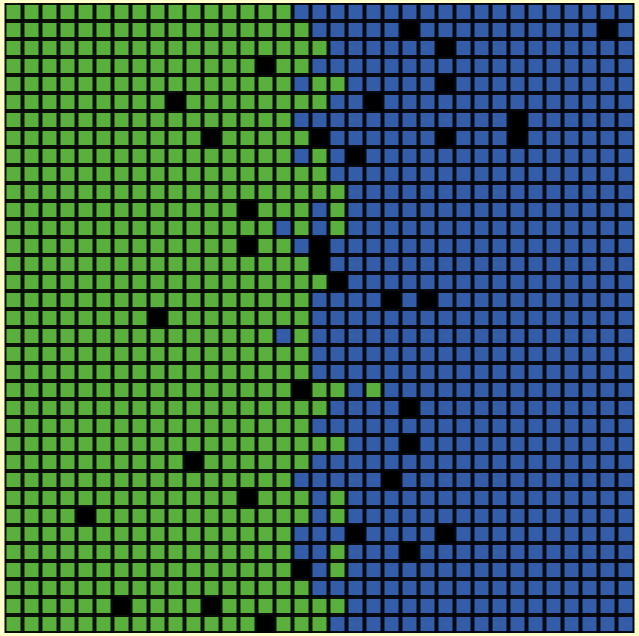
Direct Reactions of Solids

"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

$PbSO_4 + ZrO_2 + K_2CO_3 \rightarrow K_2SO_4 + PbZrO_3 + CO_2$

Reaction Types

Solid – solid synthesis – dissociation **AB → A + B**

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

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

Solid State Reactions

Oxides

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

$UF_6 + H_2 + 2\ H_2O \rightarrow UO_2$ (powder) + 6 HF at 873 K
dust = radiological hazard, milling, sintering to UO_2 pellets

YBCO 123 Superconductor (1987)

$Y_2O_3 + BaCO_3 + CuO \rightarrow YBa_2Cu_3O_{7-x}$ 1223 K in air, then 473 K in oxygen

$Tl_2O_3 + 2BaO + 3CaO + 4CuO \rightarrow Tl_2Ba_2Ca_3Cu_4O_{12}$ at 1130 K

Aluminosilicates

$NaAlO_2 + SiO_2 \rightarrow NaAlSiO_4$

Solid State Reactions

Pnictides

$Na_3E + ME + E \rightarrow Na_2M_3E_4$ at 1100 K M = Eu, Sr, E = P, As

Metals

$UF_4 + 2\ Ca \rightarrow U + 2\ CaF_2$ Manhattan Project

Chlorides

$6\ NH_4Cl + Y_2O_3 \rightarrow 2\ YCl_3 + 3\ H_2O + 6\ NH_3$
$6\ NH_4Cl + Y \rightarrow (NH_4)_3YCl_6 + 1.5\ H_2 + 3\ NH_3$
$4\ NH_4Cl + 3\ NH_4ReO_4 \rightarrow 3\ Re + 12\ H_2O + 3.5\ N_2 + 4\ HCl$

Chalcogenides

$Pb + Mo + S \rightarrow PbMo_6S_8$ Chevrel phases
($M_xMo_6X_8$, M = RE, Sn, Pb, Cu, X = S, Se, Te)

Experimental Considerations

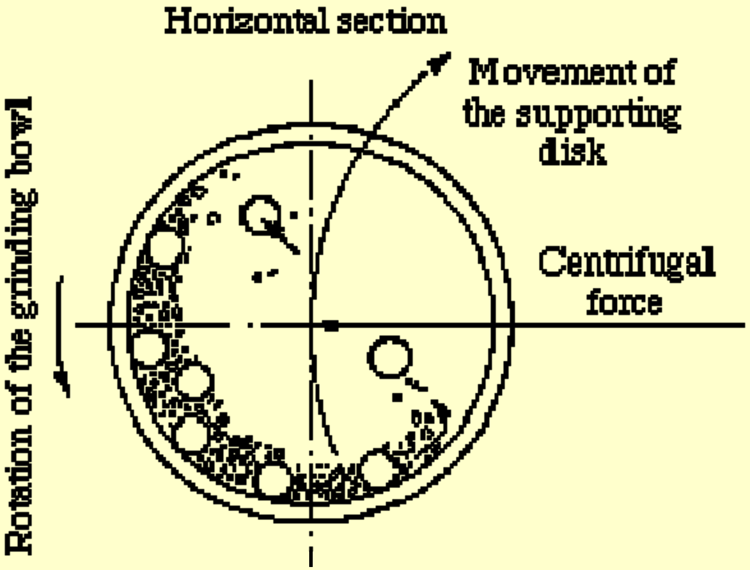
Powder Mixing Method

- 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



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

Milling

Atritor mill

Compaction - Pressing

Hydraulic Uniaxial Press

Maximum pressure: 120 MPa

Warm Isostatic Press

Max. pressure: 400 MPa
Max. temperature: 80 ^{o}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 ^{o}C 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

💣 Reaction Process

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

Experimental Considerations

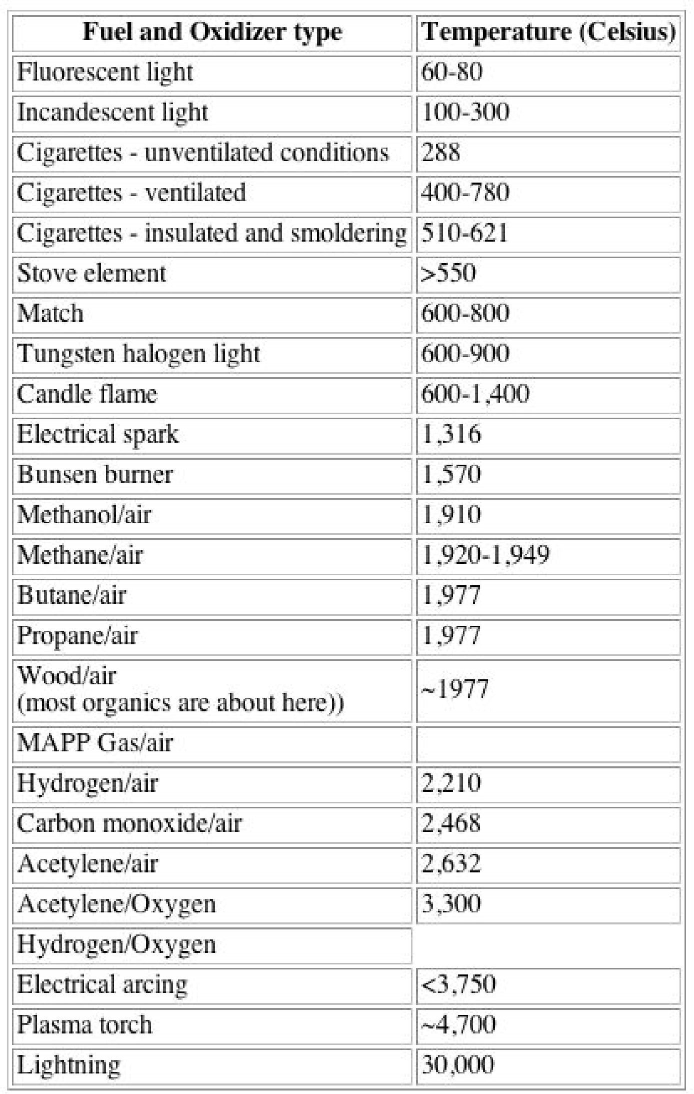
Heating Program

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

Parameters in 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

Parameters in Direct Reactions of Solids

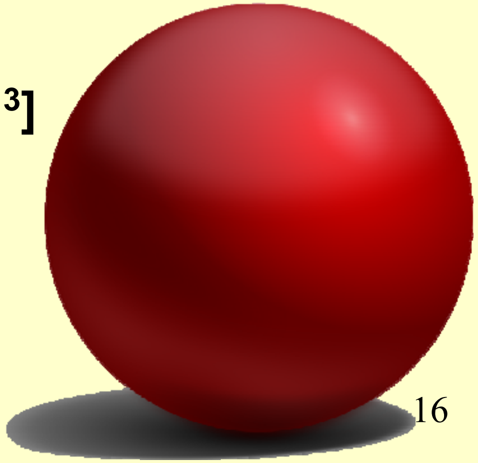
CONTACT AREA and surface area (SA) of reacting solids control:

- **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/cm³]

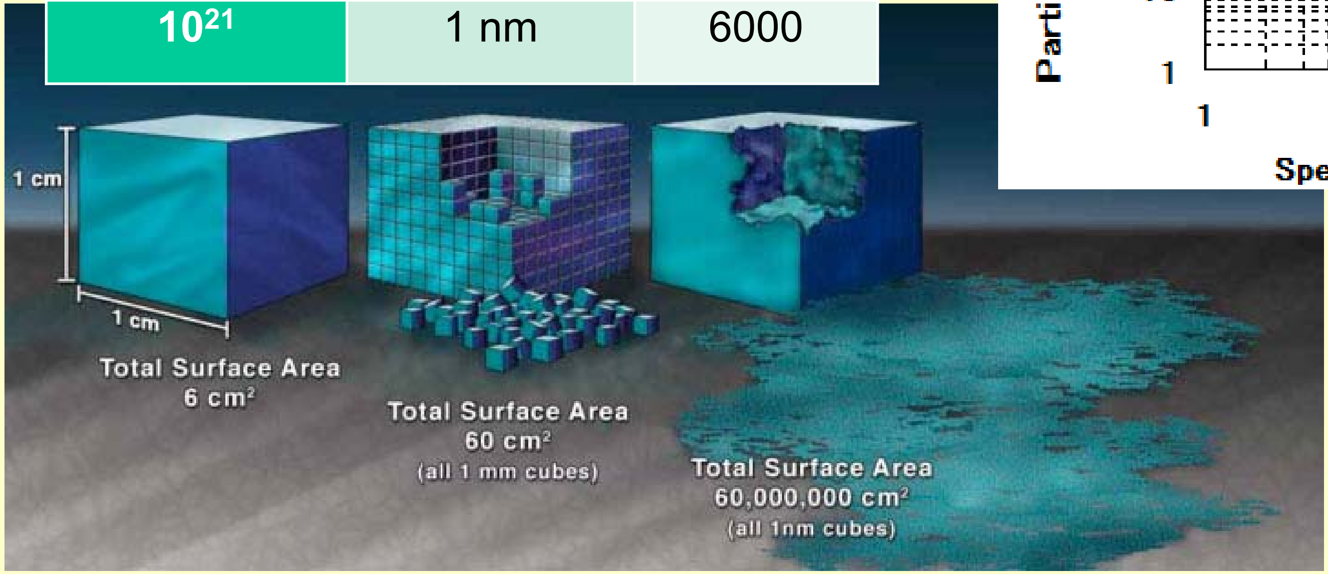


$$SA = A/m = \frac{4\pi r^2}{4/3\pi r^3.\rho} = 3000/r\rho \quad [m^2/g]$$

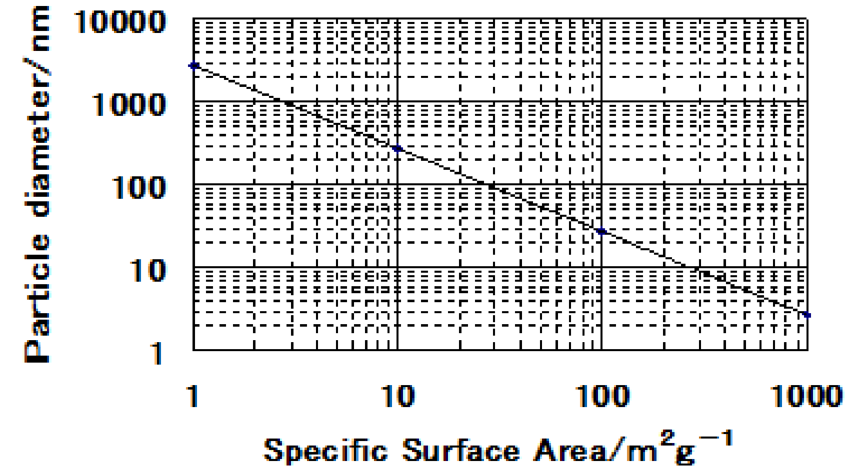
Parameters in Direct Reactions of Solids

Consider 1 g of a material, density 1.0 g/cm^3 , cubic crystallites

Number of cubes	Edge length	SA, m^2/g
1	1 cm	6.10^{-4}
10^3	1 mm	6.10^{-3}
10^{12}	1 μm	6
10^{21}	1 nm	6000

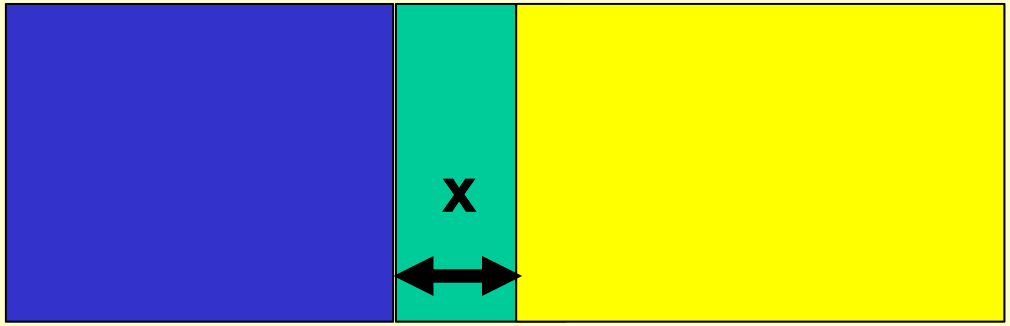


Silica



The smaller the particle size, the larger the surface area

Parameters in Direct Reactions of Solids



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

$$dx/dt = k/x$$

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

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

Thus particle sizes and surface area inextricably connected and obviously

$$x \sim d_{particle}$$

and SA particle size affect the interfacial thickness $A_{contact} \sim 1/ d_{particle}$

Parameters in 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 - 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

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

Parameters in Direct Reactions of Solids

DIFFUSION RATE

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

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 $D > 10^{-12}$

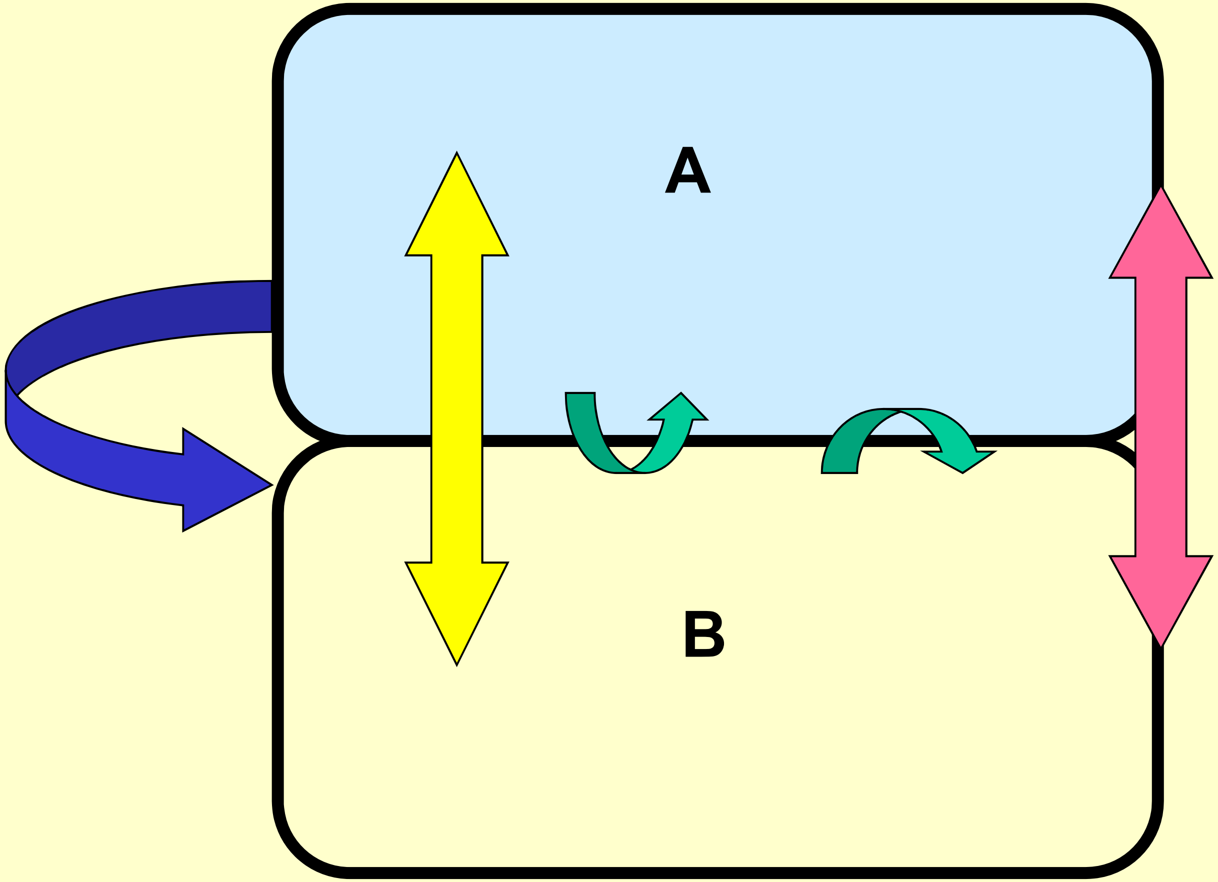
D increases with temperature, rapidly as you approach the melting point

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

Factors influencing cation diffusion rates:

- **Charge, mass and temperature**
- **Interstitial versus substitutional diffusion**
- **Number and types of defects in reactant and product phases**
- **All types of defects enhance diffusion of ions (intrinsic or extrinsic, vacancies, interstitials, lines, planes, dislocations, grain boundaries)**

Reaction Paths between Two Solids



🟦 **gas phase diffusion**

🟨 **volume diffusion**

🟩 **interface diffusion**

🟥 **surface diffusion**

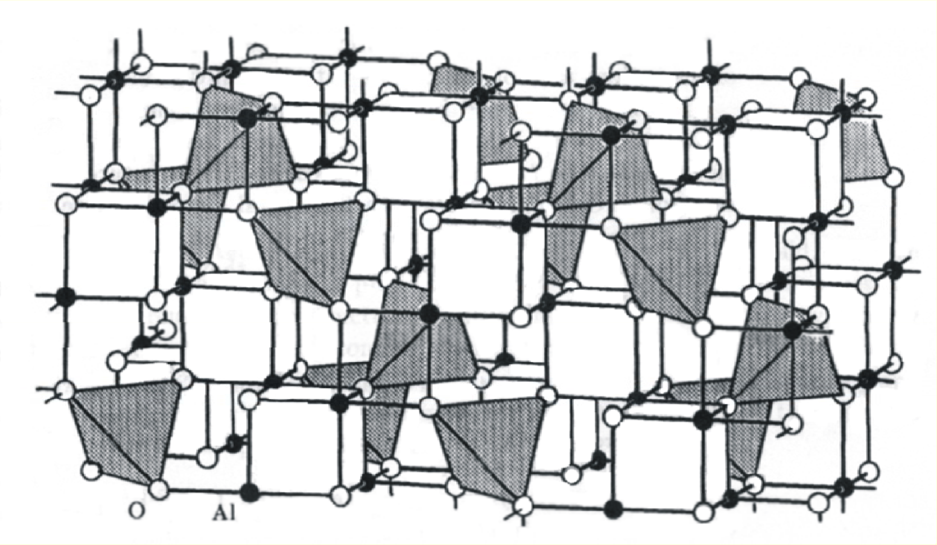
Direct Reactions of Solids

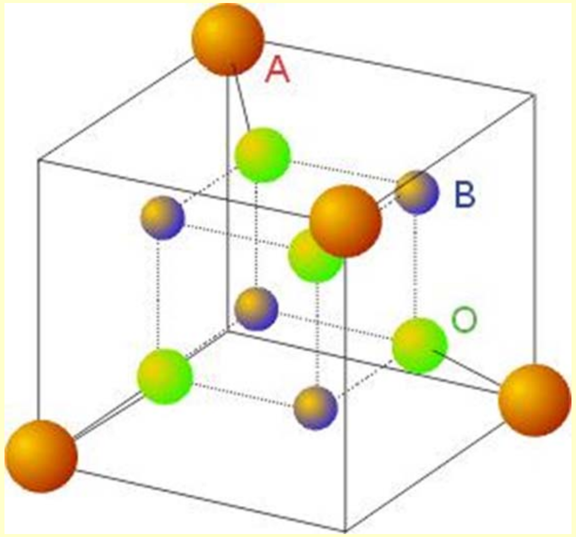
(A) $[B]_2 O_4$ Stoichiometric formula of spinel

ccp array of O^{2-}
(A) occupy 1/8 T_d
[B] occupy 1/2 O_h

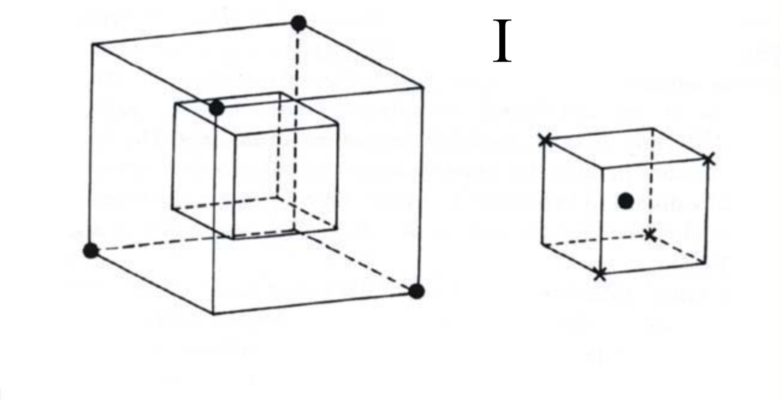
normal spinels: (A) $[B]_2 O_4$ - $MgAl_2O_4$, Co_3O_4

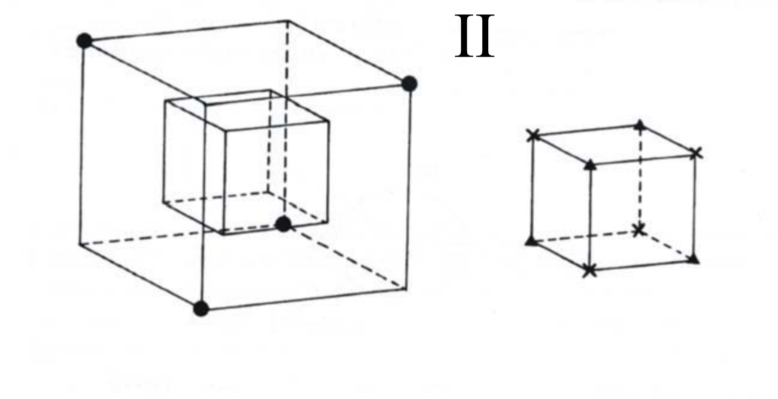
inverse spinel: (B) [AB] O_4 - Fe_3O_4: $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$



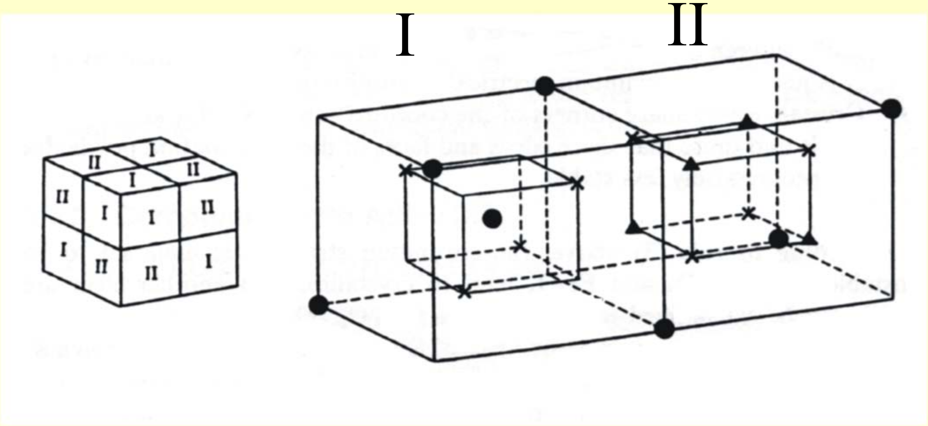


The Spinel Structure: $MgAl_2O_4$





$(A)[B]_2O_4$



• = Mg

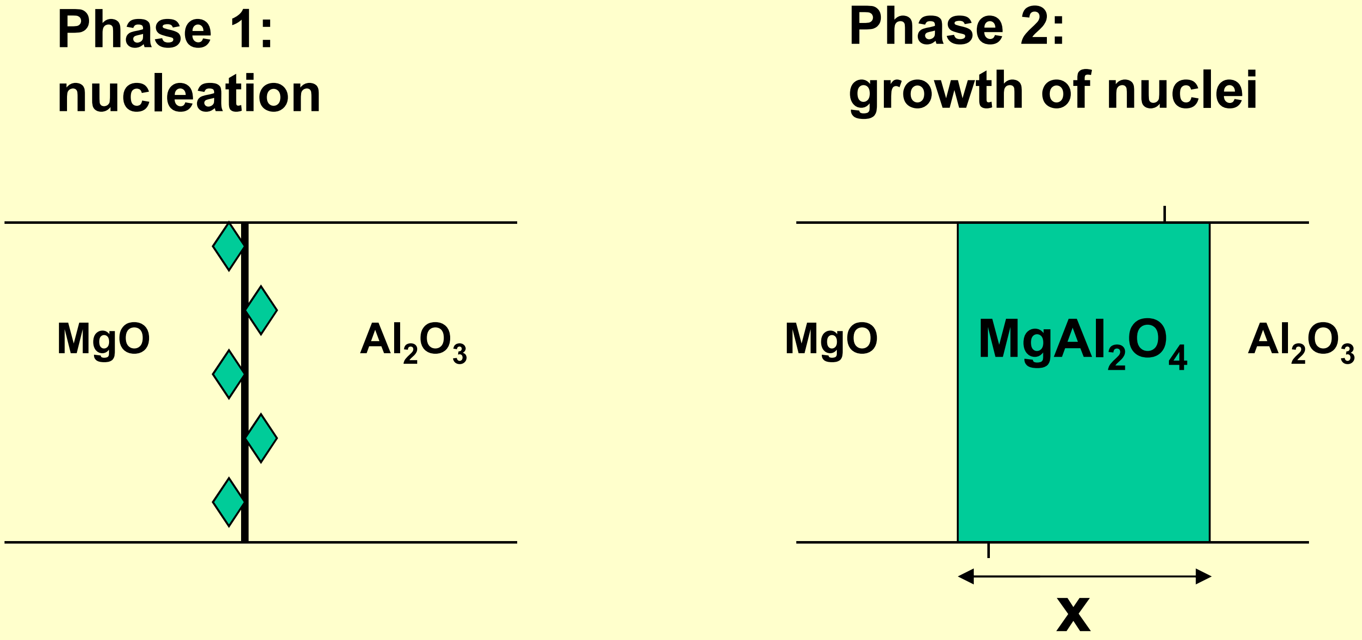
x = O

▲ = Al

Direct Reactions of Solids

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

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



Direct Reactions of Solids

Model reaction, well studied: $MgO + Al_2O_3 \rightarrow MgAl_2O_4$ **(Spinel)**

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

Interfacial growth rates 3 : 1

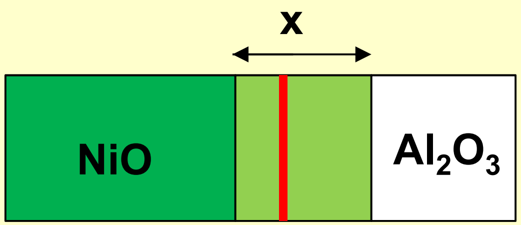
$$dx/dt = k/x$$

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

- **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: $dx/dt = k/x$

$$x^2 = kt$$

Kinetics of Reactions in Solids

Linear dependency of x^2 vs. t plots observed
In k vs. 1/T experiments provide Arrhenius activation energy E_a for the solid-state reaction

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

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

$3\,Mg^{2+}$ diffuse in opposite direction to $2\,Al^{3+}$

$MgAl_2O_4/Al_2O_3$ Interface (I):

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

$MgO/MgAl_2O_4$ Interface (II):

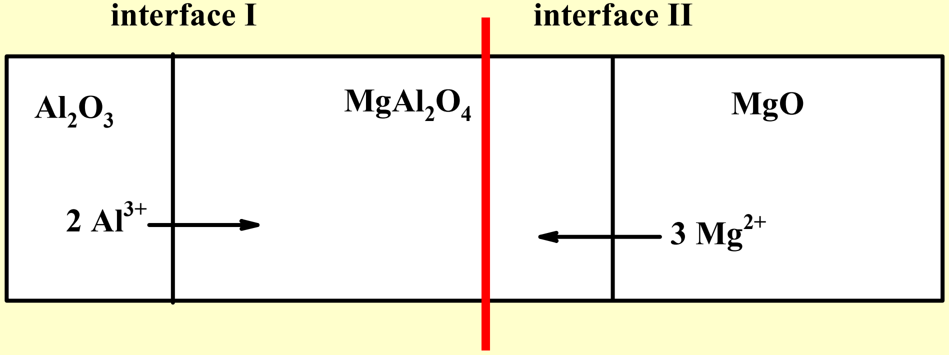
$$2\,Al^{3+} - 3\,Mg^{2+} + 4\,MgO \rightarrow 1\,MgAl_2O_4$$

Overall Reaction:

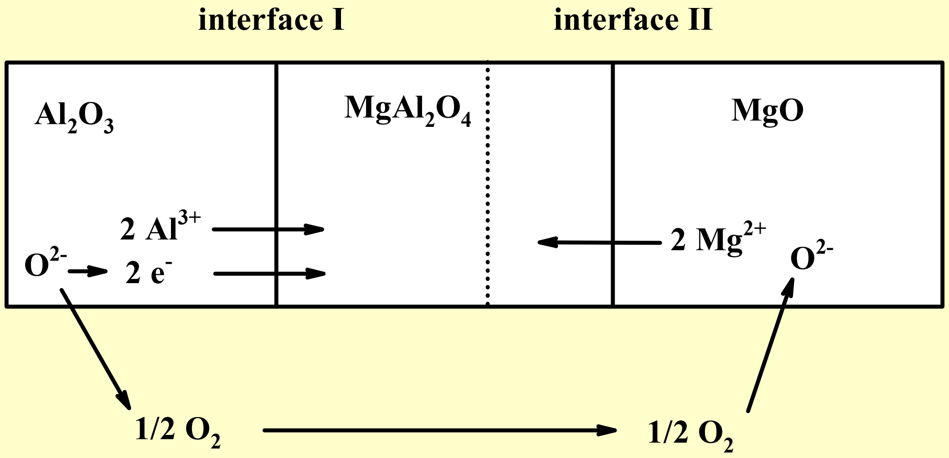
$$4\,MgO + 4\,Al_2O_3 \rightarrow 4\,MgAl_2O_4$$

the Kirkendall Effect : growth rate of interfaces = 3/1

Reaction Mechanism



the **Kirkendall** Effect : growth rate of interfaces = **3/1**



Kinetics of Reactions in 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: $k(T) = k_0 \exp(-E_a/RT)$

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

$$\alpha = 0 - 1$$

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

e.g., P_t = mass loss, x, ……

Experimentally evaluate α at different t
Fit data into a $g(\alpha) = k(T) \times t$ expression to obtain k(T) and the type of mechanism model

Kinetics of Reactions in Solids

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

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

Decreasing reaction rate dx/dt as spinel product layer (x) thickens

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

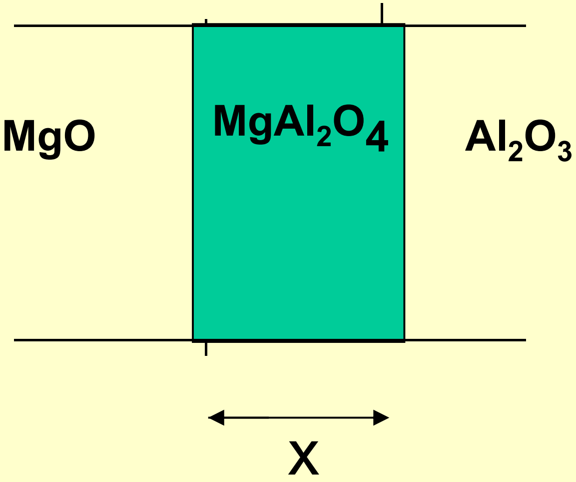
$$\alpha = 0 - 1$$

Here α = x

Parabolic rate law:

$dx/dt = k/x$

$x^2 = kt$



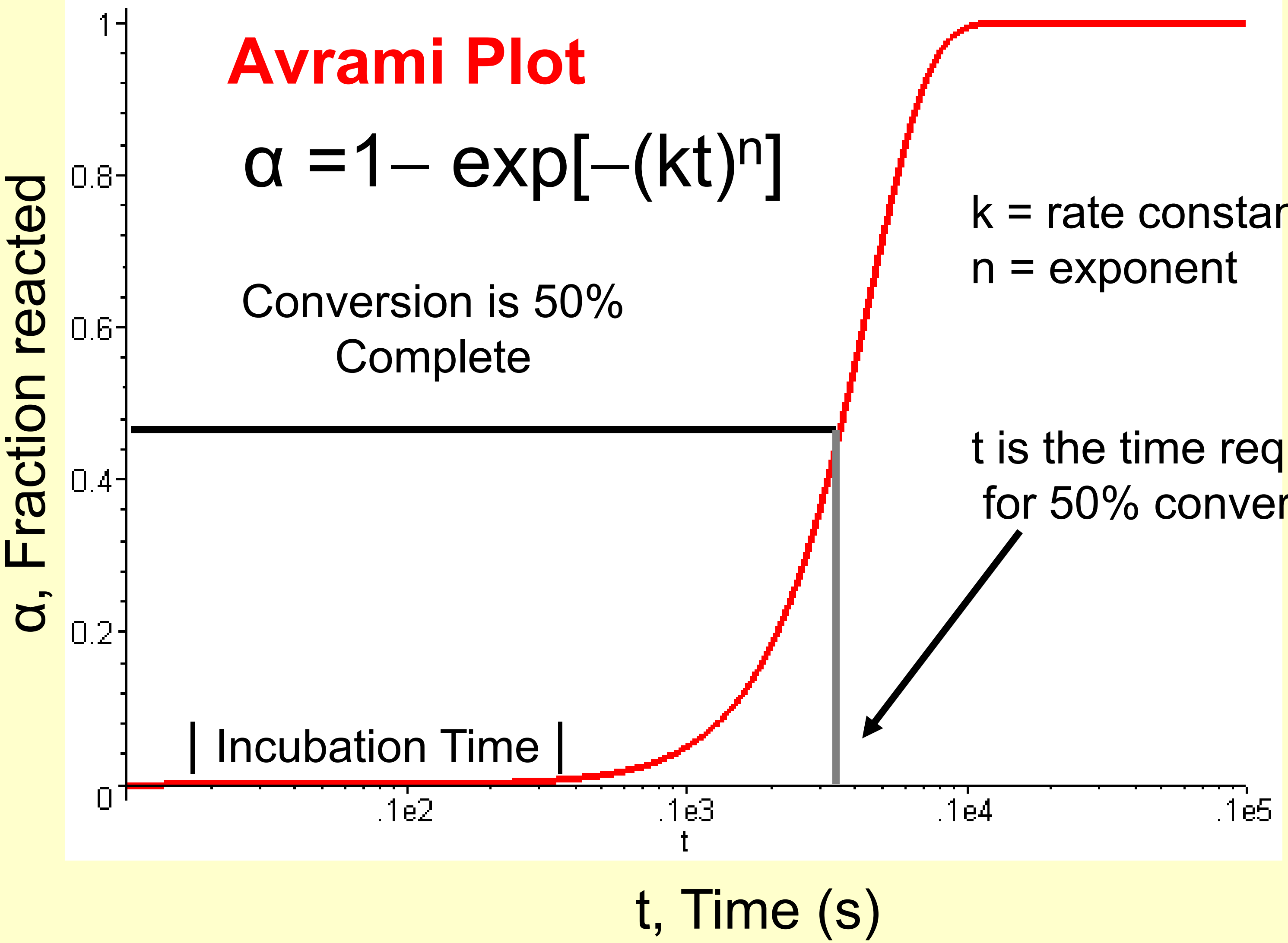
Reaction Mechanism

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

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

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

Kinetics of Reactions in Solids



Avrami Plot

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

Conversion is 50%
Complete

| Incubation Time |

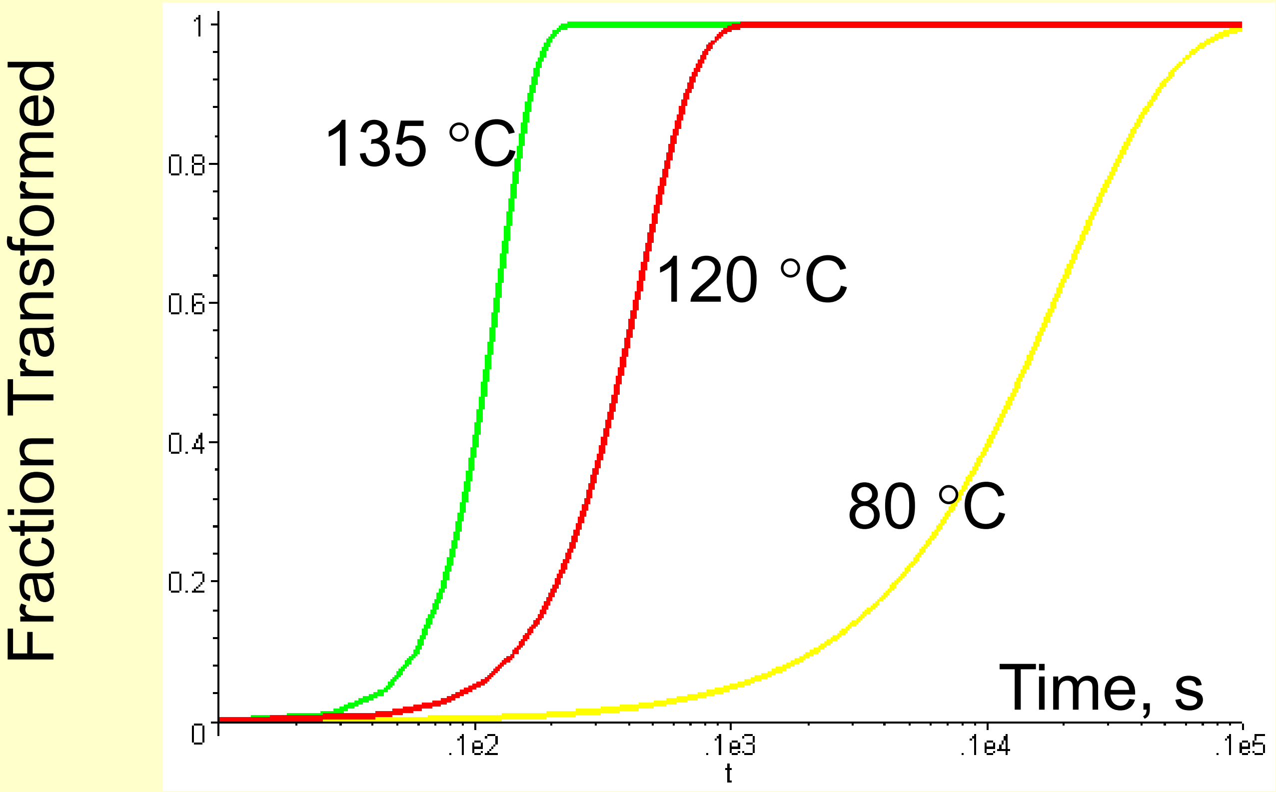
k = rate constant
n = exponent

t is the time required
for 50% conversion

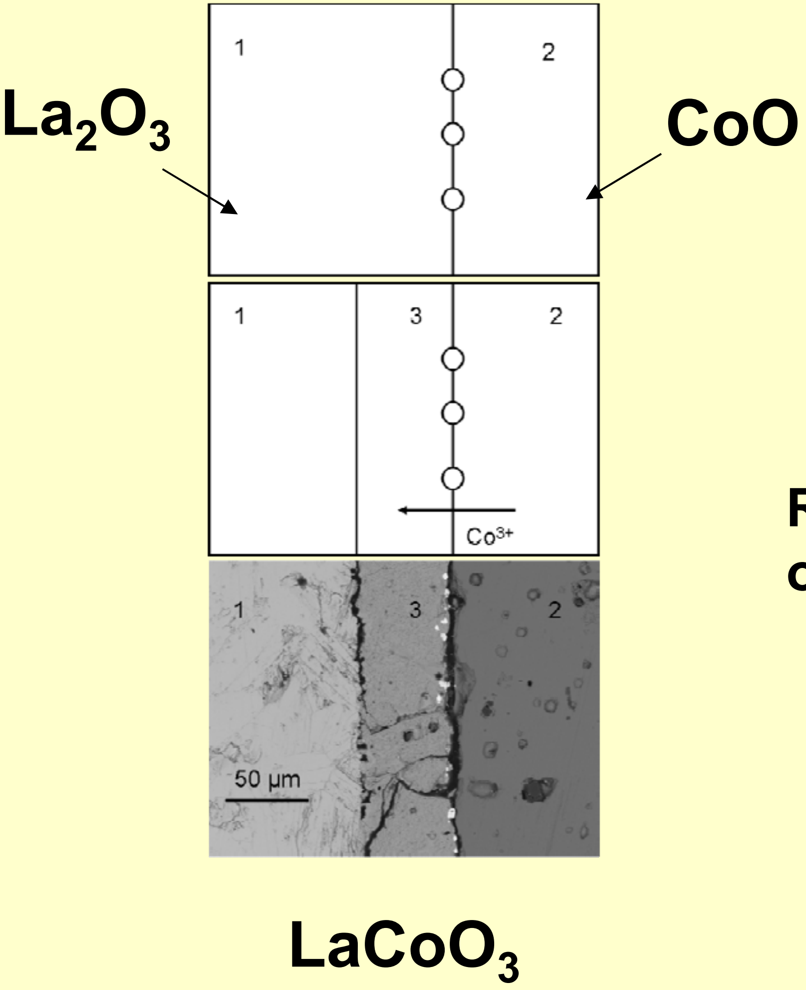
Kinetics of Reactions in Solids

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 $LaCoO_3$



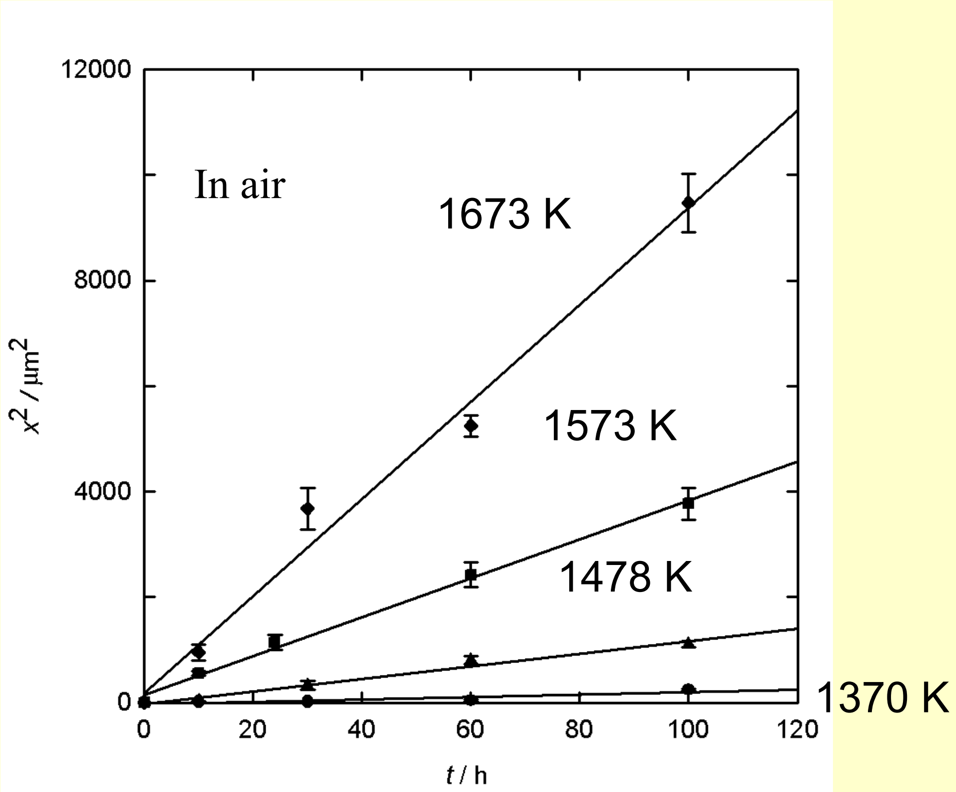
Marker experiments

Experimental result:

$\boxed{D_{Co} >> D_{La}}$

Rate-determining step is the diffusion of Co cations

Growth Kinetics of $LaCoO_3$



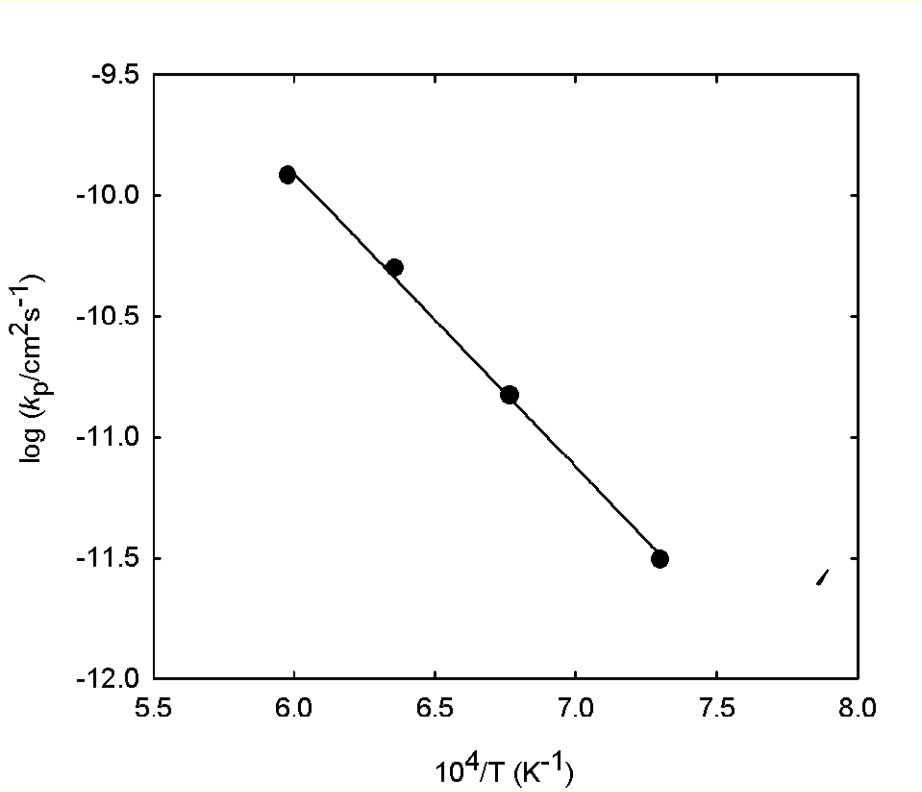
$$x^2 = kt$$

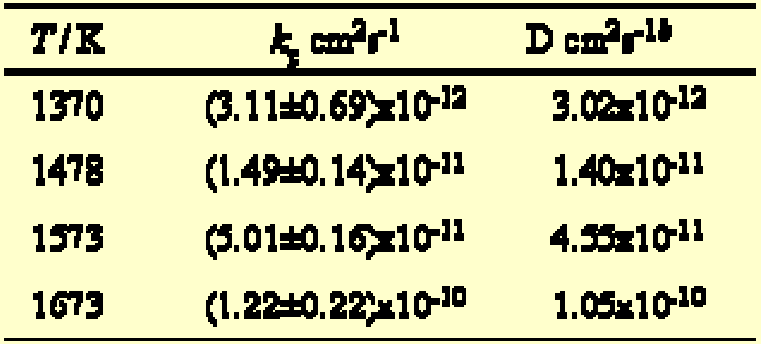
Evaluate *k* as the slope

at several temperatures

Parabolic rate law valid = process is controlled by one-dimensional diffusion = rate limiting step

Growth Kinetics of $LaCoO_3$





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

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

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

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

Nucleation

Homogeneous nucleation

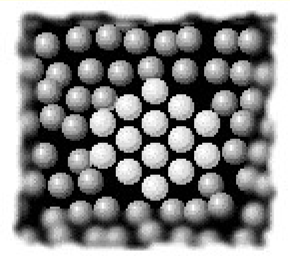
Liquid melt to crystalline solid
Cluster formation on cooling

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

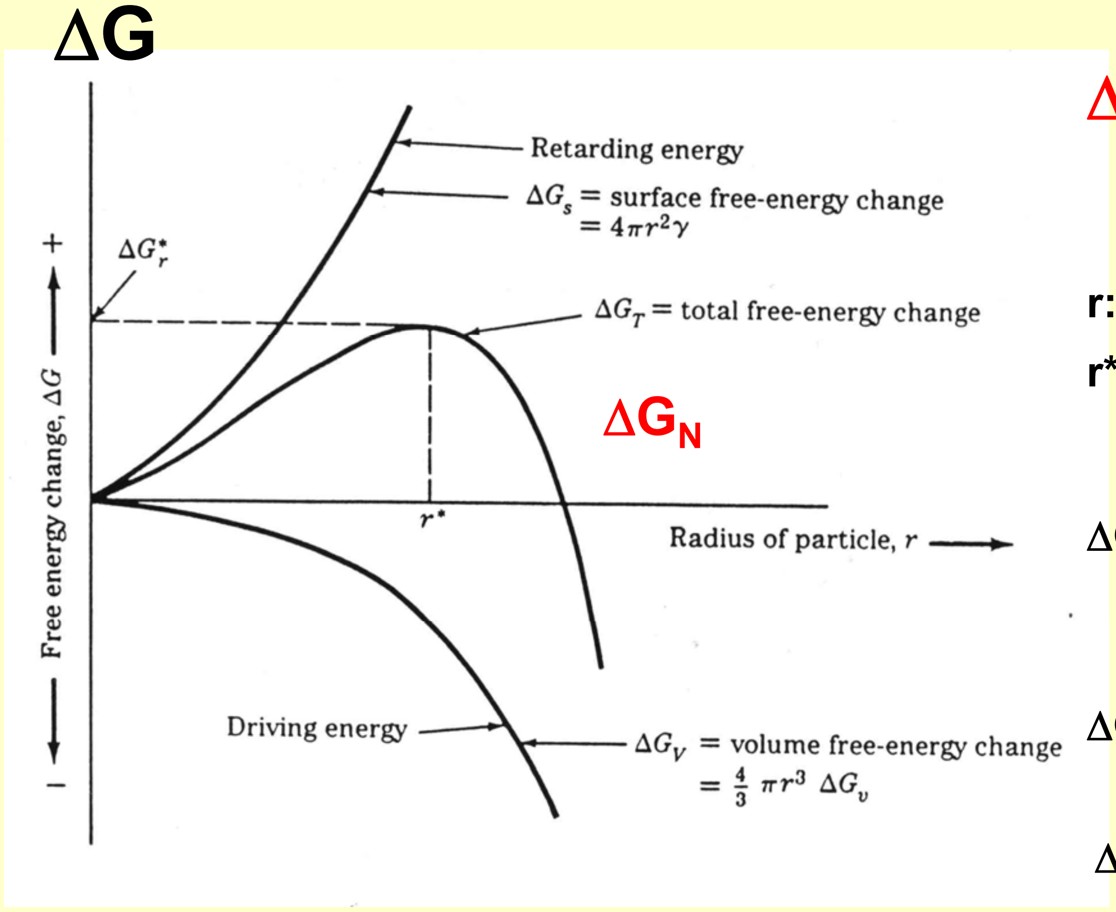
ΔG_v = driving force for solidification (negative)
Spontaneous below the equilibrium melting temperature, T_m
$\Delta T = T_m - T$ = undercooling, ΔH_v = enthalpy of solidification (negative)

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



Nucleation



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

r: radius of spherical seed

r*: critical radius

ΔG_N: total free energy change

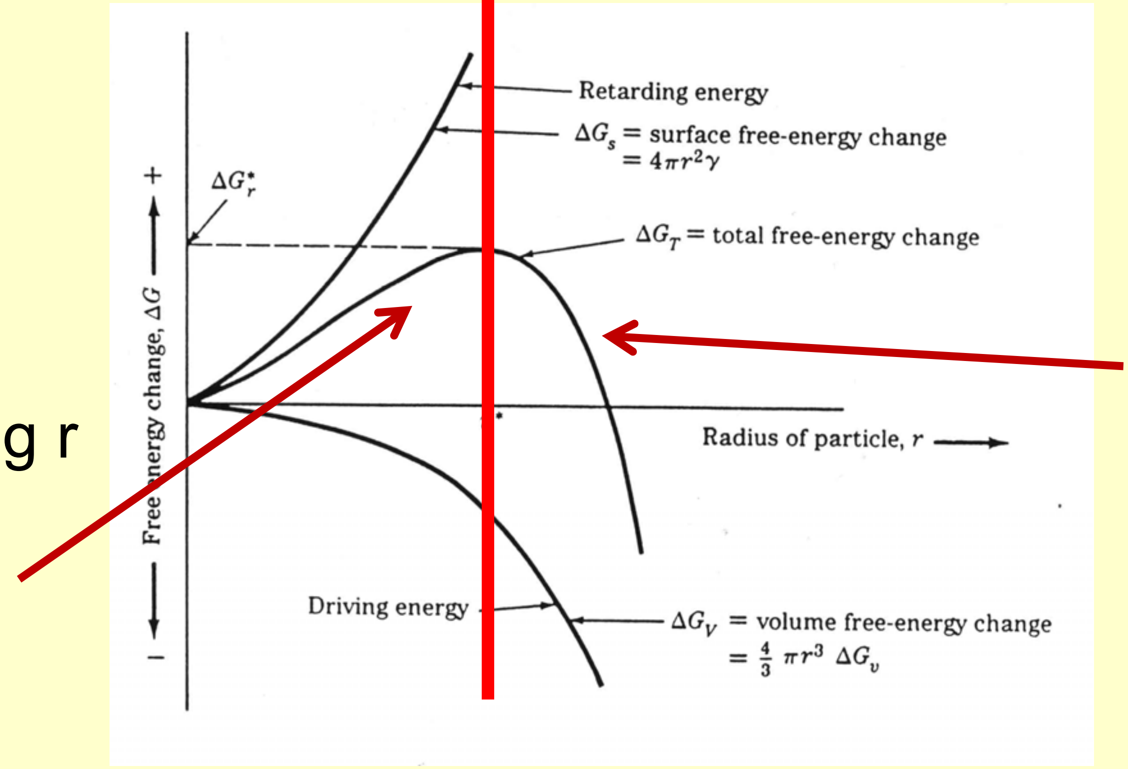
ΔG_s: surface free energy change

ΔG_v: volume free energy change

Critical Radius r*

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

$\Delta G < 0$

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 ($\Delta T = T_m - T$ = undercooling)

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

Nucleation Rate *n*

Nucleation rate *n*

Liquid to solid

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

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

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

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

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

Heterogeneous Nucleation

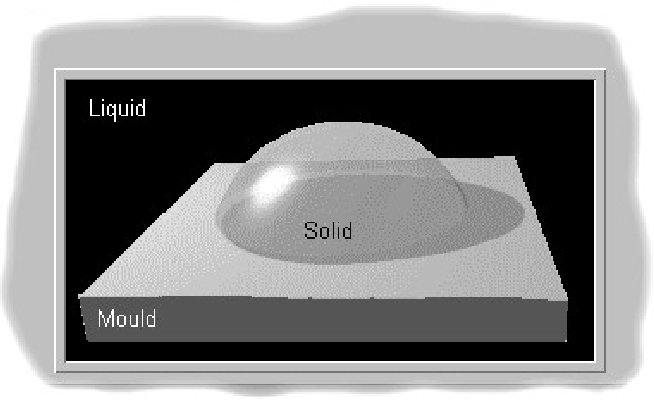
Nuclei can form at preferential sites: flask wall, impurities, catalysts, …..

The energy barrier to nucleation, ∆G*, is substantially **reduced**

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

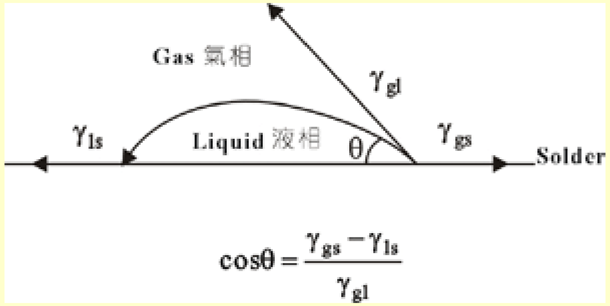
a solid cluster forming on a wall:

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



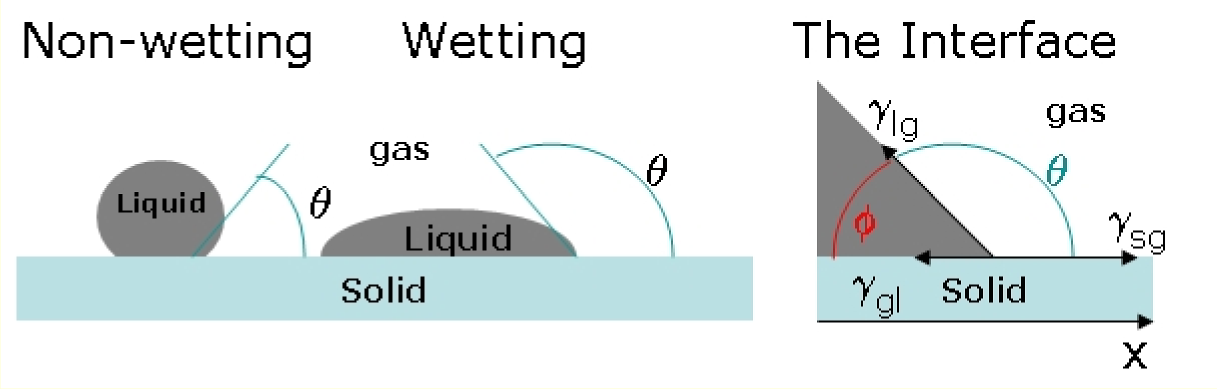
Wetting Angle

Force equilibrium

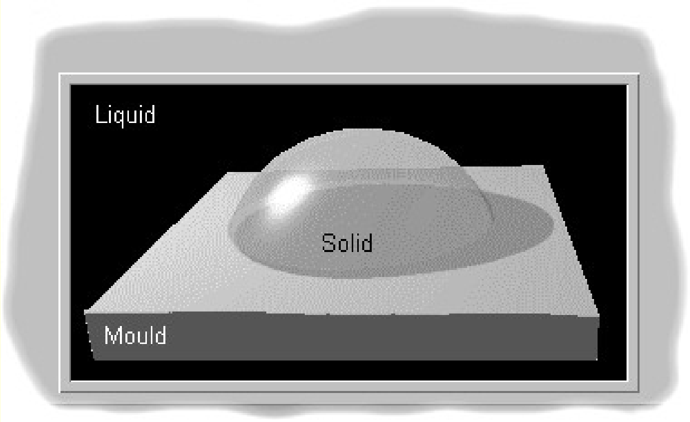


$$\gamma_{GS} = \gamma_{GL} \cos\theta + \gamma_{SL}$$

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



Heterogeneous Nucleation



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

θ = wetting angle
W = wall

Shape factor S(θ)

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

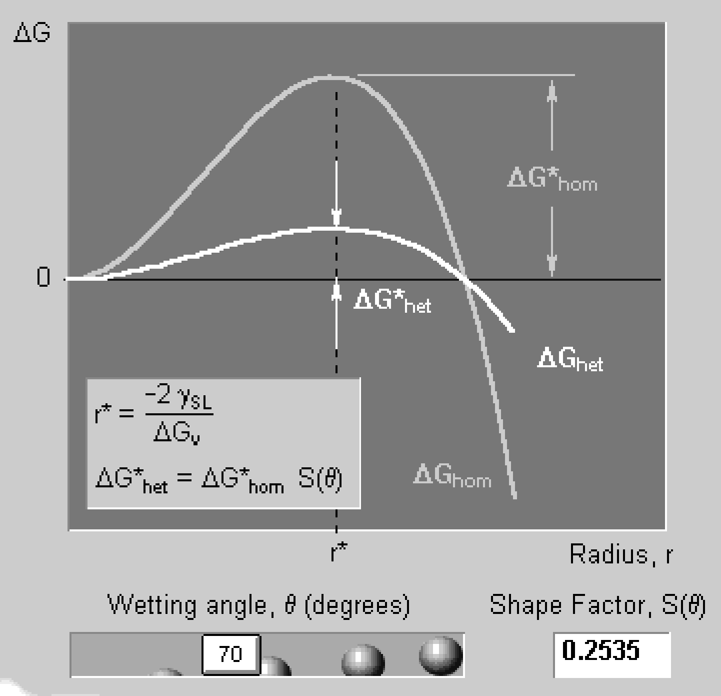
Critical radius r*

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

The energy barrier to heterogeneous nucleation

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

Heterogeneous Nucleation



Wetting angle, θ (degrees): 70

Shape Factor, $S(\theta)$: 0.2535

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

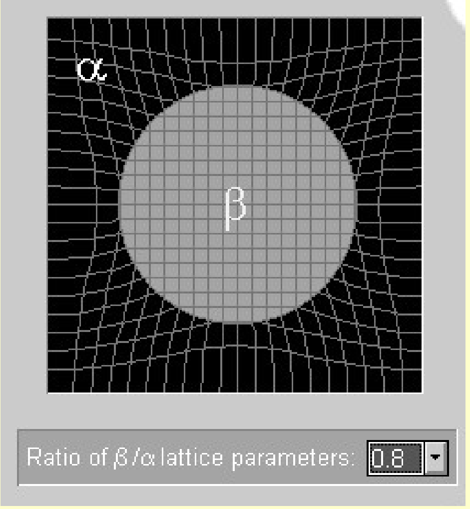
One solid phase changing to another (α to β)

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

- 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, $\Delta G_s = V\,\varepsilon$

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

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



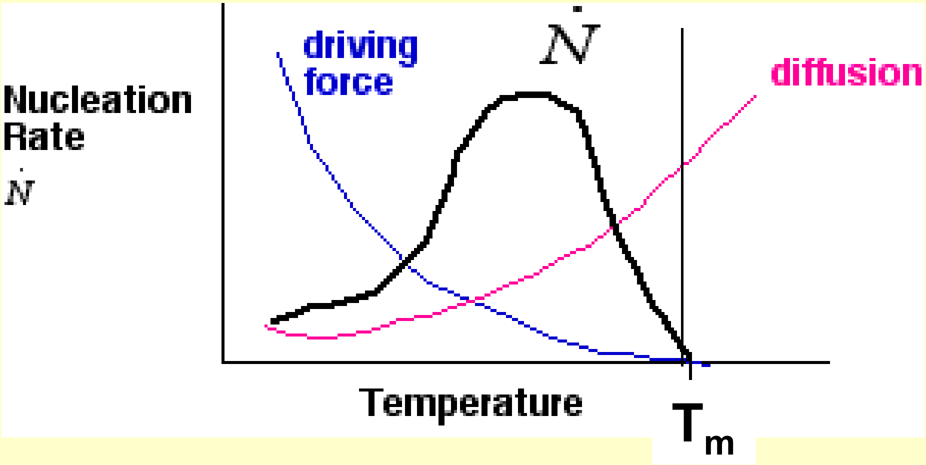
Ratio of β/α lattice parameters: 0.8

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

Nucleation

Transformation from liquid to solid phase requires:

- **Nucleation of a new phase**
- **Growth of a 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

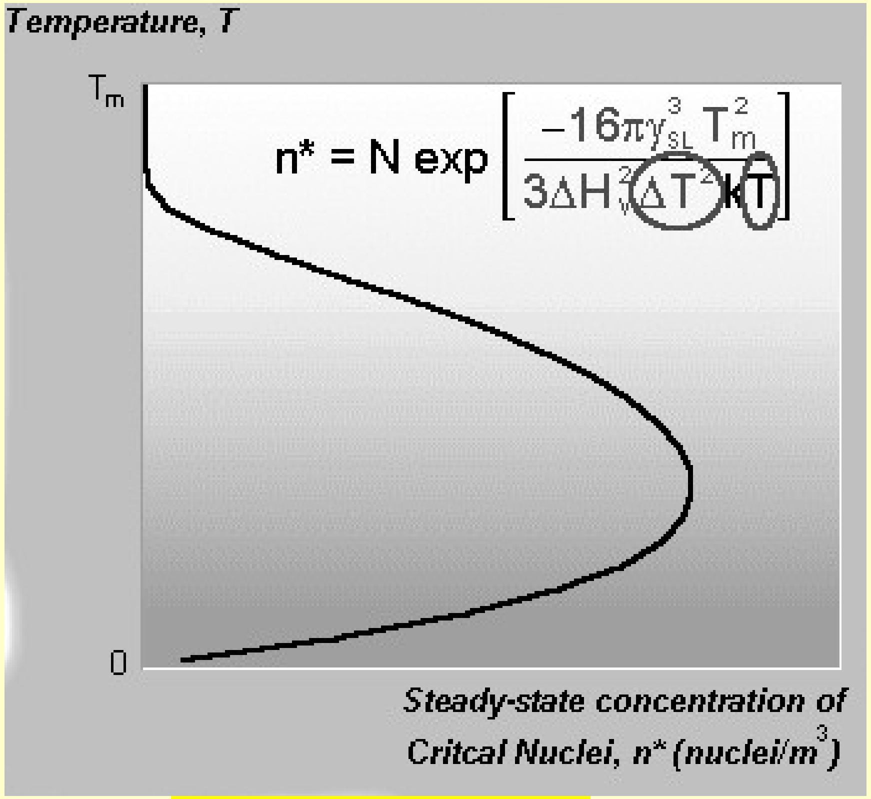
$$\beta = \omega \exp(-Q / kT)$$

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

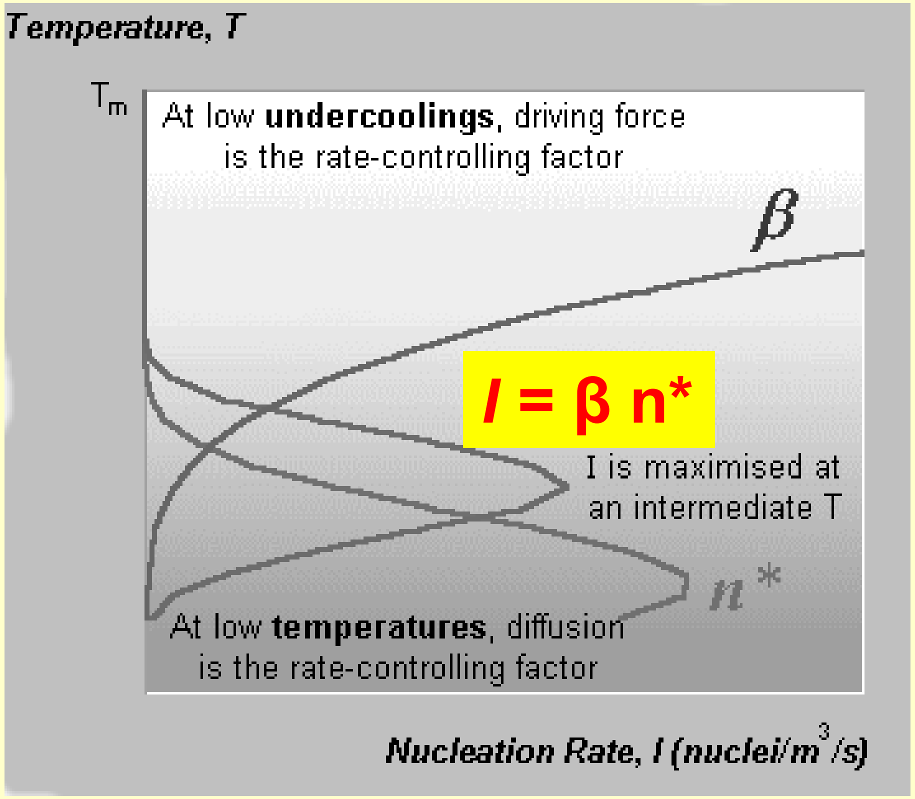
Nucleation rate *I*

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

β = the rate at which atoms join critical nuclei (s^{-1}) = growth rate



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



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

$I = \beta n^*$

I is maximised at an intermediate T

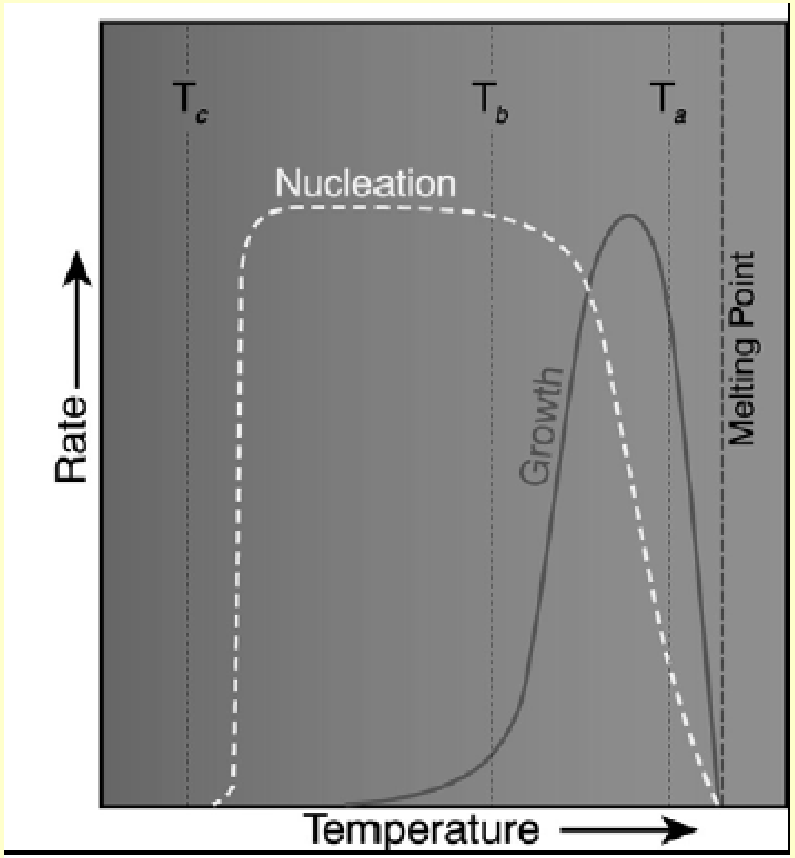
At low **temperatures**, diffusion is the rate-controlling factor

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

Nucleation vs. Crystal Growth (solution or melt)

Undercooling = cooling below the melting point

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



T_a = small undercooling: few nuclei, growth rate high – fast diffusion close to the m.p. = few coarse crystals

T_b = large undercooling: rapid spontaneous nucleation, slow growth rate - high viscosity, slow diffusion = many small nuclei, nanocrystals

T_c = very rapid cooling, nearly no nucleation = glass

Direct Reactions of Solids

Nucleation requires structural similarity of reactants and products

Less reorganization energy = faster nucleation of product phase within reactants

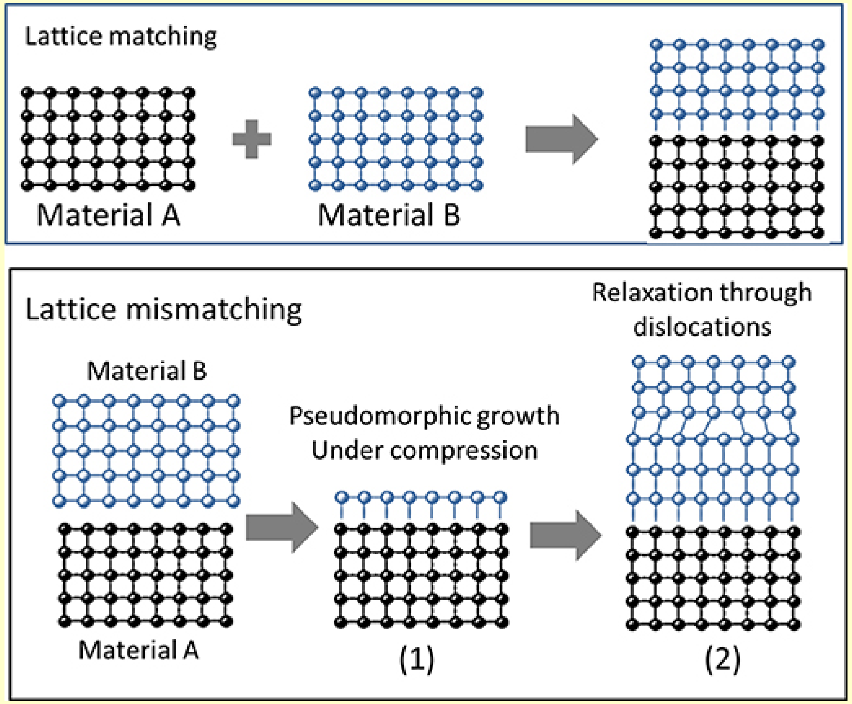
Example: MgO, Al_2O_3, $MgAl_2O_4$
MgO (rock salt) and $MgAl_2O_4$ (spinel) similar ccp O^{2-}
but distinct to hcp O^{2-} in Al_2O_3 phase

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

Epitactic Reactions

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



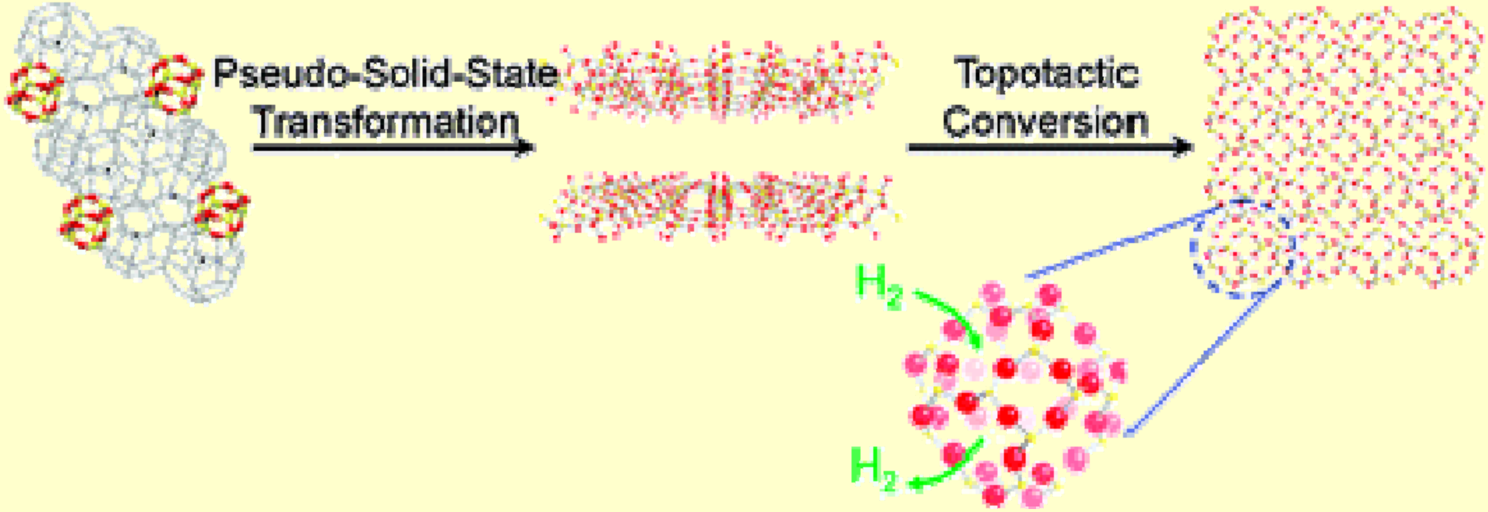
Best with less than 0.1% lattice mismatch, causes elastic strain at interface, slight atom displacement from equilibrium position, strain energy reduced by misfit-dislocation, creates dangling bonds, localized electronic states, carrier scattering by defects, luminescence quenching, killer traps, generally reduces efficacy of electronic and optical devices, can be visualized by HR-TEM imaging

Topotactic Reactions

Orientation effects in the bulk regions of solids
Implies structural relationships between reagent and product
Topotaxy occurs in bulk, 1-, 2- or 3-D

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

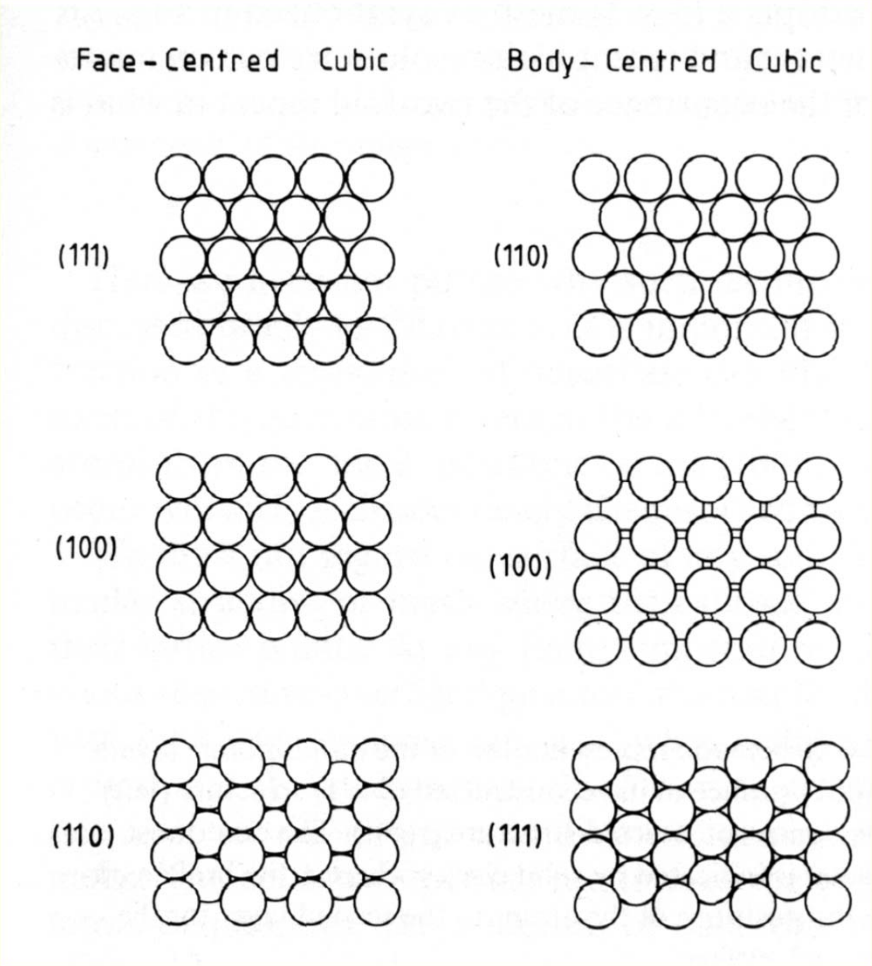
Topotaxy: involves lock-and-key ideas of self-assembly, molecule recognition, host-guest inclusion, clearly requires available space or creates space in the process of adsorption, injection, intercalation etc.



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

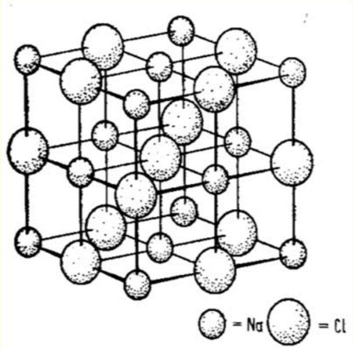


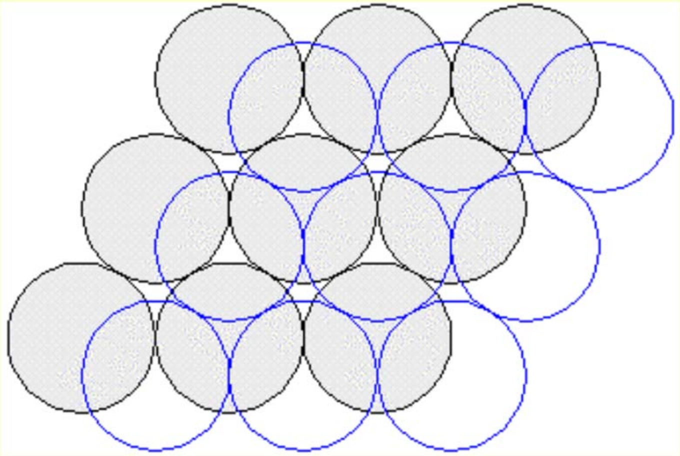
Surface Structure and Reactivity

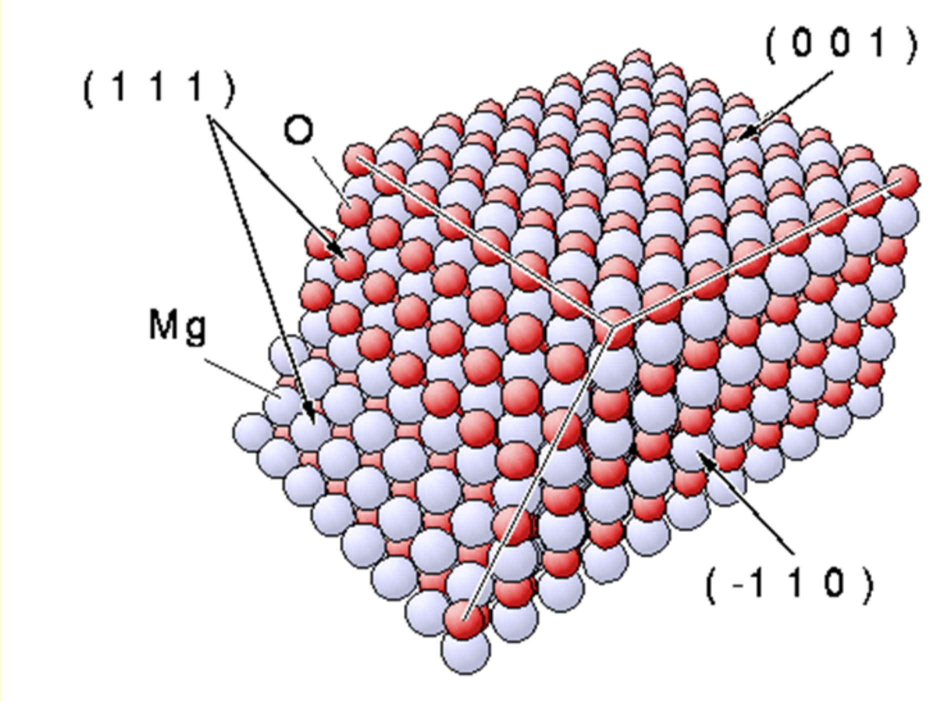
Example: MgO (rock salt)

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

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

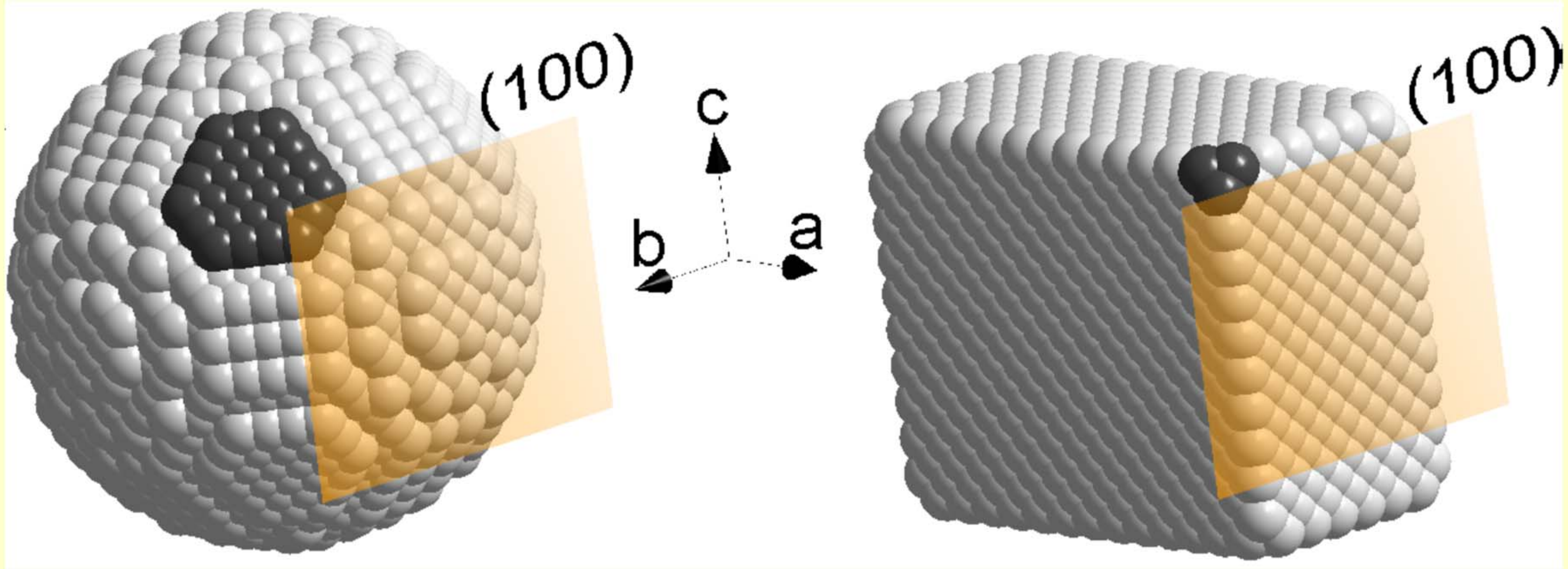






Cubic (rocksalt) MgO crystal: different netplanes

Surface Structure and Reactivity

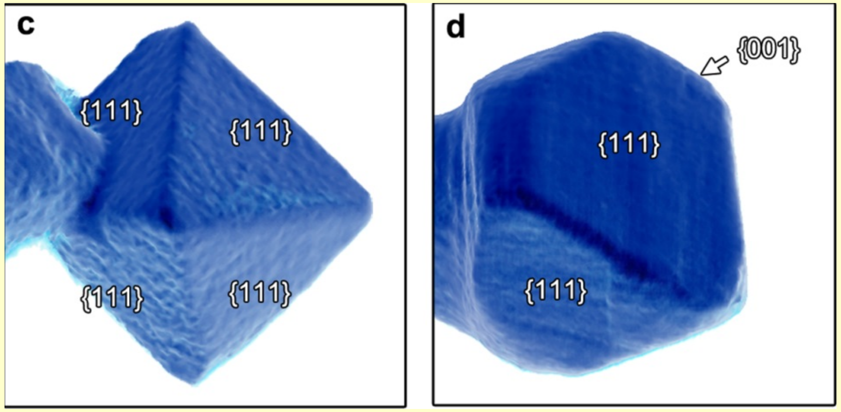


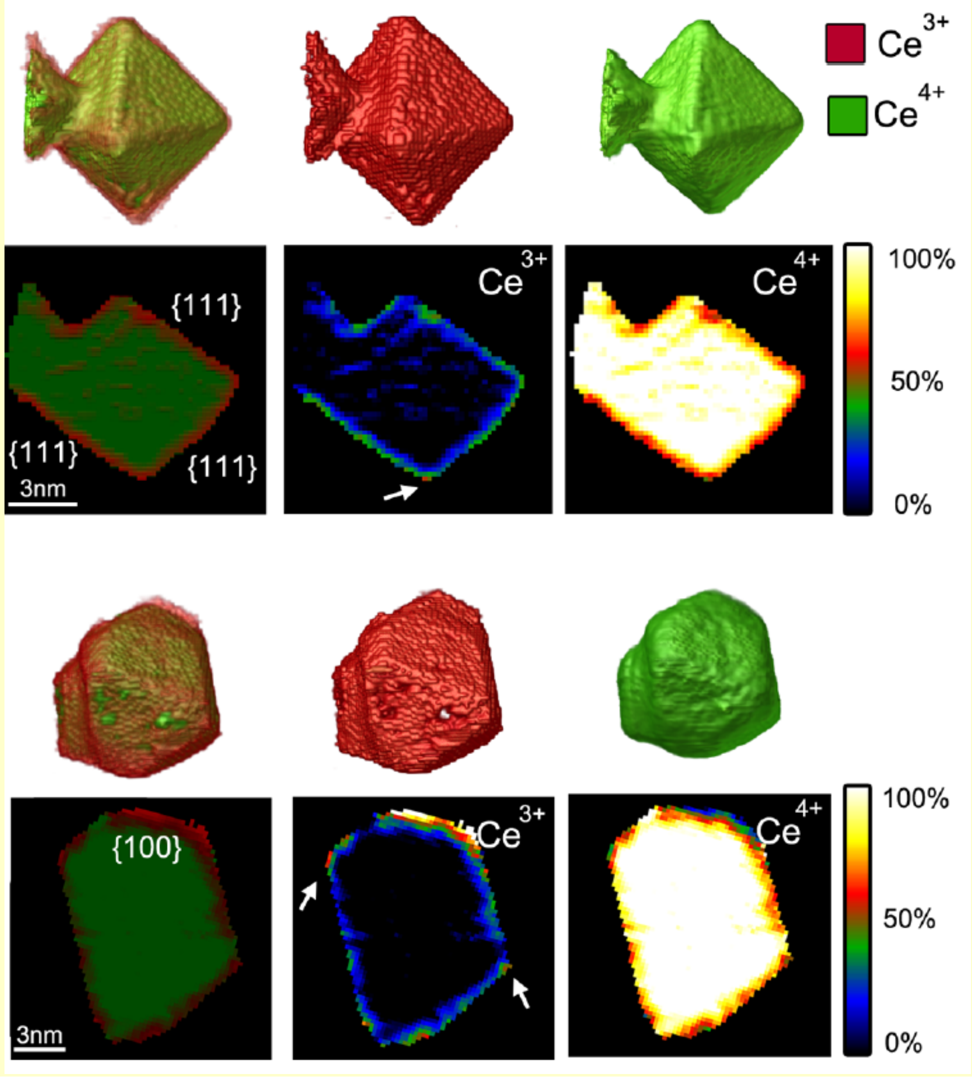
Atoms located in (111) and (100) crystal planes for spherical and cuboid particles

Model particles = fcc structure of Pt 4 nm size

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

Surface Facet Reactivity



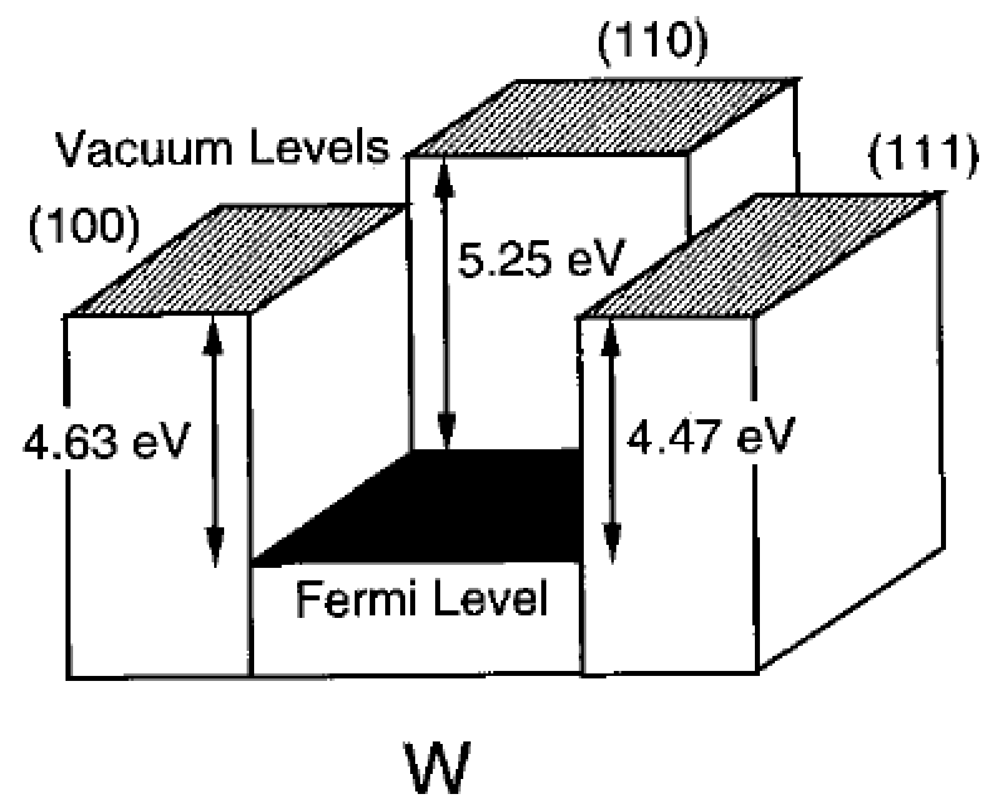


Electron tomography and electron energy loss spectroscopy (EELS) map the valency of the Ce ions in CeO_{2-x} nanocrystals in 3D

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

Surface Structure and Reactivity

Work function of different crystal planes of W



Crystal Growth

Growth rate of specific surfaces controls morphology
Different crystal habits possible, depends on rate of growth of different faces = octahedral, cubooctahedral, cubic possible and variants in between

Depends on area of a face, structure of exposed face, accessibility of a face, adsorption at surface sites, surface defects

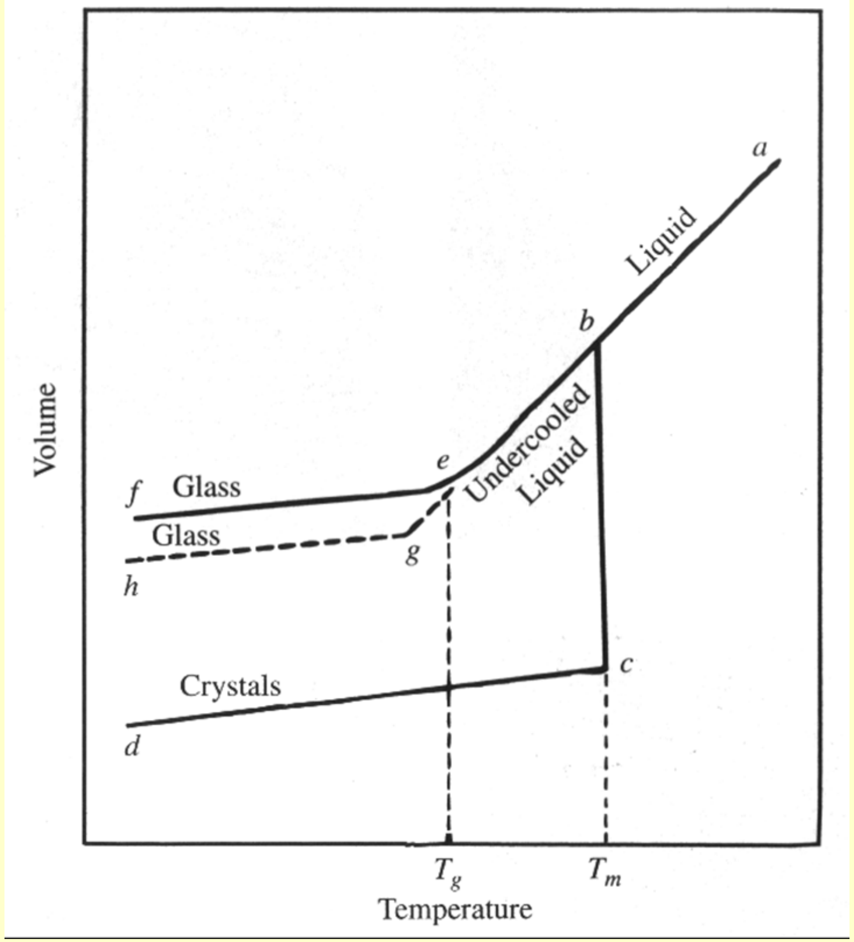
Play major role in reactivity, nucleation, crystal growth, materials properties (electronic, optical, magnetic, charge-transport, mechanical, thermal, acoustical etc)

Fusion-Crystallization from Glass

Glass = 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

Spontaneously relax ultimately, in the limit of infinite time, 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

Production of abrasive grains

Al_2O_3 + MgO → melt at 2100 K, solidify, crush, size

Crystallizing an inorganic glass, lithium disilicate

$Li_2O + 2\ SiO_2 + Al_2O_3 \rightarrow Li_2Si_2O_5$ at 1300 K, Pt crucible

$Li_2Si_2O_5$ forms as a melt, hold at 1100 °C for 2-3 h
Homogeneous, rapid cooling, fast viscosity increas
Quenches to transparent glass

$Li_2Si_2O_5$, T_g ~ 450 °C glass, hold at 500 - 700 °C, $Li_2Si_2O_5$ crystals in 2-3 h

Crystallizing a glass above its glass transition

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**

Carbothermal Reduction

High-temperature process

Acheson process

$SiO_2 + 3\,C \rightarrow 2\,CO + SiC$ at 2000 K, $\Delta H = 478$ kJ

$C + SiO_2 \rightleftarrows SiO(g) + CO$
$SiO_2 + CO \rightleftarrows SiO + CO_2$
$C + CO_2 \rightleftarrows 2\,CO$
$2\,C + SiO \rightleftarrows SiC + CO$

$3\,SiO_2 + 6\,C + 2\,N_2 \rightarrow 6\,CO + Si_3N_4$

Carbothermal Reduction

Borides

$TiO_2 + B_2O_3 + 5\ C \rightarrow 5\ CO + TiB_2$ at 1300 K

$2\ TiO_2 + B_4C + 3\ C \rightarrow 4\ CO + 2\ TiB_2$ at 2300 K

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

Carbides

$2\ Al_2O_3 + 9\ C \rightarrow Al_4C_3 + 6\ CO$ at 2200 K

$2\ B_2O_3 + 7\ C \rightarrow B_4C + 6\ CO$ at 1820 K

$WO_3 + 4\ C \rightarrow WC + 3\ CO$ at 970 K

Nitrides

$Al_2O_3 + N_2 + 3\ C \rightarrow 2\ AlN + 3\ CO$ at 1970 K

$2\ TiO_2 + N_2 + 4\ C \rightarrow 2\ TiN + 4\ CO$ at 1820 K

Direct Reactions of Solids

Heat from chemical reaction energy

Azide Method

$3\ NaN_3 + NaNO_2 \rightarrow 2\ Na_2O + 5\ N_2$

$5\ NaN_3 + NaNO_3 \rightarrow 3\ Na_2O + 8\ N_2$

$9\ NaN_3 + 3\ NaNO_2 + 2\ ZnO \rightarrow 2\ Na_6ZnO_4 + 15\ N_2$

$8\ NaN_3 + 4\ NaNO_2 + Co_3O_4 \rightarrow 3\ Na_4CoO_4 + 14\ N_2$

$2\ NaN_3 + 4\ CuO \rightarrow 2\ NaCu_2O_2 + 3\ N_2$

Driving force - enthalpic and entropic ?

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 redox reaction - high temperatures, $T_f = 1500\text{-}3000$ °C
Frontal mode, reaction wave velocity $u = 1 - 10$ mm.s^{-1}
High thermal gradients - metastable phases
Byproduct removal - washing

State of the substance in the reaction front:

- **solid ($T_f < T_m$) „solid flame“**
- **liquid, melt ($T_f > T_m$)**
- **gaseous**

Thermite reaction: $Zr + Fe_2O_3 \rightarrow Zr_{1-x}Fe_xO_2 + Fe$

Self-Propagating Metathesis

Alkali metal halides as products - large lattice energy

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

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

$$3\ HfCl_4 + 4\ Li_3P \rightarrow 3\ c\text{-}HfP + 12\ LiCl + P$$

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

Self-Propagating Metathesis

Silicon production: $Na_2SiF_6 + 4\ Na \rightarrow 6\ NaF + Si$

Hard materials production:

$TaCl_5 + Li_3N + NaN_3 + NH_4Cl \rightarrow$ c-TaN $+ LiCl + NaCl + N_2 + HCl$

Chemical control of the reaction:

$CrCl_3 + Li_3N + NH_4Cl \rightarrow Cr + Cr_2N +$ c-CrN
$CrI_3 + Li_3N \rightarrow Cr_2N$
$CrI_3 + Li_3N + NH_4Cl \rightarrow$ c-CrN

$MoCl_5 + Li_3N \rightarrow$ explosion
$MoCl_5 + Ca_3N_2 + NH_4Cl \rightarrow$ cubic γ-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

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

(Balance this equation)

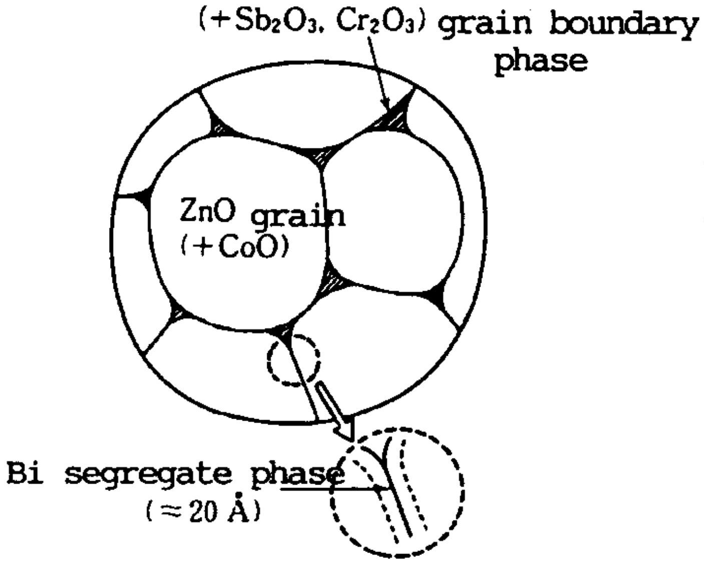
Combustion Synthesis

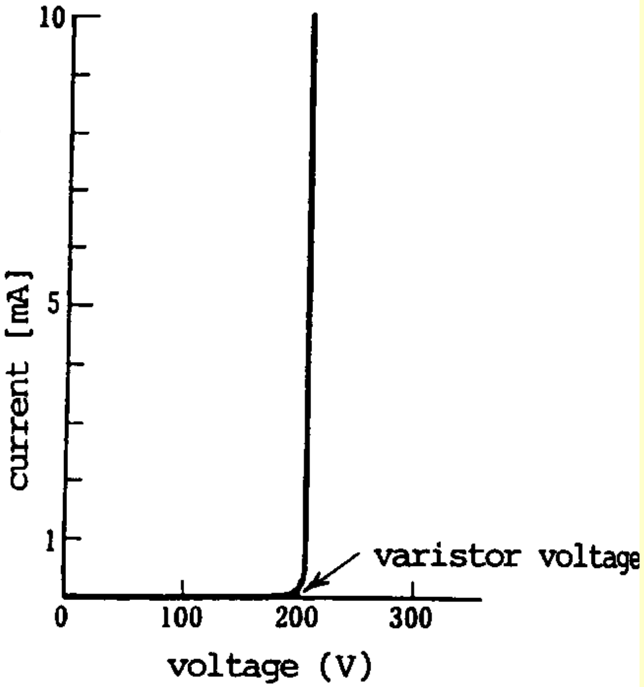
Varistors

ZnO(90%) - Bi_2O_3 - Sb_2O_3

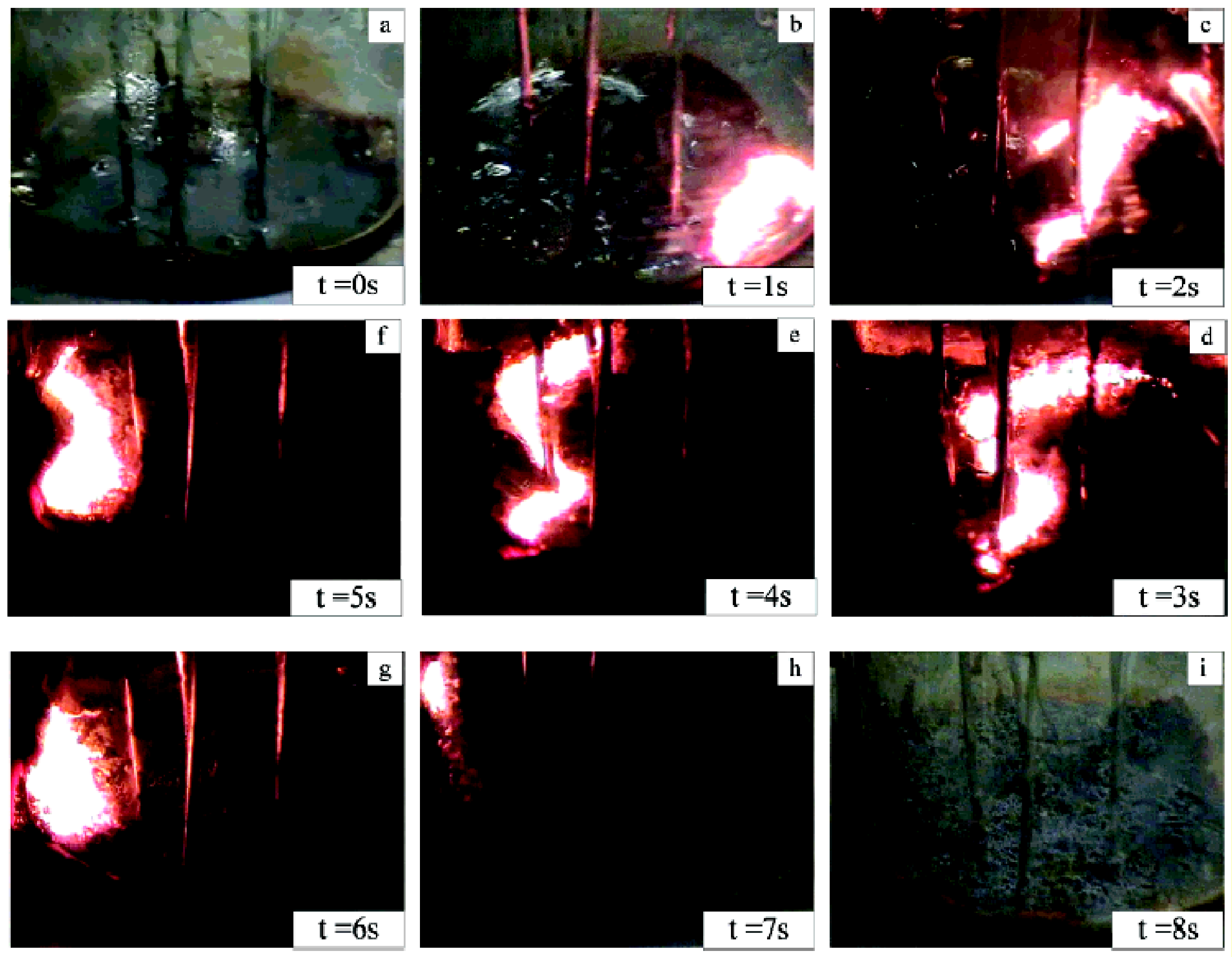
Non-Ohmic behavior $I = (U/C)^a$ C, a = constants, a = 50

Voltage stabilization, surge absorption





Combustion Synthesis

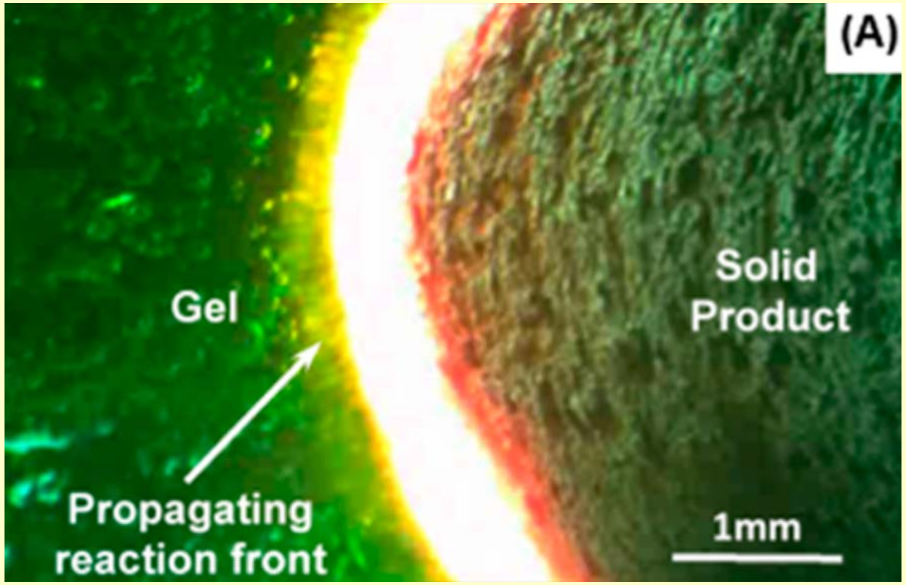


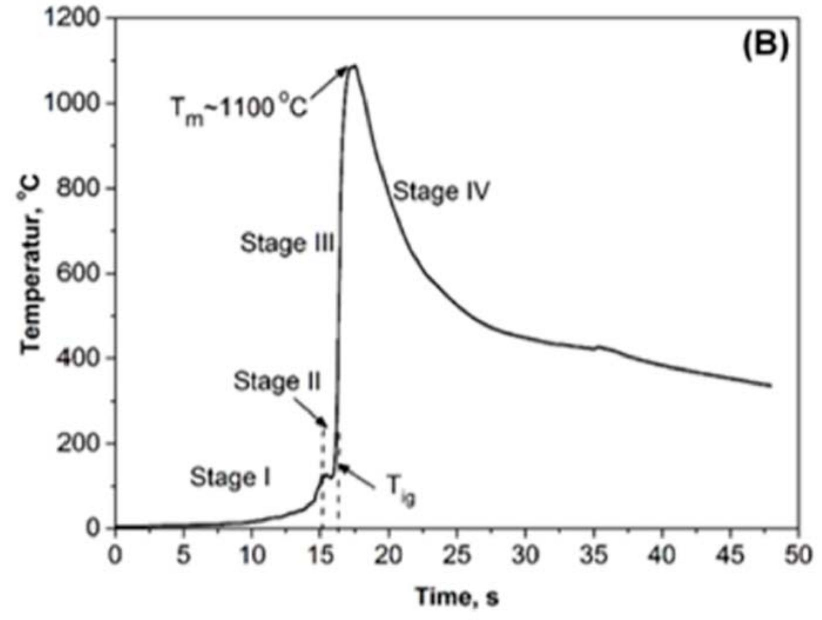
Reaction front propagation: glycine-iron nitrate

Combustion Synthesis

$LiNO_3 + NH_4VO_3 + (NH_4)_2MoO_4$ + glycine → $LiVMoO_6$

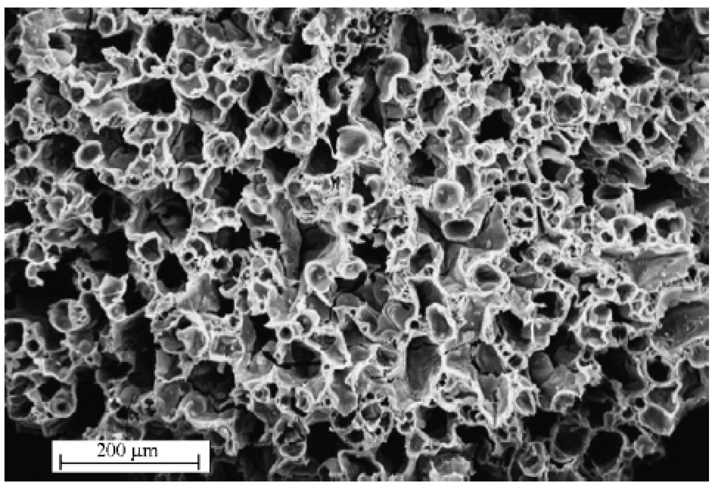
Mixing 1:1:1 in aqueous solution, drying at 90 °C
Combustion at 250 °C
Calcination to $LiVMoO_6$ cathode material for Li-ion





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