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*

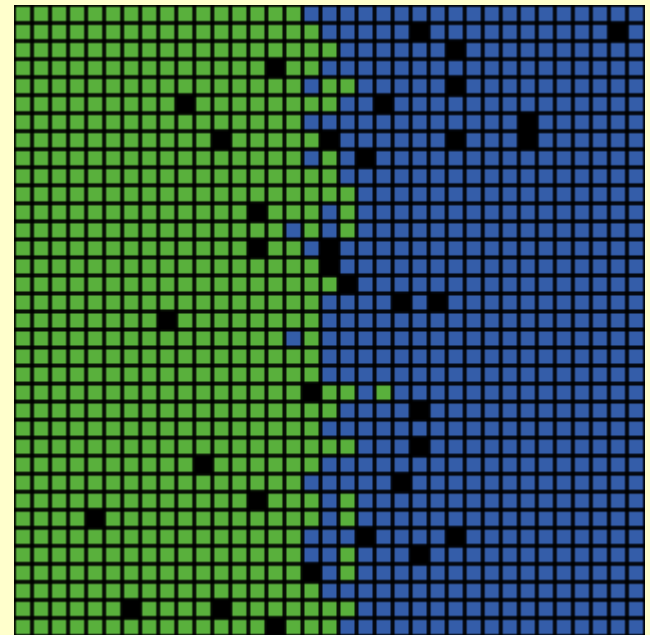**Reactions in a lattice of atoms**

Atomic mobility

No mobility without defects – perfect crystal = no chemistry

High temperatures

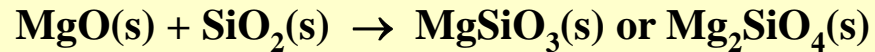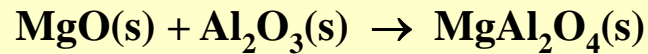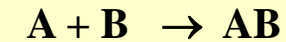**Reactions on the interphase between phases**

Microstructure - crystallite size, shape, defects

Diffusion controls the reaction rate

Reaction Types

Solid - solid synthesis - addition $A + B \rightarrow AB$

$MgO(s) + Al_2O_3(s) \rightarrow MgAl_2O_4(s)$

$MgO(s) + SiO_2(s) \rightarrow MgSiO_3(s)$ or $Mg_2SiO_4(s)$

Solid - solid synthesis – exchange, metathesis $AB + C \rightarrow AC + B$

$CaCO_3(s) + SiO_2(s) \rightarrow CaSiO_3(s) + CO_2(g)$

$Ge(s) + 2\ MoO_3(s) \rightarrow GeO_2(s) + 2\ MoO_2(s)$

Solid - solid synthesis – exchange and addition
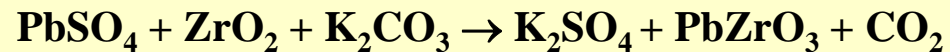
$PbSO_4 + ZrO_2 + K_2CO_3 \rightarrow K_2SO_4 + PbZrO_3 + CO_2$

Solid - solid synthesis - dissociation $AB \rightarrow A + B$
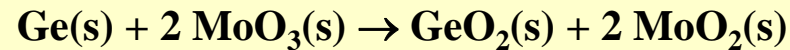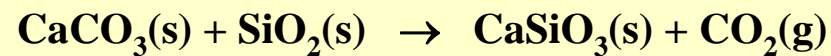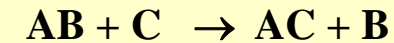
$Ca_3SiO_5(s) \rightarrow Ca_2SiO_4(s) + CaO(s)$

Reaction Types

Solid - solid synthesis - addition $\qquad$ $A + B \;\rightarrow\; AB$

$MgO(s) + Al_2O_3(s) \;\rightarrow\; MgAl_2O_4(s)$
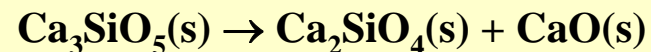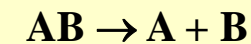
$MgO(s) + SiO_2(s) \;\rightarrow\; MgSiO_3(s) \text{ or } Mg_2SiO_4(s)$

Solid - solid synthesis – exchange, metathesis $\qquad$ $AB + C \;\rightarrow\; AC + B$

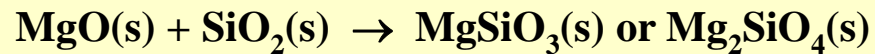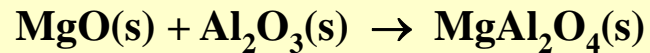$CaCO_3(s) + SiO_2(s) \;\rightarrow\; CaSiO_3(s) + CO_2(g)$

$Ge(s) + 2\,MoO_3(s) \rightarrow GeO_2(s) + 2\,MoO_2(s)$

Solid - solid synthesis - dissociation $\qquad$ $AB \rightarrow A + B$

$Ca_3SiO_5(s) \rightarrow Ca_2SiO_4(s) + CaO(s)$

3
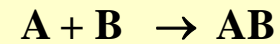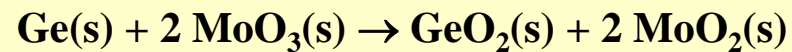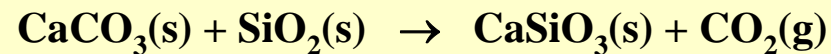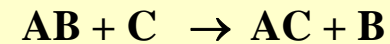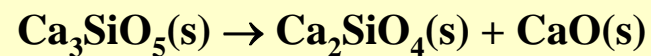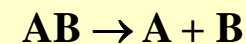
Reaction Types

Solid – gas synthesis $A + B \rightarrow AB$

$2 \, Fe_3O_4(s) + 1/2 \, O_2(g) \rightarrow 3 \, Fe_2O_3(s)$

$2 \, SiCl_4(g) + 4 \, H_2(g) + Mo(s) \rightarrow MoSi_2(s) + 8 \, HCl(g)$
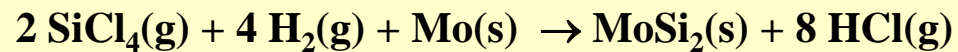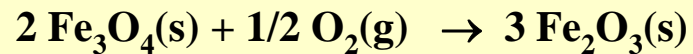
High temperature corrosion of metals in air

Solid – gas dissociation $AB \rightarrow A + B$

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$Al_4Si_4O_{10}(OH)_8(s) \rightarrow Al_4(Si_4O_{10})O_4(s) + 4 \, H_2O(g)$
Kaolinite   Metakaolinite
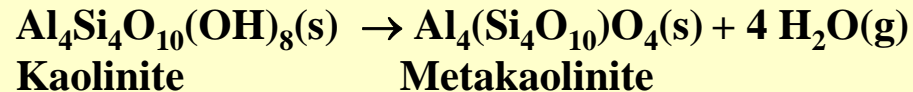
Reaction Types

Other Examples

Oxides

$$BaCO_3 + TiO_2 \longrightarrow BaTiO_3 + BaTi_2O_5 + CO_2$$

$$UF_6 + H_2 + 2\,H_2O \xrightarrow{873\ K} UO_2\ (powder) + 6\ HF$$
dust = radiological hazard, milling, sintering to UO_2 pellets
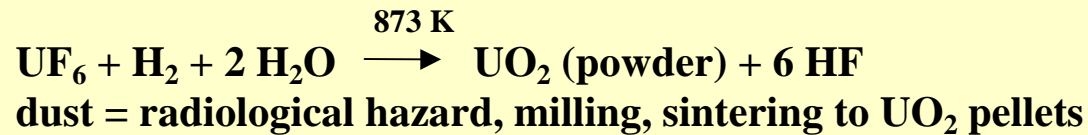
YBCO 123 Superconductor (1987)

$$Y_2O_3 + BaCO_3 + CuO \xrightarrow[air]{1223\ K} \xrightarrow[O_2]{473\ K} YBa_2Cu_3O_{7-x}$$

$$Tl_2O_3 + 2BaO + 3CaO + 4CuO \xrightarrow{1130\ K} Tl_2Ba_2Ca_3Cu_4O_{12}$$
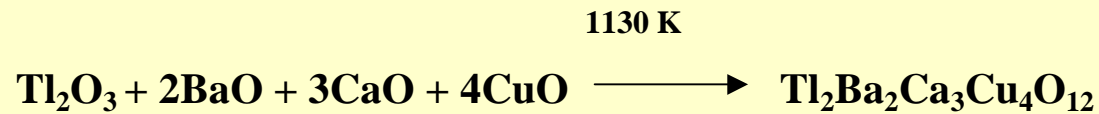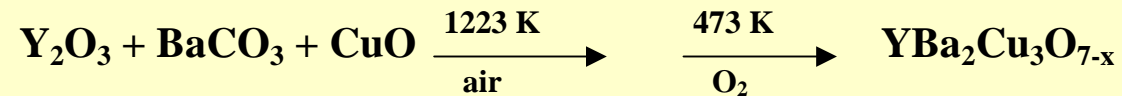
Reaction Types

Other classes than oxides

Pnictides

$$Na_3E + ME + E \xrightarrow{\text{1100 K}} Na_2M_3E_4 \qquad M = Eu, Sr, \ E = P, As$$

Metals

$$UF_4 + 2\ Ca \longrightarrow U + 2\ CaF_2 \quad \textbf{Manhattan Project}$$
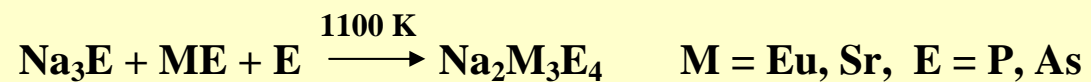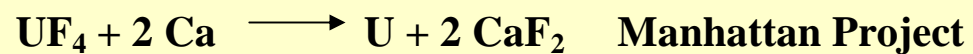
Reaction Types

Chlorides

$$3 \text{ CsCl} + 2 \text{ ScCl}_3 \longrightarrow \text{Cs}_3\text{Sc}_2\text{Cl}_9$$

$$6 \text{ NH}_4\text{Cl} + \text{Y}_2\text{O}_3 \longrightarrow 2 \text{ YCl}_3 + 3 \text{ H}_2\text{O} + 6 \text{ NH}_3$$
$$6 \text{ NH}_4\text{Cl} + \text{Y} \longrightarrow (\text{NH}_4)_3\text{YCl}_6 + 1.5 \text{ H}_2 + 3 \text{ NH}_3$$
$$4 \text{ NH}_4\text{Cl} + 3 \text{ NH}_4\text{ReO}_4 \longrightarrow 3 \text{ Re} + 12 \text{ H}_2\text{O} + 3.5 \text{ N}_2 + 4 \text{ HCl}$$

Aluminosilicates

$$\text{NaAlO}_2 + \text{SiO}_2 \longrightarrow \text{NaAlSiO}_4$$

Chalcogenides

$$\text{Pb} + \text{Mo} + \text{S} \xrightarrow{1400 \text{ K}} \text{PbMo}_6\text{S}_8$$
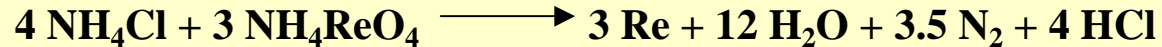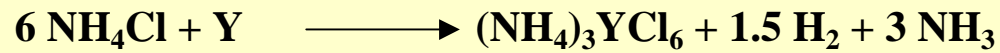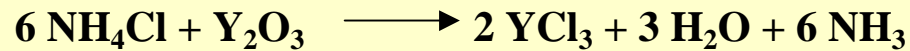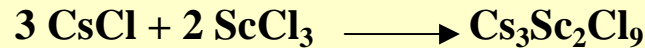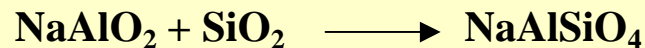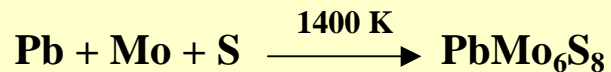
Chevrel phases
($\text{M}_x\text{Mo}_6\text{X}_8$, M = RE, Sn, Pb, Cu,
X = S, Se, Te)

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 °C)

Firing/grinding cycles

Milling

Planetary ball mill

Rotation and counter-wise spining

Horizontal section

Movement of the supporting disk

Centrifugal force

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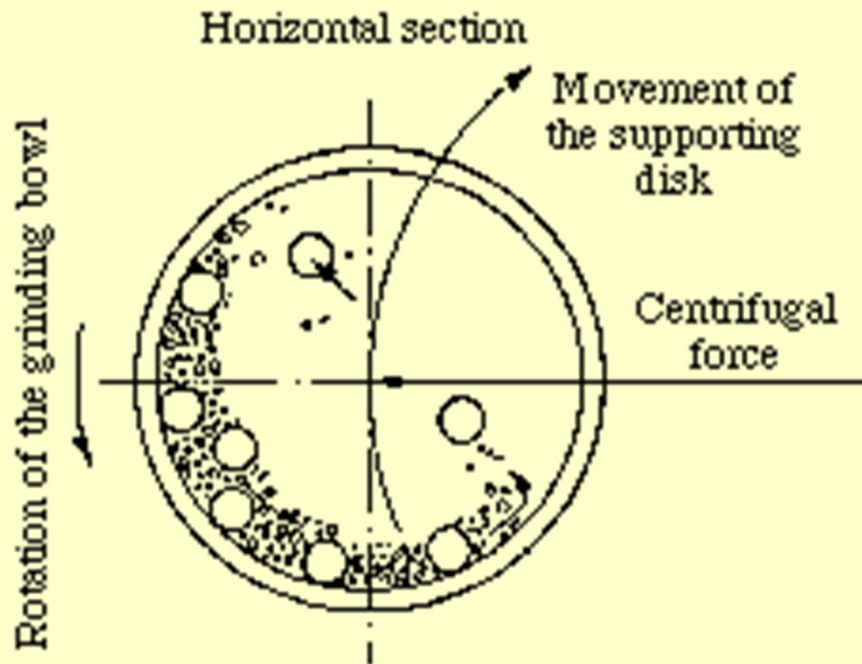
Rotation speed: **up to 400 rpm**
Milling jars: **alumina, YSZ, tungsten carbide, agate**

9

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 controled atmosphere
Maximum temperature: 1450 ºC or 1600 °C
Furnace-tube diameter: up to 75 mm

Vacuum Furnace
in vacuum or Ar, N_2, O_2 atmosphere
Maximum temperature: 1200 °C
Chamber Dimensions: 150x200x250 mm^3

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_2O, PbO, …)

        uptake of ambient gas (O_2 in superconductors)

Experimental Considerations

💣 **Reagents**

Drying, fine grain powders for maximum SA, surface activation ($Mo + H_2$), in situ decomposition (CO_3^{2-}, OH^-, O_2^{2-}, $C_2O_4^{2-}$) 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 $x10^6,\ K^{-1}$	Other Properties
Pyrex	770	GOOD	1.13	3.2	Permeable to air at high T
CaF_2	1420	FAIR	-	24	-
SiO_2	1530	VERY GOOD	1.38 - 2.67	0.4 - 0.6	Permeable to air at high T, devitrification above 1670 K
Si_3N_4	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_2O_3	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_2	2570	GOOD	1.97	4.5	-
Ir	2600	VERY GOOD	148	6.8	-
MgO	2870	FAIR	37.7	25	High vapor pressure
ThO_2	3070	FAIR	4.19	6	Reacts with C above 2290 K

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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
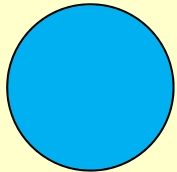
KEY FACTORS IN SOLID STATE SYNTHESIS

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
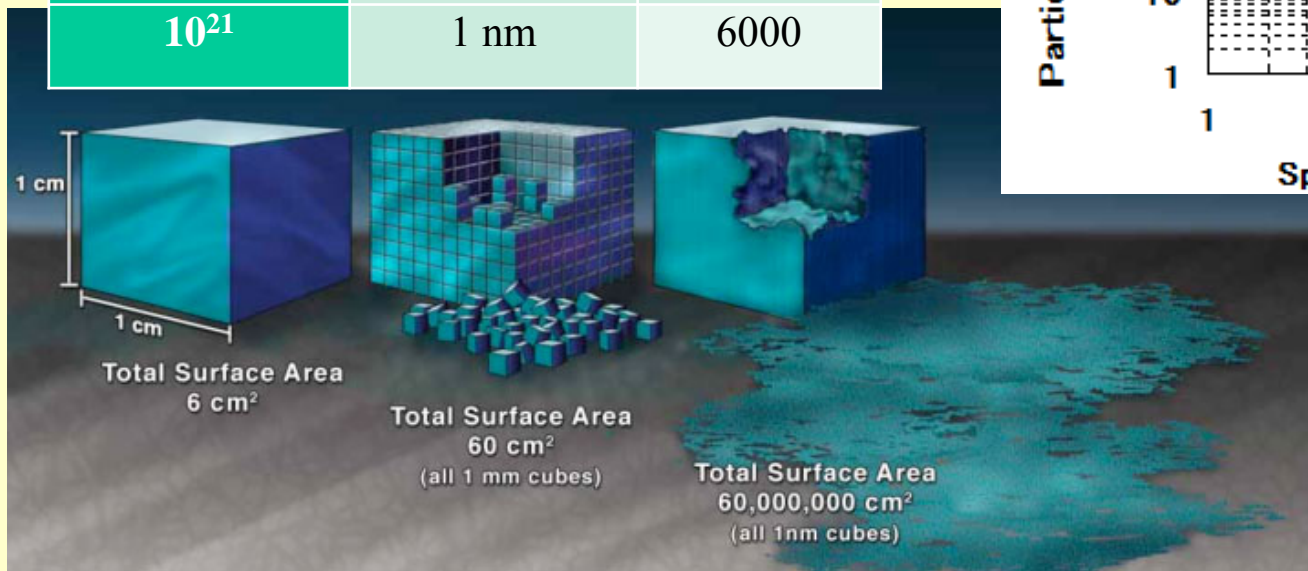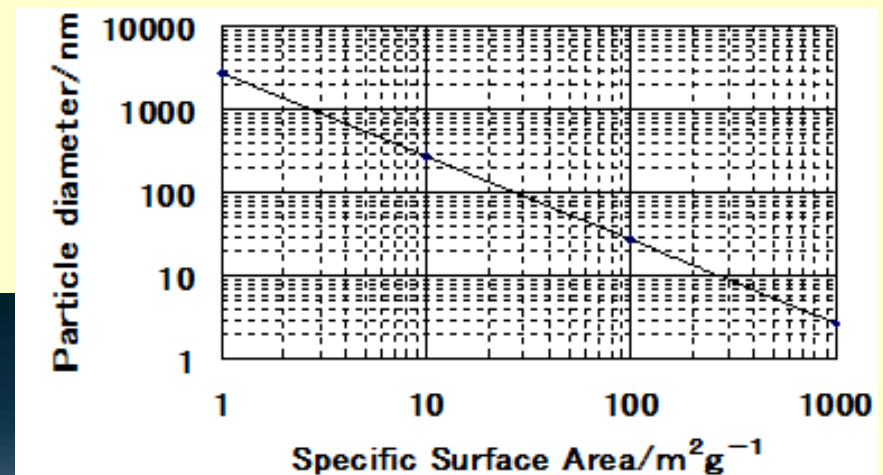
spherical particles, radius r [nm], density ρ [g/cm^3]

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

Direct Reactions of Solids

Consider 1 g of a material, density 1.0 g/cm³ , cubic crystallites

number of cubes	edge length	SA, m²/g
1	1 cm	6.10^{-4}
10^3	1 mm	6.10^{-3}
10^{12}	1 μm	6
10^{21}	1 nm	6000

Silica

Direct Reactions of Solids

Contact area
not in reaction rate expression for product layer thickness versus time:

$dx/dt = k/x$

But for a constant product volume $(V = x A)$: $x \sim 1/A_{contact}$

and furthermore $A_{contact} \sim 1/d_{particle}$

Thus particle sizes and surface area inextricably connected and obviously

$x \sim d$

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^{2}s
(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 ot 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

A

B

�\ gas phase diffusion		▪ interface diffusion
▪ volume diffusion		▪ surface diffusion
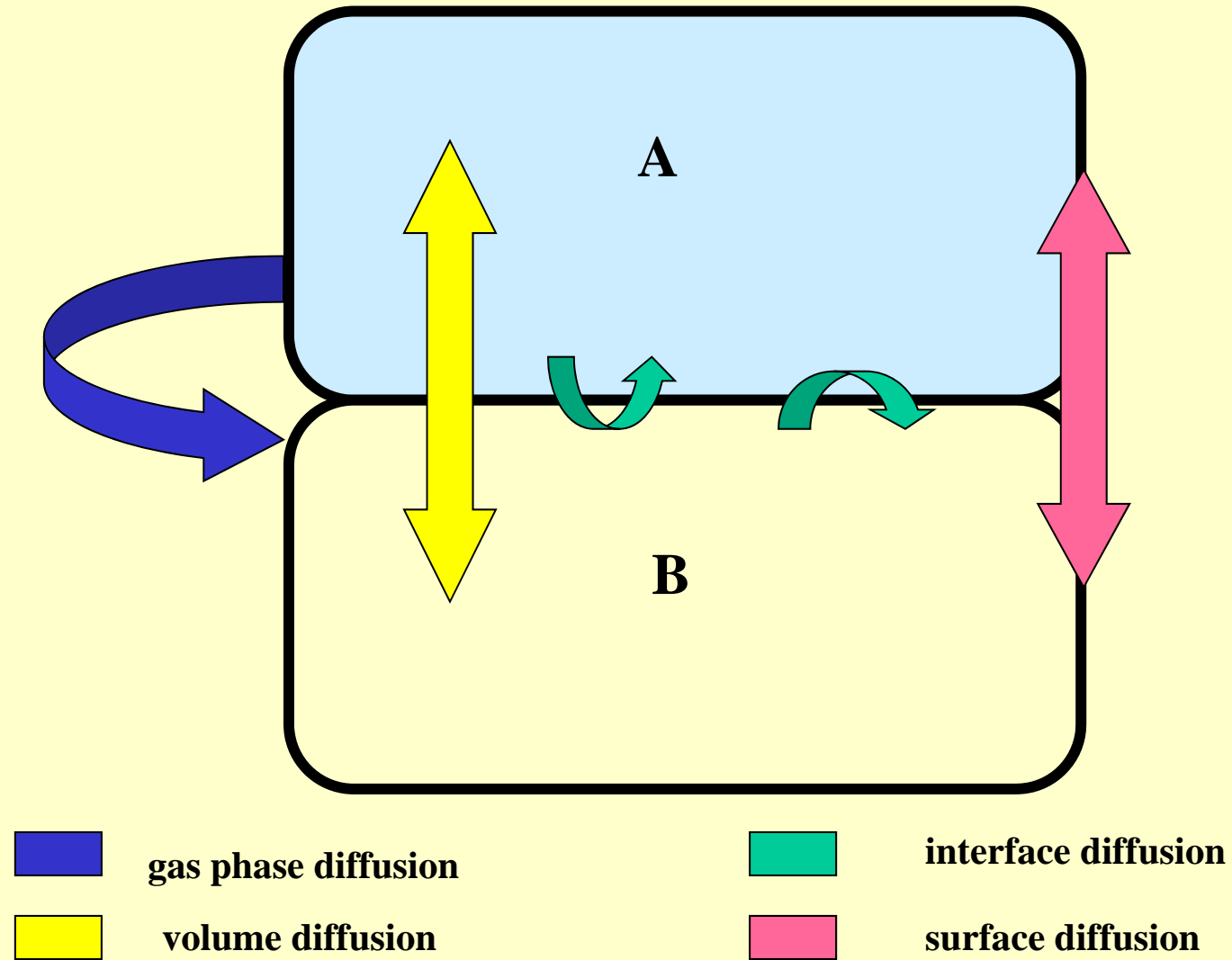
Direct Reactions of Solids

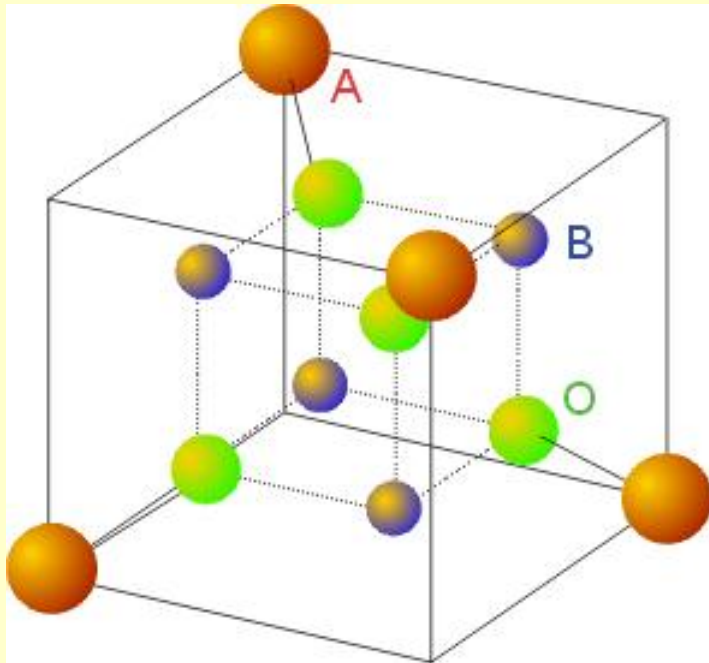A_x B_y O_z Stoichiometric formula of spinel

ccp O^{2-}

A   occupy 1/8 T_d

B   occupy 1/2 O_h

The Spinel Structure: $(A)[B_2]O_4$

fcc array of O^{2-} ions, A occupies 1/8 of the tetrahedral and B 1/2 of the octahedral holes
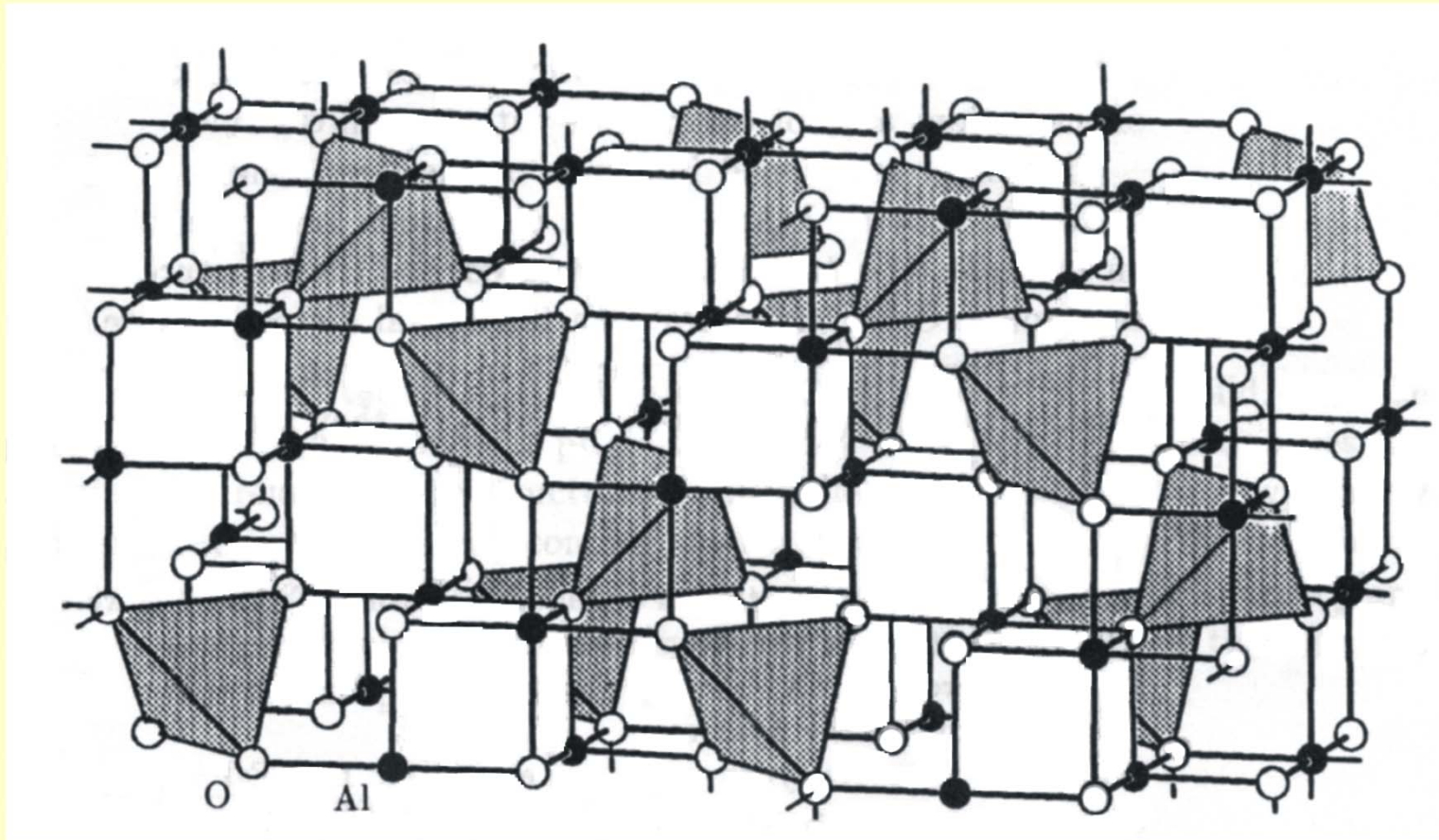
→ **normal spinel**: AB_2O_4

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**
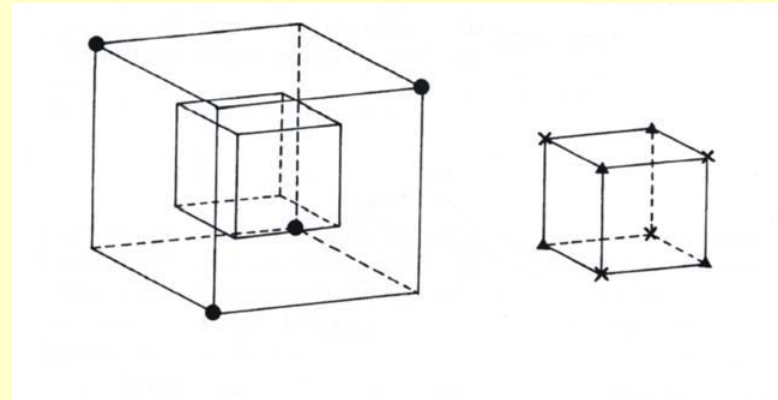
The Spinel Structure: MgAl$_2$O$_4$

(A)[B$_2$]O$_4$

The Spinel Structure: $MgAl_2O_4$

$(A)[B_2]O_4$

I

II

I   II
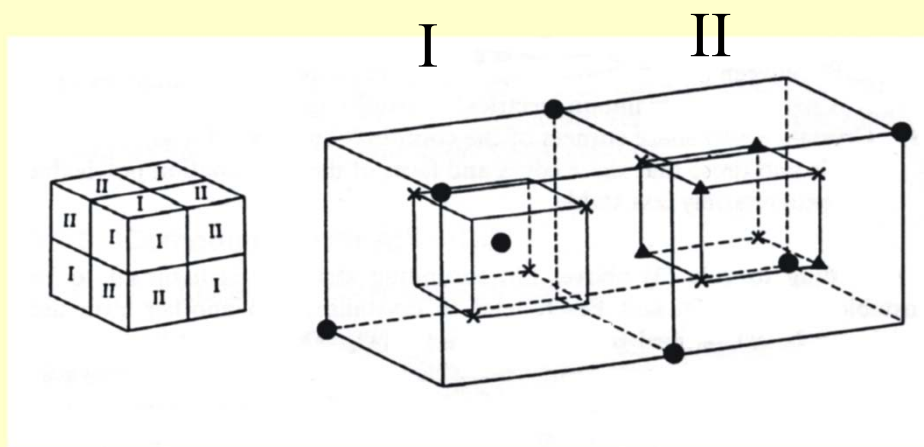
• = Mg

x = O

▲ = Al

Direct Reactions of Solids

Model reaction, well studied:

$MgO + Al_2O_3 \rightarrow MgAl_2O_4$ **Spinel**
(ccp O^{2-}, Mg^{2+} 1/8 T_d, Al^{3+} 1/2 O_h)
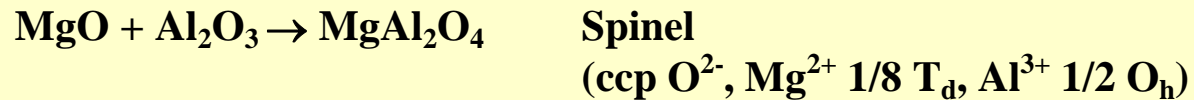
Single crystals of precursors, interfaces between reactant grains

On reaction, new reactant-product $MgO/MgAl_2O_4$ and $Al_2O_3/MgAl_2O_4$ interfaces are formed

Free energy negative, favors reaction but extremely slow at normal temperatures (several days at 1500 ºC)
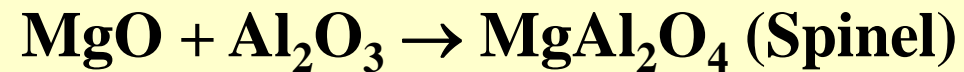
Interfacial growth rates 3 : 1

Linear dependence of interface thickness x^2 versus t

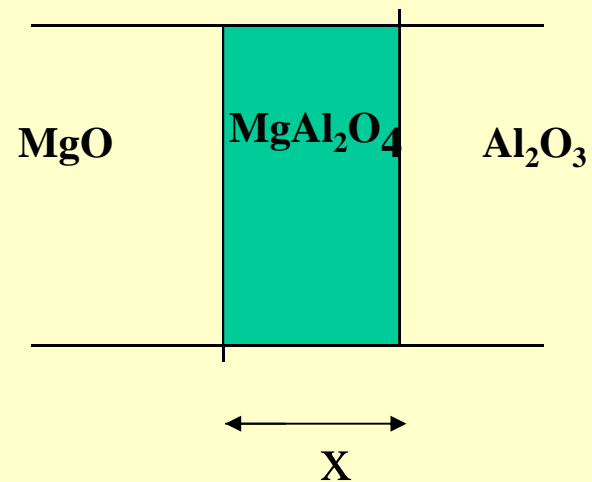**Easily monitored rates with colored product at interface, T and t**
$NiO + Al_2O_3 \rightarrow NiAl_2O_4$
$MgO + Fe_2O_3 \rightarrow MgFe_2O_4$
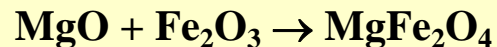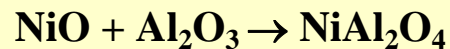
Direct Reactions of Solids

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

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4 \text{ (Spinel)}$$

Phase 1:
nucleation

Phase 2:
growth of nuclei

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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

$$x^2 = kt$$

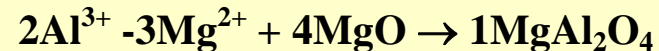30

Direct Reactions of Solids

Kinetics:

Linear x^2 vs. t plots observed

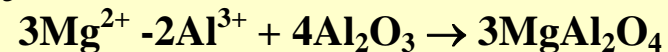**ln k vs. 1/T experiments provide Arrhenius activation energy E_a for the solid-state reaction**

Reaction mechanism requires charge balance to be maintained in the solid state interfacial reaction:
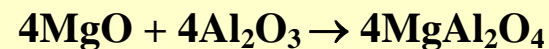
$$3Mg^{2+} \text{ diffuse in opposite way to } 2Al^{3+}$$

$MgO/MgAl_2O_4$ Interface:

$$2Al^{3+} -3Mg^{2+} + 4MgO \rightarrow 1MgAl_2O_4$$

$MgAl_2O_4/Al_2O_3$ Interface:

$$3Mg^{2+} -2Al^{3+} + 4Al_2O_3 \rightarrow 3MgAl_2O_4$$

Overall Reaction:

$$4MgO + 4Al_2O_3 \rightarrow 4MgAl_2O_4$$

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

Reaction Mechanism

interface I   interface II

Al_2O_3 $MgAl_2O_4$ MgO

$2\ Al^{3+}\longrightarrow$ $\longleftarrow 3\ Mg^{2+}$

interface I   interface II

Al_2O_3 $MgAl_2O_4$ MgO

$2\ Al^{3+}\longrightarrow$

$O^{2-}\rightarrow 2\ e^{-}\longrightarrow$ $\longleftarrow 2\ Mg^{2+}$ O^{2-}

$1/2\ O_2 \longrightarrow 1/2\ O_2$

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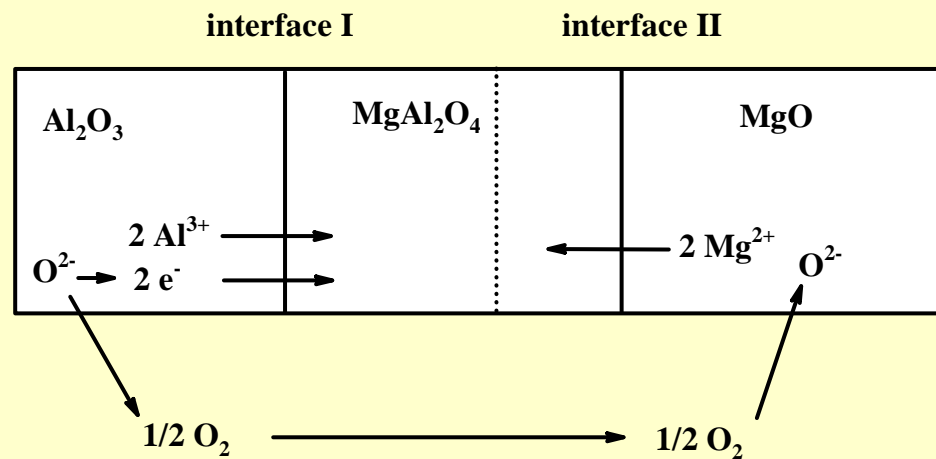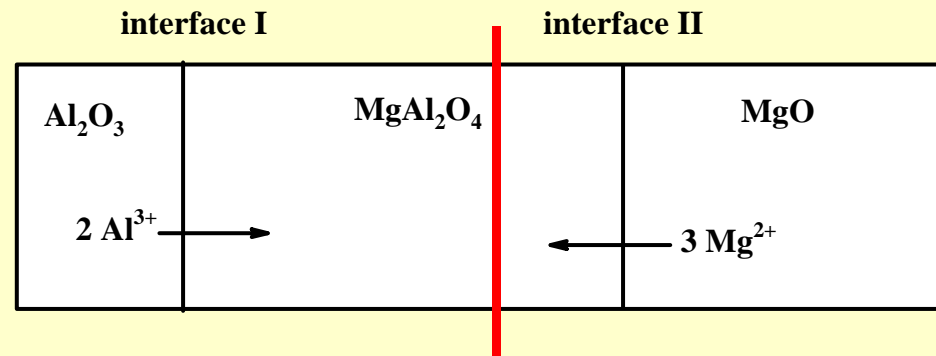
Direct Reactions of Solids

General kinetic expression

Reaction rate
Rate constant
Reaction order

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

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

α – the molar fraction of the reacted product at a time t
k(T) – the rate constant of the process

Experimentally evaluate α at different t
Fit data into a g(α) = 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, ...

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Direct Reactions of Solids

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

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

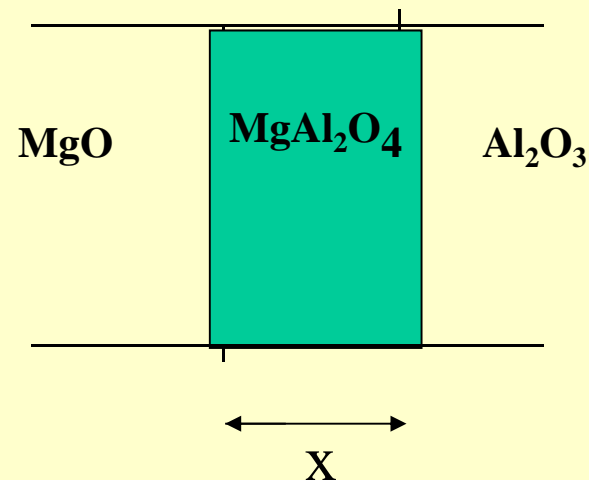**Decreasing reaction rate as spinel product layer (x) thickens**

Here $\alpha = x$

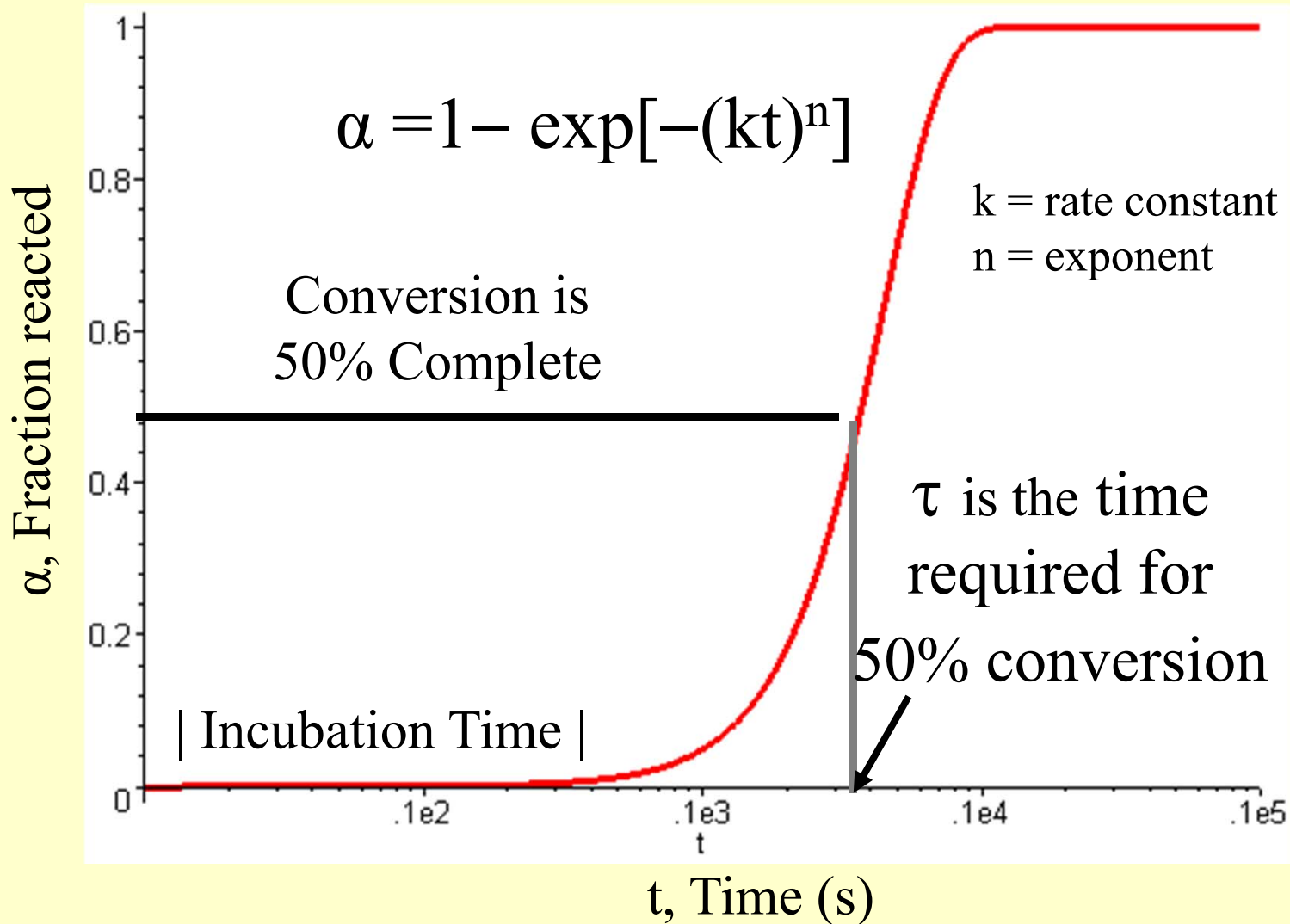$$\alpha = \frac{P_t - P_0}{P_e - P_0}$$

$$\alpha = 0 - 1$$

Parabolic rate law:

$dx/dt = k/x$

$x^2 = kt$

MgO MgAl$_2$O$_4$ Al$_2$O$_3$

X

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Mechanism model	$g(\alpha)$
Diffusion controlled	
One-dimensional	α^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	$(1 + \alpha)^{2/3} + (1 - \alpha)^{2/3}$
Growth controlled	
General	$[1 - (1 - \alpha)^{1-n}]$
First order, n = 1	$[-\ln(1 - \alpha)]$
Nucleation controlled	
Power law	$\alpha^{1/n}$
Nucleation-Growth controlled	
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

$$\alpha = 1 - \exp[-(kt)^n]$$

k = rate constant
n = exponent

Conversion is
50% Complete

τ is the time
required for
50% conversion

| Incubation Time |

α, Fraction reacted

t

t, Time (s)

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Direct Reactions of Solids

Perform the measurements in a range of temperatures T
use Arrhenius equation to evaluate the activation energy E_a
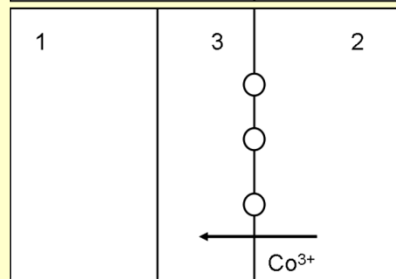
$$k(T) = k_0 \exp(-E_a/RT)$$
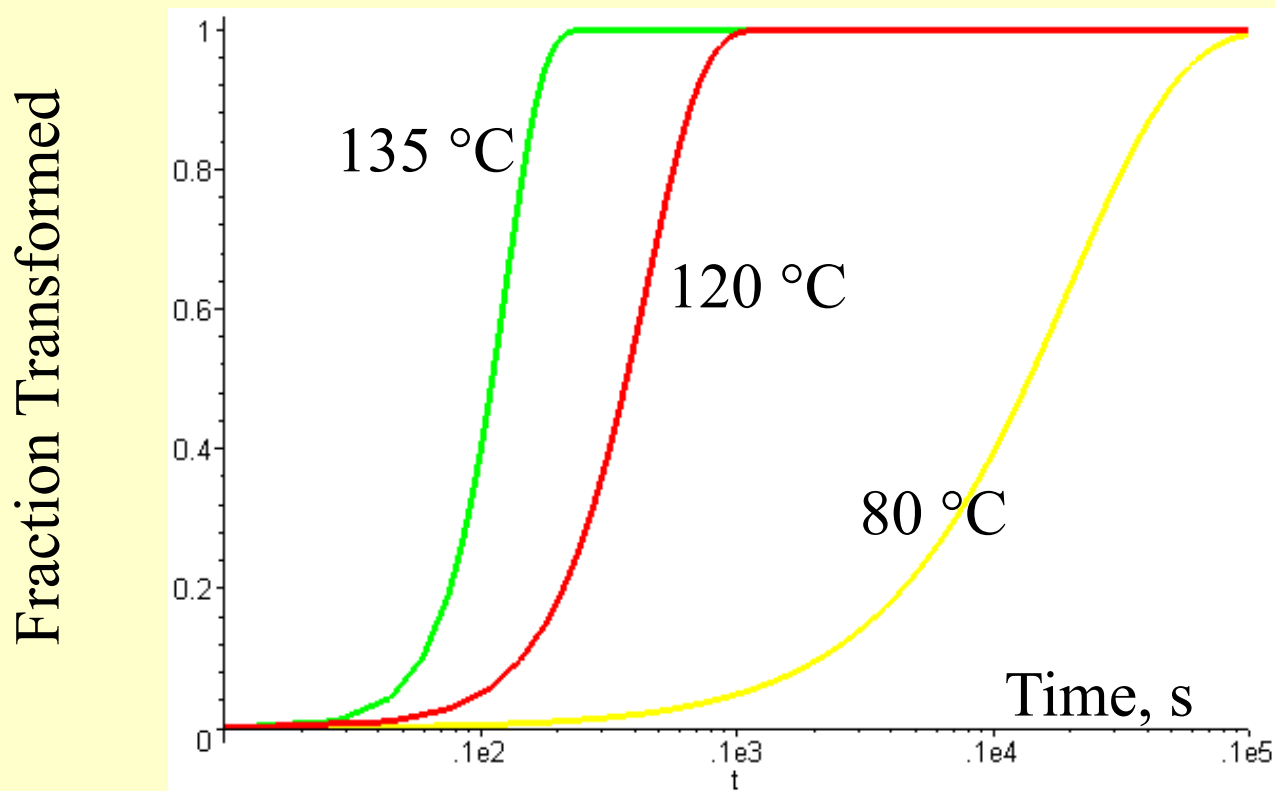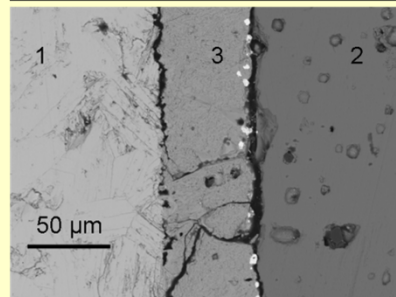
Cation Diffusion in LaCoO$_3$

Marker experiments

La$_2$O$_3$

CoO
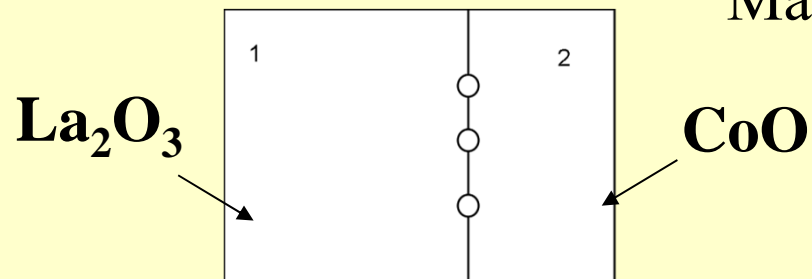
LaCoO$_3$

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

Rate-determining step:

Diffusion of Co cations

Growth Kinetics of LaCoO$_3$
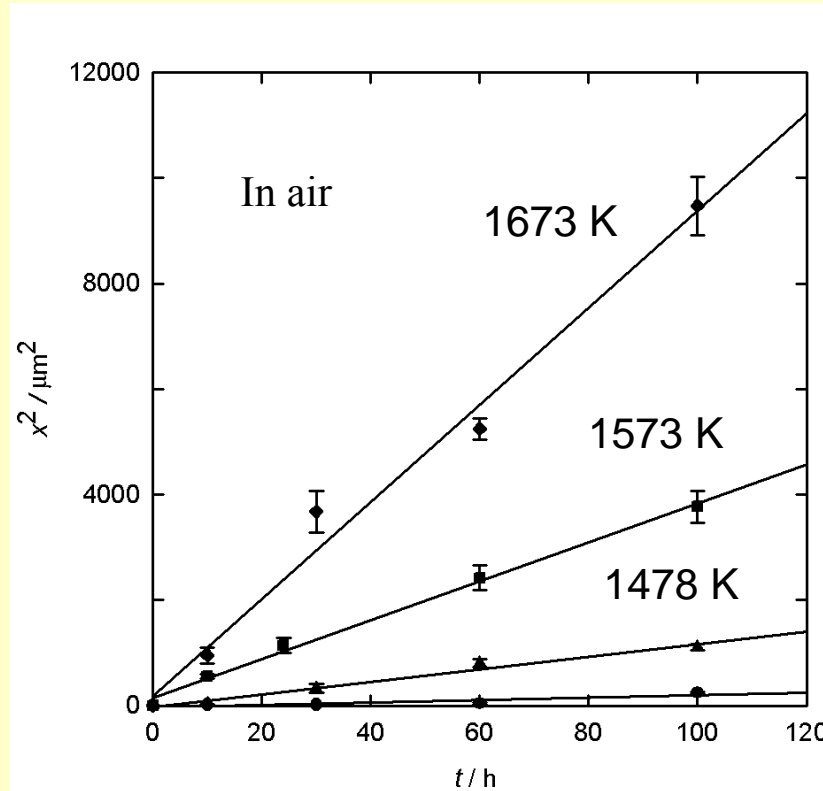
$$x^2 = kt$$

Parabolic rate law valid = diffusion controlled process

Growth Kinetics of LaCoO$_3$
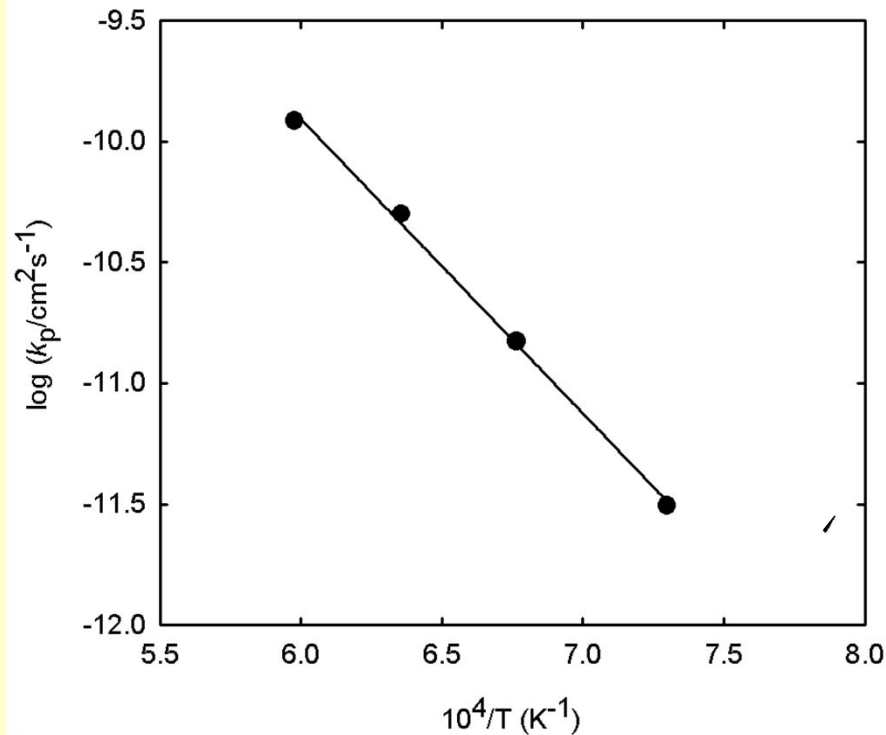
T / K	k_p cm^{2}s^{-1}	D cm^{2}s^{-1b}
1370	$(3.11\pm0.69)\times10^{-12}$	3.02×10^{-12}
1478	$(1.49\pm0.14)\times10^{-11}$	1.40×10^{-11}
1573	$(5.01\pm0.16)\times10^{-11}$	4.55×10^{-11}
1673	$(1.22\pm0.22)\times10^{-10}$	1.05×10^{-10}

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

$$\log k = \log k_0 - E_a/RT$$

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

Nucleation

Homogeneous nucleation

Liquid melt to crystalline solid
Cluster formation

$$\Delta G_V = \frac{\Delta H_V \Delta T}{T_m}$$

ΔG_v = driving force for solidification (negative)
below the equilibrium melting temperature, T_m
ΔT = undercooling, ΔH_v = enthalpy of solidification (negative)

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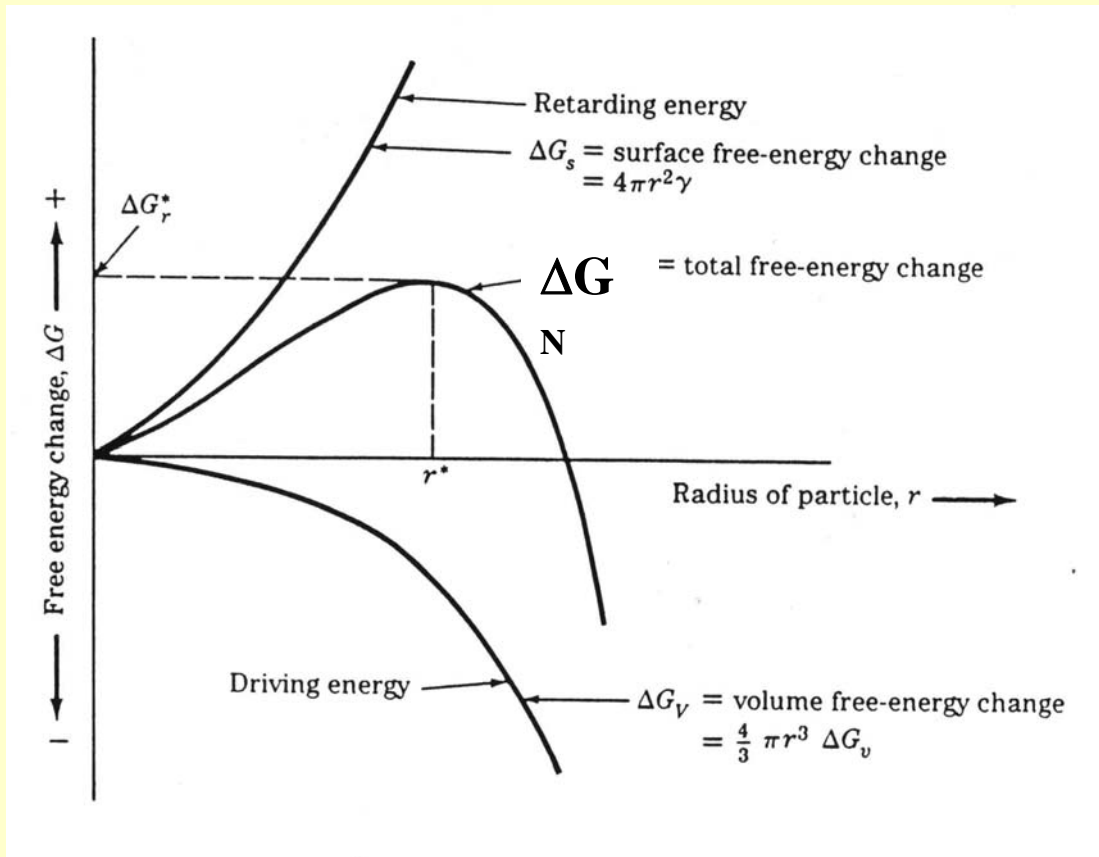motion of atoms within the liquid

Driving force is opposed by the increase in energy due to the creation of a
new solid-liquid interface
γ_{SL} = the solid/liquid interfacial energy

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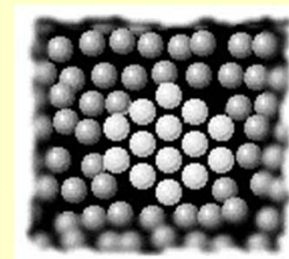
Nucleation

ΔG

r: radius of spheric seed

r*: critical radius

ΔG_N: <u>total</u> free energy change

ΔG_s: <u>surface</u> free energy change

ΔG_v: <u>volume</u> free energy change

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

Critical Radius r*

The critical radius r* = the radius at which ΔG_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

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

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

$\Delta G < 0$

Retarding energy

ΔG_s = surface free-energy change
= $4\pi r^2 \gamma$

ΔG_T = total free-energy change

ΔG_r^*

Free energy change, ΔG

Radius of particle, r

Driving energy

ΔG_V = volume free-energy change
= $\frac{4}{3}\pi r^3 \Delta G_v$

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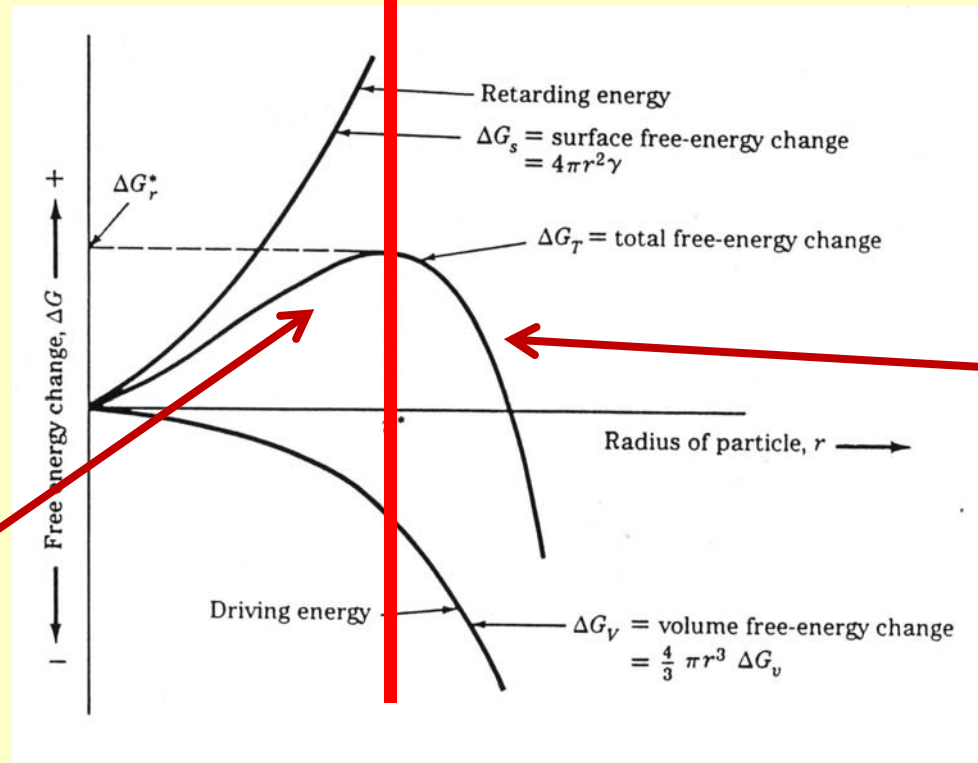
Nucleation rate *n*

Nucleation rate *n*

Liquid to solid

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

ΔG_N = thermodynamic barrier to nucleation

ΔG_D = kinetic barrier to diffusion across the liquid/nucleus interface

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

ΔG_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, ΔG^*, 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)
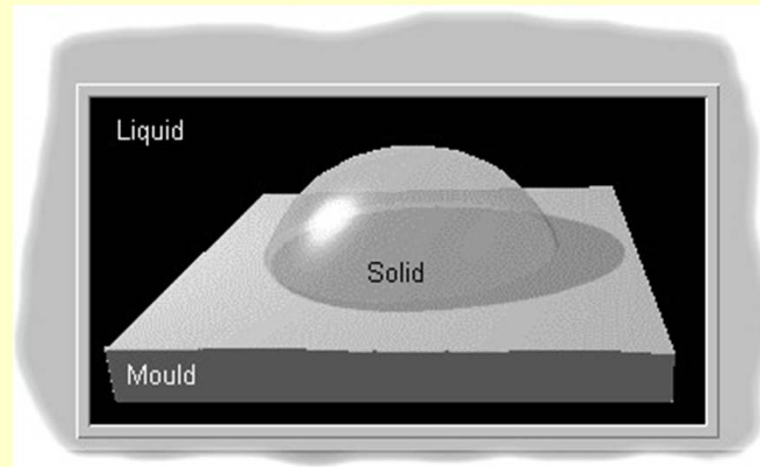
Heterogeneous Nucleation
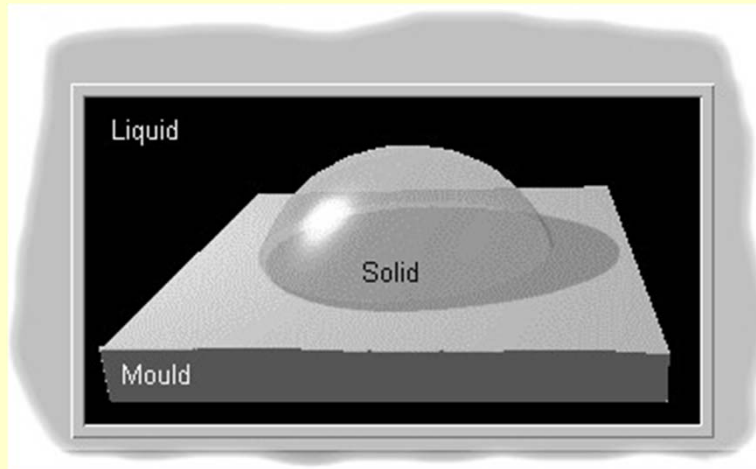
$$\cos\theta = \frac{\gamma_{WL} - \gamma_{WS}}{\gamma_{SL}}$$

θ = wetting angle

Shape factor S(θ)

$$r^*_{het} = \frac{-2\gamma_{SL}}{\Delta G^r_v} = r^*_{hom}$$

$$\Delta G^*_{het} = \frac{16\pi\gamma^3_{SL}}{3\Delta G^2_v} S(\theta) = \Delta G^*_{hom} S(\theta)$$

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

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Wetting Angle

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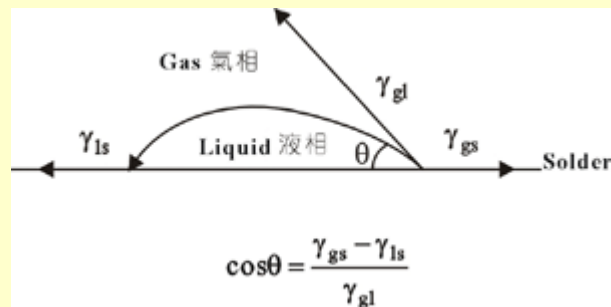
$$\gamma_{GS} = \gamma_{GL} \cos\theta + \gamma_{SL}$$

$$\cos\theta = \frac{\gamma_{GS} - \gamma_{SL}}{\gamma_{GL}}$$
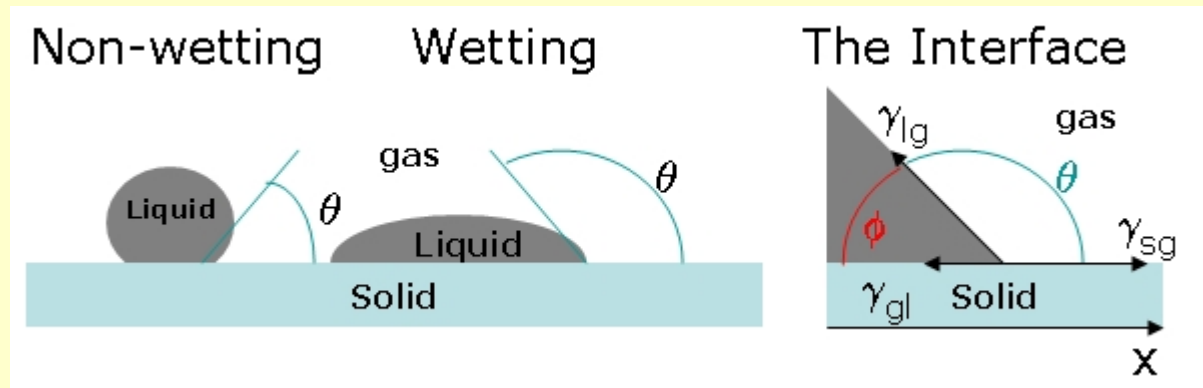
Heterogeneous Nucleation
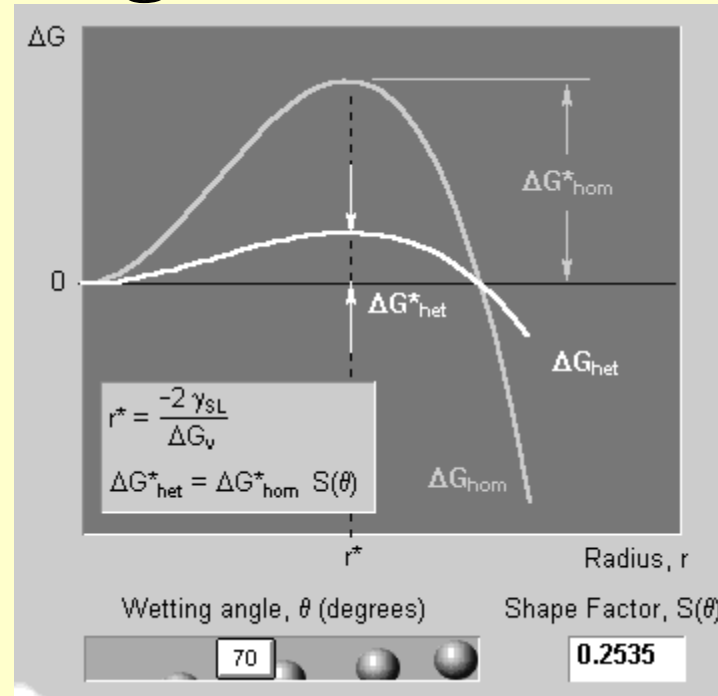
The critical radius r* is the same for both homogeneous and heterogeneous nucleation

The volume of a critical nucleus and ΔG^* can be significantly smaller for heterogeneous nucleation due to the shape factor, depending on the wetting angle, θ

Direct Reactions of Solids

Solidification

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

– **Volume free energy + surface energy**

One solid phase changing to another

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

– **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 α/β interfacial energy

Ratio of ß/α lattice parameters: 0.8
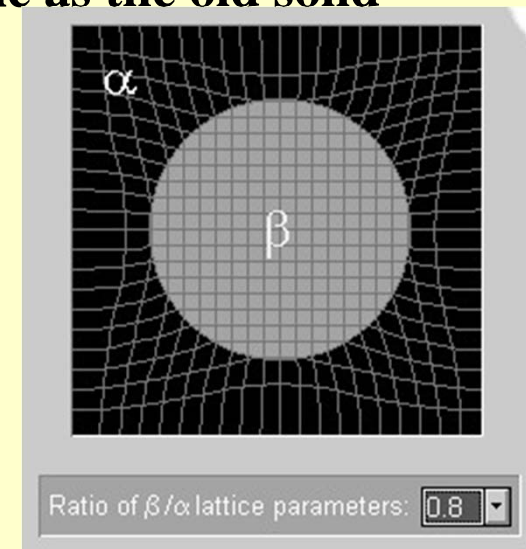
Nucleation

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
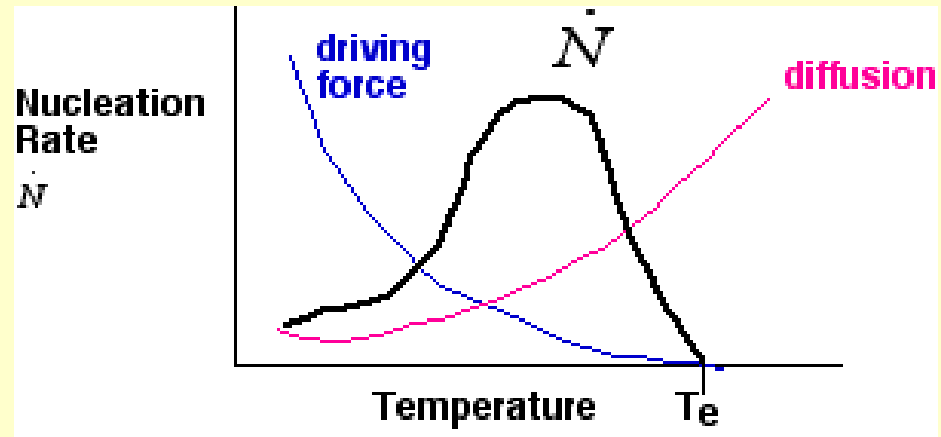
Nucleation rate *I*

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

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

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

n_0 = the number of potential nucleation sites per unit volume

ΔG^* = the critical free energy of nucleation

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

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

ω = 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 (m^{-3})

$$n^* = N \exp\left[\frac{-16\pi\gamma_{SL}^3 T_m^2}{3\Delta H_v^2 \Delta T^2 kT}\right]$$

Steady-state concentration of Critcal Nuclei, n* (nuclei/m^3)

Nucleation

Temperature, T

T_m

At low **undercoolings**, driving force is the rate-controlling factor

β

$I = \beta n^*$

I is maximised at an intermediate T

n^*

At low **temperatures**, diffusion is the rate-controlling factor

Nucleation Rate, I (nuclei/m^3/s)

Nucleation vs. Growth

Equilibrium transformation temperature

Temperature

Rate

Growth Rate

Overall Transformation Rate

Nucleation Rate

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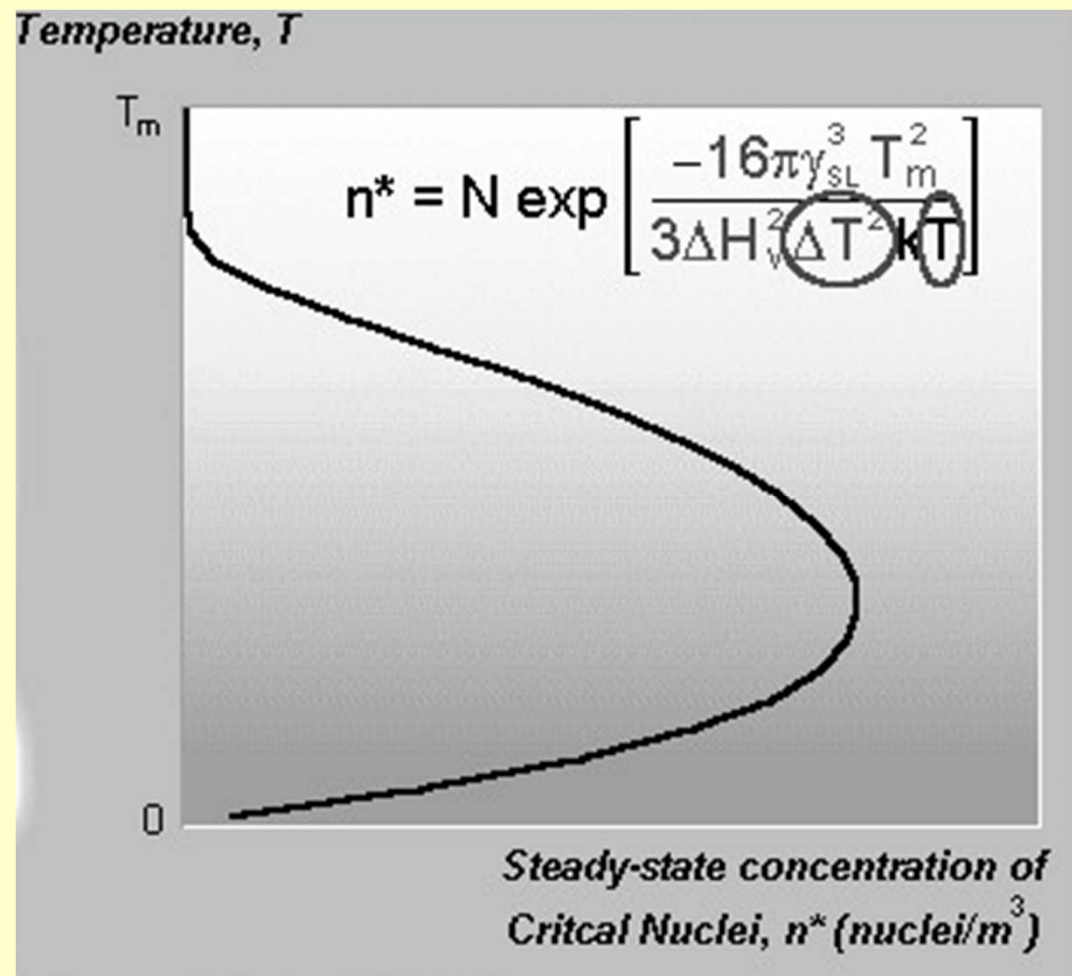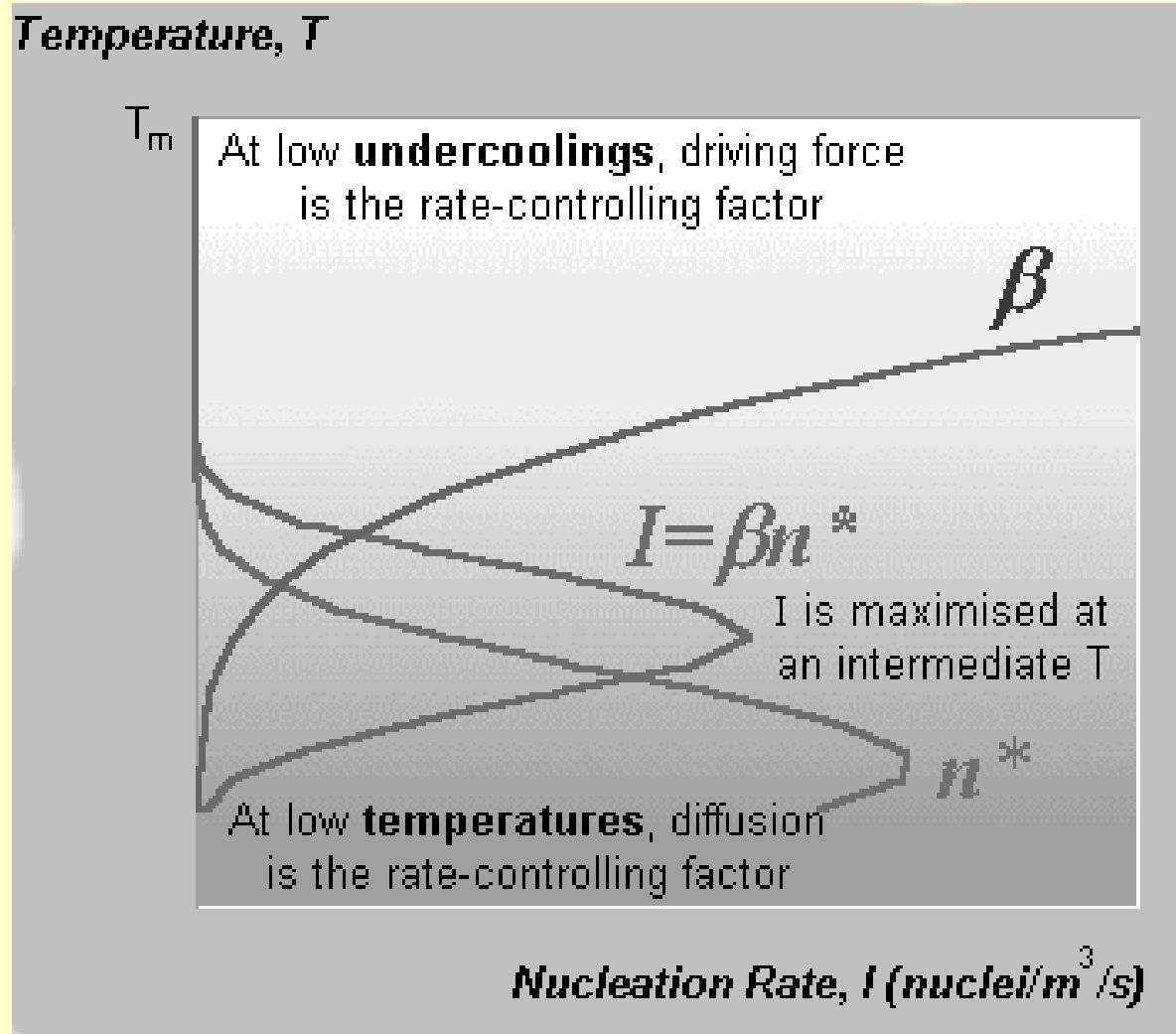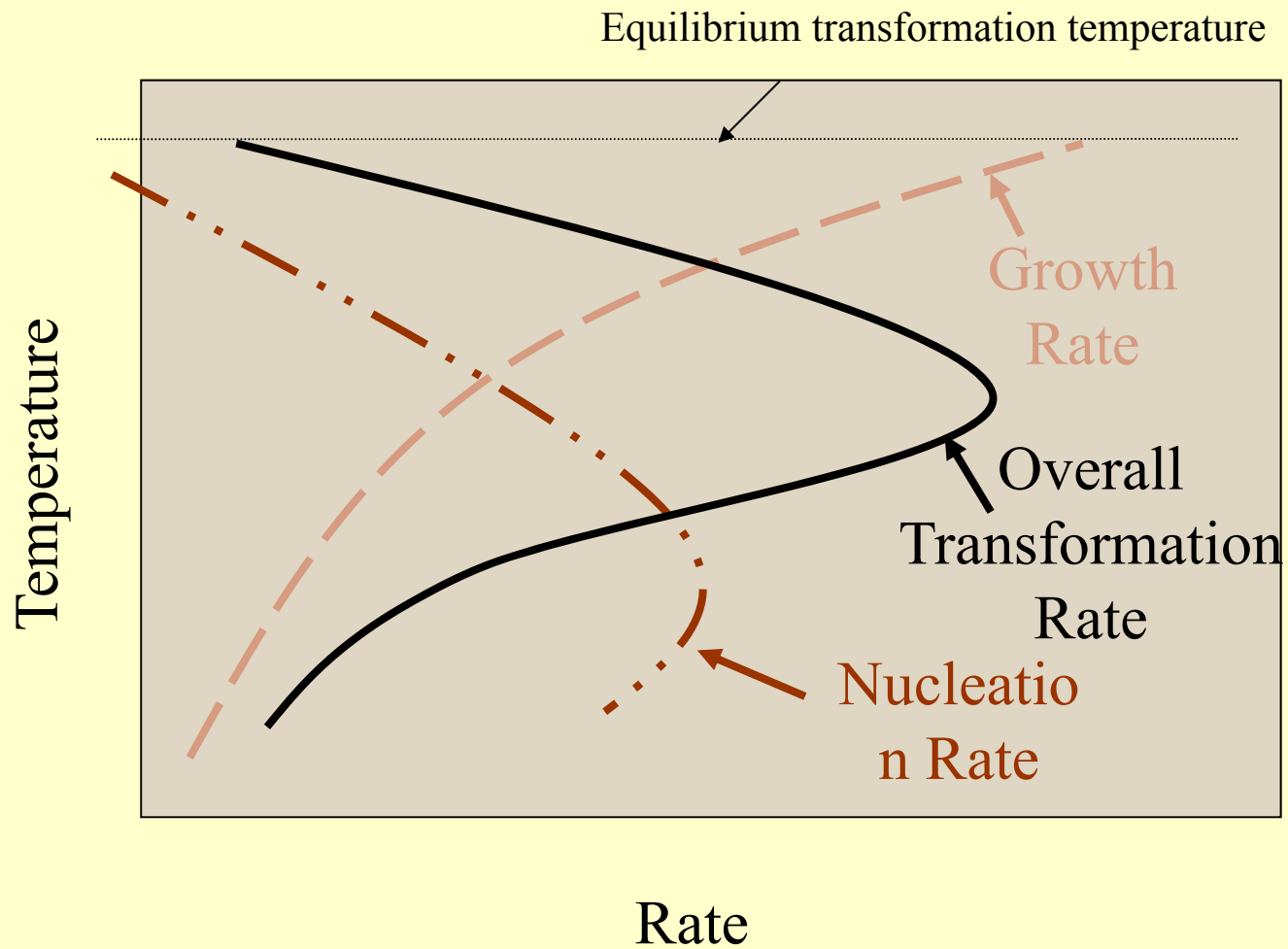
Nucleation vs. Crystal Growth
(solution or melt)

Undercooling – cooling below the melting point

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

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

small undercooling: **<u>few</u> (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
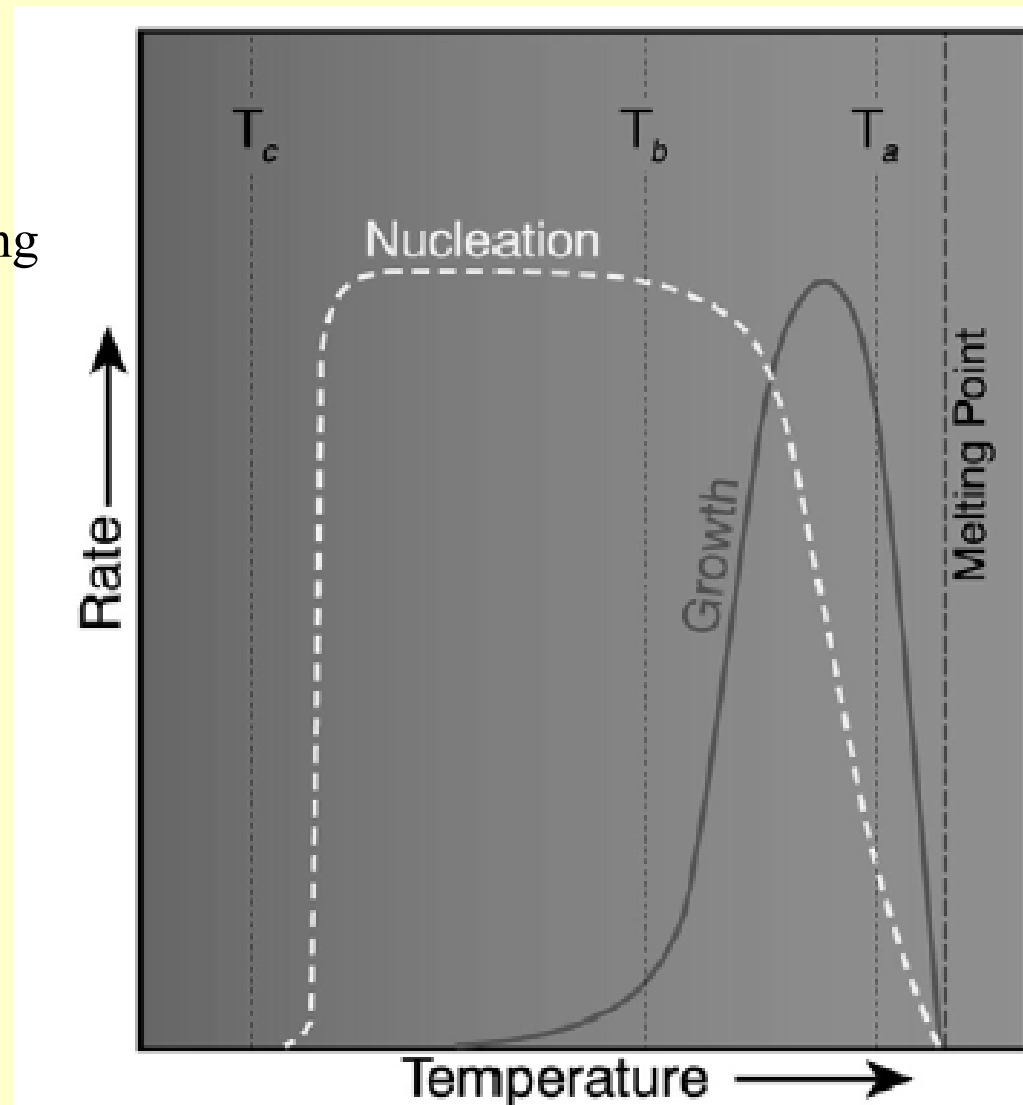
DIRECT REACTION OF SOLIDS

NUCLEATION RATE

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

MgO, Al_2O_3, $MgAl_2O_4$ example
MgO (rock salt) and $MgAl_2O_4$ (spinel) similar ccp O^{2-}
but distinct to hcp O^{2-} in Al_2O_3 phase

Spinel nuclei, matching of structure at MgO interface
Oxide arrangement essentially continuous across $MgO/MgAl_2O_4$
interface
Bottom line: structural similarity of reactants and products
promotes nucleation and growth of one phase within another
Lattice of oxide anions, mobile Mg^{2+} and Al^{3+} 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.
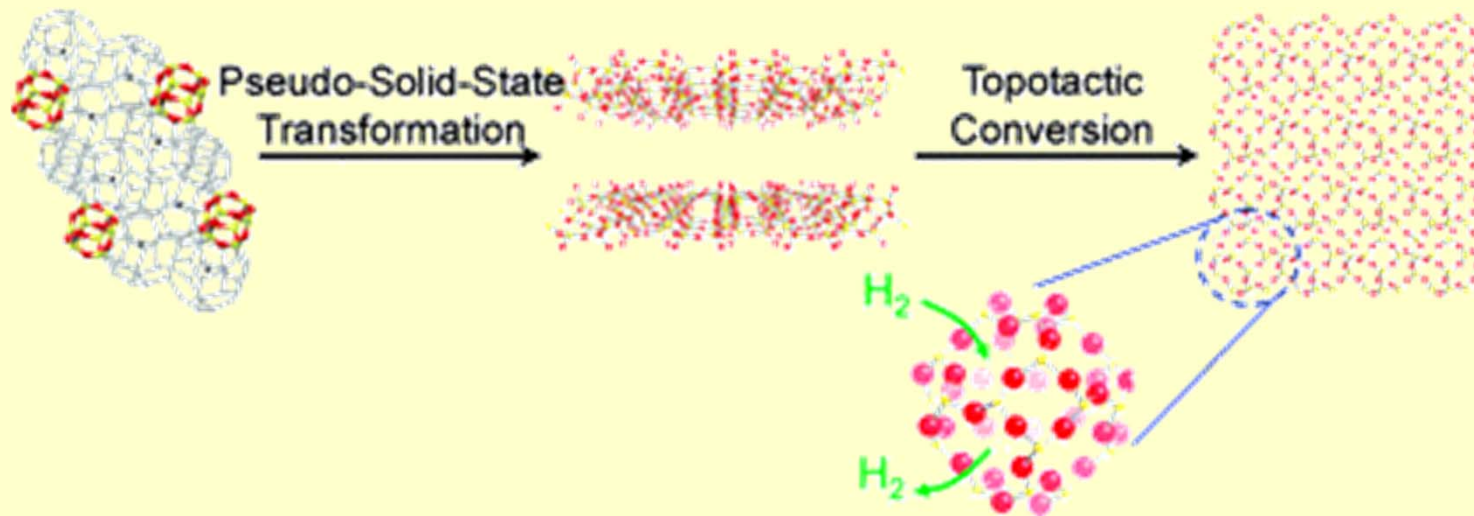
Direct Reactions of Solids

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.

Face-Centred Cubic (111), (100), (110); Body-Centred Cubic (110), (100), (111)
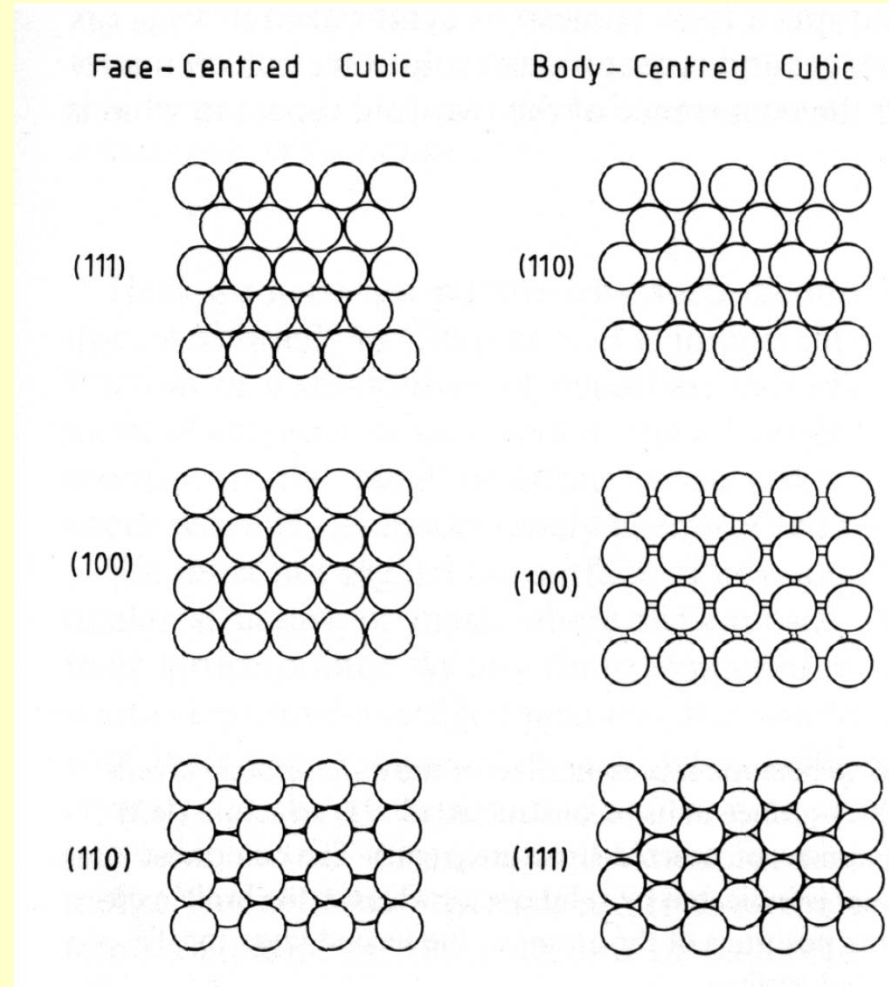
Direct Reactions of Solids

Example: MgO (rock salt)

{100} MgO alternating Mg^{2+}, O^{2-} at corners of square grid
{111} MgO, Mg^{2+} or O^{2-} hexagonal arrangement

= Na   = Cl

Direct Reactions of Solids

Cubic (rocksalt) MgO crystal: different netplanes
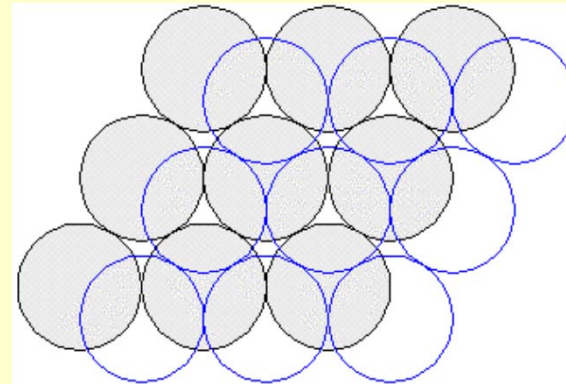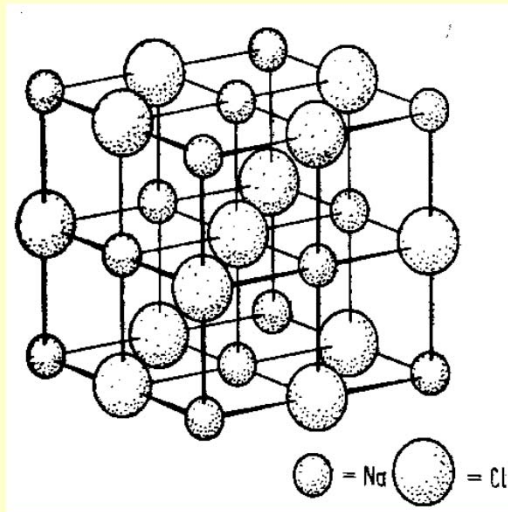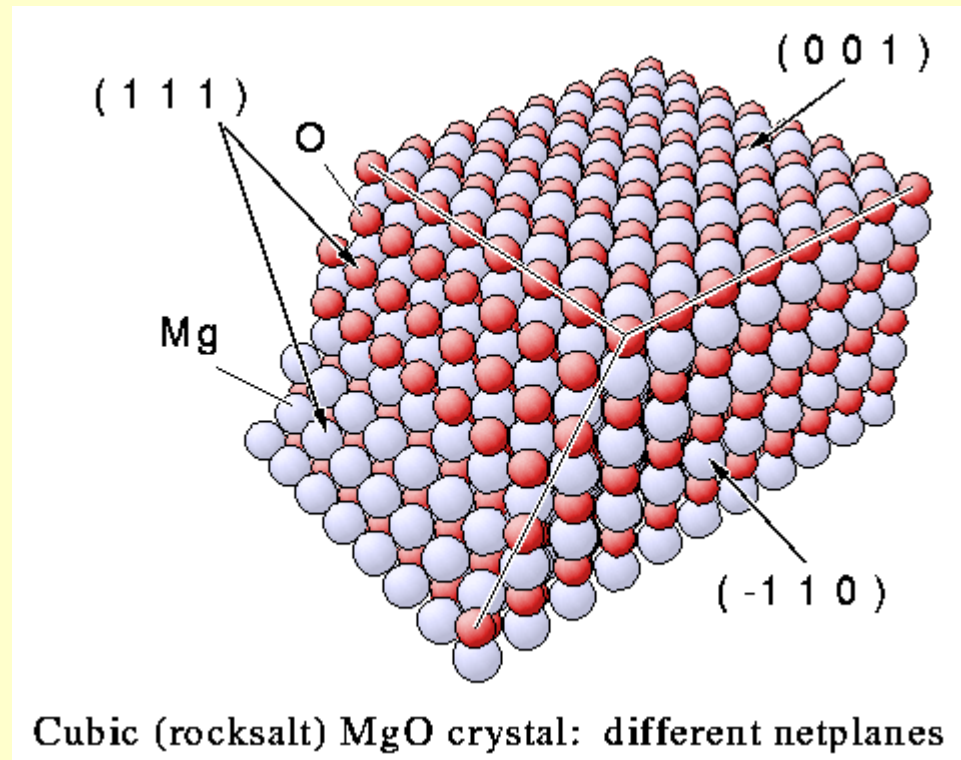
Direct Reactions of Solids
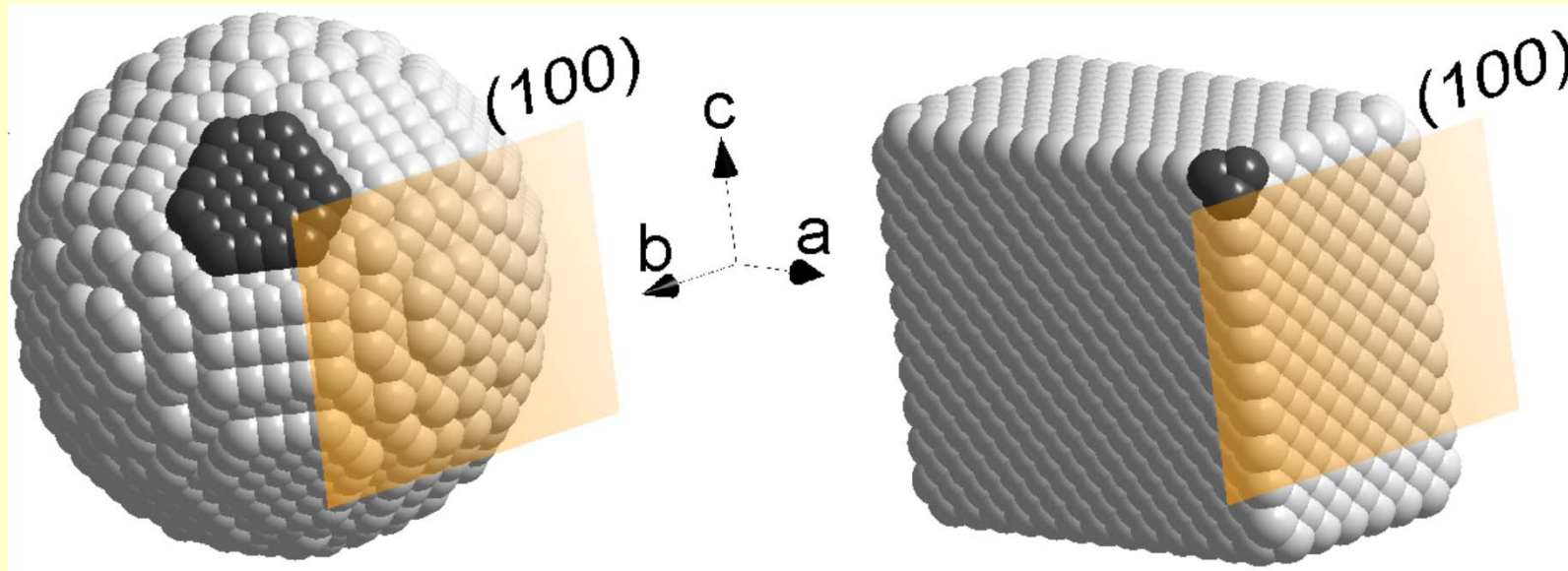
**Atoms located in (111) and (100) crystal planes for spherical
and cuboid particles**

Model particles = fcc structure of Pt 4 nm size

Dark grey = atoms located in (111)-surface
Light orange = the (100) face

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Surface Facet Reactivity
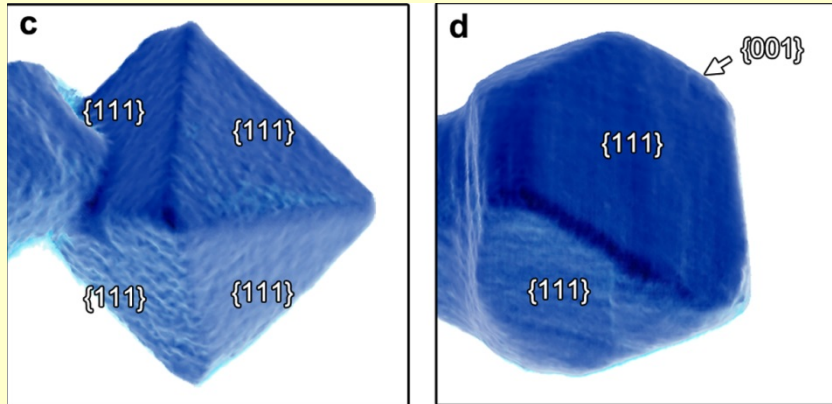
Electron tomography and electron energy loss spectroscopy (EELS) map the valency of the Ce ions in CeO_{2-x} nanocrystals in 3D.
A facet-dependent reduction shell at the surface; {111} facets show a low surface reduction, whereas at {001} surface facets, the cerium ions are more reduced.
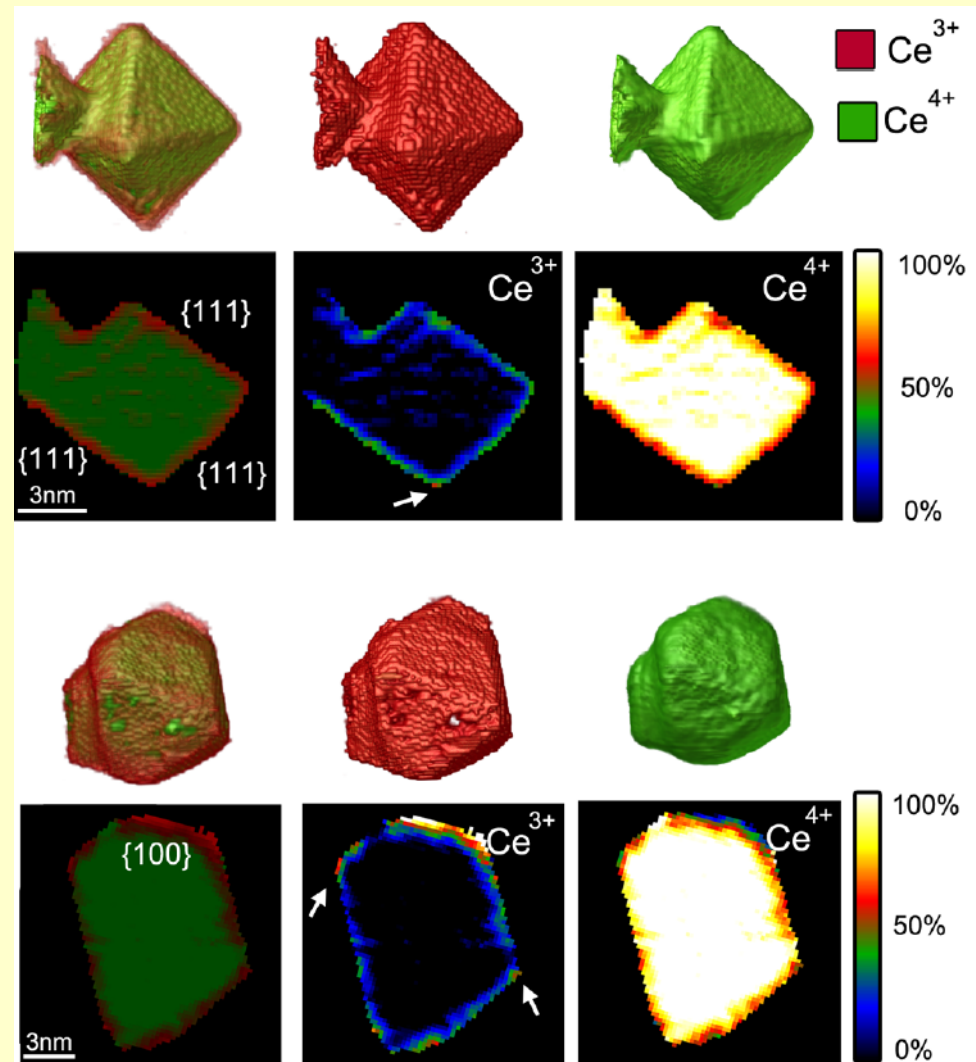
Work function of different crystal planes
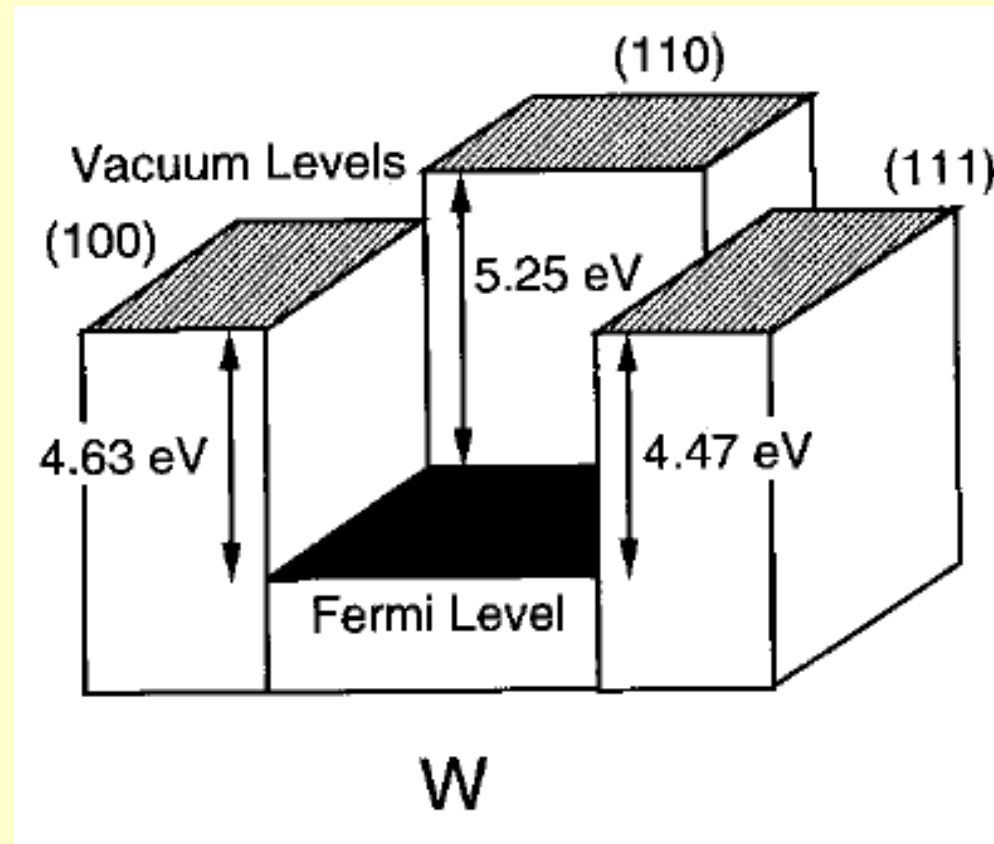
Planar density on (111) plane in a Simple Cubic Structure:

- 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 atom / $0.866a^2$ =
  $= 0.577 / a^2$

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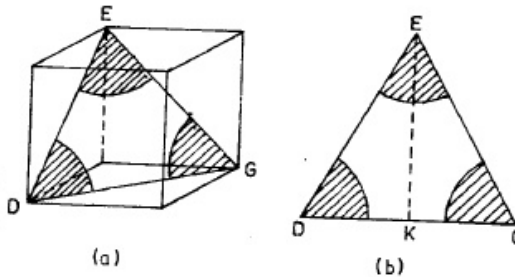
Planar density on (100) plane in a Body Centred Cubic Structure:

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

ly

/4

is

(a)   (b)

67
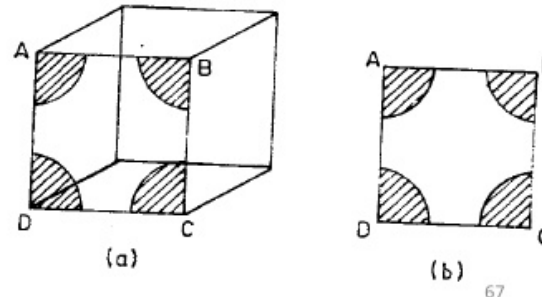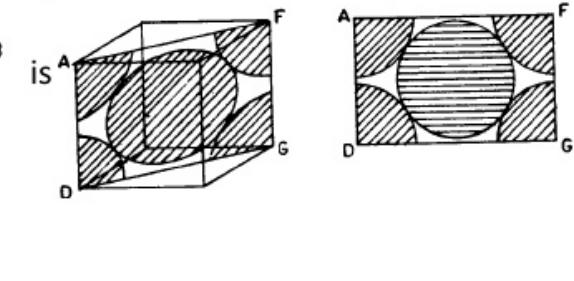
Body Centered Cubic Structure:

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

(a)   (b)

68
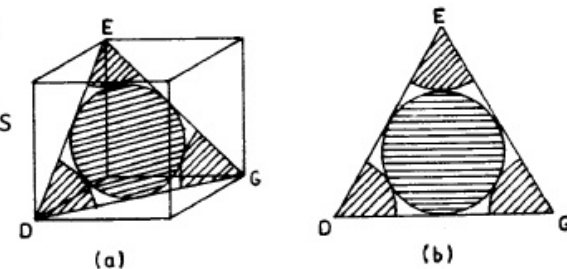
Direct Reactions of Solids

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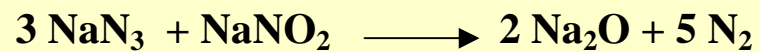
CRYSTAL GROWTH

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

$3 \text{ NaN}_3 + \text{NaNO}_2 \longrightarrow 2 \text{ Na}_2\text{O} + 5 \text{ N}_2$

$5 \text{ NaN}_3 + \text{NaNO}_3 \longrightarrow 3 \text{ Na}_2\text{O} + 8 \text{ N}_2$

$9 \text{ NaN}_3 + 3 \text{ NaNO}_2 + 2 \text{ ZnO} \longrightarrow 2 \text{ Na}_6\text{ZnO}_4 + 15 \text{ N}_2$

$8 \text{ NaN}_3 + 4 \text{ NaNO}_2 + \text{Co}_3\text{O}_4 \longrightarrow 3 \text{ Na}_4\text{CoO}_4 + 14 \text{ N}_2$

$2 \text{ NaN}_3 + 4 \text{ CuO} \longrightarrow 2 \text{ NaCu}_2\text{O}_2 + 3 \text{ N}_2$
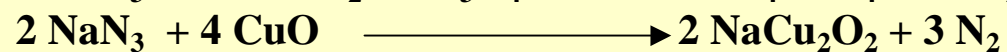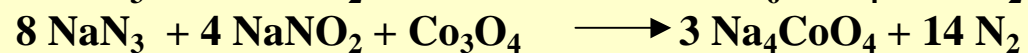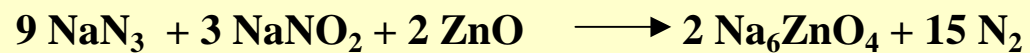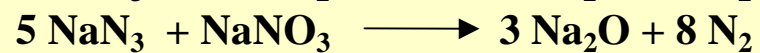
Self-Sustained High-Temperature Synthesis (SHS)

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, $T_f = 1500 - 3000 \,°C$
♠* 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
$Zr + Fe_2O_3 \longrightarrow Zr_{1-x}Fe_xO_2 + Fe$
$Ti + C \longrightarrow TiC$
$Ti + B \longrightarrow TiB$
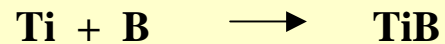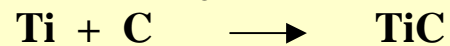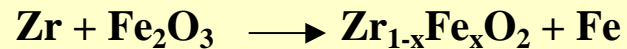
Self-Propagating Metathesis

Grinding of components in a glove box
addition of NaCl, KCl or NH_4Cl as a heat sink,
S.S. vessel, ignition by a resistively heated wire, reaction time 1 s,
washing products with MeOH, water, drying

$$3\ ZrCl_4 + 4\ Na_3P \longrightarrow 3\ c\text{-}ZrP + 12\ NaCl + P$$

$$3\ HfCl_4 + 4\ Li_3P \longrightarrow 3\ c\text{-}HfP + 12\ LiCl + P$$
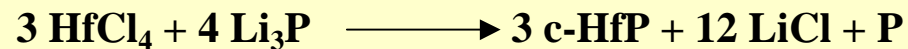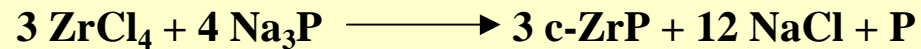
c-ZrP and c-HfP hard and chemically inert materials,
hexagonal to cubic transitions: ZrP 1425 °C, HfP 1600 °C

DIRECT REACTION OF SOLIDS
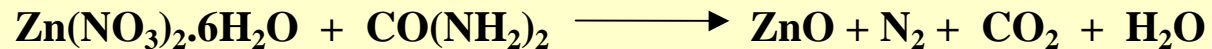
Self-Propagating Metathesis

Silicon production

$$Na_2SiF_6 + 4\,Na \longrightarrow 6\,NaF + Si$$
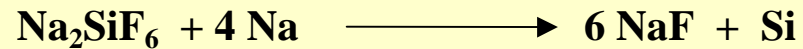
Hard materials production

$$TaCl_5 + Li_3N + NaN_3 + NH_4Cl \to c\text{-}TaN + LiCl + NaCl + N_2 + HCl$$

$$CrCl_3 + Li_3N + NH_4Cl \longrightarrow Cr + Cr_2N + c\text{-}CrN$$

$$CrI_3 + Li_3N \longrightarrow Cr_2N$$

$$CrI_3 + Li_3N + NH_4Cl \longrightarrow c\text{-}CrN$$

$$MoCl_5 + Li_3N \longrightarrow explosive$$

$$MoCl_5 + Ca_3N_2 + NH_4Cl \longrightarrow cubic\ \gamma\text{-}Mo_2N$$
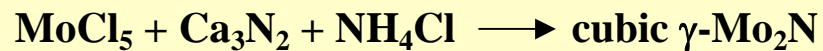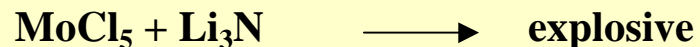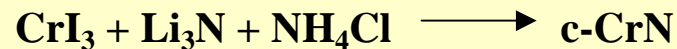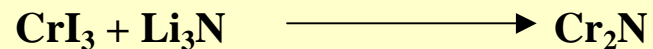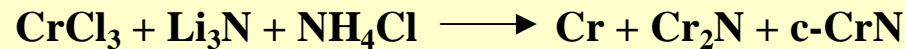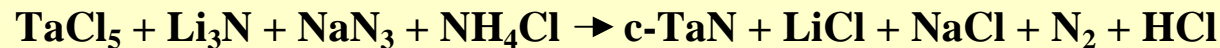
Combustion Synthesis

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
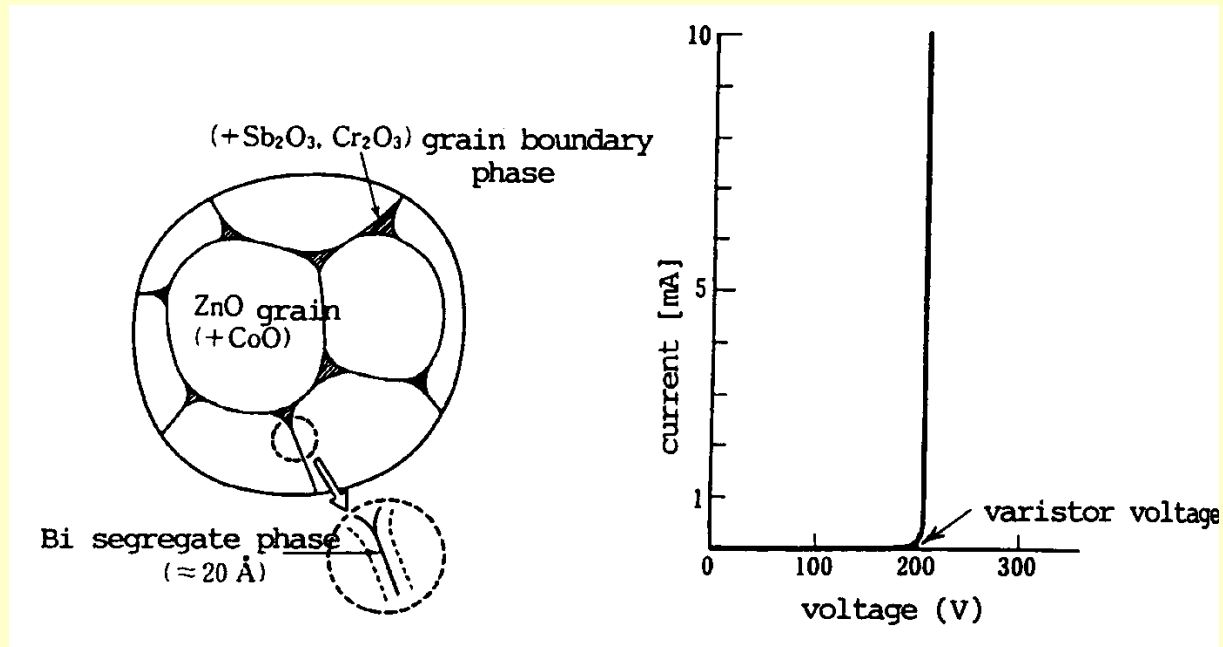**product dry foam, crumbles to a fine powder.**

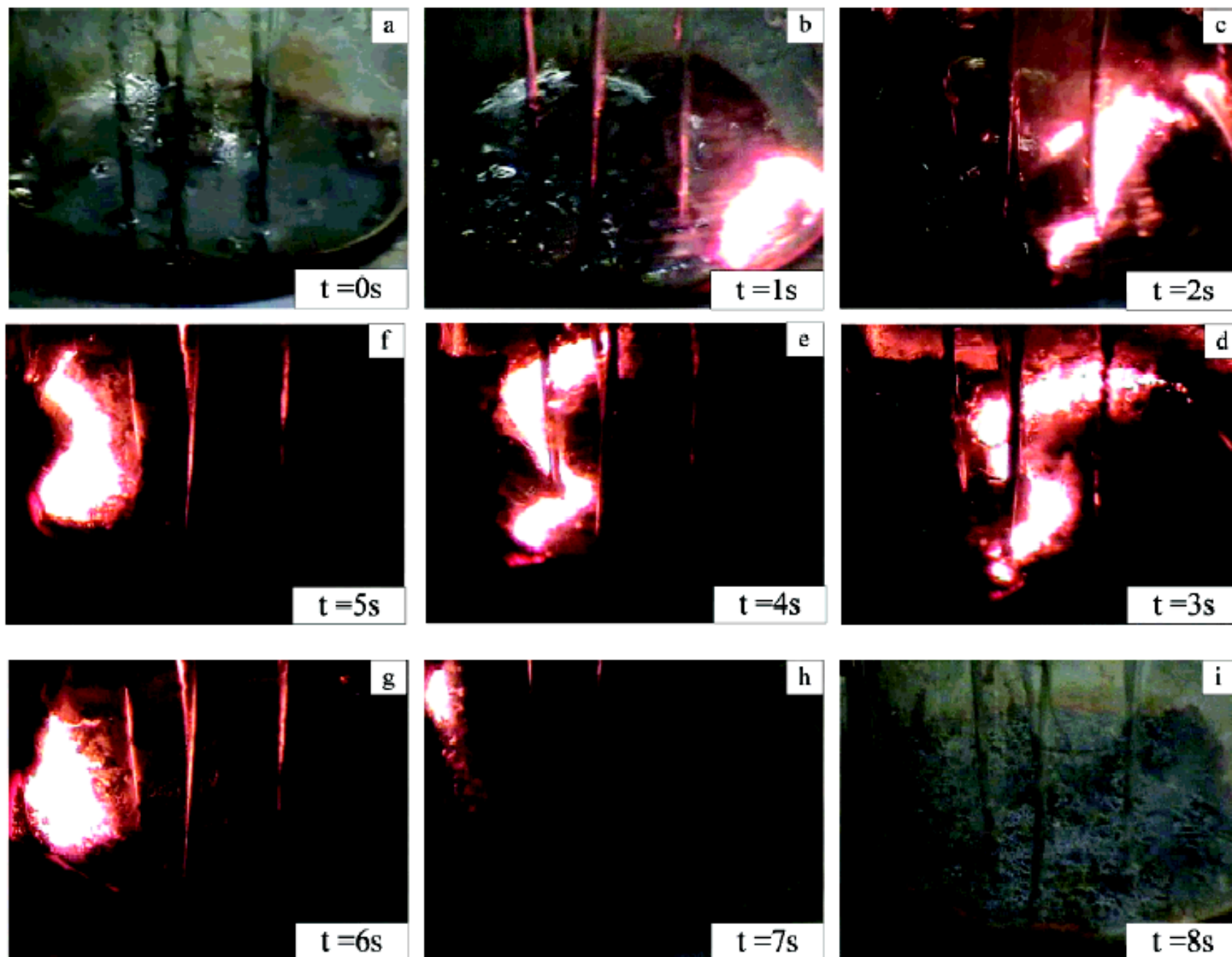$$Zn(NO_3)_2 \cdot 6H_2O \ + \ CO(NH_2)_2 \longrightarrow ZnO + N_2 + \ CO_2 \ + \ H_2O$$

Combustion Synthesis

Examples
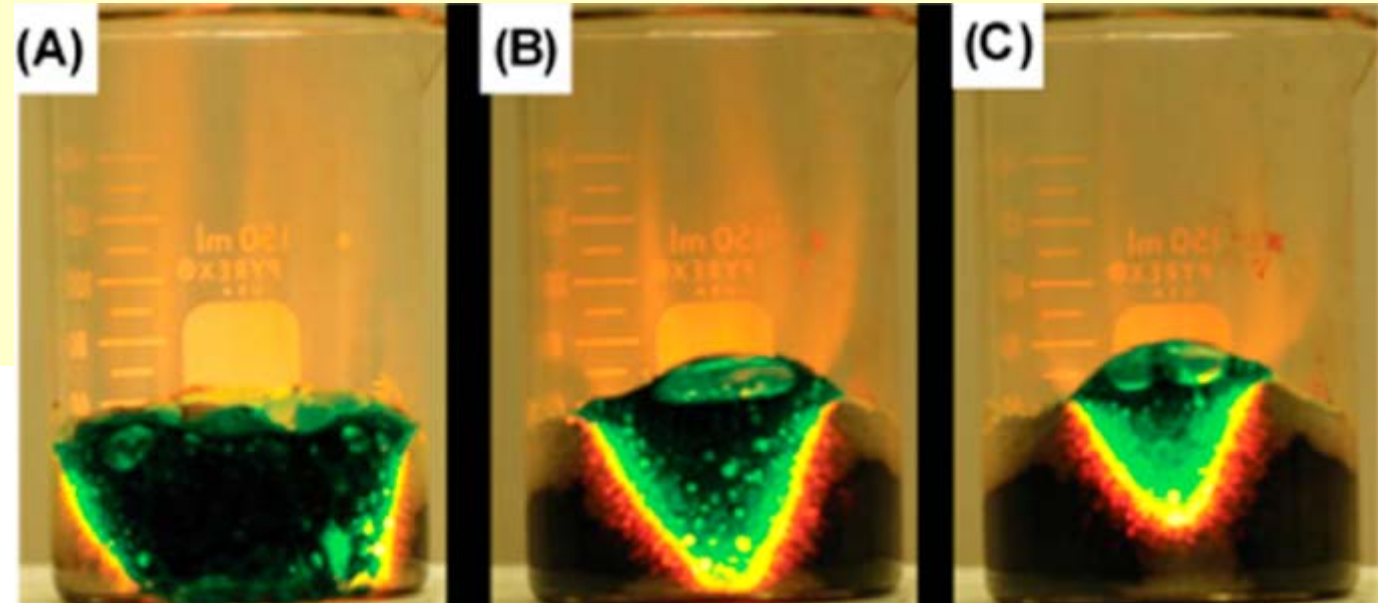
ZnO(90%) - Bi$_2$O$_3$ - Sb$_2$O$_3$

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

Reaction front propagation: glycine-iron nitrate
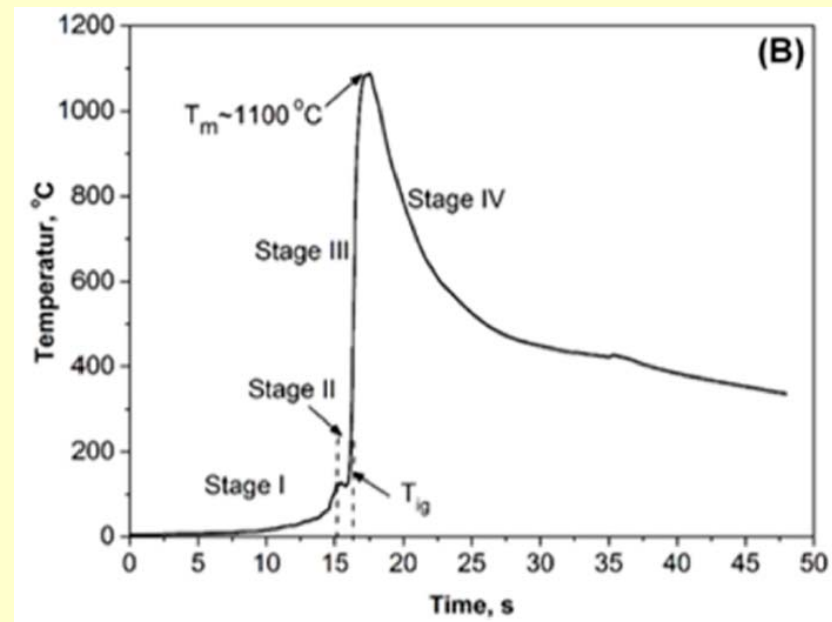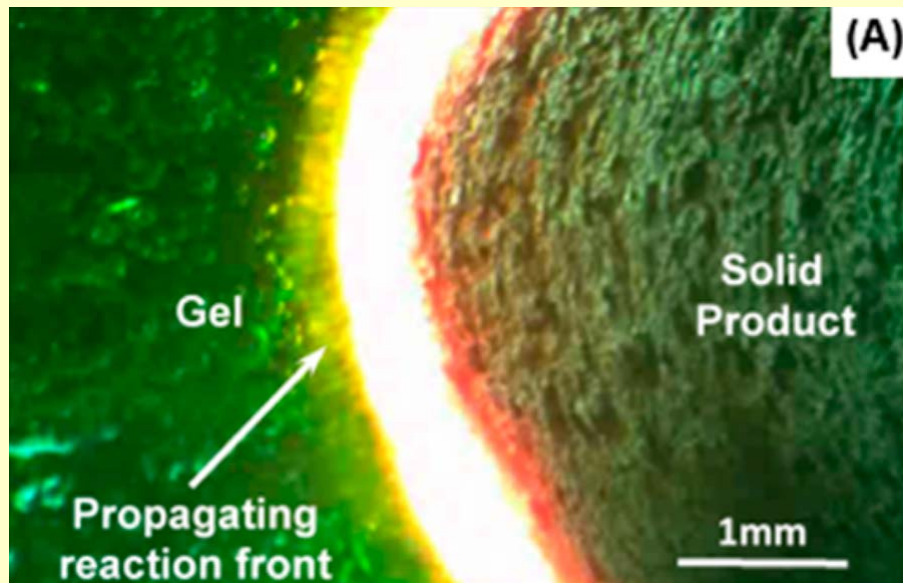
Self-Propagating Metathesis

Combustion Synthesis

Examples

$LiNO_3 + NH_4VO_3 + (NH_4)_2MoO_4 + glycine \rightarrow LiVMoO_6$
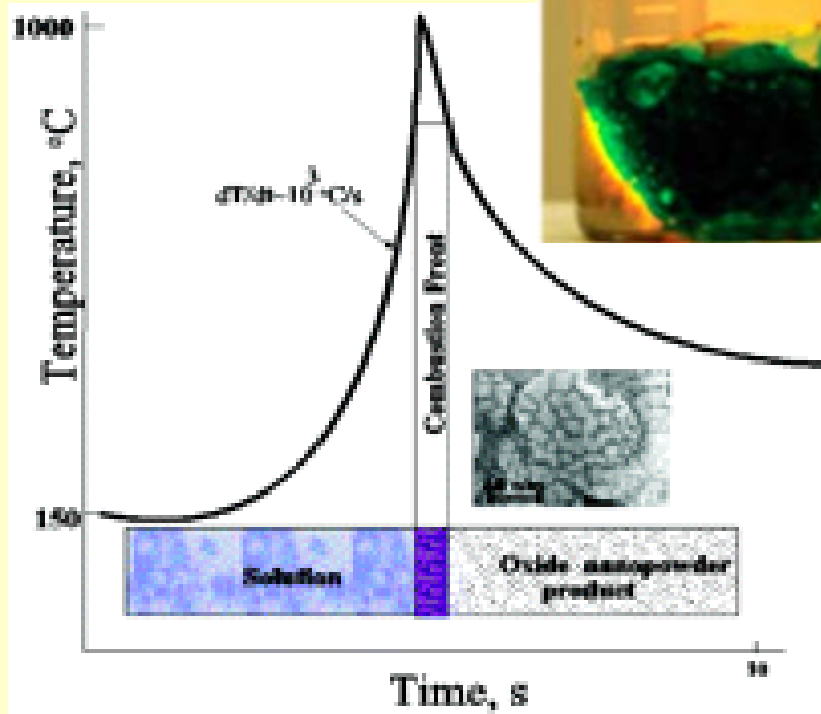
mixing 1:1:1 in aqueous solution, drying at 90 °C
combustion at 250 °C
calcination to $LiVMoO_6$ cathode material for Li-ion
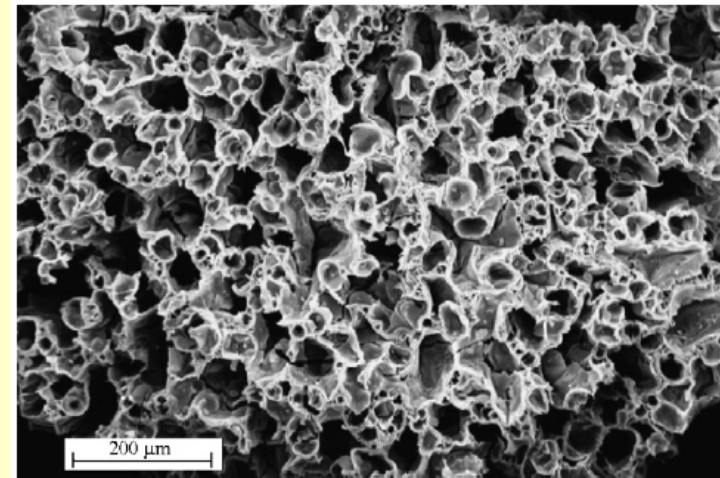
Solution Combustion Synthesis

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

Metal nitrates (MN) = oxidants

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

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

Citric acid monohydrate (CA) = fuel
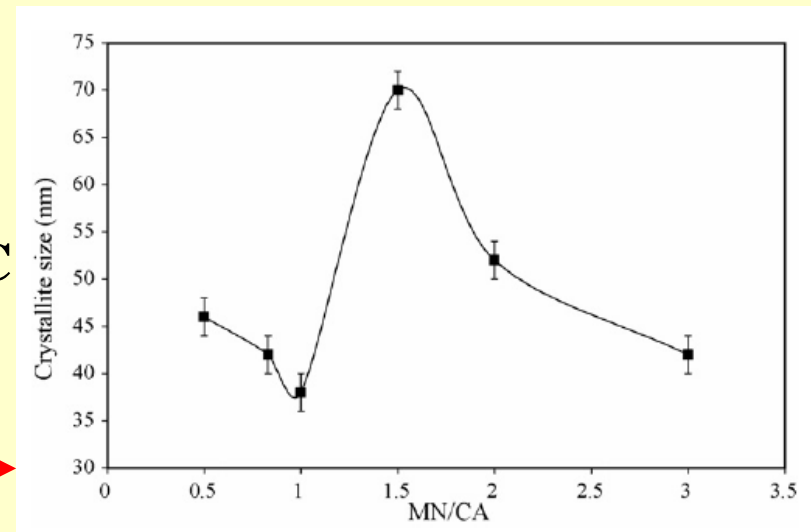
Solution in water $Y:Fe = 3:5$

The solution evaporated at 85 °C

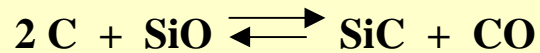**stirrred until viscous gel**

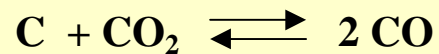**Increasing the temperature up to 250 ° C**
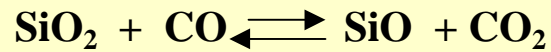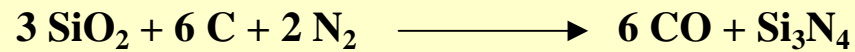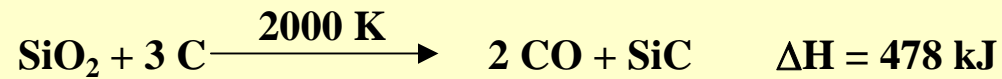
ignition of the gel

MN/CA ratio controls the size

DIRECT REACTION OF SOLIDS

Carbothermal Reduction

Acheson

$$SiO_2 + 3\ C \xrightarrow{\ 2000\ K\ } 2\ CO + SiC \qquad \Delta H = 478\ kJ$$

$$3\ SiO_2 + 6\ C + 2\ N_2 \longrightarrow 6\ CO + Si_3N_4$$

$$C\ +\ SiO_2 \rightleftharpoons SiO(g)\ +\ CO$$

$$SiO_2\ +\ CO \rightleftharpoons SiO\ + CO_2$$

$$C\ + CO_2 \rightleftharpoons 2\ CO$$

$$2\ C\ +\ SiO \rightleftharpoons SiC\ +\ CO$$

DIRECT REACTION OF SOLIDS

Carbothermal Reduction

Borides

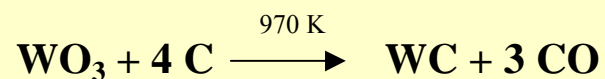$$TiO_2 + B_2O_3 + 5\ C \xrightarrow{\ 1300\ K\ } 5\ CO + TiB_2$$

$$2\ TiO_2 + B_4C + 3\ C \xrightarrow{\ 2300\ K\ } 4\ CO + 2\ TiB_2$$

$$Al_2O_3 + 12\ B_2O_3 + 39\ C \xrightarrow{\ 1820\ K\ } 2\ AlB_{12} + 39\ CO$$

Carbides

$$2\ Al_2O_3 + 9\ C \xrightarrow{\ 2220\ K\ } Al_4C_3 + 6\ CO$$

$$2\ B_2O_3 + 7\ C \xrightarrow{\ 1820\ K\ } B_4C + 6\ CO$$

$$WO_3 + 4\ C \xrightarrow{\ 970\ K\ } WC + 3\ CO$$

Nitrides

$$Al_2O_3 + N_2 + 3\ C \xrightarrow{\ 1970\ K\ } 2\ AlN + 3\ CO$$

$$2\ TiO_2 + N_2 + 4\ C \xrightarrow{\ 1820\ K\ } 2\ TiN + 4\ CO$$
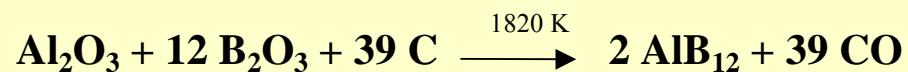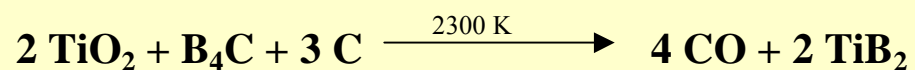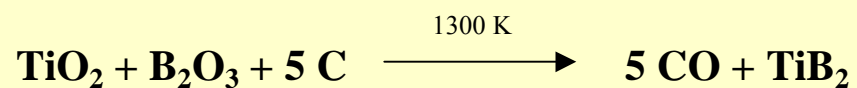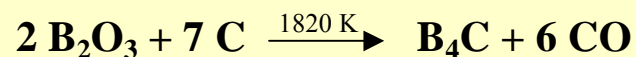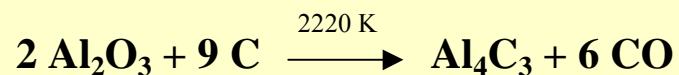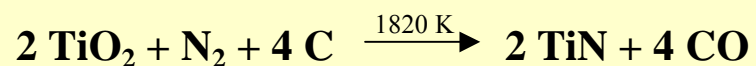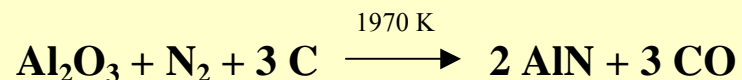
Fusion-Crystallization from Glass

Glass is a non-equilibrium, non-crystalline condensed state of matter that exhibits a glass transition. The structure of glasses is similar to that 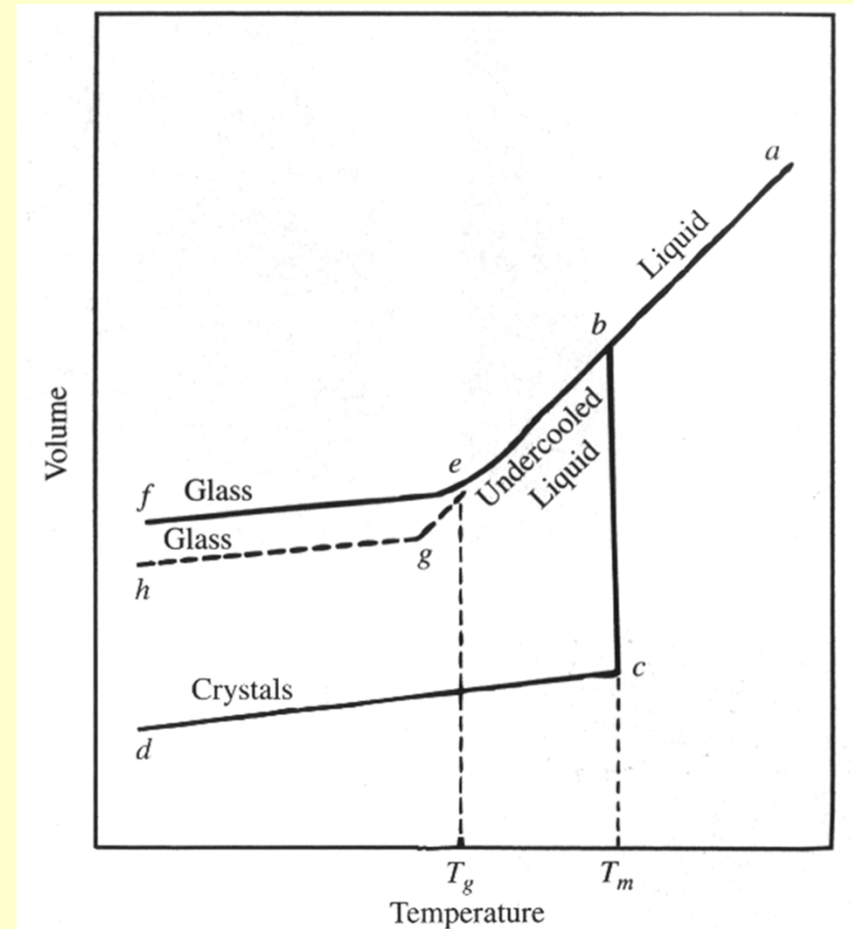of their parent supercooled liquids (SCL), and they spontaneously relax toward the SCL state. Their ultimate fate, in the limit of infinite time, is to crystallize.

Fusion-Crystallization from Glass

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

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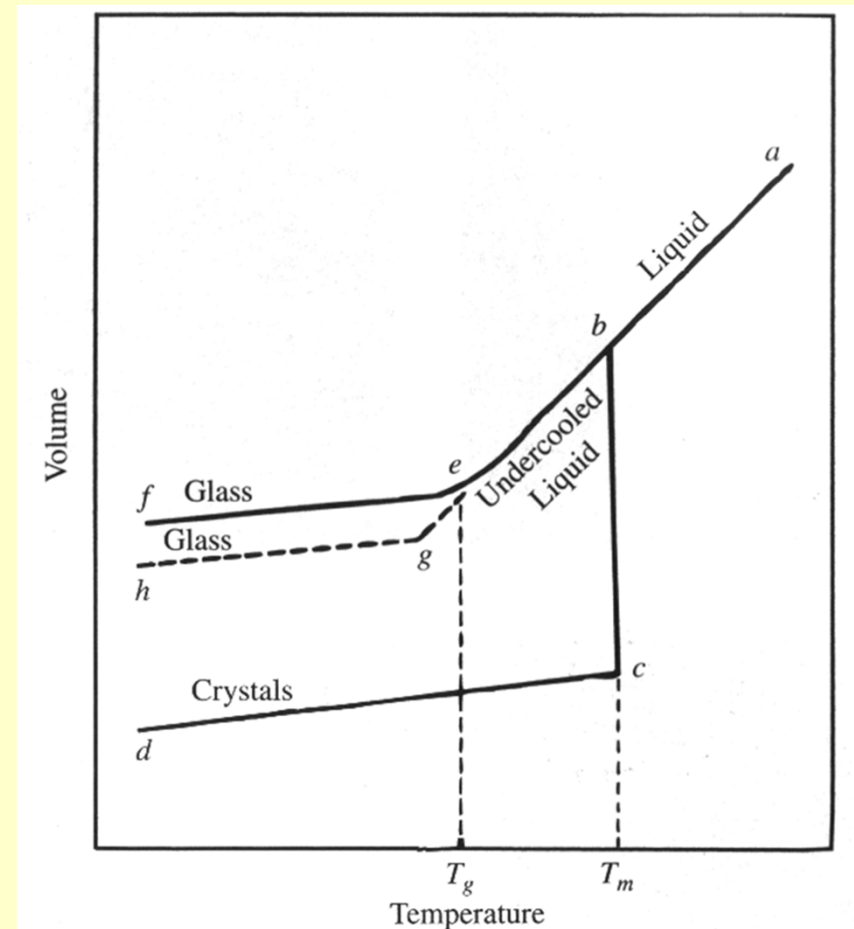- **volatility of reagents**

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

Fusion-Crystallization from Glass

Production of window glass

Abrasive grains

$$Al_2O_3 + MgO \xrightarrow{\text{2100 K}} \text{melt, solidify, crush, size}$$
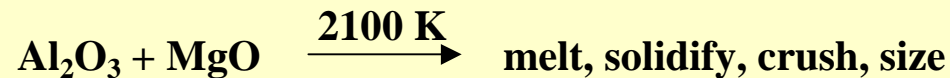
Crystallizing an inorganic glass, lithium disilicate

$$Li_2O + 2SiO_2 + Al_2O_3 \xrightarrow{\text{1300 K, Pt crucible}} Li_2Si_2O_5$$
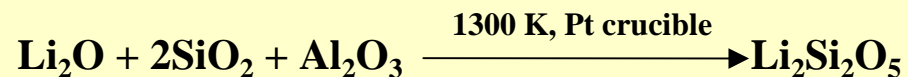
$Li_2Si_2O_5$ forms as a melt. Hold at 1100°C for 2-3 hrs. Homogeneous, rapid cooling, fast viscosity increase, quenches transparent glass

**$Li_2Si_2O_5$, glass 500-700°C, $T_g \sim 450$°C from DSC $\rightarrow Li_2Si_2O_5$, crystals in 2-3 hrs.,
principle of crystallizing a glass above its glass transition**

85

Fusion-Crystallization from Glass

Fusion-Crystallization from Glass

Glass Ceramics
polyxtalline materials made by controlled xtallization of glasses

Cooking utensils
$Li_2O/SiO_2/Al_2O_3(>10\%)$ nucl. TiO_2 β-spodumene

Vacuum tube components
$Li_2O/SiO_2/Al_2O_3(<10\%)$ nucl. P_2O_5 Li-disilicate, quartz

Missile radomes
$MgO/SiO_2/Al_2O_3$ nucl. 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_2 to form calcium carbonate through carbonatation

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_3SiO_5	Alite	50-70
B-dicalcium silicate	C2S	Ca_2SiO_4	Belite	15-30
Tricalcium aluminate	C2A	$Ca_3Al_2O_6$	Aluminate	5-10
Tetracalcium aluminoferrite	C4AF	$Ca_2(Al/Fe)O_5$	Ferrite	5-15

Chemical Cement Nomenclature

S	SiO_2	C	CaO
A	Al_2O_3	F	Fe_2O_3
T	TiO_2	M	MgO
K	K_2O	N	Na_2O
H	H_2O		
$\bar{C}$	CO_2		
$\bar{S}$	SO_3		