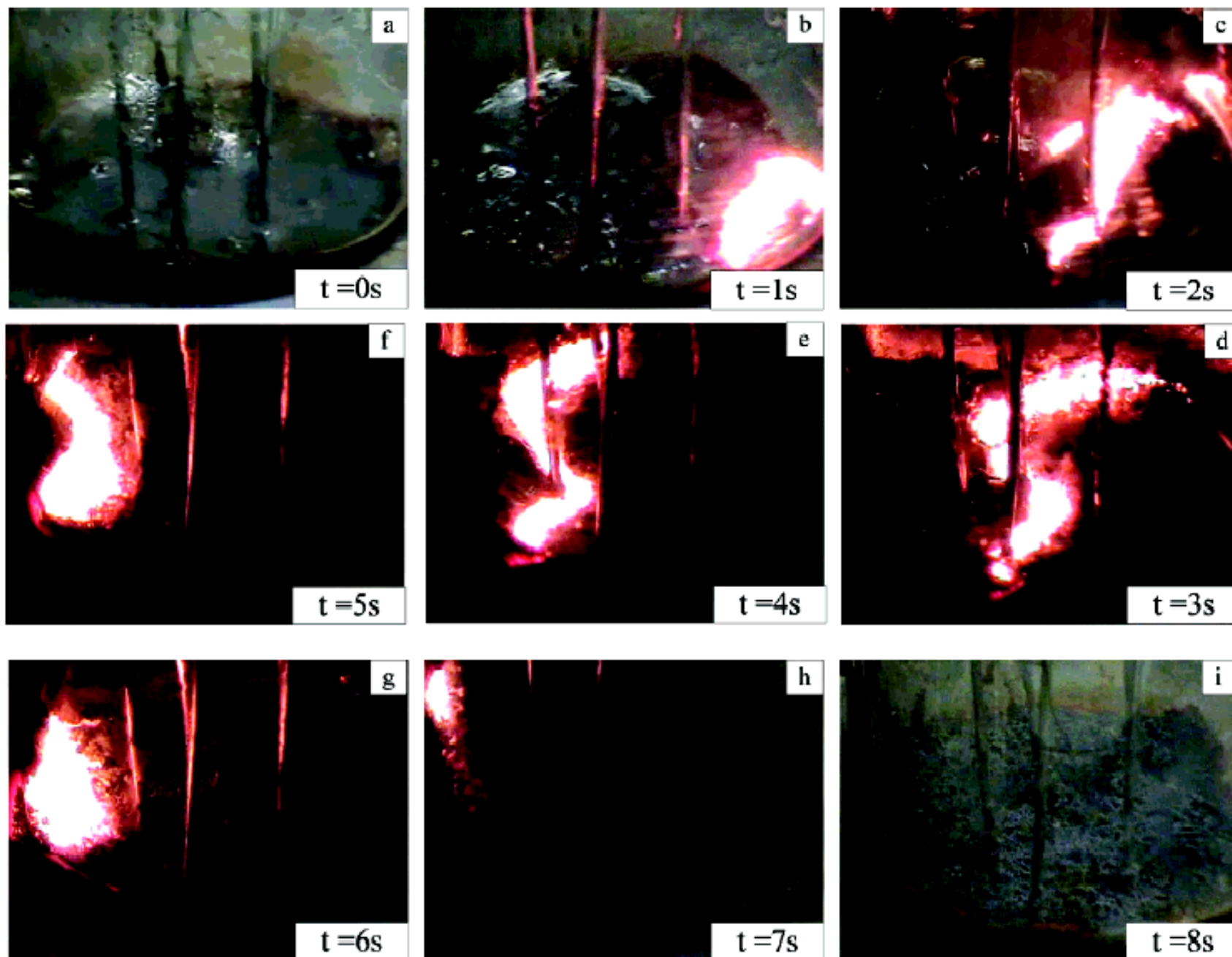
## Examples

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

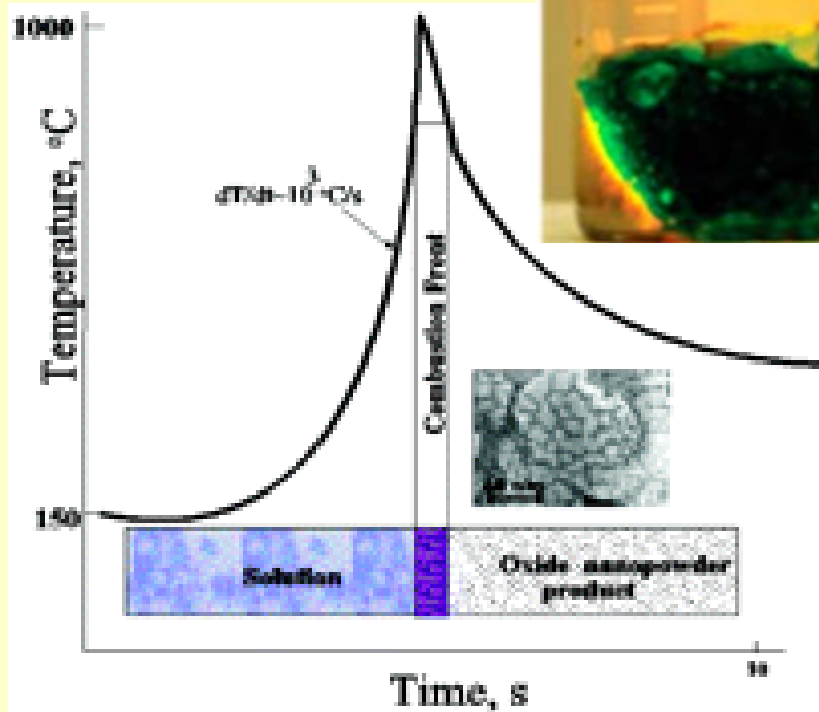
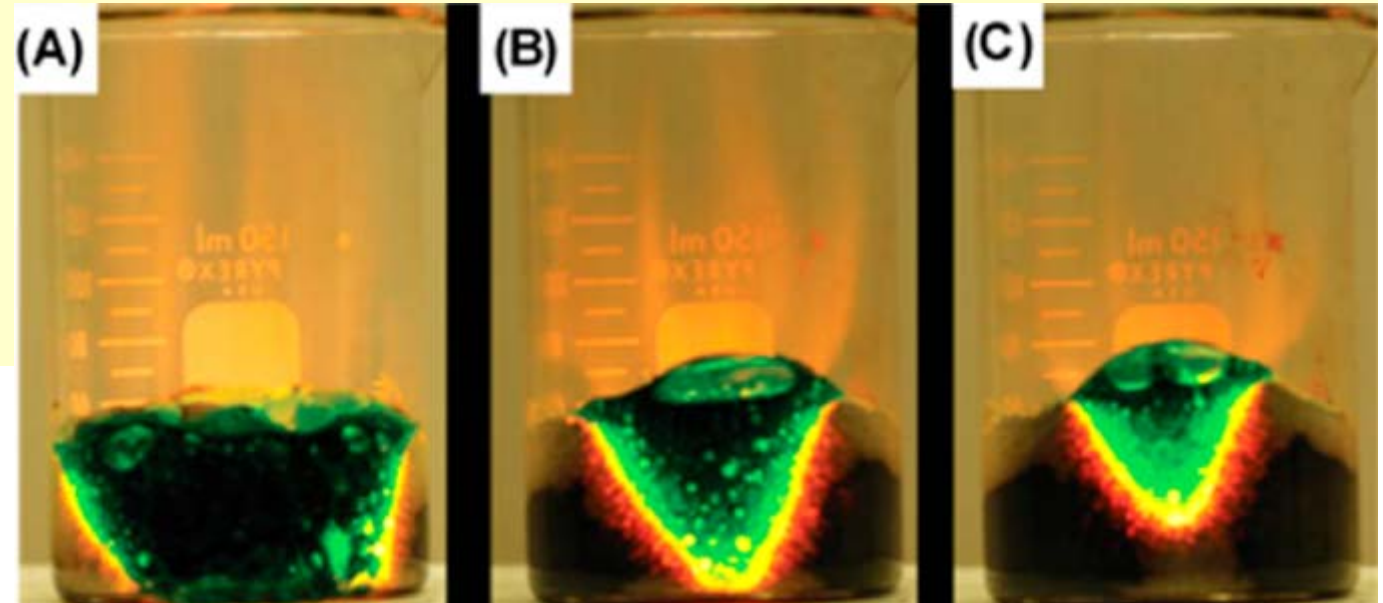
Non-Ohmic behavior  $I = (U/C)^a$  C, a = constants, a = 50  
Voltage stabilization, surge absorption



## Reaction front propagation: glycine-iron nitrate



# Self-Propagating Metathesis



# Combustion Synthesis

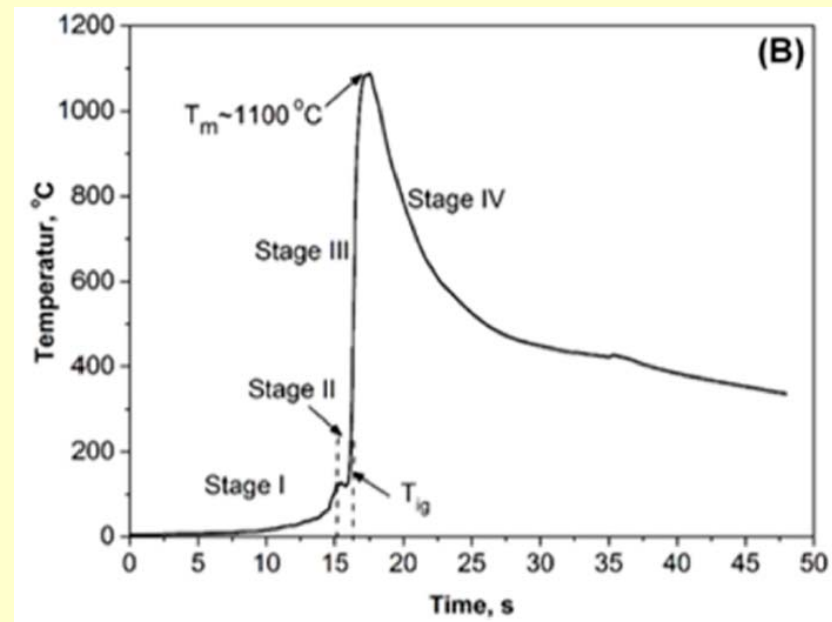
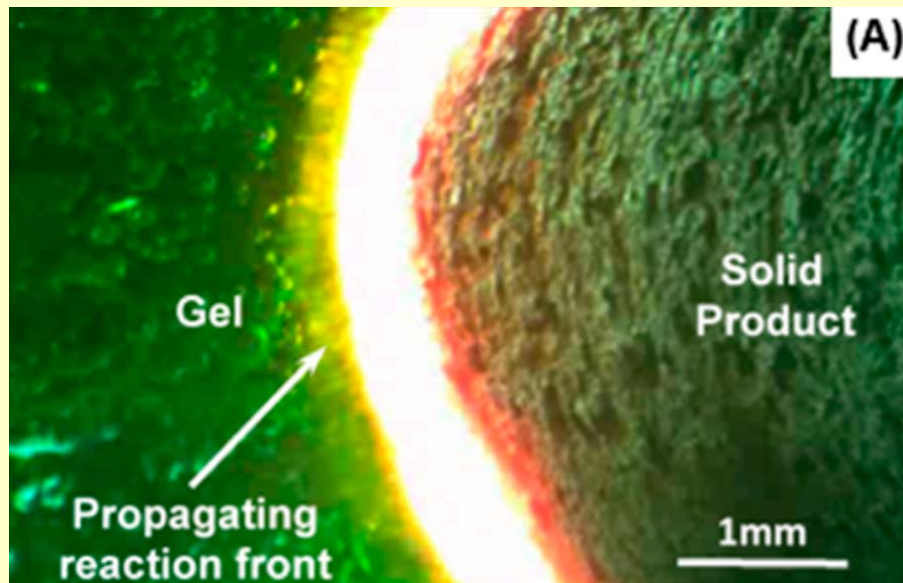
## Examples



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

combustion at 250 °C

calcination to  $\text{LiVMoO}_6$  cathode material for Li-ion



# Solution Combustion Synthesis

**Yttrium Iron Garnet (YIG)  $Y_3Fe_5O_{12}$**

**$Y(NO_3)_3 \cdot 6H_2O$**

**$Fe(NO_3)_3 \cdot 9H_2O$**

**citric acid monohydrate**

**Solution in water Y:Fe = 3:5**

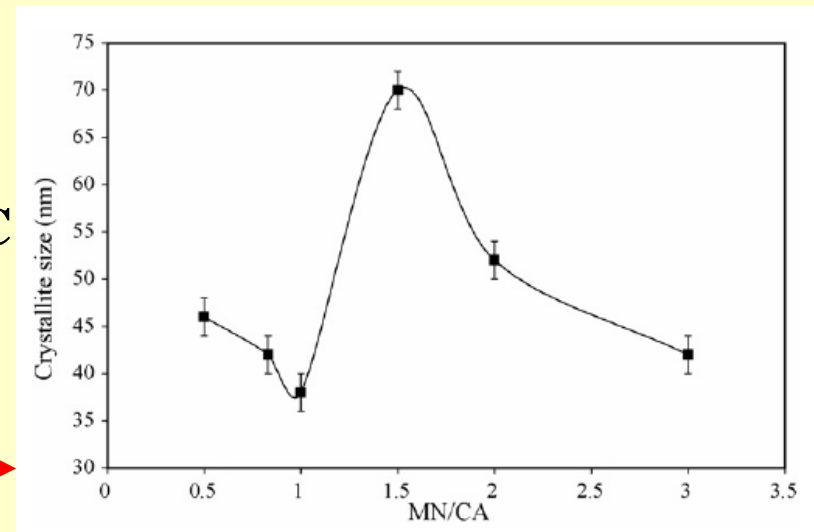
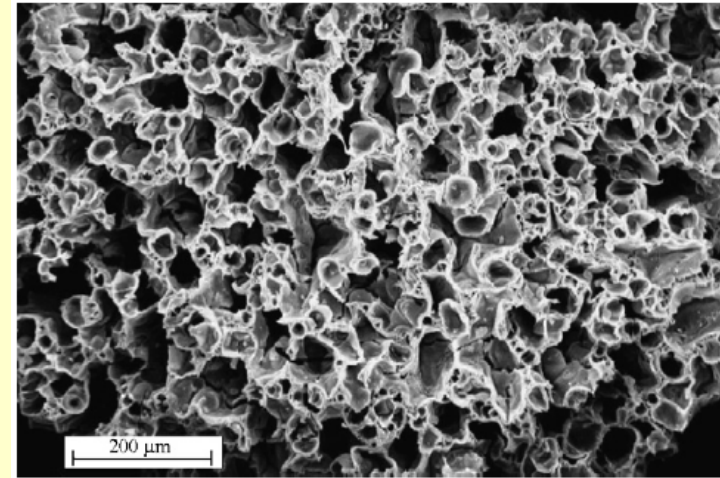
**The solution evaporated at 85 °C**

**stirred until viscous gel**

**Increasing the temperature up to 250 °C**

**ignition of the gel**

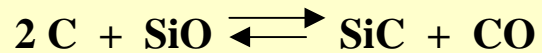
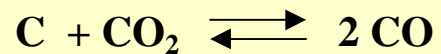
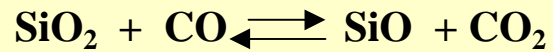
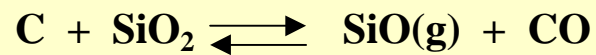
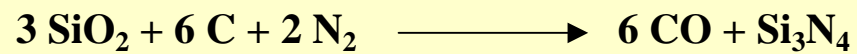
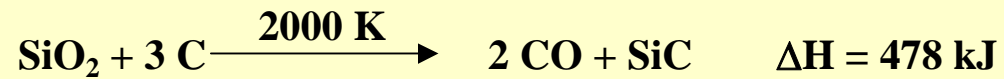
**MN/CA ratio controls the size**



## DIRECT REACTION OF SOLIDS

### Carbothermal Reduction

#### Acheson

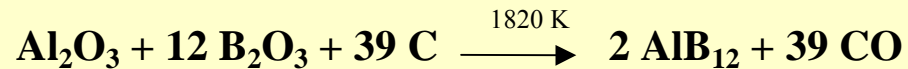
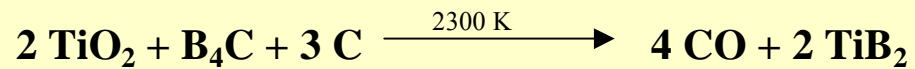
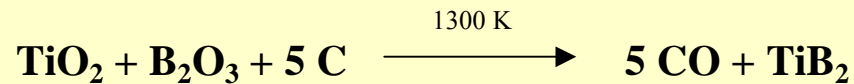




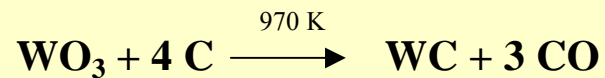
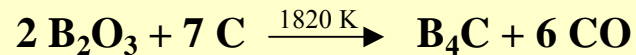
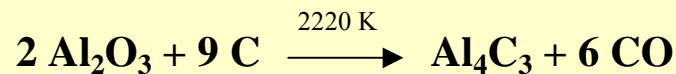
## DIRECT REACTION OF SOLIDS

### Carbothermal Reduction

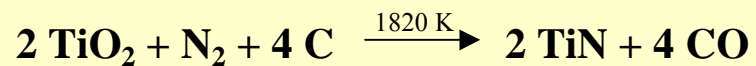
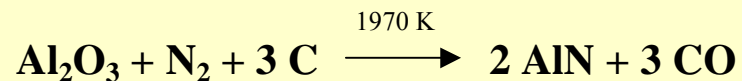
#### Borides



#### 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**

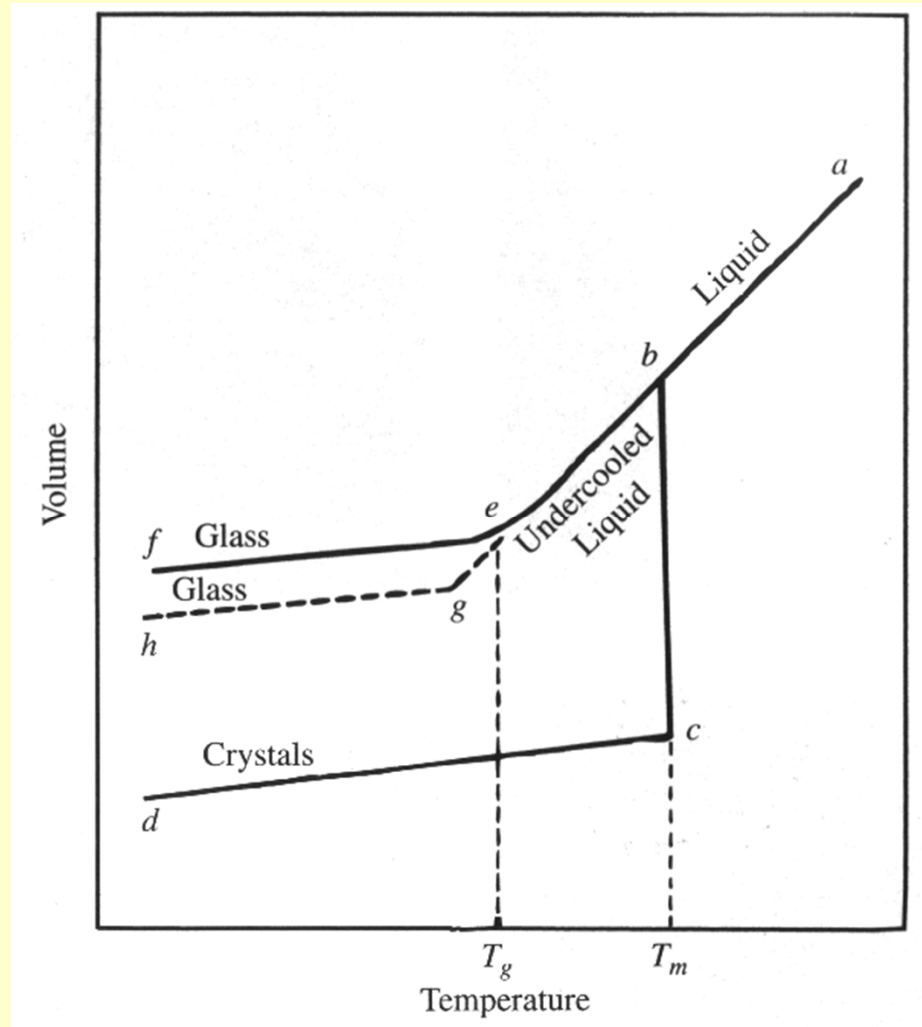
**Slow transport of precursors to seed**

**Lowest possible crystallization temperature**

**Crystallizing a glass above its glass transition**

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

# Fusion-Crystallization from Glass



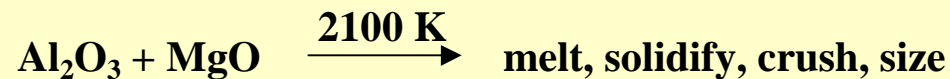
## DIRECT REACTION OF SOLIDS

# Fusion-Crystallization from Glass

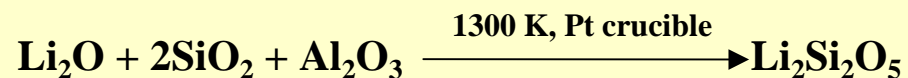
## Fusion-Crystallization from Glass

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°C for 2-3 hrs. Homogeneous, rapid cooling, fast viscosity increase, quenches transparent glass

$\text{Li}_2\text{Si}_2\text{O}_5$ , glass 500-700°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

## 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

# Cements

5600 BC - the floor of a villa in Serbia, a red lime binder (calcium oxide). Lime obtained by burning gypsum, limestone or chalk

2589-2566 BC - Egypt, the Great Pyramid of Cheops, gypsum-derived binders

800 BC the Greeks, 300 BC the Romans, limestone-derived cements became widespread

Vitruvius, *De Architectura*

the Appian Way, the Coliseum, the Pantheon

cements based on a mixture of natural and synthetic aluminosilicates with lime - pozzolan

1756 John Smeaton, lighthouse, a pozzolanic binder from lime, volcanic ash and copper slag, able to withstand the harsh coastal environment

1824 Joseph Aspdin, Leeds, England, developed and patented Portland cement.

**Portland cement** - made by heating at 1450°C chalk, shale, and clay or **limestone** in a kiln to form a partially fused mixture – clinker, which is then finely ground with gypsum

# Cements

**Hydraulic cements** - materials that set and harden by reacting with water, produce an adhesive matrix, combined with other materials, are used to form structural composite materials.

**Non-hydraulic cements** - lime and gypsum plasters, set by drying out, must be kept dry, gain strength slowly by absorption of CO<sub>2</sub> to form calcium carbonate through carbonation

**Concrete** - a mixture of cement (binding agent) and water with aggregate (varying amounts of coarse and fine sand and stone). Consumption of concrete - 2.5 tonnes per person per year.

**Mortar** - used to bind bricks together, made from cement but with finer grade of added materials.

## Portland cement

Component	Formula	Phase	wt%
Tricalcium silicate	C3S     Ca <sub>3</sub> SiO <sub>5</sub>	Alite	50-70
B-dicalcium silicate	C2S     Ca <sub>2</sub> SiO <sub>4</sub>	Belite	15-30
Tricalcium aluminate	C2A     Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	Aluminate	5-10
Tetracalcium aluminoferrite	C4AF     Ca <sub>2</sub> (Al/Fe)O <sub>5</sub>	Ferrite	5-15

# Chemical Cement Nomenclature

S	$\text{SiO}_2$	C	$\text{CaO}$
A	$\text{Al}_2\text{O}_3$	F	$\text{Fe}_2\text{O}_3$
T	$\text{TiO}_2$	M	$\text{MgO}$
K	$\text{K}_2\text{O}$	N	$\text{Na}_2\text{O}$
H	$\text{H}_2\text{O}$		
C̄	$\text{CO}_2$		
S̄	$\text{SO}_3$		

